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Josette Garnier, Gilles Billen, Julien Tournebize, Pierre Barré, Bruno Mary, et al.. Storage or loss of soil active carbon in cropland soils: The effect of agricultural practices and hydrology. *Geoderma*, 2022, 407, pp.115538. 10.1016/j.geoderma.2021.115538 . hal-03410039

**HAL Id: hal-03410039**

**<https://hal.science/hal-03410039v1>**

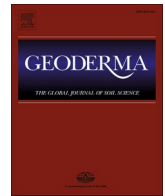
Submitted on 4 Jun 2022

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# Storage or loss of soil active carbon in cropland soils: The effect of agricultural practices and hydrology

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## ARTICLE INFO

Handling Editor: Daniel Said-Pullicino

### Keywords:

Carbon soil leaching  
Active and stable soil carbon  
Soil carbon storage and loss  
AMG model  
Seine watershed

## ABSTRACT

Few studies have simultaneously addressed the issue of the short- and long-term hydrological control of organic carbon (OC) export from soils and the role of the leaching process in the long-term dynamics of the soil OC pool. We combined short- and long-term approaches by investigating dissolved organic carbon (DOC) at the outlet of a small drainage catchment and establishing a relationship between DOC concentrations ( $3.5 \pm 1.8 \text{ mgC L}^{-1}$  on average) and subsurface runoff ( $175 \text{ mm yr}^{-1}$  on average). We then calculated the annual DOC export as a function of average annual water runoff for a 9-year period. We assumed that the annual flux of leaching is proportional to the active soil OC stock, which we compared with data from the literature. We added a leaching function to the AMG two-compartment model of soil carbon dynamics. The innovative use of the Rock-Eval method for agricultural soils made it possible to determine the stable and active carbon fractions ( $\text{OC}_p$  and  $\text{OC}_A$ , respectively), necessary to characterize the system in the model, for 52 plots in organic and conventional agricultural farms in the Seine Basin. No significant difference was found in OC for the two agricultural systems ( $11.4 \pm 2.5 \text{ gC kg}^{-1}$  vs.  $12.3 \pm 4.2 \text{ gC kg}^{-1}$ , respectively, for the 0 to 30 cm layer).

Using the AMG model with its leaching function, we calculated the equilibrium value of  $\text{OC}_A$ , representing the size of the  $\text{OC}_A$  pool that would be reached in the long term under constant farming practices and hydrological conditions in a given plot. Deviation from this equilibrium indicates whether carbon storage or loss occurs. Overall, for the plots sampled in the Seine Basin, an annual carbon loss of  $\sim -0.24 \text{ \% yr}^{-1}$  of the total OC pool was found. This may increase by 15% (i.e., to  $\sim -0.28 \text{ \% yr}^{-1}$ ) under higher subsurface runoff, which is plausible under ongoing climate change (e.g.,  $600 \text{ mm yr}^{-1}$  vs.  $175 \text{ mm yr}^{-1}$  currently observed).

## 1. Introduction

The pool of organic matter in soils is recognized as a major component of the global carbon cycle, and its variations can considerably affect the greenhouse gases responsible for climate change (Caddeo et al., 2019; Friedlingstein et al., 2020 and other references therein). Regarding cropland, declining trends in the soil organic carbon (OC) content of agricultural soils have often been evidenced by long-term monitoring studies (e.g., Gregorich et al., 2001; Heikkinen et al., 2013; Hobbey et al., 2018) and experimental agricultural assays in Europe (Clivot et al., 2019; Autret et al., 2016). Several models have been proposed to quantitatively assess the effect of agricultural practices

on how the soil OC stock evolves over long periods of time, Century and Roth-C being the most well-known with multiple compartments (Parton, 1996; Coleman et al., 1997, respectively). Recently, six different soil models were compared and combined for a better prediction of soil OC (Riggers et al., 2019). In addition, a number of studies have addressed the issue of leached organic matter and the role of hydrology in the dynamics of soil OC. Indeed, OC exports by rivers have long been found to be related to their discharge and the land cover of their watershed (Meybeck, 1982; Hope et al., 1994) or to the carbon/nitrogen (C/N) ratio of soil organic matter on a biome basis (Aitkenhead and McDowell, 2000). Soil dissolved organic carbon (DOC) lost from leaching is not only problematic because of the decline in soil OC, but also because,

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<https://doi.org/10.1016/j.geoderma.2021.115538>

Received 27 March 2021; Received in revised form 9 October 2021; Accepted 11 October 2021

Available online 30 October 2021

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transformed and transported along the land-to-sea continuum, it may potentially affect the ecological functioning of aquatic systems in terms of the production vs. respiration ratio, to the same extent as organic matter input from urban point sources (Garnier and Billen, 2007). In addition to being processed by detritivores and mineralized by microbes leading to CO<sub>2</sub> evasion over the water course (Cole et al., 2007; Battin et al., 2009; Marescaux et al., 2020), DOC may also impact marine coastal systems by modifying community structures (Manninen et al., 2018). In coastal systems, riverine DOC can potentially be taken up by mixotrophic microorganisms causing eutrophication and hypoxia (Gilbert, 2017; Ghyoot et al., 2017).

Carbon losses from soils to rivers (and to the atmosphere) are very complex and require studies at the land-water interface. With climate change, most experts predict an increase in extreme events (IPCC, 2014), conditions that could affect soil OC (dissolved [DOC] and particulate [POC]) deliveries to surface water. At the annual scale, the largest proportions of DOC and POC are known to occur during floods, so that 30–90% of POC and 20–50% of water and DOC fluxes occur during short (10%) periods of the year (Meybeck et al., 2003; Meybeck, 2009). Several studies have also shown the discharge dependency of OC fluxes during rainy events (Manninen et al., 2018; Strohmeier et al., 2013; Wagner et al., 2008). Further, DOC leached to surface waters is controlled by the seasonality of not only the hydrology but also temperature (Sinsabaugh and Findlay, 2003). In addition to climate, soil features play a major role in OC losses (Lal, 2004, 2016; Hobley et al., 2018). While POC (OC attached to soil mineral particles) can be eroded and exported with surface runoff, DOC is mostly lost by soil leaching, both leading to soils losing carbon (Chaplot et al., 2019). Such processes of soil OC loss tend to decrease soil fertility and may be exacerbated by land use changes (e.g., Bellamy et al., 2005; Chaplot et al., 2019; Chaplot and Cooper, 2015; Chahal and Van Eerd, 2020; Sheng et al., 2015). Although carbon storage at a rate of 0.4% per year (the 4 per mil

initiative, Pellerin and Bamière, 2019) would help compensate greenhouse gas emissions from fossil carbon use, any OC loss due to increased runoff may not only hamper soil storage, but this lost carbon as DOC or POC may also return to the atmosphere as CO<sub>2</sub> (Menichetti et al., 2015).

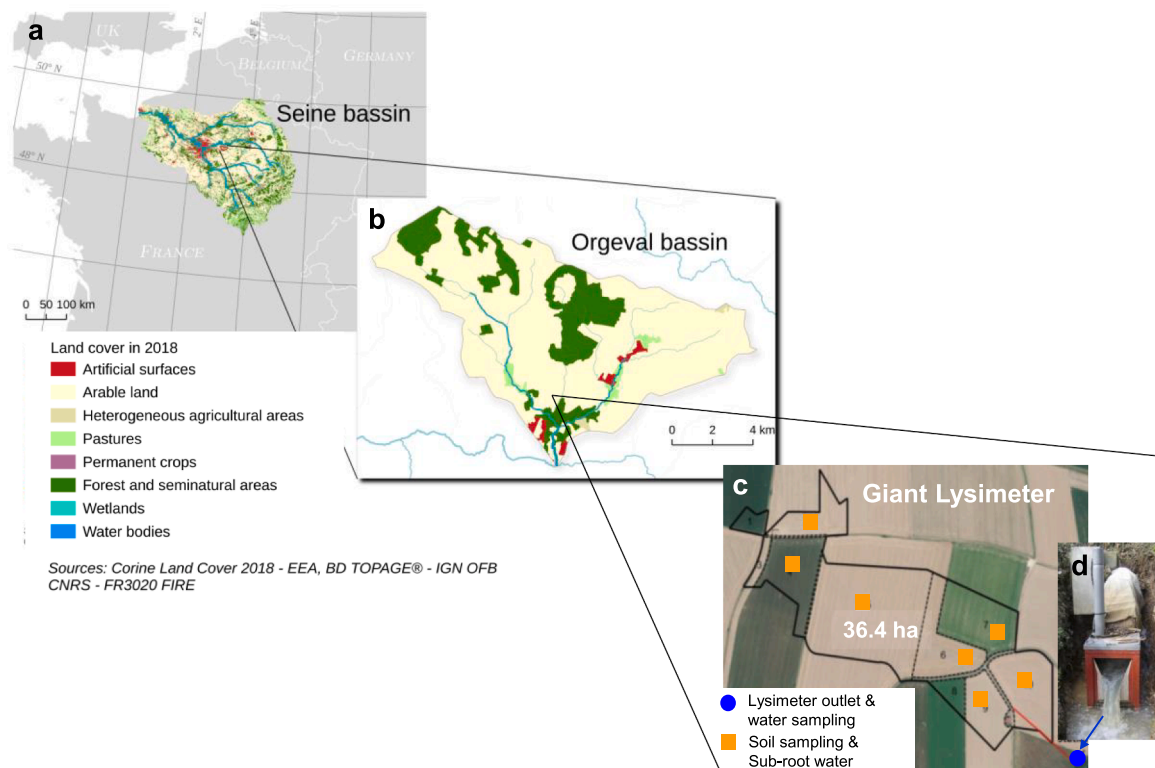
The overall objective of the present study was to link the dynamics of OC in soils with its DOC leaching to surface water in agricultural settings. To accomplish this, we chose a small drained experimental catchment in the Seine Basin, representative of its temperate climate, with both conventional and organic crops, and where erosion is very limited (Guerrini et al., 1998).

Aiming to quantify is the size of the effect of DOC lost by leaching on soil OC storage, we needed to relate OC dynamics in soils and DOC in sub-surface runoff. To combine the soil and water compartments, a soil OC dynamic model was upgraded with a leaching module for the first time. The existing AMG model of soil OC dynamics was chosen (Clivot et al., 2017; Clivot et al., 2019). At an annual time step, it simulates three compartments of OC: fresh OC coming from crop residues or organic amendments and two soils OC pools, stable and active. The relevant information needed to upgrade the AMG with the DOC leaching module was gathered by analyzing DOC and subsurface water runoff in this small drained catchment. The upgraded model was used to quantify how much DOC leaching affects soil OC dynamics, by means of a dual approach on soils OC dynamics and DOC leaching.

