Geogenic organic carbon in terrestrial sediments and its contribution to total soil carbon

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Abstract

Geogenic organic carbon (GOC) from sedimentary rocks is an overlooked fraction in soils that has not been quantified yet, influencing the composition, age and stability of total organic carbon (OC) in soils. In this context GOC is referred to as the OC in bedrocks deposited during sedimentation. However, the contribution of GOC to total soil OC varies with the type of bedrock. So far studies investigating the contribution of GOC derived from different terrestrial sedimentary rocks to soil OC contents are missing.

In order to fill this gap, we analysed 10 m long sediment cores at three sites recovered from Pleistocene Loess, Miocene Sand and Triassic Red Sandstone and calculated the amount of GOC based on ^{14}C measurements. ^{14}C ages of bulk sedimentary OC revealed that OC represents a mixture of biogenic and geogenic components. Biogenic refers to OC that entered the sediments recently from plant sources. All sediments contain considerable amounts of GOC (median amounts of 0.10 g kg^{-1} at the Miocene Sand, 0.27 g kg^{-1} at the Pleistocene Loess and 0.17 at Red Sandstone) in comparison to subsoil OC contents (between 0.53-15.21 g kg^{-1}). Long-term incubation experiments revealed that this GOC seemed to be comparatively stable against biodegradation. Its possible contribution to subsoil OC stocks (0.3-1.5 m depth) is ~ 2.5 % in soil developed in the Miocene Sand, ~ 8 % in the Loess soil and ~ 12 % at the Red Sandstone site. Thus GOC having no detectable ^{14}C contents influences ^{14}C ages of subsoil OC and thus may partly explain the strong ^{14}C ages increase observed in many subsoils. This is particularly important in soils on terrestrial sediments with comparatively low amounts of OC, where GOC can considerably contribute to total OC stocks

Keywords Geogenic organic carbon; sedimentary organic carbon; ^{14}C; terrestrial sediments; incubation experiment

1. Introduction

On a global average soils store more than 50 % of OC in the subsoil below 30 cm depth (Batjes, 2014). This carbon is considered as a highly stabilised carbon pool due to its high apparent ^{14}C ages (Mathieu et al., 2015, Schrumpf et al., 2013). This, however, may also be explained by an contribution from geogenic organic carbon (GOC), which is defined here as OC that originates from deposition during sedimentation and rock formation, and may increasingly influence subsoil OC with increasing depth (Graz et al., 2010, Kögel-Knabner et al., 2008, Schrumpf et al., 2013, Trumbore, 2009). GOC in most cases is devoid of ^{14}C and thus may lead to an overestimation of ancient OC sources although a number of studies showed the importance of root derived, young OC inputs to subsoils (Angst et al., 2016, Crow et al., 2009). The contribution of GOC to soils has been investigated in reclaimed mine soils where Vindušková et al. (2015) found contributions from GOC between 26 and 99 % to total soil OC. Furthermore especially OC rich sediments with contents of 2-7 g kg^{-1} (Hemingway et al., 2018) or 28-105 g kg^{-1} (Frouz et al., 2011) have been investigated. The impact of GOC on soils derived from sediments or sedimentary rocks with lower OC contents, however, has not been investigated so far. Considering the fact that approximately 65 % of the continental earth’s surface is covered with sediments and sedimentary rocks (Amiotte Suchet et al., 2003) a potentially large fraction of soils could contain GOC that contributes to soil OC stocks, even though a lot of them might be derived from recent sedimentation processes. So far there is not much literature about sediments with only low amounts of OC. There are estimations that assume sandstones to be GOC free (van der Voort et al., 2018) or, in contrast, a storage model that assumes generally high GOC amounts of 2.4 g kg^{-1} for all sandy deposits (Copard et al., 2007). Therefore, more information about the amounts of OC in sediments is needed.

To estimate the possible contribution of GOC to subsoil OC stocks, it is further necessary to know about the amount of OC in sediments that comes from sedimentation (GOC) and to distinguish it from OC that is derived from current vegetation (biogenic OC). There are many soil- and substrate-specific factors that might influence the OC contribution from current vegetation to sedimentary OC like potential rooting depth or hydraulic conductivity. So far no method could be established that would allow a direct quantification of GOC in different soils or sediments, apart from promising methods to quantify the graphitic part of GOC in soils (Zethof et al., 2019). The only reliable approach to distinguish both sources is the use of ^{14}C. Because deposition of sediments mostly took place > 50,000 yrs. BP, they do not contain any ^{14}C, which has a mean half life time of 5,730 yrs. (Libby, 1952). In addition, $\delta^{13}C$ values of OC in the sediments allow to distinguish carbonaceous from organic sources. Thus, using both carbon isotopes can reveal if the OC is a mixture of GOC and OC from the vegetation that is younger than 50,000 yrs. A quantification of the geogenic part of OC in the sediments is only possible if the average ^{14}C age of biogenic OC is known or can be estimated.

One important question regarding a possible contribution from GOC in soils is, if this GOC will be mineralised when it becomes part of the soil. Due to the fact that GOC resists degradation since it has been deposited, it can be assumed that it already exhibits a strong inherent recalcitrance. Nevertheless, this could also be due to a physical protection that prevented microbial accessibility. However, when it becomes part of the subsoil during progressing soil development, the infiltration of water, oxygen, fresh nutrients and microorganisms might cause the degradation of this OC pool. The direct microbial coal degradation has already been observed via incubation experiments in mine soils (Rumpel and Kögel-Knabner, 2002, Waschkies and Huttl, 1999) or in shale bedrocks directly exposed to the surface (Soulet et al., 2017). If GOC is degradable in OC-poor sediments or sedimentary rocks has not been investigated so far but might be different since the amount of OC can also drive microbial respiration (Colman and Schimel, 2013).

To the best of our knowledge there is only one study by van der Voort et al. (2018) investigating the amount of GOC in soils and estimating this to make up about 80 % of soil OC in a moraine derived soil. This reveals that GOC might considerably contribute to soil OC. But beside the study from van der Voort et al. (2018) on a very specific sediment, further direct calculations of the amount of GOC in soils are missing.

Our aim was to quantify GOC in different terrestrial sediments and a sedimentary rock and investigate its stability in incubation experiments to make assumptions about its possible contribution to soil OC stocks in soil profiles at the same site. Our main research questions were i) what is the relation between sedimentary and subsoil OC contents? ii) is OC in sediments ^{14}C free and how much is really geogenic? iii) will sedimentary GOC be degraded? and iv) how much does GOC contribute to soil OC?

2. Material and methods

2.1 Site description

Three sites were selected with different sedimentary bedrocks derived from a single geologic substrate, that can be found close to the surface and that is homogeneous down to 10 m depth. The sites represented one sedimentary rock and two soft sediments. The sedimentary rock was a sandstone (Solling Formation, Triassic) under European beech forest (*Fagus sylvatica*) 11.5 km north-east of Göttingen (51°35.012' N; 10°3.960' O) in the following referred to as "Red Sandstone". The soil was classified as a Cambisol according to World Reference Base for Soil Resources (WRB, 2006). The sediments were loessic deposits (Weichselian Glacial) under agricultural landuse for the past decades, 30 km north of Göttingen (51°48.101 N; 9°58.002' O) referred as "Loess" and terrestrial sandy deposits from the Miocene (Neogene formerly named Tertiary) in a European beech forest 13 km south-west of Göttingen (51°28.673 N; 9°45.323' O) referred to as "Miocene Sand". To the best of our knowledge, the forest sites were never under agricultural use. The associated soils are classified as a Luvisol and a Cambisol respectively. Mean annual air temperature and precipitation were 9.2 °C and 647 mm (1981-2010) at the nearby weather station including all three sites.

2.2 Sampling and sample preparation

Two 10 m long sediment cores with a diameter of 15 cm were drilled at each site in April 2017. For the soft sediments (Loess and Miocene Sand), drilling was conducted as percussion drilling and for the hard sediment (Red Sandstone) as cable core drilling with water as flushing solution. The replicates per site were drilled in a distance of approximately 10 m. We subdivided the sampled cores into 1 m increments. For further chemical analysis, we took material from respectively 85-95 cm depth of each 1 m increment and removed the outer 5 cm to avoid possible contaminations. This means e.g. for a sample increment from 1-2 m, the sample represents the 1.85-1.95 m depth.

One sample from each depth increment (1-2 m, 2-3 m, 3-4 m , 4-5 m, 5-6 m, 6-7 m, 7-8 m, 8-9 m, 9-10 m) for chemical analysis was oven dried at 60°C and sieved to pass 2 mm. The Red Sandstone samples were crushed with a hammer before drying and sieving was conducted. Additionally, approximately 1 m deep soil profiles were dug and soil samples were taken from the different classified layers to obtain corresponding soil parameters (Fig. 1).