## 2. Material and methods

### 2.1. Study sites

The DOC samples were taken at the outlet of a small fully drained 36.4 ha experimental catchment (herein referred to as a giant lysimeter; Klavivko et al., 2001), which, in the late 2000s, was instrumented with a device for continuously measuring subsurface flows and collecting



**Fig. 1.** Land use of a. the Seine Basin and b. the embedded Orgeval catchment. c. Location of the small experimental catchment (giant lysimeter) in the Orgeval catchment. d. Device for automatic measurements of water flow and concentration in water quality variables at its outlet. The black line represents the drainage perimeter of the giant lysimeter, and the blue dot shows its outlet. Orange squares represent the seven plots of the giant lysimeter where soils were auger sampled and suction cups were installed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

samples at its outlet (Fig. 1, Tournebize et al., 2015). It is located in the Orgeval watershed, which covers 104 km<sup>2</sup> and is located 70 km east of Paris in the Seine Basin (Seine-et-Marne department, France). This tile drainage network, consisting of perforated pipes installed 10 m apart and buried 0.8–1 m deep, was installed starting in the 1950s to facilitate the evacuation of excess water during winter and thus reducing the clogging and anoxia phases of these hydromorphic soils (Beaudoin et al., 2012; Arlot, 1999). This subsurface drainage, applied on a large scale, led to a redistribution of the water balance, reducing the share of deep infiltration in favor of subsurface runoff. Runoff refers to the amount of water per surface area flowing more or less rapidly through the soil profile to ultimately joining rivers. In the specific case of this giant lysimeter subsurface runoff is actually measured and represents by far the most important share of total runoff. More generally, runoff (in mm yr<sup>-1</sup>) is estimated by dividing the annual river flow by the catchment area.

The climate is semi-oceanic, with 727 mm annual precipitation (2011–2019) and annual averaged minimum and maximum daily air temperature reaching 7.3 °C and 16 °C, respectively, for the same period. The average humidity for the Seine Basin (rainfall–potential evapotranspiration) is approximately 200 ± 39 mm yr<sup>-1</sup>. Homogeneous in terms of climate, the Orgeval watershed is also rather uniform in elevation (mean altitude, 148 m). It is located in the upper Tertiary Brie Formation with siliceous and marly limestone, covered by Quaternary loess deposits and enriched in clay, resulting in low permeability and waterlogged soil during winter. In the Orgeval watershed, agricultural land dominates (82%) with conventional cereal cropping (wheat, maize, barley, and rapeseed), based on mineral nitrogen fertilization and short crop rotations. The remaining surface is covered by woods (17%), pasture close to streams (<1 %), and the rest is urban or artificialized zones (Fig. 1). Organic farming accounts for only 4.1 % of the agriculture in this area and is based on long crop rotations, eight to nine successive crops: typically, 2–3 years of alfalfa, 2 years of cereals, 1 year of grain legumes, 2 years of cereals and 1 year with flax or hemp (Benoit et al., 2014; Benoit et al., 2016).

Agriculture in this giant lysimeter is representative of the Orgeval watershed as well as the Seine Basin watershed, i.e., intensive conventional cropping systems dominated by cereals with rather short rotation cycles (Mignolet et al., 2007; Garnier et al., 2016). Therefore, we also included here other similar investigations on cropped soils in the Seine Basin for additional organic farming references: in the Yonne, Eure, and Oise departments, in addition to Seine-et-Marne. These are part of a network of farms that have been surveyed since 2011 (known as the “ABAC network,” see supplementary material, Fig. 1 SM), together with those of the Orgeval catchment (Benoit et al., 2014; Benoit et al., 2016), comprising the giant lysimeter area.

## 2.2. Sampling

Water flow rates were continuously recorded in the main drainage collector outlet of the giant lysimeter from 2011 to 2020, in a gradient of hydrological conditions. The water level measurement devices (SE-200 OTT and Druck PDCR1830 sensors) were installed in a weir box equipped with baffles to still the water and a 90-cm V-notch section situated on the main drain. Discharge gauges were used to relate water levels to flow rates by means of rating curves with a 15-min time step. During the period from November 2018 to March 2020, 25 water samples were taken periodically at bi-weekly or monthly intervals at the outlet of the drainage collector for DOC analysis, when the drain was flowing. Using an ISCO automatic sampler (model 3700, Teledyne Isco), five flood episodes were also sampled in February, May, and December 2019, and February and March 2020, for which 5, 12, 19, 12, and 24 samples were analyzed, respectively (Table 1).

Sub-root water and soils were sampled from seven farm plots covering 82% of the giant lysimeter surface area (Fig. 1c). Six ceramic suction cups (SDEC, France, SPS Ø 31 mm, 85 cm long) per plot were

**Table 1**  
Sampling frequency for water and soil analysis.

Water sampling			Number of samples
DOC from the tile drain of the giant lysimeter	Punctual	28 Nov 2018–13 March 2020	25
	Continuous, 1	6–12 Feb 2019	5
	Continuous, 2	10–11 May 2019	12
	Continuous, 3	21–25 Dec 2019	19
	Continuous, 4	12–17 Feb 2020	12
BDOC from tile drain	Continuous, 5	5–6 March 2020	24
	Punctual and continuous	02 Feb 2018–13 March 2020	61
DOC from suction cups in the giant lysimeter	Punctual (7 plots and 6 suction cups per plots)	10 Dec 2019–13 March 2020	51
BDOC from suction cups	idem	10 Dec 2019–13 March 2020	51
Soil sampling			Number of plots
Soils OC content from the Seine Basin, including the 7 from the giant lysimeter	0–30 cm, auger sampling	Nov 2016 or 2017	52
Flux of fresh aerial root and crop residues			
fOC <sub>F</sub>	Farmer interviews of C input to soils	2013–2018	52

installed vertically 90-cm deep with a manual auger of the same diameter, the head placed below the ground surface (–5 cm) to allow for shallow tillage (Benoit et al., 2014; Benoit et al., 2016). They were arranged 2 m apart on a line parallel to the soil tillage. Sub-root water samples were taken fortnightly, after 48 h of vacuum setting, during the rainy hydrological season (between the end of November and the end of March). Soils sampled over the 0- to 30-cm horizon with the auger for the six suction cups were pooled for analysis. Other farm plots (45) were sampled in the Seine Basin, in the same way for soils as the seven in the Orgeval watershed; a total of 52 farm plots from 14 farming systems, six of which were in organic (OF) and eight in conventional farming (CF), respectively represented 32 and 20 farm plots (see location in Fig. 1 SM). Soils samples were collected in mid-November when the suction cups were installed. Water and soil samples were stored in a cooler on the field and at 4 °C when back in the laboratory. Following Autret et al. (2016) and Veloso et al. (2018), we sought to determine whether the effect of OF practices would differ from CF practices in terms of carbon storage.

As required by the AMG model, we determined the average annual input of fresh OC to the soil on the basis of recorded detailed interviews with farmers, which were conducted to document the practices of the 14 farming systems (OF and CF) and 52 farm plots (crops, sowing and harvest dates, yield; type of residue and residue management and biomass left on the field; mineral and organic fertilizer application, other inputs; introduction of intermediate crops and their sowing, harvest/destruction dates, associated biomass; soil preparation, tillage).

## 2.3. Water chemical analysis

Samples were filtered on the sampling day. The DOC was analyzed on the filtrate (filtration through GF/F 0.7-µm filters, 25 mm, pre-combusted for 4 h at 500 °C). One fraction (T0) of the filtrate (30 mL) was immediately acidified by adding 0.1 mL of sulfuric acid (3 M) to

determine DOC. For biodegradable dissolved organic carbon (BDOC), another filtered fraction (250 mL) was re-inoculated with the corresponding water sample and its native bacterial assemblage (1% in final concentration) and batch-incubated for 45 days (T45) in the dark at 20 °C under constant agitation. At the end of the incubation time, 30 mL of the batch was filtered and stored in the same conditions as its corresponding T0 sample (Servais et al., 1995). DOC analysis was performed using infrared chromatography (TOC analyzer, Aurora 1030). BDOC is estimated as the difference between the DOC on the sampling day (T0) and the DOC after incubation (T45).

A total of 97 DOC and 61 BDOC samples from the subsurface water drained by the giant lysimeter were analyzed (Table 1). Overall, 51 DOC and BDOC samples were analyzed from the sub-root water in the suction cups. Combined with the flow measurements, these data made it possible to estimate the flux of organic carbon leaching. As also shown in Table 1, soil samples and farmer interviews for 52 plots allowed us to determine the three carbon fractions for the AMG model.

#### 2.4. Soil chemical analysis for total carbon and its fraction of permanent carbon

To characterize the soil from the 52 plots (including the seven from the giant lysimeter), samples from their 0 to 30-cm horizon were freeze-dried, ground, and sieved at 2 mm. The contents in clay, CaCO<sub>3</sub>, as well as in carbon and nitrogen were classically measured in accordance with the respective standard methods, NF X 31-107, NF ISO 10693, NF ISO 10694, and NF ISO 13878; the latter two were dry combustion methods (DC). The C/N ratio was then calculated.

The Rock-Eval (RE) method was used on the same 52 samples at the ISTeP Laboratory with an RE turbo device (Vinci Technologies, France; see Behar et al. (2001) for details on the equipment). The analytical procedure was adapted from the procedure developed for the analysis of soil organic matter by Disnar et al. (2003). Briefly, approximately 60 mg of ground sample was subjected to two consecutive heating treatments, first in a pyrolysis oven (200–650 °C; thermal ramping rate, 30 °C·min<sup>-1</sup>; under N<sub>2</sub> atmosphere) then in a combustion oven (300–850 °C; thermal ramping rate, 20 °C·min<sup>-1</sup>; under laboratory air atmosphere). At the beginning of the pyrolysis stage, the sample was kept at 200 °C for 180 s during which the free hydrocarbons (HC) were thermovaporized (S1 peak). The pyrolysis effluents (mostly HC) were quantified with flame ionization detection, while CO and CO<sub>2</sub> were quantified using infrared detection during both the pyrolysis and oxidation stages. One of the major advantages of the RE method is that it provides TOC values without preliminary treatment such as decarbonation as required for the determination of the OC using classic combustion techniques (Disnar et al., 2003; Baudin et al., 2015).

Moreover, this innovative approach using RE data can quantify the proportion of centennially stable soil organic carbon (OC<sub>s</sub>) and active soil OC pools for each plot (OF or CF), in any temperate soils (Cécillon et al., 2018; Cécillon et al., 2021). A statistical model based on Rock-Eval® thermal analysis (PARTYSOC Cécillon et al., 2021) optimally partitions the active and stable pools of AMG (Kanari et al., 2021). This statistical model uses Rock-Eval thermal analyses data as entry variables and provides the proportion of C stable in the analyzed sample. The proportion of stable C was then multiplied by TOC to calculate the C stable content. The content of active C was determined by the difference between the two.

#### 2.5. The AMG model

The AMG model was built for simulating the long-term dynamics of organic matter in agricultural soils under the effect of different climatic or crop factors (Bouthier et al., 2014; Clivot et al., 2017). The AMG model has been intensively verified and validated based on a large number of experimental plots for which long chronicles of soil organic carbon measurements were available (see Clivot et al., 2019 and

references herein). In addition to fresh organic matter soil inputs to soils, it considers two soil OC compartments (Fig. 2): (i) an active OC (OC<sub>A</sub>), fed from the initial decomposition of this fresh organic matter inputs to soils (fOC<sub>F</sub>), such as unharvested above and belowground crop residues as well as organic amendments, and subjected to mineralization, and (ii) a stable OC (OC<sub>S</sub>) pool, considered fully inert at the timescale of the simulation (typically less than 50 years).

The “humification” coefficient for OC inputs (h<sub>i</sub>, see Fig. 2) determines the proportion of the C from fresh organic residues and amendments remaining after 1 year of decomposition. It therefore corresponds to the fraction of OC that is entering the OC<sub>A</sub> active soil carbon pool. This “humification” coefficient is considered dependent only on the nature of the original material, with a negligible influence of pedoclimatic properties (Clivot et al., 2019; Levavasseur et al., 2020). The mean residence time of OC<sub>A</sub> is ca. 30 years, which is about the mean residence time measured for lignin compounds in temperate soils. It is also on the same order of magnitude as the “hum” pool of the Roth-C model. The rate of OC<sub>A</sub> mineralization depends on the pedoclimatic characteristics of each farm plot (Fig. 2). The balance between annual humified carbon inputs and mineralization of the active carbon determines how the soil OC stock evolves. The first-order constant rate of OC<sub>A</sub> mineralization (k<sub>m</sub>, see Fig. 2) varies as a function of clay content, calcium carbonate (CaCO<sub>3</sub>) content, pH, C/N ratio, water balance (W, in mm·yr<sup>-1</sup> = rainfall – potential evapotranspiration), and temperature (T), according to the following functions (Clivot et al., 2017; Clivot et al., 2019):

$$k_m (\text{yr}^{-1}) = k_0 * f(\text{clay}) * f(\text{CaCO}_3) * f(\text{pH}) * f(\text{C/N}) * f(\text{W}) * f(\text{T}) \quad (1)$$

with:

$$k_0 = 0.1 \text{ yr}^{-1}$$

$$f(\text{clay}) = \exp(-a * \text{clay}) \text{ where } a = 2.72 \text{ and clay is the clay content in}$$

g<sub>clay</sub>/g<sub>soil</sub>

$$f(\text{CaCO}_3) = 1/(1 + b * \text{CaCO}_3) \text{ with } b = 0.15 \text{ and CaCO}_3 \text{ the calcium carbonate content in g/g}_{\text{soil}}$$

$$f(\text{pH}) = \exp(-c * (\text{pH} - \text{pH}_{\text{ref}})^2) \text{ with } c = 0.112 \text{ and } \text{pH}_{\text{ref}} = 8.5$$

$$f(\text{C/N}) = 0.8 * \exp(-d * (\text{C/N} - 11)^2) + 0.2 \text{ with } d = 0.06$$

$$f(\text{W}) = 0.989$$

$$f(\text{T}) = x/(1 + (x-1) * \exp(-t * (\text{T} - \text{T}_{\text{ref}}))) \text{ with } x = 20; t = 0.12 \text{ } ^\circ\text{C}^{-1}; \text{T}_{\text{ref}} = 15 \text{ } ^\circ\text{C}$$

#### 2.6. Determination of soil active carbon inputs

Detailed interviews with farmers allowed us to assemble, for each of the 52 plots and over 3–6 consecutive years, a comprehensive data set of farming practices (see section 2.2, Table 3 SM). C inputs from above- and underground residues of main and intermediate crops were calculated from crop yields using the allometric functions provided by Bollinder et al. (2007). Depending on the plant and the organ (root, stubble, etc.), a fraction of the fresh C inputs is transferred annually to OC<sub>A</sub> depending on its specific humification coefficient, h<sub>i</sub> (Clivot et al., 2019; Levavasseur et al., 2020). The same was done for inputs of organic fertilizers such as manure, droppings, vinasse, etc.

From these data, it was possible to calculate the corresponding total active humified carbon flux (fOC<sub>AH</sub>) (values provided in Table 2 SM).

#### 2.7. Statistical tests

The Student test was used to compare the DOC concentrations measured in drained sub-surface water (n = 97) from the drain collector, and those from sub-root water from suction cups (n = 51). The flux of active humified OC to soils (fOC<sub>AH</sub>) and DOC concentrations were compared for OF (n = 20) and CF (n = 37) farming plots with a Mann–Whitney–Wilcoxon rank test, given that observations did not follow a normal distribution. Similarly, the differences in biodegradable DOC in drained sub-surface water runoff (n = 59) and in sub-root water from

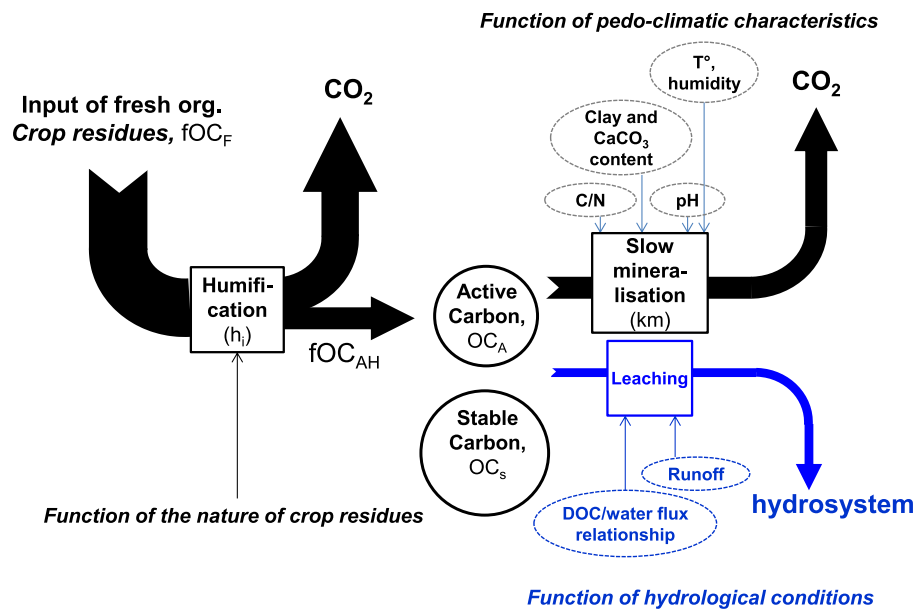


Fig. 2. Schematic representation of the AMG model: carbon fluxes and stocks.  $fOC_F$  is the flux of fresh organic matter input to soils;  $h_i$  is the humification rate ( $yr^{-1}$ ) of each organic input (Clivot et al., 2019; Levassasseur et al., 2020);  $fOC_{AH}$  is the flux of active humified organic carbon input to soils,  $k_m$  is the mineralization constant of active soil carbon ( $yr^{-1}$ ). The representation of leaching loss of active  $OC_A$  has been added in this study.

suction cups ( $n = 51$ ) were tested with the Mann–Whitney–Wilcoxon rank test. All statistical tests were performed using R software (R version 4.0.3 (2020–10–10)).

### 3. Results

#### 3.1. Soil organic carbon pools

The mean characteristics of soils necessary for running the AMG model are shown in Table 2. The loamy clay soils of the Seine Basin and the Orgeval watershed (including the giant lysimeter) contain on average 73% silt and 20% clay for the 0- to 30-cm horizon. OC and nitrogen soil contents amounted to roughly 13.5 and 1.3  $g\ kg^{-1}$  for a C/N ratio of 10.1, very close to 10, a ratio generally cited for French arable soils (Nicolardot et al., 2001). The pH measured at the soil surface during the 2018–2019 period averaged 6.79, very close to the value of 6.8 provided by the RMQS (2000–2020) network for the area studied (Martin et al., 2019).

The total OC measured using the RE technique has been previously shown to be closely related to the elemental analysis. Here, the average total OC (Rock-Eval) amounted to  $11.8 \pm 3.3\ gC/kg_{DWsoil}$ .

$OC_s$  and  $OC_A$  (stable and active OC, respectively) accounted for  $58 \pm 6\%$  and  $42 \pm 6\%$  of total OC in the 0- to 30-cm layer. Interestingly, no

Table 2

Average characteristics of the soils (0–30 cm) of the farm plots studied in terms of clay and silt, organic carbon ( $OC_{DC}$ ), total nitrogen (TN), C/N, and pH. Humidity was calculated for the Seine Basin using data from hydrological records (<https://www.ecologie.gouv.fr/banque-hydro>). Average  $CaCO_3$  values were proposed for the Ile-de-France region by the RMQS (2000–2020) database ([www.gissol.fr/tag/rmqqs](http://www.gissol.fr/tag/rmqqs), Martin et al., 2019).

	Units	Values
Clay	$g\ kg^{-1}$	$203.6 \pm 43.4$
Silt 2–50 $\mu m$	$g\ kg^{-1}$	$730.1 \pm 44.6$
$OC_{DC}$	$g\ C\ kg^{-1}$	$13.5 \pm 4.5$
N	$g\ N\ kg^{-1}$	$1.3 \pm 0.3$
C/N		$10.1 \pm 1.5$
pH		$6.79 \pm 0.71$
$CaCO_3$	$g\ kg^{-1}$	0.1
Humidity	$mm\ yr^{-1}$	$200 \pm 39$

significant difference (Wilcoxon–Mann–Whitney test,  $p = 0.1675$ ) was found between the amount of the different carbon forms on the farm plots in OF and CF, respectively (Table 3).

#### 3.2. Carbon leaching from the soils to the hydrosystem

Continuous records of subsurface runoff at the outlet of the drainage collector are shown from 2011 to 2020 (Fig. 3a, b). A hydrological year is considered from September 1 to August 31 of the following year, i.e., after the crops have been harvested, with soils prepared for the next cropping year. The hydrological years 2011–2012 and 2016–2017 were particularly dry, with water runoff of  $\sim 63$  and  $42\ mm\ yr^{-1}$ , respectively, less than half the average over the 2011–2020 period ( $175\ mm\ yr^{-1}$ ). The wettest yearly subsurface water runoff was observed during 2017–2018 ( $380\ mm\ yr^{-1}$ ).

Overall, the measurements of DOC concentration in water samples from the giant lysimeter averaged  $3.6\ mgC\ L^{-1}$  ( $SD = 1.8, n = 97$ ). These values showed a hyperbolic relationship with subsurface runoff ( $mm\ d^{-1}$ ) (Fig. 4). Interestingly, the averaged DOC measured in suction cups (sub-root concentrations) for plots within the giant lysimeter were close to those from the collector (mean  $3.8\ mgC\ L^{-1}$   $SD = 2.5, n = 51$ , Student test,  $p = 0.521$ ), with a lower DOC concentration for OF than CF farming plots ( $2.8$  vs.  $4.4\ mgC\ L^{-1}$ ), but not significantly different (Mann–Whitney test,  $p = 0.003$ ).