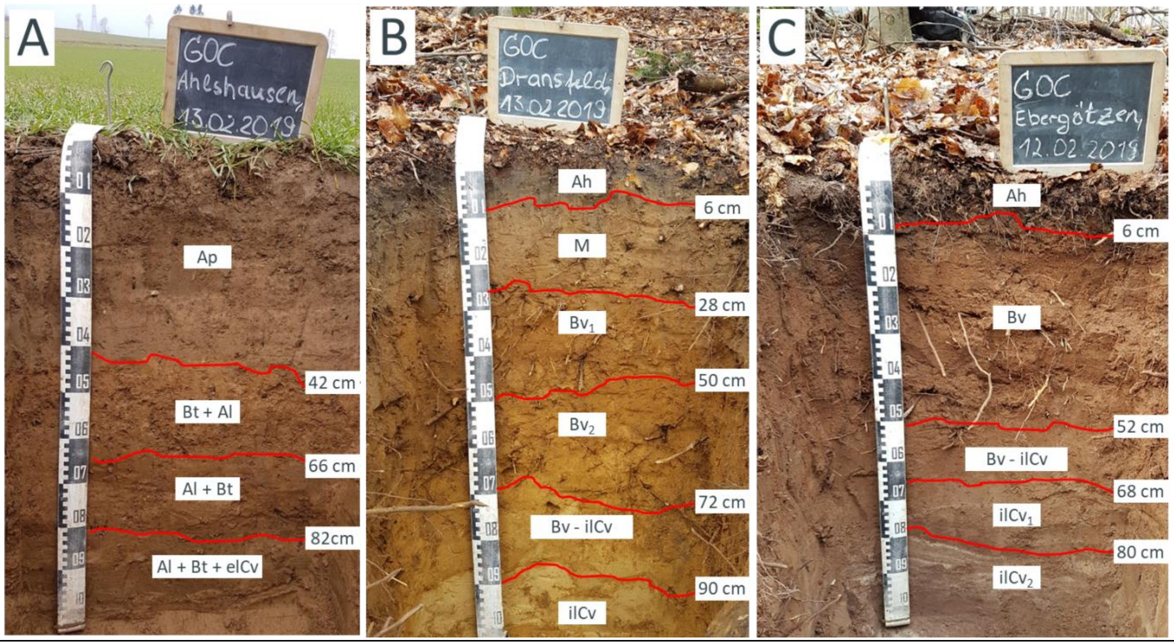

Fig. 1: Respective soil profiles of the Loess (A), Miocene Sand (B) and Red Sandstone (C) site. Soil classification was conducted using the German classification system for soil horizons {Eckelmann, 2006 #445}. Depth transitions to the beginning sediment were 82 cm for the Loess (Al + Bt + elCv), 72 cm for the Miocene Sand (Bv - ilCv) and 68 cm for the Red Sandstone (ilCv$_1$).

Samples were oven dried at 60°C and stored and sieved to pass 2 mm. For the determination of OC and ^{13}C samples were ground in a planetary ball mill. For ^{14}C analysis, subsamples were decarbonized with 1M HCl and heated for 1 h at 80 °C followed by 10 h at room temperature.

2.3 Chemical analysis and calculations

Three aliquots of each sieved sample was analysed by dry combustion for total C and total N content (TruMac CN LECO, St. Joseph, MI, USA). Samples with a pH value of > 6 (measured in 0,01 mol L^{-1} CaCl) were analysed for carbonates after ignition of the sample at 450 °C for 16 h in a muffle kiln to remove the organic part of total C. The OC concentration was calculated by subtracting carbonaceous C from total C and expressed as g OC kg^{-1} dry matter. Homogenised samples were further analysed for δ^{13}C values after removing carbonates in an isotope ratio mass spectrometer (Delta Plus, Thermo Fisher, Waltham, MA, USA) coupled to an elemental analyser (FLASH EA 1122 NA 1500; Wigan, United Kingdom). Resulting δ^{13}C values (‰) were expressed relative to the international standard of Vienna Pee Dee Belemnite. The bulk densities for the soil samples were obtained with 250 cm³ sampling rings from each layer of the soil profile. For the sedimentary Loess and Miocene Sand samples, the bulk density of the deepest soil sample (in 94 and 100 cm respectively) was used. The bulk densities and the densities without pore space of the intact Red Sandstone cores were determined on four subsamples (from 1.6, 3.6, 7 and 9 m depth) with a Dryflow-pycnometer (GeoPyc 1360) and a gas pycnometer (AccuPyc 1330) respectively. Bulk densities for the missing depth increments were linearly interpolated. For radiocarbon (^{14}C) analysis, the sediment samples were first treated with acid to remove inorganic C and where then transferred into pre-combusted quartz ampoules together with copper oxid and silver wool. The ampoules were evacuated, flame sealed, then combusted at 900°C, and the CO_2 evolved was purified on a vacuum ring (Rethemeyer et al., 2019). ^{14}C contents were measured with the MICADAS accelerator mass spectrometry (AMS) system at the ETH Zürich, Switzerland. If possible one sedimentary sample per depth increment and site and one sample per soil layer was analysed. Due to the very low OC contents in some sediment samples, ^{14}C contents could only be determined for three samples from the Miocene Sand (from 1.9, 4.9 and 7.9 m depth) and four from the Red Sandstone (1.9, 4.9, 7.9 and 9.9 m depth). For the Loess, ^{14}C of bulk OC was measured in all depth intervals (1.9-9.9 m).

Total OC stocks (Mg ha^{-1}) were calculated according to Eq. 1:

$$OC\ stock = OC \cdot BD\ \cdot (1 - stone\ content) \cdot depth \cdot 0.1 \qquad \text{Eq. 1}$$

where *OC* is the weight based OC content, either in the fine soil <2-mm fraction of the soil profiles, or in the sediments (g kg^{-1}), *BD* is the bulk density of the fine soil (g cm^{-3}), stone content is the volume based proportion of stones (cm³ cm^{-3}) and depth is the thickness of the depth increment (cm). To be able to compare OC stocks and contributions from GOC later on we decided to set the boarders between top- and subsoils to 0.3 m and the transition from subsoils to the sediments to 1.5 m. According to Richter and Markewitz (1995) this represents a common boarder for the transition from soil to sediment We further subdivided the sediments into an upper and a lower part at 4 m depth.

In a second step we calculated the amount of GOC and biogenic OC in the sediments considering GOC as one carbon pool free of ^{14}C. For the sediments we calculated the proportion of biogenic OC ($f_{biogenic}$) on the total amount of OC with a two pool model (Eq. 2) used by Cerri et al. (1985):

$$f_{biogenic}\ (\%) = \frac{F_{biogenic\ OC} - F_{GOC}}{F_{sample} - F_{GOC}} \cdot 100 \qquad \text{Eq. 2}$$

where *F* represents the ^{14}C content in fraction modern carbon ($F^{14}C$) from a source compared to the ^{14}C content of an oxalic standard (Stuiver and Polach, 1977, Torn et al., 2009). Sources were the GOC fraction (F_{GOC}), the sample (F_{sample}) and the biogenic OC fraction ($F_{biogenic\ OC}$). Since the ^{14}C content of the GOC fraction can be set to zero, this equation can be simplified to:

$$f_{biogenic}\ (\%) = \frac{F_{biogenic\ OC}}{F_{sample}} \cdot 100 \qquad \text{Eq. 3}$$

For the biogenic OC in the sediments we assumed an average ^{14}C age ranging from 1,000-4,000 yrs. BP. We assumed this range based on published ^{14}C results of dissolved OC reaching greater depths (Artinger et al., 1996, Schiff et al., 1997). The ^{14}C contents in the sediment from 2 to 4 m depth of the loess led to ages < 3,000 yrs. BP and were therefore even younger than in 74 cm depth (4,413 yrs.

BP). Thus, they were treated like the soil part for the calculation of a GOC fraction in the following. Respective times were converted into ^{14}C contents ($F_{biogenic\ OC}$) according to Torn et al. (2009):

$$F_{biogenic\ OC} = e^{(\frac{t}{-8033})} \qquad \text{Eq. 4}$$

where t represents the ^{14}C age (1,000 or 4,000 yrs. BP respectively) and 8033 yrs. the mean life of radiocarbon. The proportion of GOC in the sediments (f_{GOC}) consequently is the remaining portion (Eq. 5).

$$f_{GOC} = 100\,\% - f_{biogenic} \qquad \text{Eq. 5}$$

For the depth increments without measured ^{14}C ages (Tab. S1) we linearly interpolated the calculated amounts with measured ^{14}C ages from over- and underlying samples. This was done by assuming a depth dependent correlation and using the adjacent values. To calculate the amount of GOC in the soil profiles we first calculated the weight-based amount of GOC in the sediments by multiplying its fraction (f_{GOC}) with the respective OC content (in g OC per kg^{-1} dry mass). We then took the median amount of GOC (g GOC per kg^{-1} dry mass) of these sedimentary values and calculated its proportion on the soil OC content (g OC per kg^{-1} fine soil) in the soil profile. This was done for the proportion of GOC in the sediments calculated with a 1,000 and a 4,000 year old biogenic OC fraction ($F_{biogenic\ OC}$ in Eq. 3) to obtain a range of GOC contributions. We assumed that the GOC fraction resisted degradation during soil formation. Therefore, this proportion represents the highest possible amount of GOC that may contribute to soil OC stocks. Under this assumption we were also able to define the influence of GOC in the soil profile on the resulting ^{14}C ages. Since the calculated ^{14}C ages represent a mixture of the ^{14}C content from the GOC and the biogenic fraction (Eq. 5), the GOC fraction has the same influence on the soil ^{14}C age as on bulk OC (according to Eq. 3). Reducing the age by this fraction would therefore represent an “unbiased” age of soil derived OC.

2.4 Incubation experiment

To assess the potential stability of OC in the sediments against microbial decay, two laboratory incubation experiments were conducted at 20°C for 50 and 63 days respectively. This was done to reveal the potential degradation of OC from the sediments. A temperature of 20°C was chosen because we expected only very low degradation rates. The first, 50 days lasting experiment was conducted with intact Red Sandstone core samples, while the second experiment was performed after crushing the Red Sandstone to sizes < 2 mm. This was done to simulate the process of weathering when the intact sediment or sedimentary rock becomes part of the (sub)soil. For the incubations, four subsamples with 1,340-6,890 g per sample from different depth intervals were used. The sample material was stored at room temperature until the incubation experiment started. We took four samples from each sediment and from each of four depth ranges for the Miocene Sand (1.2-2.8, 3.2-4.8, 6.1-7.8 and 8.2-9.9 m), the Red Sandstone (2-3, 4-5.8, 7-8 and 8.4-9.8 m) and the Loess (1.4-2, 2.7-3, 4.8-6 and 9.1-10 m). A water content corresponding to 40 % of the water holding capacity based on the poured bulk density was adjusted. The material for the four repetitions was mixed in big plastic vats and water was added before the respective four subsamples were transfered into incubation vessels. Additionally four blank samples with no material were installed. Based on preliminary tests and its calculated bulk density and porosity, the intact Red Sandstone samples were kept in a barrel with pure water for 14 hours to reach a water content of nearly 40 %. Samples were placed in polycarbonate vessels with a volume of 7069 cm³ and closed air-tight. The lids contained two tube connectors so that the samples could be flushed with ambient air. After flushing, samples were set to a starting pressure of about 1,300 mbar and kept closed until the end of the incubation. Nine gas samples were taken in evacuated glass vials (20 mL), 0, 3, 7, 13, 21, 30, 59 and 63 days after the incubation started. Samples were analysed for CO_2 concentrations by gas chromatography (Agilent 7890A, GC, Agilent Technologies, Santa Clara, USA) to account for the amount of accumulated CO_2. Three additional gas samples were taken 0, 30 and 63 days after the incubation started and analysed with an isotope ratio mass spectrometer (Delta Plus XP, Thermo Fisher Scientific, Bremen, Germany) to account for the development of $\delta^{13}C$ of CO_2 during the respiration. Corresponding pressure was measured at each sampling date. When the over-pressure of a vessel was lost due to leakages, it was removed from the sampling because a contamination with ambient air could not be excluded. This happened for one third of all samples.

The amount of respired CO_2-C (mg CO_2-C d^{-1}) was calculated with Eq 6.

$$CO_2 - C = \frac{0.1 \cdot p \cdot x_i \cdot M \cdot V}{R \cdot T \cdot t} \qquad \text{Eq. 6}$$

where p is the pressure (mbar), x_i is the difference of the CO_2 concentration between the samplings (ppm), M is the molar mass of C (g mol^{-1}), V the air volume of the sample (m³), R is the molar gas constant (J $kmol^{-1}$ K^{-1}), T is the incubation temperature (K) and t is the elapsed time (d) between the samplings. Based on the $\delta^{13}C$ values of CO_2 the proportion of CO_2 derived from carbonates was subtracted according to Bertrand et al. (2007) if necessary. This respiration rate was related to the OC content of the samples (called “OC-normalised respiration”) by dividing it by the total amount of OC in g in the sample.

Since we observed a nearly linear respiration behaviour in both incubation experiments we fitted a simple linear regression model to describe the mineralisation rate per time (mineralised OC (%) = $k \cdot t$)

2.5 Statistics

Statistical analyses were conducted using the statistical environment R (R Core Team (2018) including "*lm*" to fit linear models and the package *ggplot2* (Wickham, 2016) for graphical presentationModels were tested for deviations from homoscedasticity, normality of residuals and absence of collinearity. The tests revealed heteroscedasticity of the residuals. This can be explained by an increasing standard deviation with time. We are further aware of not having normally distributed residuals since the dependent variable, representing the proportion of OC being mineralised, only allows values between 0 and 1. Keeping this in mind the results have to be treated as an indicator for the differences between the samples and a scale for the mineralisation of a the OC pool. We therefore also omitted calculations of standard errors and significance of the parameters since this would not lead to reasonable results with the used model.

3. Results

3.1 Relation between sedimentary and subsoil organic carbon

In all analysed sediments measured OC contents were above the detection limit. This was ensured by using three laboratory replicates per sample and the comparison with muffled samples. The mean relative standard deviation of the laboratory replicates was 9.5 %. In terms of the detection limit, the sample with the lowest total C content (mean of 0.04 mg C g^{-1} soil) showed values between 0.00 and 0.01 mg C g^{-1} soil after OC was removed at 450°C. Thus the range from 0.00 to 0.01 mg C g^{-1} soil was assumed to be random noise from the measurement.The amount of OC in the sediments from 1 to 10 m depth was comparatively low in the Miocene Sand and Red Sandstone (0.04-0.71 g kg^{-1} and 0.01-0.53 g kg^{-1}, respectively). Considerably higher OC contents of 0.21-9.71 g C kg^{-1} were found in the Loess (Fig. 1 a). The median OC content of the sediments was in a range comparable to those in the respective deepest subsoil horizon. This deepest horizon was a Cv horizon in 94 cm depth for the Loess, 100 cm depth for the Miocene Sand and 74 cm depth for the Red Sandstone. In detail, the median OC content in the sediments, compared to the respective Cv horizons, corresponded to 27 % for the Loess, 29 % for the Miocene Sand and 39 % for the Red Sandstone. The Loess OC contents were highly variable, highlighting the changing sedimentary conditions during the past glacial and interglacial periods (Jordan and Schwartau, 1993). In 4-5 m depth, OC contents of the Loess were even higher (9.7 g kg^{-1}) than in the subsoil (3 g kg^{-1}). In the Miocene Sand and the Red Sandstone no clear depth gradient of OC was found in 2-10 m depth (Fig. 1 a). Even though OC content in the sediments are low, OC stocks can be considerable large. A comparison of OC stocks in topsoils (0-0.3 m), subsoils (0.3-1.5 m) and the sediments down to 10 m depth revealed quite high OC stocks in the sediments. For the Loess, OC in the sediment contributed up to 71 % of the total OC amount while it was 51 % for the Red Sandstone and 21 % for the Miocene Sand (Table 1).

The distribution of the $\delta^{13}C$ values of OC in the soil and sediment profiles showed an increase of $\delta^{13}C$ with increasing depth in the soil down to 1 m depth (Fig. 1 b). Contrastingly, the $\delta^{13}C$ values of OC in the sediments showed no clear trend with increasing depth but they all were in the range of C_3 plant material. A value above -25 ‰ for the Red Sandstone in 4 m depth can be explained by corresponding high values of inorganic carbon (IC) in this depth. It can be assumed that decarbonisation of this sample was not completely successful. Unexpectedly high amounts of IC were found in parts of the Red Sandstone, indicating the presence of calcareous deposits in this terrestrial material (Fig. 1 c). The Loess also includes some distinct calcareous layers in 5 and 10 m depth, while there were only small amounts around 0.1 mg IC g^{-1} soil in the other depths. This could be due to the fact that the investigated loess deposits belongs to the "Leine Ilme Basin" a region with aoelian loamy loess that has been decalcified during weathering and soil genesis (Wagner, 2011) while the contents in the soil profile can be explained by liming.

Meanwhile no ICwas present in the Miocene Sand.