Regarding the biodegradable DOC fraction (BDOC, after 45 days

Table 3

Average contents in soils with organic and conventional farming practices. Total organic carbon: OC; stable organic carbon:  $OC_s$ ; active organic carbon:  $OC_A$ .

Farming systems	Units	Values
OC		
Organic	$gC\ kg^{-1}$	$11.4 \pm 2.5$
Conventional	$gC\ kg^{-1}$	$12.3 \pm 4.2$
$OC_s$		
Organic	$gC\ kg^{-1}$	$6.5 \pm 1.3$
Conventional	$gC\ kg^{-1}$	$7.1 \pm 2.1$
$OC_A$		
Organic	$gC\ kg^{-1}$	$4.9 \pm 1.5$
Conventional	$gC\ kg^{-1}$	$5.3 \pm 2.7$

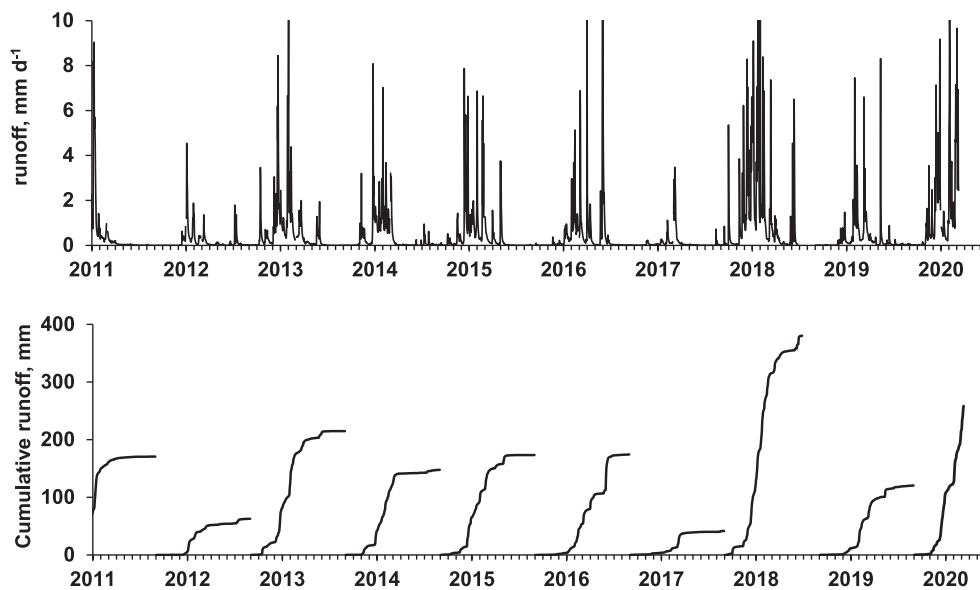


Fig. 3. a. Measurements of daily variations in subsurface runoff ( $\text{mm d}^{-1}$ ) drained from the experimental catchment (2011–2020) b. Cumulative subsurface runoff for the hydrological years (September 1 to August 31 of the following year).

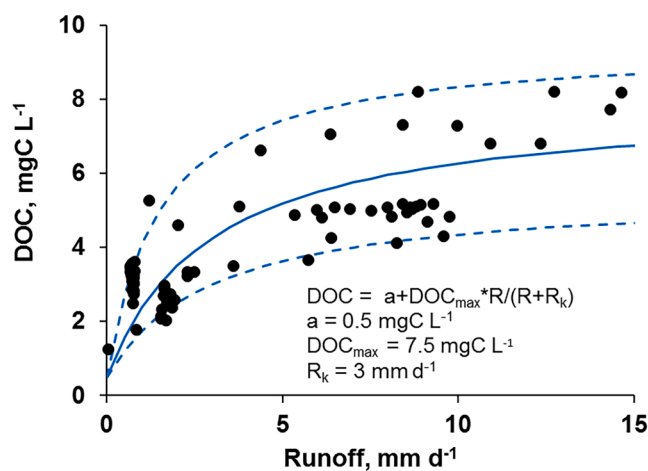


Fig. 4. Relationship between concentrations of dissolved organic carbon (DOC) and subsurface runoff values ( $R$ ,  $\text{mm d}^{-1}$ ) at the outlet of the experimental basin. The relationship can be formalized as a hyperbolic function:  $\text{DOC} = a + \text{DOC}_{\text{max}} * R / (R + R_k)$ , with  $\text{DOC}_{\text{max}}$  the asymptotic value of DOC at high  $R$ , and  $R_k$  the subsurface runoff value for which DOC reaches half of the  $\text{DOC}_{\text{max}}$  value.

incubation) in the water from the giant lysimeter outlet, a rather low average of 11.5% was found ( $\text{SD} = 6.3$ ,  $n = 59$ ), without identifying any relationship for either DOC concentrations or the specific period. A BDOC average of 22.8% ( $\text{SD} = 14.2$ ,  $n = 51$ ) was found in the sub-root water from suction cups, although the differences were not significant on average (Mann–Whitney test,  $p = 0.14$ ).

This relationship shown in Fig. 4 was then made used to reconstruct the daily export of DOC by leaching from agricultural soils. This depended largely on the cumulative discharge of the drained water (Fig. 5a) and therefore varied considerably from one hydrological year to another. At the annual scale, a linear relationship between total DOC export and annual runoff was found (Fig. 5.b).

### 3.3. Incorporating leaching in the model of organic carbon dynamics in soils

It is important to determine the extent to which DOC leaching is

likely to affect the stock of OC in soils, which can be conceptually represented as in Fig. 2 (above, in blue). Since mineralization of soil OC by micro-organisms requires soluble OC (generally produced by the action of exoenzymes) to enter microbial cells, it is logical to consider that the leaching process preferentially concerns the active carbon stock of the soil rather than the stable OC, which is inert at a centennial timescale.

If we then consider that the annual flux of DOC leaching ( $\text{flx}_{\text{leach}}$ , in  $\text{tC ha}^{-1} \text{ yr}^{-1}$ ) is a linear function of the annual runoff (runoff in  $\text{mm yr}^{-1}$ ) (Fig. 5b) and proportional to the soil active OC stock ( $\text{OC}_A$   $\text{tonC ha}^{-1}$ ), it can be expressed as:

$$\text{flx}_{\text{leach}} = (a_{\text{leach}} * \text{runoff}) * \text{OC}_A \quad (2)$$

The leaching constants ( $a_{\text{leach}}$ , in  $\text{mm}^{-1}$ ) can be calibrated from the observations shown in Fig. 5b ( $y = 0.04x$ ,  $R^2 = 0.96$ ), considering an average stock of active OC ( $\text{OC}_A$ ) in soils of the experimental area amounting to  $20 \pm 8 \text{ tC ha}^{-1}$ , obtained from an average  $\text{OC}_A$  content of  $5 \text{ g kg}^{-1}$  over 30 cm and considering an apparent density of  $1.3 \text{ ton m}^{-3}$ :

$$a_{\text{leach}} = 0.04 / 20 / 1000 = 2.10^{-6} \text{ mm}^{-1}$$

This also assumes that DOC mostly originated from the 0- to 30-cm horizon and that this contribution was homogeneous for the soils studied.

The equation for OC dynamics in soils can then be written as:

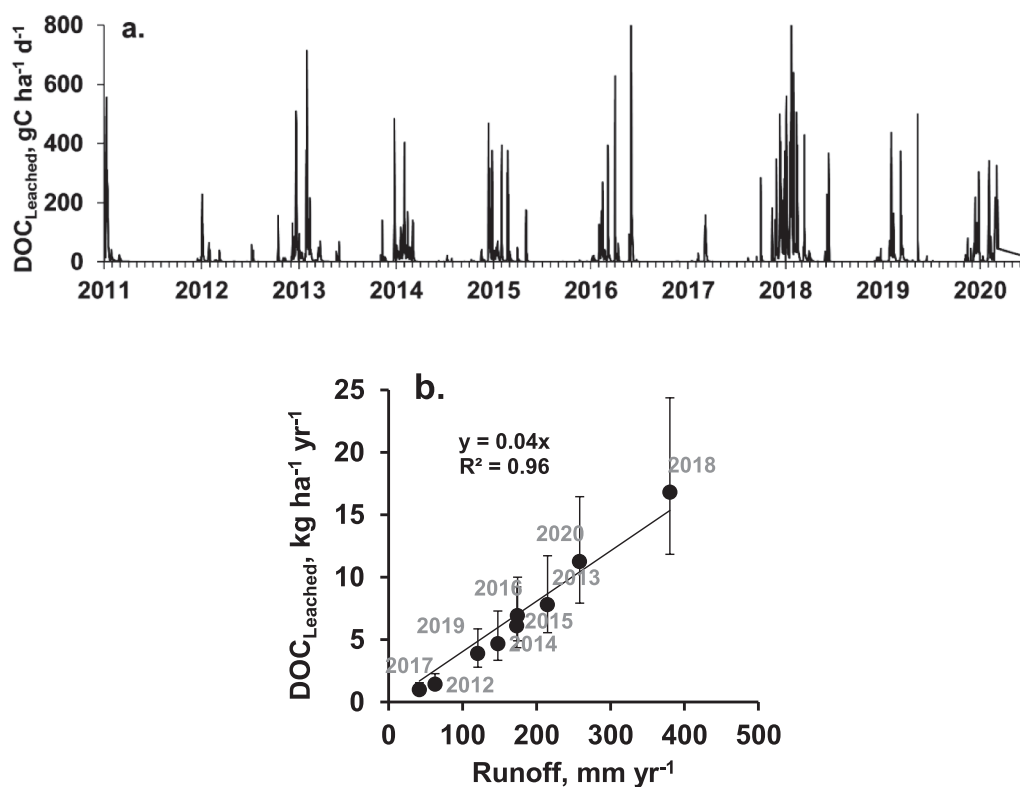
$$d\text{OC}_A / dt = f\text{OC}_{\text{AH}} - k_m * \text{OC}_A - (a_{\text{leach}} * \text{runoff}) * \text{OC}_A \quad (3)$$

where active humified carbon inputs ( $f\text{OC}_{\text{AH}}$ ) represent the average yearly inputs ( $\text{tonC ha}^{-1} \text{ yr}^{-1}$ ) depending on agricultural practices, and  $k_m$  ( $\text{yr}^{-1}$ ) the mineralization constant depending on soil-pedoclimatic conditions.