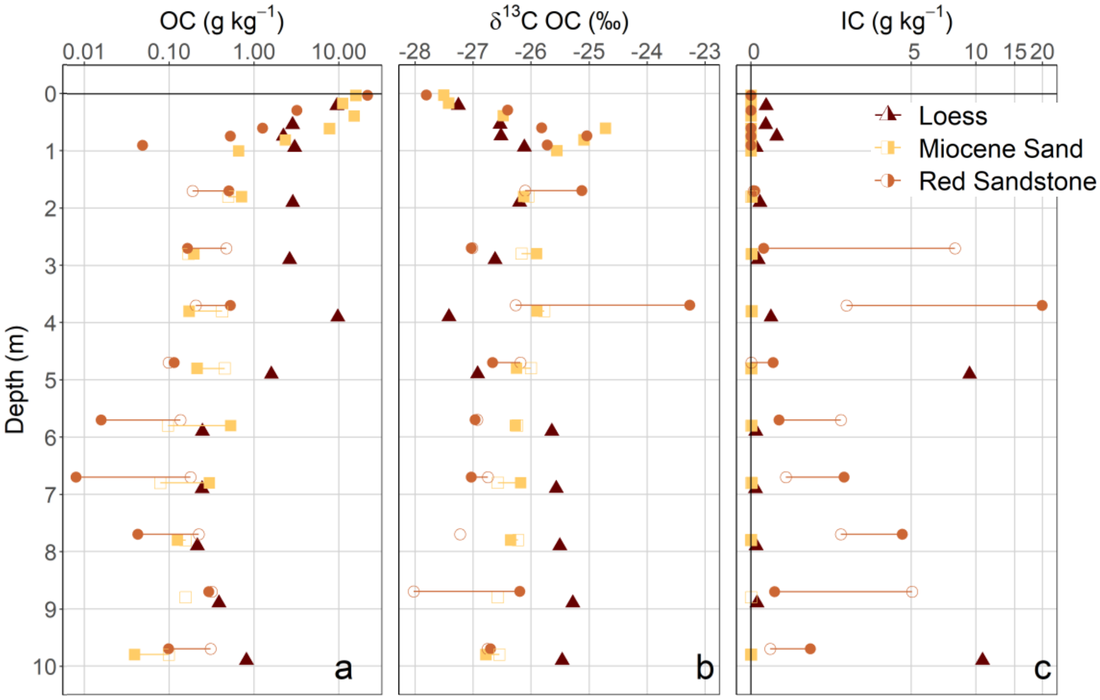

Fig. 2: Depth distribution of different bulk properties of the soil profiles and the deep drilling cores. Presented parameters include the log scale organic carbon (OC) and inorganic carbon (IC) content (a and c) and δ^{13}C values of the organic carbon (b) related to the amount of fine soil or dry mass respectively. Filled and unfilled symbols represent the two different cores. For the Loess only one core could be analysed.

Table 1: OC stocks and proportions for the three sites down to 10 m depth. Proportions of biogenic and geogenic OC were calculated based on ^{14}C results and assumptions described in the material and methods section. Represented ranges are calculated based on the assumption of a 1,000 or 4,000 year old biogenic OC fraction reaching the sediments.

			TOC		OC stocks (Mg ha^{-1})				Proportion of OC (%)[b]			
Substrate	Layer	Depth (m)	(Mg·ha^{-1})	(%)[a]	geogenic		biogenic		geogenic		biogenic	
					4,000 yrs.	1,000 yrs.	1,000 yrs.	4,000 yrs.	4,000 yrs.	1,000 yrs.	1,000 yrs.	4,000 yrs.

Loess	Topsoil	0.0 - 0.3	40.6	11	1.1 - 1.2	40 - 39	3 - 3	97 - 97
	Subsoil	0.3 - 1.5	66.0	17	5.1 - 5.3	61 - 61	8 - 8	92 - 92
	Upper Sediment	1.5 - 4.0	218.6	57	10.6 - 11.0	208 - 208	5 - 5	95 - 95
	Lower Sediment	4.0 - 10.0	55.1	15	42.9 - 46.7	8 - 12	78 - 85	15 - 22
Red andstone	Topsoil	0.0 - 0.3	22.2	30	0.6 - 0.7	22 - 22	3 - 3	97 - 97
	Subsoil	0.3 - 1.5	13.7	19	1.6 - 1.7	12 - 12	12 - 12	88 - 88
	Upper Sediment	1.5 - 4.0	18.7	25	13.1 - 14.9	4 - 6	70 - 80	20 - 30
	Lower Sediment	4.0 - 10.0	19.3	26	14.1 - 15.7	4 - 5	73 - 82	18 - 27
Miocene Sand	Topsoil	0.0 - 0.3	39.1	31	0.3 - 0.3	39 - 39	1 - 1	99 - 99
	Subsoil	0.3 - 1.5	60.8	48	1.3 - 1.6	59 - 60	2 - 3	97 - 98
	Upper Sediment	1.5 - 4.0	10.6	8	3.7 - 5.8	5 - 7	34 - 55	45 - 66
	Lower Sediment	4.0 - 10.0	16.3	13	8.3 - 10.8	6 - 8	51 - 66	34 - 49

[a] % of total OC stock from 0-10 m

[b] % of OC stock in the respective depth increment

3.2 Ages of organic carbon in soils and sediments and contributions from geogenic organic carbon

The ages of OC in the Loess soil profiles revealed a modern like carbon signature (0 yrs. BP) in 0.3 m depth with a sharp increase up to 4,413 ± 51 yrs. BP in 0.7 m depth (Fig. 2 a). For the Red Sandstone soil profile there was only an increase in the ages from a modern like signature in 0.04 m to 532 ± 41 yrs. BP in 0.3 m depth. The Miocene Sand soil profile in 0.4 m depth showed an increase from 1,277 ± 41 to 1,771 ± 44 yrs. BP in 0.6 m depth. Thus, OC of the subsoil (around 0.6 m depth) in the Loess was more than twice as old as in the Miocene Sand. Contrastingly, the Loess has a modern like signature in 0.3 m while the soil developed in Red Sandstone showed an average age of 532 ± 41 yrs. BP in 0.3 m depth. This could be due to the observed plough layer at the Loess site mixing up the upper 30 cm with a predominantly modern ^{14}C signature.

The ages of OC in the sediments ranged from 2,200-30,730 yrs. BP, with respective mean ages of 9,077 ± 3,234 yrs. BP for the Miocene Sand, 13,674 ± 9,632 yrs. BP for the Loess, and 14,463 ± 1,992 yrs. BP for the Red Sandstone. For all sediments, 11 out of 16 samples contained a ^{14}C content that led to an apparent ^{14}C age older than the soil age of 11,600 yrs. BP, assuming that soil development started after the latest glacial period at this time (Litt et al., 2007). Therefore sediments contain a mixture of geogenic (^{14}C free) and biogenic (with ^{14}C) OC. Despite being the youngest sediment, the Loess partly revealed the highest apparent ^{14}C ages with up to 30,730 ± 631 yrs. BP (Fig. 2 a). The ages of OC in the sediment of the Red Sandstone and the Miocene Sand ranged from 12,940 ± 132 to 17,390 ± 206 yrs. BP and from 6,750 ± 86 to 12,770 ± 151 yrs. BP, respectively revealing no depth trend with higher ages in the deeper sediment. The calculated GOC fraction in the sediments was highest for the Red Sandstone, ranging from 67 to 87 % with a mean of 77 % (Fig. 2 b). For the three samples of the Miocene Sand the GOC fraction ranges from 29 to 77 % with a mean of 53 %. The

Loess showed a sharp increase at a depth of five metres where GOC contribution went up to 71 to 98 % while it was only 5 to 19 % in 2 to 4 m depth.

The calculated weight based content of GOC in the sediment revealed a comparatively uniform distribution for all sediments with depth, except the extremely high contents of the Loess in 5 m depth (Fig. 2 c). The investigated sediment depths revealed a quite narrow range of GOC contents with 0.10 ± 0.03 g kg^{-1} for the Miocene Sand, 0.17 ± 0.12 g kg^{-1} for the Red Sandstone and 0.27 ± 0.08 g kg^{-1} for the Loess.

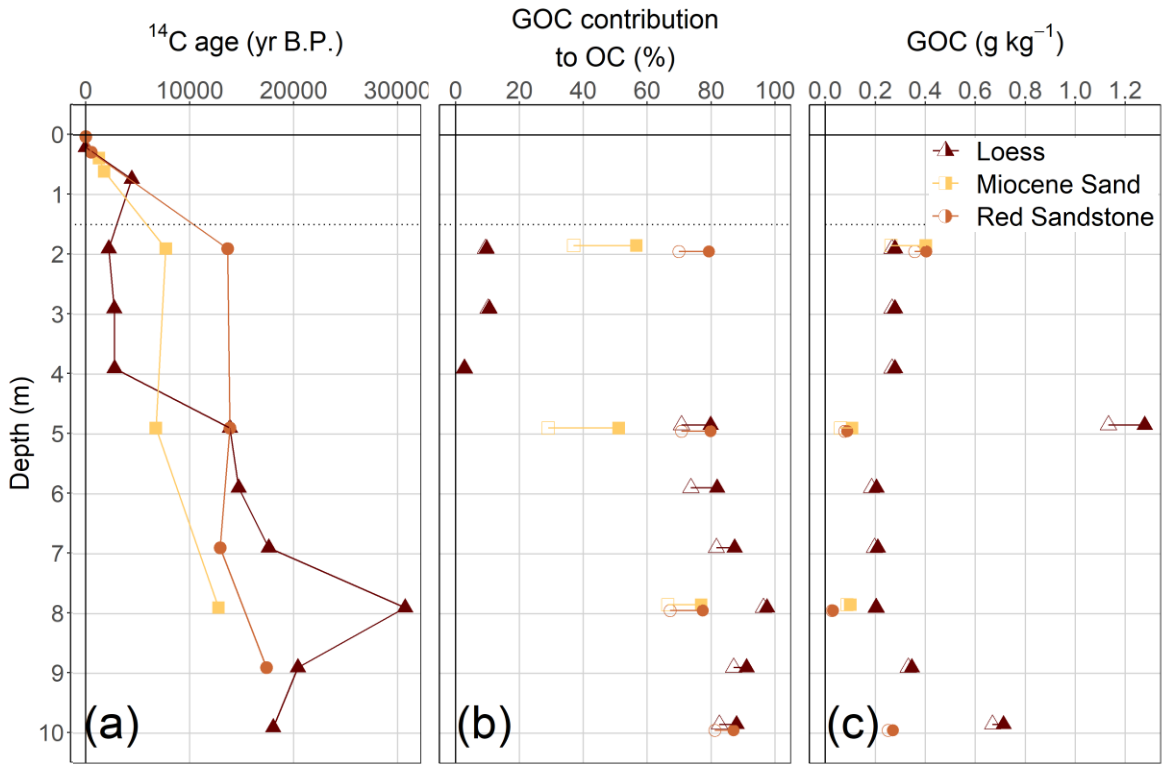

Fig. 3: Depth distribution of apparent ^{14}C ages (in yrs. BP) (a), GOC contribution to OC contents in the sediments (b) and resulting weight based amounts of GOC (c) in the sediments. The range in the contribution from GOC is due to the assumption of an average biogenic OC age of 4,000 (empty shapes) and 1,000 years (filled shapes).

3.3 Biodegradability of sedimentary derived organic carbon

The incubation experiment revealed a potential but low biodegradability of OC for all samples, but without a clear depth gradient from 1 to 10 m (Fig. 3). To compare the effect of crushing on the respiration of Red Sandstone samples, we compared the mineralisation rates from the first incubation experiment with the mineralisation rates of the second incubation experiment (Table 3). While the Red Sandstone showed very low mineralisation when the samples were incubated as intact cores (0.3-1.0 mg CO_2-C g^{-1} OC y^{-1}), the mineralisation rate constants were up to five times higher when the samples were crushed (1.0-2.1 mg CO_2-C g^{-1} OC y^{-1}). Comparing the Loess and the Miocene Sand both revealed high differences between samples with lowest (1.2 and 1.8 mg CO_2-C g^{-1} OC y^{-1}) and highest

(34.2 and 12 mg CO_2-C g^{-1} OC y^{-1}) respiration rate constants. Interestingly, there was no depth gradient for the different substrates but samples from 7 and 9 m depth of the Miocene Sand tended to show up to 6.8 times lower respiration rate constants compared to samples from 2 and 4 m depth. Additionally, there was a very high variation between samples from the same depth (see Fig. A1) as revealed by the high standard devations Assuming a constant mineralisation rate constant over time, the results of the incubation experiment would result in mean residence times between 29 and 135 yrs. for the Loess, 83 and 556 yrs. for the Miocene Sand and between 476 and 1,000 yrs. for the crushed Red Sandstone. Since CH_4-levels of the samples remained on a low level (Fig. A3) there were no indications for oxygen limited conditions during the incubation.

Table 2: Comparison of mineralisation rate constants between the first (Red Sandstone samples intact) and the second incubation experiment (crushed Red Sandstone samples) calculated with linear models.

Substrate	Depth (m)	Mineralisation rate constant (mg CO_2-C g^{-1} OC y^{-1})[a]
Miocene Sand	2	12.0
	4	10.5
	7	1.8
	9	2.9
Loess	1.7	7.4
	2.9	34.2
	5.4	10.2
	9.6	1.3
Uncrushed Red Sandstone	2.5	0.3
	5	1.0
	7.5	0.4
	9	0.4
Crushed Red Sandstone	2.5	1.3
	5	2.1
	7.5	2.0
	9	1.0

[a] represents the slope of the fitted linear model for the respiration during the incubation experiment.

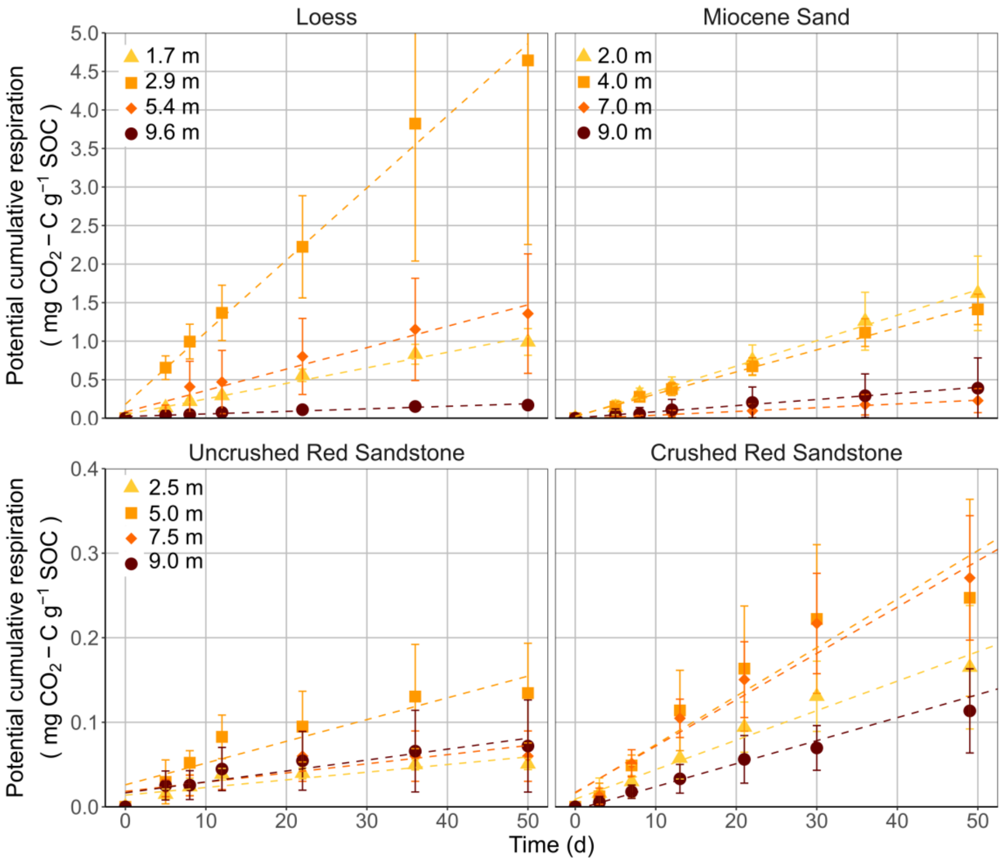

Fig. 4: Potential degradability of sedimentary OC from three sites. Results represent cumulative respiration from Loees and Miocene Sand samples andboth Red Sandstone incubation experiments with uncrushed and crushed samples with respective standard deviations (n = 4). Dashed lines represent a fitted linear model to the respiration data.

3.4 Possible contribution from geogenic organic carbon to soil organic carbon

When the bedrock is weathering it becomes part of the soil and also GOC becomes soil OC. The potential amount of GOC in the subsoil was dependent on the sedimentary bedrock (Fig. 4). In the subsoil of the Miocene Sand it added up to 2-3 %, at the Loess site it was 8 % and at the Red Sandstone site it was 12 % (Table 1). For the defined topsoils (0-30 cm depth), contributions of GOC to soil OC were smaller with 0.7-0.9 % for the Miocene Sand, 2.8-2.9 % for the Loess and 2.8-3.0 % for the Red Sandstone.

The presence of ^{14}C-free GOC to soil OC reduces the mean bulk soil OC ^{14}C ages depending on its proportion on soil OC content. Topsoils that developed in the Loess and the Red Sandstone had a modern ^{14}C content of 1.029 and 1.035 F^{14}C similar to the atmospheric ^{14}C content in 1950. Because of the large proportion of biogenic OC, an influence of a geogenic fraction is not detectable in the topsoil of these sites. No ^{14}C data are available for the topsoil of the Miocene Sand. For all subsoils, influence of GOC on bulk soil OC ^{14}C contents depends strongly on the depth and the corresponding OC contents. For the Loess the possible influence on ^{14}C ages in the subsoils would be quite high, with an average of 10 % reduction in mean apparent ^{14}C ages in the subsoil. It would therefore reduce the measured age from 4,413 yrs. BP in 74 cm depth by 532-555 yrs. BP. Geogenic OC potentially reduces the mean apparent radiocarbon age of 1,277 yrs. BP in 0.39 m depth in the Miocene Sand by about 7-9 yrs and the radiocarbon age of 1,771 yrs. BP in 0.61 m depth by 20-24 yrs.. This reduction is below the respective standard deviations of the measurement. Nevertheless, in 1 m depth a given possible proportion of 13.1-16.3 % would reduce an interpolated ^{14}C age of 3,053 yrs. BP by 399-497 yrs. For the Red Sandstone the influence of GOC on ^{14}C ages would be highest in the subsoil. In 74 cm depth it would influence an age of 1,453 yrs. BP by 451-490 yrs. BP. Due to the low amounts of soil OC in 90 cm depth at the Red Sandstone site, the weight based median amount of GOC in the sediments is even four times higher than the biogenic amount of soil OC.