From equation (3), an equilibrium value of  $\text{OC}_A$  ( $\text{eqOC}_A$ ) can be derived, representing the value of  $\text{OC}_A$  that would be reached in the long term under constant farming practices (i.e., constant  $f\text{OC}_{\text{AH}}$ ) and constant hydrological conditions (i.e., constant annual runoff):

$$\text{eqOC}_A = f\text{OC}_{\text{AH}} / (k_m + a_{\text{leach}} * \text{runoff}) \quad (4)$$

The calculation shows that, compared with a hypothetical situation with no leaching, the effect of runoff on the equilibrium stock of  $\text{OC}_A$  is rather low. At the average values of runoff observed during the 2011–2020 period in the giant lysimeter ( $175 \text{ mm yr}^{-1}$ ), the equilibrium stock is decreased by only 1% compared with a situation with no

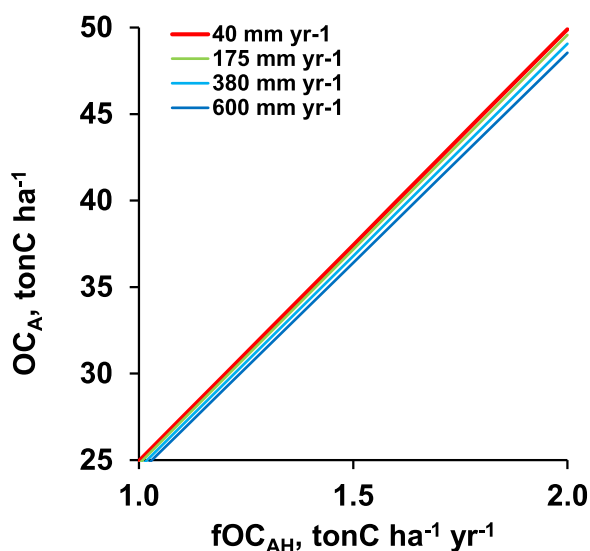


**Fig. 5.** a. Calculated daily variations of the leached flux of dissolved organic carbon ( $DOC_{leached}$ ) for the 2011–2020 period. b. Total annual export of dissolved organic carbon according to total water subsurface runoff for the 9 hydrological years.

leaching. A further 1% and 2% decrease can be expected, respectively, at higher runoff such as  $380 \text{ mm yr}^{-1}$  observed during 2017–2018 and  $600 \text{ mm yr}^{-1}$  possibly reached in very wet years (Fig. 6).

### 3.4. Net storage or loss of soil organic carbon in cropland soils

The concept of the equilibrium of active OC in soil ( $eqOC_A$ ) defined in the previous section can be used to determine whether the organic



**Fig. 6.** Relationship between the stock of active organic carbon ( $OC_A$ ) and the flux of active humified carbon ( $fOC_{AH}$ ) for different annual values of subsurface runoff (minimum  $40 \text{ mm yr}^{-1}$  during 2016–2017; maximum  $380 \text{ mm yr}^{-1}$  during 2017–2018; mean  $175 \text{ mm yr}^{-1}$  for the 2011–2020 period; a hypothetical extreme value of  $600 \text{ mm yr}^{-1}$ ).

matter pool of a given agricultural plot, for which the  $OC_A$  value has been determined using the RE method, is currently increasing or decreasing, considering its current agricultural practices and hydrological conditions. The idea is simply to compare the  $OC_A$  value measured with its equilibrium value on the way to being reached, calculated from equation (4).

The mineralization constant  $k_m$  was calculated using equation (1) from the AMG model according to the pedological characteristics of the soils (Table 1). It varied from  $0.031$  to  $0.058 \text{ yr}^{-1}$  for the 52 farm plots and averaged  $0.042 \pm 0.07 \text{ yr}^{-1}$ . The average runoff values obtained from the last 10 years (2011–2020) of hydrological records (<https://www.ecologie.gouv.fr/banque-hydro>) varied from  $150$  to  $320 \text{ mm yr}^{-1}$ , and were used for the various locations of the plots in the Seine Basin.

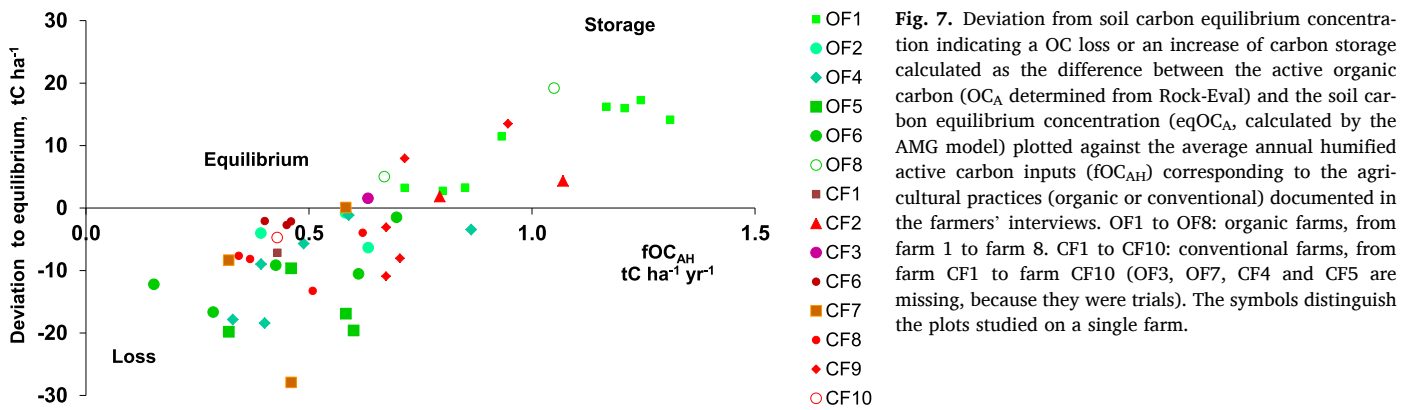
For each plot, the equilibrium active organic carbon ( $eqOC_A$ ) was calculated and compared with the actual  $OC_A$  value measured with the RE method. If  $OC_A$  is lower than  $eqOC_A$ , this indicates that the soil is experiencing a phase of storing carbon; otherwise, the soil is likely in a process of OC loss (Fig. 7). At the farm level, the different plots investigated in a given farm most often were all storing (e.g., OF1, CF2) or losing carbon (e.g., OF5, CF7), but occasionally some plots in the same farm were losing carbon while others were storing carbon. The results showed no systematic difference in this regard between OF and CF farms (Fig. 7, and see Table 2 SM).

## 4. Discussion

### 4.1. The Rock–Eval method for quantifying the two major carbon pools in soils

A large (30–70%) proportion of OC in soils is not expected to be mineralized at the centennial timescale (i.e., stable at a secular or multidecadal scale) (e.g., Balesdent et al., 1987; Barré et al., 2010). Until recently, no analytical method was able to quantify this pool, a step





currently done using default values provided by Clivot et al. (2017, 2019) or the difference between the measured total OC values and the active OC modeled values (Nemo et al., 2016; Le Noë et al., 2019).

Recent studies have evidenced that the RE method can be used to determine the stable carbon pool in temperate soils (Cécillon et al., 2018; Cécillon et al., 2021) and here we used this pool to characterize the AMG model. Other pool-compartment models at a small scale (Roth-C: Coleman et al., 1997; JULES, based on Roth-C: Nakhavali et al., 2018; Century: Parton, 1996) and even at the global scale (Davidson et al., 2014; Luo et al., 2016) could similarly benefit from the determination of this stable carbon pool. The distinction of an active and stable pool of OC is indeed crucial for evaluating carbon dynamics in soils. Here, the RE method (see Cécillon et al., 2018; Cécillon et al., 2021) again appeared to be an efficient and rapid tool for directly determining these two stable and active carbon pools characterizing the 52 agricultural soils, and for running the AMG model. In addition, RE can evaluate the total OC with a difference of about 10% or less (9%: Disnar et al., 2003; 6%: Behar et al., 2001).

#### 4.2. Carbon storage and loss in cropped soils: Organic vs. Conventional farming systems

In this survey of 52 plots in the Seine Basin, whereas the flux of active humified OC to soils ( $fOC_{AH}$ ) did not systematically differ between organic and conventional farming (OF and CF respectively), carbon loss and sequestration appear to indifferently occur for both CF and OF plots, contrary to the view that OF would increase carbon in soils owing to a higher occurrence of legumes in crop rotations (Gregorich et al., 2001; Gattinger et al., 2012; Autret et al., 2016; Veloso et al., 2018). In fact, the dynamics of the soil OC pool primarily depends on the intensity of above- and underground crop residues inputs, which is largely dependent on the production intensity of the cropping system. In general, OF systems are less intensive than CF systems in the same pedoclimatic context (approximately 30% lower total N fertilization and yield, Benoit et al., 2016). There are, however, quite intensive OF systems, providing high active humified carbon inputs ( $fOC_{AH}$ ), leading to high carbon storage (e.g., OF1, see Fig. 7 and Table 2 SM), in clear contrast to extensive OF systems with no external N inputs, which lose OC (e.g., OF6, see Fig. 7 and Table 3 SM). In CF systems, soil OC storage is often associated with solid manure inputs, as shown by the example of CF9, the plots of which either store or lose OC according to the input of solid manure (see Table 3 SM). Fertilization with mineral fertilizers, or by C-poor methanizer digestate (CF6), do not by themselves enhance soil OC storage.

Although storage or loss of soil carbon depends on current practices, it also depends on the legacy of previous land use. For example, a

cultivated plot settled on plowed previous grassland might show losses for more than a decade (Guo and Gifford, 2002). This might well be the case for plots (cf. Fig. 7; Fig. 1 SM) located in the Orgeval watershed where pasture and milk production for Brie cheese were traditional; only after drains were installed in these clayey soils were wet pastures converted into arable cereal croplands (Garnier et al., 2016).

We analyzed the 0- to 30-cm horizon, but several studies have demonstrated complex interactions for subsoils, between the root system and carbon dynamics (Hobley et al., 2018), especially in the context of global warming (Jia et al., 2019). In contrast to other studies mostly considering only top soils as reactive (e.g., Blanco-Canqui et al., 2017), Nakhavali et al. (2018) implemented a soil profile over 3 m in the JULES model, while Hobley et al. (2018) reported a gain in carbon over a 1-m soil depth. We sampled ten soils for three horizons (0–30 cm, 30–60 cm, and 60–90 cm) for which  $OC_A$  in the top layer (0–30 cm) accounted for 61% of the total  $OC_A$  (0–90 cm) (data not shown): this result indicates an underestimation of OC loss by approximately 40 %, arguing in favor of considering carbon in subsoils, in agreement with Sheng et al. (2015 and references herein).

In the cropland soils investigated herein, the relative yearly increase (or decrease) in OC can be calculated as the difference between inputs ( $fOC_{AH}$ ) and losses ( $k_m \cdot OC_A + \text{leaching}$ ). Dividing this increase rate by the current size of the total OC pool provides a relative annual rate of storage (or loss if negative). The results of the present study show an average relative rate of  $-0.24\% \text{ yr}^{-1}$  (ranging from  $-2.7\% \text{ yr}^{-1}$  to  $+2.3\% \text{ yr}^{-1}$  depending on the agricultural plots). Increasing the carbon storage rate in agricultural soils to the level of the recommended  $0.4\% \text{ yr}^{-1}$  (4 per mil initiative) would thus require huge efforts in increasing crop residue input, the establishment of intermediate crops, the introduction of temporary grassland within crop rotations, etc. (see Lal, 2016; Pellerin and Bamière, 2019).