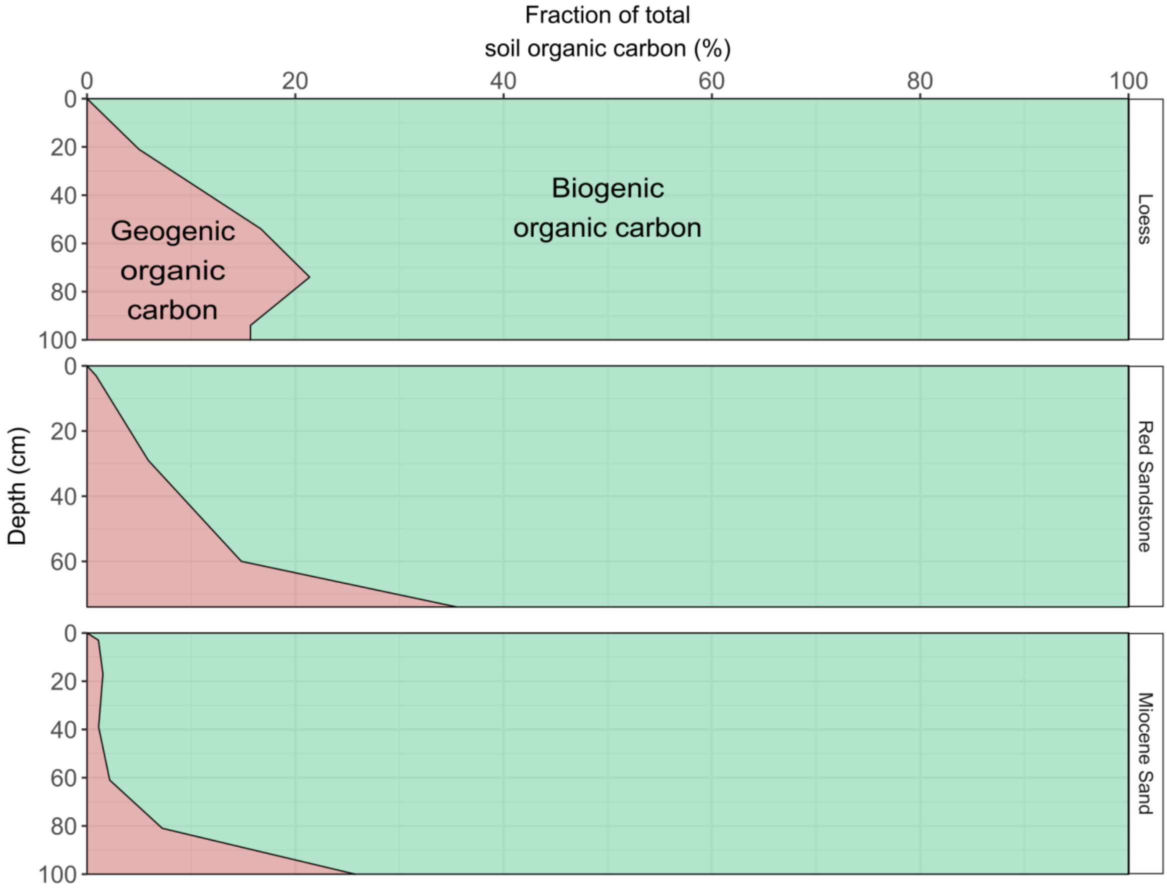

Fig. 5: Highest possible contribution from GOC to OC (red area) in relation to the bulk OC content. Here the median GOC contents of the sediments were taken into account for the respective horizontal weight based OC contents. The contribution from GOC is the mean amount based on the assumption of an average biogenic OC age between 4,000 () and 1,000 years

4. Discussion

4.1 Geogenic OC in the sediments

4.1.1 Site dependent contents of GOC

Regarding our calculated contribution from GOC to OC in the sediments, the assumed range of biogenic ^{14}C ages from 1,000-4,000 yrs. BP is within the typical range for ages of dissolved OC leaching from soils (Artinger et al., 1996, Jia et al., 2019). Despite this, the range from 1,000-4,000 yrs. BP did not greatly influence the range of calculated sedimentary contribution from GOC, especially for the Loess (~ 6 % difference) and the Red Sandstone (~ 9 % difference). The calculated GOC contribution for the Miocene Sand was comparatively low (29-77 %) compared to the contribution for the Red Sandstone and the Loess, especially in 5 m depth. Compared to the Red Sandstone this could be due to deep biogenic carbon inputs e.g. as roots and root exudates from the trees (Angst et al., 2016, John et al., 2016, Kirfel et al., 2017, Tückmantel et al., 2017), since the loosely bedded Miocene Sand allows for a deep infiltration compared to the Red Sandstone site with its shallow bedrock as a root restricting layer (Schneider and Don, 2019). Although we could not define the exact rooting depth for the Miocene Sand, it can be expected that this depth will probably not exceed 4 m referring to Schenk and Jackson (2005). Therefore the increase in sedimentary contribution from 5 to 8 m depth of the Miocene Sand could be due to the decreasing influence of roots and root exudates in 8 m depth.

In the Loess, the low ^{14}C ages in 2-4 m depth (2,200-2,770 yrs. BP) in contrast to a ^{14}C age of 4,413 yrs. BP in 0.74 m depth were surprising. This might indicate past anthropogenic activities or erosion driven material movement that might have mixed up the upper part of the profile. Nevertheless, at depths below 4 m the high ^{14}C ages of OC in the sediments indicated a large proportion of GOC. This could be due to different sedimentation periods, soil forming and also soil burial processes (Chaopricha and Marin-Spiotta, 2014) that took place during the Pleistocene. These processes can lead to the presence of buried layers in the Loess with varying amounts of rather recalcitrant OC as it was shown by Marin-Spiotta et al. (2014). For the investigated Loess site we can expect different sedimentation and soil forming processes due to the presence of completely different material in the cores in terms of colour and measured OC contents. This is in accordance to Jordan and Schwartau (1993) who investigated the same site assigned the different layers to specific Pleistocene sedimentation periods. In summary, the contribution from GOC to sedimentary OC was substrate dependent. A loosely bedded sediment like the Miocene Sand with extremely low concentrations of OC is more prone for infiltration of biogenic OC. This resulted in contributions of biogenic OC to the sediments of about 50 %. In contrast, the Loess site with comparatively low infiltration rates or the Red Sandstone site with reduced possibilities for deep rooting seemed to contain relative constant contributions from GOC of around 80 %.

We found that the GOC contribution within the sediments did not increase with increasing soil depth. This is in contrast to the results of Frouz et al. (2011) showing that different sediment types from a Miocene clay sediment had higher weight based carbon contents in 150 m compared to 30 m depth. However, a comparison with the present study is rather difficult since Frouz et al. (2011) did not distinguish between the geogenic and the biogenic OC fraction and OC contents were by far higher (28-112 g kg^{-1} dry mass compared to 0.008-10 g kg^{-1} dry mass in our results). But this also underlines the importance of different sedimentation processes for the amount and depth distribution of OC in sediments and sedimentary rocks.

4.1.2 Geogenic OC in the Miocene Sand and the Red Sandstone compared to other studies

A comparison of the weight based amounts of GOC in terrestrial sediments is difficult, since most studies in that field rarely determine the amounts of OC in terrestrial sediments, or pre-assume that e.g. sandy sediments contain no considerable amounts of OC (Artinger et al., 1996). Quite high amounts of OC were found in the skeleton part of different soils on sandstones with 0.61-1.97 t ha^{-1} Corti et al. (2002). Nevertheless, they mentioned the possible high influence of organic substances from the soil solution without quantifying it and they did not directly investigated OC in the sediments. Additionally Copard et al. (2007) assumed an OC amount of 2.4 g kg^{-1} from an unknown source for all sandy sediments in a global storage modelling approach for the first metre of the sediments. This would fit to the amounts of around 1 and 5 mg OC g^{-1} found by Krummholz et al. (1997) for Dakota sandstone layers in > 180 m depth but is much higher than the median GOC amount in the Red Sandstone (0.2 g kg^{-1}) and the Miocene Sand (0.1 g kg^{-1}). More data are thus needed to constrain the OC pool in sedimentary bedrock since it will also influence the soil carbon pool in our study.

*4.1.3 Geogenic OC in the Loess compared to other studies*Loess deposits are comparably well investigated as archive for paleoenvironmental conditions (Hatté et al., 1998, Head et al., 1989, Murton et al., 2015, Wang et al., 1996). The median amount of 0.27 g kg^{-1} from our study is low compared with studies from Hatté et al. (1998), Wang et al. (1996) and Strauss et al. (2012). Hatté et al. (1998) investigated 20 m depth loess deposits in the Rhine valley and found OC contents between 1.0-8.6 g kg^{-1}, Wang et al. (1996) investigated 12 m depth loess deposits in China and found OC contents of 31.2 ± 30.5 g kg^{-1} and Strauss et al. (2012) found OC contents of 15 ± 14 g kg^{-1} in Yedoma loess deposits in Siberia. This shows that the deposits from our investigated site stored comparatively low GOC contents, although most of the studies mentioned above did not distinguish between a biogenic and a geogenic OC pool. Nevertheless, also in our study Loess is, compared to other sediments, a sedimentary bedrock with a high OC content. This was in line with highest OC contents in subsoils at the Loess site and may indicate the importance and contribution of bedrock OC to subsoil OC.

4.2 Is sedimentary derived organic carbon biodegradable?

The incubation experiment revealed a mineralisation of OC within the sediments with values between 0.1 and 3.4 % of total OC being mineralised after one year, assuming a constant mineralisation rate. Thereby it has to be considered that the incubation temperature of 20°C is above the typical mean temperatures in the subsoils at the investigated sites having a mean annual temperature of 9.2°C. Assuming a Q_{10} value of around 2 for the assumable difference (Hamdi et al., 2013), the respiration rate at typical subsoil temperatures would be roughly half as high. A direct mineralisation of OC from sediments is in accordance with several studies investigating the direct mineralisation from outcrops (Copard et al., 2007, Horan et al., 2017, Petsch et al., 2000, Soulet et al., 2017, Seifert et al., 2001). The difference to our study is, that these studies observed this mineralisation when the sediments were directly exposed to the surface or/and part of a very fast eroding area. Thus GOC from the sediments already is in touch with the atmosphere and inputs of the recent vegetation. However, Frouz et al. (2011) conducted an incubation experiment with sedimentary samples from OC rich Miocene clay sediments. They found quite high respiration rate constants with values between 3.5-12.3 mg CO_2-C g^{-1} OC y^{-1} within a 91 day incubation experiment. They attributed this to the prevailing presence of aliphatic compounds in their samples being decomposed. Also Kieft and Rosacker (1991) found high respiration rates of sedimentary samples with values between 0.9-9.5 mg CO_2-C g^{-1} OC y^{-1} which they primarily attributed to the physiological status of the soil microbial community expressed as adenylate energy charge. These results fit quite well to our observed respiration rate constants (1 – 34.2 mg CO_2-C g^{-1} OC y^{-1}). Meanwhile, compared to subsoil incubation experiments, the mineralisation found in our incubation experiment was quite low. For example, in subsoil incubation experiments at 20°C, Wordell-Dietrich et al. (2017) found that between 5-9.5 mg CO_2-C g^{-1} OC of OC are mineralised after incubation for 63 days, Wang et al. (2013) reported values between 5-15 mg CO_2-C g^{-1} OC of after 28 days and Soucemarianadin et al. (2018) reported values between 10-12.5 mg CO_2-C g^{-1} OC after 70 days. The difference between the observed respiration rates in our incubation experiment and the results from sedimentary and subsoil incubation experiments might be a result from different microbial communities, quality of OC and the physical connection between OC and potential decomposers. As it was shown in a meta-analysis by Colman and Schimel (2013), different microbial compositions, their abundance and the quality of OC, strongly affects respiration rates. This might also be indicative by the extreme differences in respiration rates even within the same substrate and sample.

Our results indicated that there is a considerable portion of biogenic OC in the sediments. Therefore it could be the case that the observed mineralisation is primarily due to the consumption of this biogenic OC part. Furthermore, the low mineralisation rate of the Red Sandstone during the incubation as intact cores (Fig. S1) promotes the stability of GOC when it is part of the sediments. This might be due to the low accessibility of OC in the sediments for microorganisms and the low the availability of water due to a preferential flow through the sandstone (Swanson et al., 2006).

Altogether the low mineralisation rates of the OC in the sediments might be driven by alack of fresh substrates and/or microorganisms that could enhance the degradation of OC (Fontaine et al., 2007)since Seifert et al. (2011) showed that microorganisms are able to degrade sedimentary OC after the addition of glucose in black slate outcrops. Nevertheless, a mineralisation of OC could be observed only by adding water, which indicates the presence of an active microbial community in the sediments, which is a largely recognised assumption(Bomberg et al., 2017, Frederickson and Balkwill 2006, Joergensen and Wichern, 2018, Magnabosco et al., 2018). Since we did not add fresh substrates during the incubation, it has to be taken into account that respiration rates could be higher if a fresh substrate induced priming effect occurs. Furthermore the inherent and active microbial communities in the sediments might have assimilated ^{14}C free GOC into their biomass as it has been shown by Schwab et al. (2019). This means that part of the labile OC pool in the sediments might also be derived from metabolised ^{14}C free microbial biomass.

The long-term incubation cannot answer the question if GOC will be mineralised when it becomes part of the (sub-)soil. Assuming that preferably the biogenic part of OC in the sediments was mineralised during the incubation experiment, geogenic OC could still be preserved during soil formation especially in the subsoils. This is in accordance to an indirect approach to determine the mineralisation of sedimentary OC when it becomes part of the subsoil from Graz et al. (2010). They stated that 30 % of GOC resisted degradation when it becomes part of the soil due to the results from a quantitative palynofacies analysis of bedrock and soil samples. Hemingway et al. (2018) found that sedimentary OC directly exposed to the surface in a rapidly eroding tropical mountain area exhibits a considerable mineralisation down to 1 m below the surface leading to a resistant part on similar level. Based on ^{14}C measurements they found out that on average 67 ± 11 % of the OC fraction in the sediments could be lost during soil formation but did not distinguished between a biogenic and a geogenic OC fraction. This indicates that a microbial mineralisation of bedrock OC takes place but may be partly restricted to biogenic OC.

Regarding the depth distribution of GOC in the sediments, the amount of GOC (in g kg^{-1}) does not increase with depth but shows clear differences. On the one hand, this represents the sedimentation history with different initial amounts of OC and degradation during sedimentation. This is particularly evident by the high amounts of GOC in 5 m depth of the Loess. Meanwhile, contents of GOC especially in the Red Sandstone and Miocene Sand are in the same range over the whole depth. This might indicate that degradation of GOC is not depth dependend within the sediments. If there would be a stronger degradation of GOC with decreasing depth one would expect a decreasing amount of GOC due to the input of water, microorganisms and fresh nutrients from above. Furthermore, there is a relatively constant contribution from biogenic OC within the sediments. This means that, if biogenic OC enters the sediments, together with possibly degrading microorganisms, this biogenic OC might also be preferably mineralised. That degradation of OC in subsoils in subsoils is primarily limited to small hotspot areas was shown very well by Heitkötter et al. (2018). Also for sediments, Krummholz et al. (1997) showed that microbial communities are especially present in spatially discrete areas. Nevertheless Heitkötter et al. (2018) also showed that microorganisms outside the hotspots can be activated when substrate is supplied. Thus the bioavailability of GOC might be very site dependent, since e.g. root channels as microbial hotspots are less abundant and stable in sandy soils (Schneider and Don, 2019). With regard to our investigated sites, the solid Red Sandstone might only obtain water in preferential flow paths (Swanson, 2006) leading to a comparatively stable OC pool in the sediment. Meanwhile for the weathered, poorly structured sandy soil prevalent matrix flow conditions can be assumed (Flury et al., 1994). Thus the bulk GOC might be supplied with fresh substrates and water from above more frequently compared to the well-structured Loess soil with more frequent and stable preferential flow paths (Schneider and Don, 2019). This might lead to a lower accessibility and therefore slower turnover rates of OC (Dungait et al., 2012).

This leads to the conclusion that GOC can and will be degraded when it becomes part of the subsoil but probably to a comparatively low extent. Based on the mentioned literature, at least around 30 % of GOC can be assumed to resist degradation when it becomes part of the subsoil.

4.3 How much GOC contributes to soil organic carbon?

The contribution of GOC to soil OC stocks in our study is driven by the amount of OC in the soil, the amount of GOC in the respective sediment and also its assumed turnover. Our results revealed that despite differences between sediments, GOC content varied in a quite narrow range between 0.1 and 0.3 g kg^{-1}. The contribution of GOC to topsoil OC was negligible. Assuming no degradation of GOC, highest possible contributions to total subsoil OC were found for the Red Sandstone (~30 %) and lowest for the Miocene Sand (0.6 %). This was due to the range of OC contents in the subsoils (0.53 g kg^{-1}-15.21 g kg^{-1}). When soil OC contents were low, the possible contributions from GOC were high and vice versa (Fig. S2). For our investigated soils OC contents of 3 g kg^{-1} soil allowed for possible GOC contributions between 5-10 %. For OC contents around 1 g kg^{-1} soil a GOC contribution between 10-20 % seems to be possible. Thereby higher contributions came from GOC rich sediments like the Loess and lower contributions from sandy sediments. In comparison, van der Voort et al. (2018) estimated the contribution from GOC of a soil derived from glacial deposits (flysch) between 80-100 cm depth to be around 40 %. For a soil developed from a poorly consolidated sedimentary rock (calcareous and shaly moraine) they calculated the contribution from GOC to range from 20 % in 145 cm depth to 80 % in 310 cm depth. There has further been an attempt to fractionate subsoils to extract the most stable OC that may be derived from GOC. Paul et al. (2001) found that 30 % of subsoil OC was non-hydrolysable. The investigated a soil developed on loess over till with this non-hydrolysable fraction showing a ^{14}C age of 13,000 yrs. BP. They also concluded that this high age can partly be explained by a GOC fraction. These results indicate that especially deposits from the past glacial periods like flysch or till have a much higher potential for OC contributions from GOC possibly due to their higher amounts of GOC in the sediments. Since we only investigated terrestrial sediments it has to be taken into account that also marine sediments or shales contain much higher amounts of OC up to 250 g kg^{-1} (Hemingway et al., 2018, Petsch et al., 2000). Their amount of GOC and possible contribution to subsoil OC stocks might therefore be much higher.