#### 4.3. Subsurface runoff and DOC leaching

The relationship between measured DOC concentrations and runoff, similar to that reported by Fabre et al. (2019) and Wen et al. (2020) from various rivers, led to a daily carbon leached value varying along with water runoff, with maximum values up to  $0.7\text{--}0.8 \text{ kg C ha}^{-1} \text{ d}^{-1}$  during the wettest days. Therefore, meteorological conditions strongly influenced the timing of DOC leaching and its yearly load, the lowest in 2012 down to  $1.4 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  and the highest in 2018, up to  $16.8 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  ( $6.7 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  on average). These values were lower than the range reported for crops in southwestern Michigan (USA) and in the Midwestern Big Pine Creek watershed (Indiana, USA), i.e.,  $15.4 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  (Hussain et al., 2020) and  $14\text{--}19 \text{ kg C ha}^{-1} \text{ yr}^{-1}$  (Datzell et al., 2007), two sites with similar temperatures to those in the area studied,

but with 20–40% higher precipitation (i.e., ~900–1200 mm yr<sup>-1</sup> vs. 727 mm yr<sup>-1</sup> for our site). They were also much lower than for agricultural land in Finland (20–50 kg C ha<sup>-1</sup> yr<sup>-1</sup> for precipitation ranging from 533 to 740 mm yr<sup>-1</sup>, with lower temperatures (Manninen et al., 2018)), and for untilled and superficially tilled cropping systems of the Arlington Research Station (Wisconsin, USA) (8.4 and 13.3 kg C ha<sup>-1</sup> yr<sup>-1</sup>, Brye et al., 2001) where precipitation amounted to approximately 800 mm.

Regarding the biodegradable fraction of leached DOC, the 11.5% BDOC found in the drained water in the current study was on the same order as the figures reported for different land uses (6%, Autio et al., 2016; 8.7%, Manninen et al., 2018), independent of DOC variations and the sampling period. This BDOC fraction was twofold lower than in the sub-root water (22.8%), corresponding to a concentration in BDOC of 0.5 mg C L<sup>-1</sup> lower. This tends to show further degradation during the water transport from the sub-root areas to the outlet of the giant lysimeter. As reported by Autio et al. (2016) and Manninen et al. (2018), more studies are needed to classify the various factors that might control the biodegradability of DOC (type of soil and vegetation, hydrology, and agricultural practices). Overall, in the intensively cropped agriculture area in our study, where all the soils investigated have rather similar clayey silt characteristics and are located in a homogeneous temperate climatic zone, DOC export is relatively low.

#### 4.4. DOC leaching and effect on soils carbon stock

At the scale of rainfall events, our observations confirmed that intense drainage events result in an increasing DOC concentration in runoff water, enhancing total DOC leaching from agricultural soils, as already reported by several authors (Hinton et al., 1997; Royer et al., 2007; Dalzell et al., 2007; Andrews et al., 2011; Van Gaelen et al., 2014).

For higher runoffs, such as the 380 mm yr<sup>-1</sup> observed during 2017–2018 and 600 mm yr<sup>-1</sup> possibly reached in very wet years, an OC<sub>A</sub> stock decreasing by 1% and 2% was observed (see Fig. 6). Further, we can calculate a corresponding carbon loss rate, to be compared with the current rate modeled (–0.24 % yr<sup>-1</sup>). The losses would be increased by 7% and by 15% for 380 mm yr<sup>-1</sup> and 600 mm yr<sup>-1</sup>, respectively (i.e., a loss rate of, respectively, –0.26% yr<sup>-1</sup> and –0.28% yr<sup>-1</sup>). These calculations show that even new agricultural practices or management measures devoted to enhancing OC storage in soils may be unsuccessful due to the feedback effects of climate change and their interannual variations (Le Quéré et al., 2018; Sleeter et al., 2019).

In spite of this effect of the rainfall regime, a linear relationship between DOC export and total annual runoff is observed at the annual scale. This allowed us to define a weighted mean DOC leaching concentration, which is the same at low and high runoff (see Fig. 5b). The model assumed that this DOC export concentration was linearly related to the watershed soil OC stock, or more specifically to its active fraction (eq. (3); see previous section). This is consistent with the observations reported by Aitkenhead et al. (1999) that the total OC stock in soils is the single most important determinant of the amount of DOC exported from a watershed. Aitkenhead and McDowell (2000) even showed that the mean soil C/N ratio, a good proxy for soils OC degradability, would account for 99% of the variance in annual riverine DOC flux among biomes.

Examining the studies in the literature reporting annual fluxes of DOC leaching together with OC content in the watershed soils, we were able to quantitatively validate the assumption and the calibrated value used for the  $\alpha_{\text{leach}}$  factor (Fig. 8), even if the DOC concentrations seem to level off somewhat at a very high soil OC stock. Note that the studies gathered in Fig. 8 excluded those concerning watersheds with high peatland coverage, such as those reported by Aitkenhead et al. (1999), which have a much greater organic matter stock and behave differently (Autio et al., 2016).

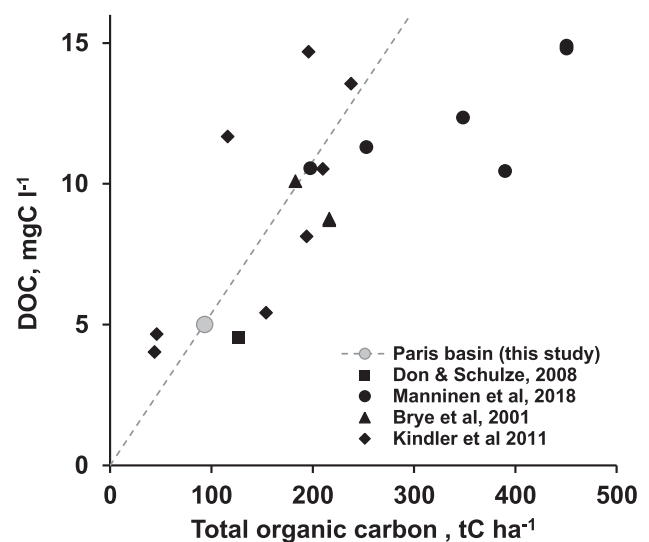


Fig. 8. Relationship between DOC concentrations (flow-weighted leaching) and total soil organic carbon stocks reported in the literature for agricultural and forested watersheds (excluding peat-rich sites). The dashed gray line is equivalent to Eq. (2), assuming an active fraction of 40% of the total soil organic carbon stock.

## 5. Conclusions

The RE approach was used in this study not only to quantify organic carbon (OC) in soils but also to distinguish the OC fractions of both centennially stable (OC<sub>S</sub>) and active (OC<sub>A</sub>) OC for 52 cropped plots in the rich deep loamy agricultural soils of the Seine Basin. Interestingly, we found no significant difference in the soil OC pool or humified C input to soils between organic and conventional cropping systems.

Using the AMG model upgraded with a leaching term, we developed the concept of a long-term equilibrium value, eqOC<sub>A</sub>, from which the deviation of actually measured OC<sub>A</sub> indicates whether the soil is losing or storing OC. Although soil OC storage is assessed in 15 of the 52 plots investigated, the average trend is a loss of soil OC at a rate of –0.24% yr<sup>-1</sup>. The loss of carbon by leaching is rather low in this agricultural temperate clayey silt soil, but could be enhanced at higher runoff.

### CRedit authorship contribution statement

**Josette Garnier:** Conceptualization, Methodology, Field coordination, AMG model extension, Writing – Original draft preparation, Project administration. **Gilles Billen:** Conceptualization, Methodology, AMG model extension, Reviewing - Writing. **Julien Tournebize:** Field Investigations, Methodology, Review & editing. **Bruno Mary:** AMG Software, Review & editing. **Pierre Barré and François Baudin:** Laboratory investigations, Review & editing.

### 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.

### Acknowledgments

This study was partially funded by the EC2CO CNRS program in the interdisciplinary framework offered by the FIRE-FR3020 research federation. The work was also supported by the PIREN-Seine program and ABAC project. We grateful to Anun Martinez, Benjamin Mercier, Cédric Chaumont, Florence Savignac, and Sophie Mery de Bellegarde for their kind and valuable contribution in the field and/or in the lab. We

are also grateful to Alexis Vanhaesebrouck who performed the statistical tests. Two anonymous reviewers are greatly acknowledged for their constructive remarks on the manuscript.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2021.115538>.

## References

- Aitkenhead, J.A., McDowell, W.H., 2000. Soil C: N ratio as a predictor of annual riverine DOC flux at local and global scales. *Glob Biogeochem. Cycles* 14, 127–138.
- Aitkenhead, J.A., Hope, D., Billett, M.F., 1999. The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. *Hydrol. Processes* 1 (3), 1289–1302.
- Andrews, D.M., Lin, H., Zhu, Q., Jin, L., Brantley, S.L., 2011. Hot spots and hot moments of dissolved organic carbon export and soil organic carbon storage in the Shale Hills Catchment. *Vadose Zone J.* 10, 943–954.
- Arlot, M.P., 1999. Nitrates dans les eaux, Drainage acteur, drainage témoin ?, Thèse de l'Université Paris VI, Géologie appliquée, spécialité "Hydrologie, hydrogéologie, géostatistiques et géochimie des eaux", 374 pp.
- Autio, I., Soine, H., Helin, J., Asmala, E., Hoikkala, L., 2016. Effect of catchment land use and soil type on bacterial degradation of riverine dissolved organic matter. *Ambio* 45 (3), 331–349.
- Autret, B., Mary, B., Chenu, C., Balabane, M., Girardin, C., Bertrand, M., Grandeau, G., Beaudoin, N., 2016. Alternative arable cropping systems: a key to increase soil organic carbon storage? results from a 16 year field experiment. *Agric Environ.* 232, 150–164. <https://doi.org/10.1016/j.agee.2016.07.008>.
- Balesdent, J., Mariotti, A., Guillet, B., 1987. Natural <sup>13</sup>C abundance as a tracer for studies of soil organic matter dynamics. *Soil Biol. Biochem.* 19 (1), 25–30.
- Barré, P., Eglin, T., Christensen, B.T., Ciais, P., Houot, S., Kätterer, T., Chenu, C., 2010. Quantifying and isolating stable soil organic carbon using long-term bare fallow experiments. *Biogeosciences* 7 (11), 3839–3850. <https://doi.org/10.5194/bg-7-3839-2010>.
- Battin, T.J., Kaplan, L., Findlay, S., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, J. D., Sabater, F., 2009. Biophysical controls on organic carbon fluxes in fluvial networks. *Nat. Geosci.* 2, 595. <https://doi.org/10.1038/ngeo602>.
- Baudin, F., Disnar, J.R., Aboussou, A., Savignac, F., 2015. Guidelines for Rock-Eval analysis of recent marine sediments. *Org. Geochem.* 86, 71–80.
- Beaudoin, N., Tournèze, J., Ruiz, L., Constantin, J., Justes E., 2012. Réduire les fuites de nitrate au moyen de cultures intermédiaires – Chapitre 4.
- Behar, F., Beaumont, V., De B. Penteado, H.L., 2001. Rock-Eval 6 technology: performances and developments. *Oil and Gas Science and Technology. Revue Institut Français Pétrole* 56, 111–134. <https://doi.org/10.2516/ogst:2001013>.
- Bellamy, P.H., Loveland, P.J., Bradley, I.R., Lark, R.M., Kirk, G.J.D., 2005. Carbon losses from all soils across England and Wales 1978–2003. *Nature* 437, 245–248.
- Benoit, M., Garnier, J., Anglade, J., Billen, G., 2014. Nitrate leaching from organic and conventional arable crop farms in the Seine Basin (France). *Nutrient Cycling in Agroecosystems. Nutr Cycl Agroecosyst* DOI 10.1007/s10705-014-9650-9.
- Benoit, M., Garnier, J., Beaudoin, N., Billen, G., 2016. A network of organic and conventional crop farms in the Seine Basin (France) for evaluating environmental performance: yield and nitrate leaching. *Agric. Syst.* 148, 105–113. <https://doi.org/10.1016/j.agsy.2016.07.005>.
- Blanco-Canqui, H., Wienhold, B.J., Jin, V.L., Schmer, M.R., Kibet, L.C., 2017. Long-term tillage impact on soil hydraulic properties. *Soil Tillage Res.* 170, 38–42. <https://doi.org/10.1016/j.still.2017.03.001>.
- Bouthier, A., Duparque, A., Mary, B., Sagot, S., Trochard, R., Levert, M., Houot, S., Damay, N., Denoroy, P., Dinh, J.-L., Blin, B., Ganteil, F., 2014. Adaptation et mise en œuvre du modèle de calcul de bilan humique à long terme AMG dans une large gamme de systèmes de grandes cultures et de polyculture-élevage. *Innovations Agronomiques* 34, 125–139.
- Brye, K.R., Norman, J.M., Bundy, L.G., Gower, S.T., 2001. Nitrogen and carbon leaching in agroecosystems and their role in denitrification potential. *J. Environ. Qual.* 30 (5), 8–70.
- Caddeo, A., Marras, S., Sallustio, L., Spano, D., Sirca, C., 2019. Soil organic carbon in Italian forests and agroecosystems: estimating current stock and future changes with a spatial modelling approach. *Agric. For. Meteorol.* 278, 107654 <https://doi.org/10.1016/j.agrformet.2019.107654>.
- Cécillon, L., Baudin, F., Chenu, C., Houot, S., Jolivet, R., Kätterer, T., Barré, P., 2018. A model based on Rock-Eval thermal analysis to quantify the size of the centennially persistent organic carbon pool in temperate soils. *Biogeosciences* 15 (9), 2835–2849. <https://doi.org/10.5194/bg-15-2835-2018>.
- Cécillon, L., Baudin, F., Chenu, C., Christensen, B.T., Franko, U., Houot, S., Kanari, E., Kätterer, T., Merbach, I., van Oort, F., Poeplau, C., Quezada, J.C., Savignac F., Soucérianadin, L.N., Barré, P., 2021. Partitioning soil organic carbon into its centennially stable and active fractions with statistical models based on Rock-Eval® thermal analysis (PARTYSOCv2.0 and PARTYSOCv2.0EU). *Geoscientific Model Development* <https://doi.org/10.5194/gmd-2021-16>.
- Chahal, I., Van Eerd, L.L., 2020. Cover crop and crop residue removal effects on temporal dynamics of soil carbon and nitrogen in a temperate, humid climate. *PLoS ONE* 15 (7), e0235665. <https://doi.org/10.1371/journal.pone.0235665>.
- Chaplot, V., Cooper, M., 2015. Soil aggregate stability to predict organic carbon outputs from soils. *Geoderma* 243–244, 205–213. <https://doi.org/10.1016/j.geoderma.2014.12.013>.
- Chaplot, V., Darboux, F., Alexis, M., Cottenot, L., Gaillard, H., Quenea, K., Mutema, M., 2019. Soil tillage impact on the relative contribution of dissolved, particulate and gaseous (CO<sub>2</sub>) carbon losses during rainstorms. *Soil Tillage Res.* 187, 31–40. <https://doi.org/10.1016/j.still.2018.11.010>.
- Clivot, H., Mary, B., Valé, M., Cohan, J.P., Champolivier, L., Piroux, F., Laurent, F., Justes, E., 2017. Quantifying in situ and modeling net nitrogen mineralization from soil organic matter in arable cropping systems. *Soil Biol. Biochem.* 111, 44–59. <https://doi.org/10.1016/j.soilbio.2017.03.010>.
- Clivot, H., Mouny, J.-C., Duparque, A., Dinh, J.-L., Denoroy, P., Houot, S., Vertes, F., Trochard, R., Bouthier, A., Sagot, S., Mary, B., 2019. Modeling soil organic carbon evolution in long-term arable experiments with AMG model. *Environ. Modell. Software* 118, 99–113. <https://doi.org/10.1016/j.envsoft.2019.04.004>.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J., 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10, 172–185.
- Coleman, K., Jenkinson, D.S., Crocker, G.J., Graced, P.R., Klir, J., Körschens, M.K., Poulton, P.R., Richter, D.D., 1997. Simulating trends in soil organic carbon in long-term experiments using RothC-26.3. *Geoderma* 81, 29–44.
- Dalzell, B.J., Filley, T.R., Harbor, J.M., 2007. The role of hydrology in annual organic carbon loads and terrestrial organic matter export from a midwestern agricultural watershed. *Geochimica Cosmochimica Acta* 71, 1448–1462.
- Davidson, E.A., Savage, K.E., Finzi, A.C., 2014. A big-microsite framework for soil carbon modeling. *Global Change Biol.* 20, 3610–3620.
- Disnar, J.R., Guillet, B., Keravus, D., Di-Giovanni, C., Sebag, D., 2003. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations. *Org. Geochem.* 34, 327–343.
- Fabre, C., Sauvage, S., Tananaev, N., Noël, G.E., Teisserenc, R., Probst, J.L., Sánchez-Pérez, J.M., 2019. Assessment of sediment and organic carbon exports into the Arctic ocean: the case of the Yenisei River basin. *Water Res.* 158, 118–135. <https://doi.org/10.1016/j.watres.2019.04.018>.
- Friedlingstein, P., Matthews, J.W., O'Sullivan, M., et al., 2020. Global carbon budget 2020. *Earth Syst. Sci. Data* 12, 3269–3340. <https://doi.org/10.5194/essd-12-3269-2020>.
- Garnier, J., Billen, G., 2007. Production vs. respiration in river systems: an indicator of a "good ecological status" evaluation. *Sci. Total Environ.* 375, 110–124.
- Garnier, J., Anglade, J., Benoit, M., Billen, G., Puech, T., Ramarson, A., Passy, P., Silvestre, M., Lassaletta, L., Trommenschlager, J.-M., Schott, C., Tallec, G., 2016. Reconnecting crop and cattle farming to reduce nitrogen losses in river water of an intensive agricultural catchment (Seine basin, France). *Environ. Sci. Policy* 63, 76–90. <https://doi.org/10.1016/j.envsci.2016.04.019>.
- Gettinger, A., Müller, A., Haeni, M., Skinner, C., Fliesbach, A., Buchmann, N., Mäder, P., Stolze, M., Smith, P., El-Hage Scialabba, N., Niggli, U., 2012. Enhanced top soil carbon stocks under organic farming. *Proc. Natl. Acad. Sci. U. S. A.* 109, 44.
- Ghyoot, C., Lancelot, C., Flynn, K.J., Mitra, A., Gypens, N., 2017. Introducing mixotrophy into a biogeochemical model describing an eutrophied coastal ecosystem: The Southern North Sea. *Progress in Oceanography* 157, 1–11. [dx.doi.org/10.1016/j.pocean.2017.08.002](https://doi.org/10.1016/j.pocean.2017.08.002).
- Glibert, P.M., 2017. Eutrophication, harmful algae and biodiversity — Challenging paradigms in a world of complex nutrient changes. *Marine Pollution Bulletin* 124, 591–606. [dx.doi.org/10.1016/j.marpolbul.2017.04.027](https://doi.org/10.1016/j.marpolbul.2017.04.027).
- Gregorich, E.G., Drury, C.F., Baldock, J.A., 2001. Changes in soil carbon under long-term maize in monoculture and legume-based rotation. *Can. J. Soil Sci.* 81, 21–31.
- Guerrini, M.-C., Mouchel, J.-M., Meybeck, M., Penven, M. J., Hubert, G., Muxart, T., 1998. Le bassin de la Seine: la confrontation du rural et de l'urbain, in La Seine en son bassin, in: Fonctionnement écologique d'un système fluvial anthropisé, edited by: Meybeck, M., de Marsily, G., and Fustec, E., Elsevier, Paris, Amsterdam, Lausanne, 29–73.
- Guo, L.B., Gifford, R.M., 2002. Soil carbon stocks and land use change: a meta analysis. *Glob. Chang. Biol.* 8, 345–360.
- Heikkinen, J., Ketoja, E., Nuutinen, V., Regina, K., 2013. Declining trend of carbon in Finnish cropland soils in 1974–2009. *Glob. Chang. Biol.* 19, 1456–1469.
- Hinton, M.J., Schiff, S.L., English, M.C., 1997. The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry* 36, 67–88.
- Hobley, E.U., Honermeier, B., Don, A., Gocke, M.I., Amelung, W., Kögel-Knabner, I., 2018. Decoupling of subsoil carbon and nitrogen dynamics after long-term crop rotation and fertilization. *Agric. Ecosyst. Environ.* 265, 363–373. <https://doi.org/10.1016/j.agee.2018.06.021>.
- Hope, D., Billett, M.F., Cresser, M.S., 1994. A review of the export of carbon in river water: Fluxes and processes. *Environ. Pollut.* 84, 301–324.
- Hussain, M.Z., Robertson, G.P., Basso, B., Hamilton, S.K., 2020. Leaching losses of dissolved organic carbon and nitrogen from agricultural soils in the upper US Midwest. *Sci. Total Environ.* 734, 139379 <https://doi.org/10.1016/j.scitotenv.2020.139379>.
- IPCC, 2014. Climate Change 2014: Synthesis Report. In: The Core Writing Team, Pachauri, R.K., Meyer, L.A. (Eds.), Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland, pp. 1–151. <https://ar5-syr.ipcc.ch/>.
- Jia, J., Cao, Z., Liu, C., Zhang, Z., Lin, L., Wang, Y., Haghpor, N., Wacker, L., Bao, H., Dittmar, T., Simpson, M.J., Yang, H., Crowther, T.W., Eglinton, T.I., He, J.-S., Feng, X., 2019. Climate warming alters subsoil but not topsoil carbon dynamics in alpine grassland. *Glob. Change Biol.* <https://doi.org/10.1111/gcb.14823>.

- Kanari, Eva, Cécillon, L., Baudin, F., Clivot, H., Ferchaud, F., Houot, S., Levasseur, F., Mary, B., Soucémariadin, L., Chenu, C., Barré, P., 2021. A robust initialization method for accurate soil organic carbon simulations. *Biogeosci. Discuss.* <https://doi.org/10.5194/bg-2021-246>. Submitted for publication.
- Kladivko, E.J., Brown, L.C., Baker, J.L., 2001. Pesticide transport to subsurface tile drains in humid regions of North America. *Crit. Rev. Environ. Sci. Technol.* 31, 1–62. <https://doi.org/10.1080/20016491089163>.
- Lal, R., 2004. Soil carbon sequestration impacts on global climate change and food security. *Science* 304, 1623–1627.
- Lal, R., 2016. Beyond COP21: potential and challenges of the “4 per thousand” initiative. *J. Soil Water Conserv.* 71 (1), 20A–25A. <https://doi.org/10.2489/jswc.71.1.20A>.
- Le Noë, J., Billen, G., Mary, B., Garnier, J., 2019. Assessing long-term soil organic carbon dynamics in cropland and identification of the main drivers of C sequestration: the case of French regions from 1852 to 2014. *J. Environ. Policy* 93, 53–65. <https://doi.org/10.1016/j.envsci.2018.12.027>.
- Le Quéré, C., Andrew, R.M., Friedlingstein, P., Sitch, S., Hauck, J., 2018. Global carbon budget 2018. *Earth Syst. Sci. Data* 10, 2141–2194. <https://doi.org/10.5194/essd-10-2141-2018>.
- Levasseur, F., Mary, B., Christensen, B.T., Duparque, A., Ferchaud, F., Kätterer, T., Lagrange, H., Montenach, D., Resseguier, C., Houot, S., 2020. The simple AMG model accurately simulates organic carbon storage in soils after repeated application of exogenous organic matter. *Nutr. Cycl. Agroecosyst.* 117, 215–229. <https://doi.org/10.1007/s10705-020-10065-x>.
- Luo, Y., Ahlström, A., Allison, S.D., Batjes, N.H., Brovkin, V., Carvalhais, N., Chappell, A., Ciais, P., Davidson, E.A., Finzi, A., Georgiou, K., Guenet, B., Zhou, T., 2016. Toward more realistic projections of soil carbon. *Dynamics by Earth system models. Global Biogeochem. Cy.* 30, 40–56. <https://doi.org/10.1002/2015GB005239>.
- Manninen, N., Soenne, H., Lemola, R., Hoikkala, L., Turtola, E., 2018. Effects of agricultural land use on dissolved organic carbon and nitrogen in surface runoff and subsurface drainage. *Sci. Total Environ.* 618, 1519–1528. <https://doi.org/10.1016/j.scitotenv.2017.09.319>.
- Marescaux, A., Thieu, V., Gypens, N., Silvestre, M., Garnier, J., 2020. Modeling the inorganic carbon dynamics in the Seine River continuum in France. *Hydrol. Earth Syst. Sci.* 24, 1–20. <https://doi.org/10.5194/hess-24-1-2020>.
- Martin, M., Dimassi, B., Millet, F., Picaut, C., Bounoua, E.-M., Bardy, M., Bispo, A., Boulonne, L., Bouthier, A., Duparque, A., Eglin, T., Guenet, B., Huard, F., Mary, B., Mathias, E., Mignolet, C., Robert, C., Saby, N., Sagot, S., Schott, C., Toutain, B., Trochard, R., 2019. Méthodes de comptabilisation du stockage de carbone organique des sols sous l'effet des pratiques culturales (CSopra). 70p. [www.ademe.fr/mediatheque](http://www.ademe.fr/mediatheque).
- Menichetti, L., Houot, S., van Oort, F., Kätterer, T., Christensen, B.T., Chenu, C., Barre, P., Vasilyeva, N.A., Ekblad, A., 2015. Increase in soil stable carbon isotope ratio relates to loss of organic carbon: results from five long-term bare fallow experiments. *Oecologia* 177, 811–821. <https://doi.org/10.1007/s00442-014-3114-4>.
- Meybeck, M., 1982. Carbon, Nitrogen, and phosphorus transport by world rivers. *Am. J. Sci.* 282, 401–450.
- Meybeck, M., Laroche, L., Dürr, H.H., Syvitski, J.P.M., 2003. Global variability of daily total suspended solids and their fluxes in rivers. *Global Planetary Change* 39, 65–93.
- Meybeck, M., 2009. Fluvial export. pp 118–130. In: *Biogeochemistry of Inland Waters: a derivative of Encyclopedia of inland waters*. Ed. E.G. Likens. Elsevier & Academic Press, ISBN 978-0-12-381996-3.
- Mignolet, C., Schott, C., Benoît, M., 2007. Spatial dynamics of farming practices in the Seine basin: methods for agronomic approaches on a regional scale. *Sci. Total Environ.* 375, 13–32.
- Nakhavali, M., Friedlingstein, P., Lauerwald, R., Tang, J., Chadburn, S., Camino-Serrano, M., Guenet, B., Harper, A., Walmsley, D., Peichl, M., Gielen, B., 2018. Representation of dissolved organic carbon in the JULES land surface model (vn4.4. JULES-DOCM). *Geosci. Model Dev.* 11, 593–609. <https://doi.org/10.5194/gmd-11-593-2018>.
- Nemo, Klumpp, K., Coleman, K., Dondini, M., Goulding, K., Hasting, A., ... Smith, P., 2016. Soil Organic Carbon (SOC) Equilibrium and Model Initialisation Methods: an Application to the Rothamsted Carbon (RothC) Model. *Environmental Modeling and Assessment*, 22(3), 215–229. <https://doi.org/10.1007/s10666-016-9536-0>.
- Nicolardot, B., Recous, S., Mary, B., 2001. Simulation of C and N mineralisation during crop residue decomposition: A simple dynamic model based on the C: N ratio of the residues. *Plant Soil* 228, 83–103.
- Parton, W. J., 1996. The CENTURY Model. In: Powlson D.S., Smith P., Smith J.U. (eds) *Evaluation of Soil Organic Matter Models. NATO ASI Series (Series I: Global Environmental Change) (Vol. 38, pp. 283–291)*. Springer Berlin, Heidelberg.
- Pellerin, S., Bamière, L. (Coord.), 2019. Stocker du carbone dans les sols français, Quel potentiel au regard de l'objectif 4 pour 1000 et à quel coût ? Synthèse du rapport d'étude, INRAE, (France), 114 p.
- Riggers, C., Poeplau, C., Don, A., Bamminger, C., Hoper, H., Dechow, R., 2019. Multi-model ensemble improved the prediction of trends in soil organic carbon stocks in German croplands. *Geoderma* 345, 17–30. <https://doi.org/10.1016/j.geoderma.2019.03.014>.
- RMQS, 2000-2020. Réseau de Mesure de la Qualité des Sols/Network of Measurements and Quality of Soil, implemented by INRAE. [www.gissol.fr/tag/rmqqs](http://www.gissol.fr/tag/rmqqs).
- Royer, I., Angers, D.A., Chantigny, M.H., Simard, R.R., Cluis, D., 2007. Dissolved organic carbon in runoff and tile-drain water under corn and forage fertilized with hog manure. *J. Environ. Qual.* 36, 855–863.
- Servais, P., Barillier, A., Garnier, J., 1995. Determination of the biodegradable fraction of dissolved and particulate organic carbon. *Annls Limnol.* 31, 75–80.
- Sheng, H., Zhou, P., Zhang, Y., Kuzyakov, Y., Zhou, Q., Ge, T., Wang, C., 2015. Loss of labile organic carbon from subsoil due to land-use changes in subtropical China. *Soil Biol. Biochem.* 88, 148–157. <https://doi.org/10.1016/j.soilbio.2015.05.015>.
- Sinsabaugh, R.L., Findlay, S., 2003. Dissolved organic matter: Out of the black box into the mainstream. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), *Aquatic ecosystems: Interactivity of dissolved organic matter*, pp. 479–498.
- Sleeter, B.M., Marvin, D.C., Cameron, D.R., Selman, P.C., LeRoy, Westerling, A., Kreitler, J., Daniel, C.J., Liu, J., Wilson, T.S., 2019. Effects of 21st-century climate, land use, and disturbances on ecosystem carbon balance in California Glob Change Biol. 2019, 00:1–20. DOI: 10.1111/gcb.14677.
- Strohmeier, S., Knorr, K.-H., Reichert, M., Frei, S., Fleckenstein, J.H., Peiffer, S., Matzner, E., 2013. Concentrations and fluxes of dissolved organic carbon in runoff from a forested catchment: insights from high frequency measurements. *Biogeosciences* 10, 905–916.
- Tournebize, J., Chaumont, C., Marcon, A., Molina, S., Bethault D., 2015. Guide technique à l'implantation des zones tampons humides artificielles (ZTHA) pour réduire les transferts de nitrates et de pesticides dans les eaux de drainage (Version 3). Rapport Final pour la Direction Départementale des Territoires de Seine et Marne. 60pp.
- Van Gaelen, N., Verschoren, V., Clymans, W., Poesen, J., Govers, G., Vanderborght, J., Diels, J., 2014. Controls on dissolved organic carbon export through surface runoff from loamy agricultural soils. *Geoderma* 226–227, 387–396. <https://doi.org/10.1016/j.geoderma.2014.03.018>.
- Veloso, M.G., Angers, D.A., Tiecher, T., Giacomini, S., Dieckow, J., Bayer, C., 2018. High carbon storage in a previously degraded subtropical soil under no tillage with legume cover crops. *Agric. Ecosyst. Environ.* 268, 15–23.
- Wagner, L.E., Vidon, P., Tedesco, L.P., Gray, M., 2008. Stream nitrate and DOC dynamics during three spring storms across land uses in glaciated landscapes of the Midwest. *J. Hydrol.* 362, 177–190.
- Wen, H., Perdrial, J., Abbott, B.W., Bernal, S., Dupas, R., Godsey, S.E., Harpold, A., Rizzo, D., Underwood, K., Adler, T., Sterle, G., Li, L., 2020. Temperature controls production but hydrology regulates export of dissolved organic carbon at the catchment scale. *Hydrol. Earth Syst. Sci.* 24, 945–966. <https://doi.org/10.5194/hess-24-945-2020>.