Nevertheless, ^{14}C ages of OC in the subsoil can be high in soils derived from igneous parent materials without GOC (Rumpel et al., 2002), although even crystalline bedrocks contain microbial communities (Purkamo et al., 2020). Furthermore, on a global scale ^{14}C ages of soil OC are primarily driven by climatic conditions, clay content and age, since soil development started (Mathieu et al., 2015). But for terrestrial sediments with comparatively low amounts of GOC that started their soil development after the latest glacial period, we could obtain a scale for possible contributions when the amount of OC is known. Thus, at a global scale the high ^{14}C age of subsoils is not only driven by the GOC fraction but the presence of GOC may considerable influence subsoil ^{14}C.

5. Conclusion

With our approach of estimating the GOC contribution to soil OC, we could show that common and abundant terrestrial sediments, with low amounts of sedimentary OC, can contribute considerably to subsoil OC stocks. One fraction of OC in the sediments is of geogenic origin and could therefore influence measured ^{14}C ages in soil, in particular in subsoils. Subsoils are known for their high ^{14}C ages and slow turnover rates and slow reaction to changing environmental condition. These properties of subsoil OC may partly be derived from the GOC in the subsoil. The sediments at the investigated sites contained OC in a range from 0.1-0.3 g kg^{-1}, allowing for contributions from GOC between 10-30 % in subsoils. Incubation of sediments seem to indicate that this geogenic contribution presents a quite stable OC pool, especially for subsoils. Thus, also sediments with comparatively low amounts of OC, could show considerable contributions from GOC.

Data availability

The data will be made available on request

Author contribution

AD conceived of and designed the study, FK performed the sampling and analysis, and wrote the first draft. All the authors contributed to generating and reviewing the subsequent versions of the manuscript.

Competing interest

The authors declare that they have no conflict of interest

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References

Amiotte Suchet, P., Probst, J. L. and Ludwig, W.: Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO2 uptake by continental weathering and alkalinity river transport to the oceans, Global Biogeochemical Cycles, 17, 2003

Angst, G., John, S., Mueller, C. W., Kogel-Knabner, I. and Rethemeyer, J.: Tracing the sources and spatial distribution of organic carbon in subsoils using a multi-biomarker approach, Scientific Reports, 6, 29478, 2016

Artinger, R., Buckau, G., Kim, J., Geyer, S. and Wolf, M.: Influence of sedimentary organic matter on dissolved fulvic acids in groundwater. Significance for groundwater dating with 14 C in dissolved organic matter, 1996

Batjes, N. H.: Total carbon and nitrogen in the soils of the world, Eur J Soil Sci, 65, 10-21, 2014

Bertrand, I., Delfosse, O. and Mary, B.: Carbon and nitrogen mineralization in acidic, limed and calcareous agricultural soils: Apparent and actual effects, Soil Biology and Biochemistry, 39, 276-288, 2007

Bomberg, M., Raulio, M., Jylha, S., Mueller, C. W., Hoschen, C., Rajala, P., Purkamo, L., Kietavainen, R., Ahonen, L. and Itavaara, M.: CO2 and carbonate as substrate for the activation of the microbial community in 180 m deep bedrock fracture fluid of Outokumpu Deep Drill Hole, Finland, AIMS Microbiol, 3, 846-871, 2017

Cerri, C., Feller, C., Balesdent, J., Victoria, R. and Plenecassagne, A.: Particle-sie fractionation and stable carbon isotope distribution applied to the study of soil organic-matter dynamics, Comptes Rendus De L Academie Des Sciences Serie Ii, 300, 423-+, 1985

Chaopricha, N. T. and Marin-Spiotta, E.: Soil burial contributes to deep soil organic carbon storage, Soil Biol Biochem, 69, 251-264, 2014

Colman, B. P. and Schimel, J. P.: Drivers of microbial respiration and net N mineralization at the continental scale, Soil Biology Biochemistry, 60, 65-76, 2013

Copard, Y., Amiotte-Suchet, P. and Di-Giovanni, C.: Storage and release of fossil organic carbon related to weathering of sedimentary rocks, Earth Planet Sc Lett, 258, 345-357, 2007

Corti, G., Ugolini, F. C., Agnelli, A., Certini, G., Cuniglio, R., Berna, F. and Sanjurjo, M. J. F.: The soil skeleton, a forgotten pool of carbon and nitrogen in soil, Eur J Soil Sci, 53, 283-298, 2002

Crow, S. E., Lajtha, K., Filley, T. R., Swanston, C. W., Bowden, R. D. and Caldwell, B. A.: Sources of plant-derived carbon and stability of organic matter in soil: implications for global change, Global Change Biology, 15, 2003-2019, 2009

Dungait, J.A.J., Hopkins, D.W., Gregory, A.S., Whitmore, A.P.: Soil organic matter turnover is governed by accessibility not recalcitrance, Global Change Biology, 18, 1781–1796, 2012

Flury, M., Flühler, H., Jury, W.A., Leuenberger, J.: Susceptibility of soils to preferential flow of water: A field study, Water Resources Research, 30, 1945-1954, 1994

Fontaine, S., Barot, S., Barre, P., Bdioui, N., Mary, B. and Rumpel, C.: Stability of organic carbon in deep soil layers controlled by fresh carbon supply, Nature, 450, 277-280, 2007

Fredrickson J. K., Balkwill, D.L.: Geomicrobial processes and biodiversity in the deep terrestrial subsurface, Geomicrobiology Journal, 23, 345-356, 2006

Frouz, J., Cajthaml, T., Kribek, B., Schaeffer, P., Bartuska, M., Galertova, R., Rojik, P. and Kristufek, V.: Deep, subsurface microflora after excavation respiration and biomass and its potential role in degradation of fossil organic matter, Folia Microbiologica, 56, 389-396, 2011

Graz, Y., Di-Giovanni, C., Copard, Y., Laggoun-Defarge, F., Boussafir, M., Lallier-Verges, E., Baillif, P., Perdereau, L. and Simonneau, A.: Quantitative palynofacies analysis as a new tool to study transfers of fossil organic matter in recent terrestrial environments, Int J Coal Geol, 84, 49-62, 2010

Hamdi, S., Moyano, F., Sall, S., Bernoux, M., Chevallier, T.: Synthesis analysis of the temperature sensitivity of soil respiration fromlaboratory studies in relation to incubation methods and soil conditions, Soil Biology and Biochemistry, 58, 115-126, 2013

Hatté, C., Fontugne, M., Rousseau, D.-D., Antoine, P., Zöller, L., Laborde, N. T. r. and Bentaleb, I.: δ13C variations of loess organic matter as a record of the vegetation response to climatic changes during the Weichselian, Geology, 26, 583-586, 1998

Head, M., Zhou, W. and Zhou, M.: Evaluation of 14 C ages of organic fractions of paleosols from loess-paleosol sequences near Xian, China, Radiocarbon, 31, 680-695, 1989

Heitkötter, J., Marschner, B.: Soil zymography as a powerful tool for exploring hotspots and substrate limitation in undisturbed subsoil, Soil Biology and Biochemistry, 124 ,210-217, 2018

Hemingway, J. D., Hilton, R. G., Hovius, N., Eglinton, T. I., Haghipour, N., Wacker, L., Chen, M.-C. and Galy, V. V.: Microbial oxidation of lithospheric organic carbon in rapidly eroding tropical mountain soils, Science, 360, 209-212, 2018

Horan, K., Hilton, R. G., Selby, D., Ottley, C. J., Gröcke, D. R., Hicks, M. and Burton, K. W.: Mountain glaciation drives rapid oxidation of rock-bound organic carbon, Science advances, 3, e1701107, 2017

Jia, J., Feng, X., Pannatier, E. G., Wacker, L., McIntyre, C., van der Voort, T., Montlucon, D. and Eglinton, T.: 14C characteristics of dissolved lignin along a forest soil profile, Soil Biology Biochemistry, 2019

Joergensen, R. G. and Wichern, F.: Alive and kicking: Why dormant soil microorganisms matter, Soil Biology and Biochemistry, 116, 419-430, 2018

John, S., Angst, G., Kirfel, K., Preusser, S., Mueller, C. W., Leuschner, C., Kandeler, E. and Rethemeyer, J.: Which are important soil parameters influencing the spatial heterogeneity of 14C in soil organic matter, Biogeosciences Discuss, 123, 2016

Jordan, H. and Schwartau, W.: Das Lößprofil von Ahlshausen und weitere tiefe Quartäraufschlüsse entlang der Bundesbahn-Neubaustrecke bei Northeim, Südniedersachsen, Quaternary Science Journal, 43, 12, 1993

Kieft, T. L. and Rosacker, L. L.: Application of respiration-and adenylate-based soil microbiological assays to deep subsurface terrestrial sediments, Soil biology Biochemistry, 23, 563-568, 1991

Kirfel, K., Leuschner, C., Hertel, D. and Schuldt, B.: Influence of Root Diameter and Soil Depth on the Xylem Anatomy of Fineto Medium-Sized Roots of Mature Beech Trees in the Top- and Subsoil, Front Plant Sci, 8, 2017

Kögel-Knabner, I., Guggenberger, G., Kleber, M., Kandeler, E., Kalbitz, K., Scheu, S., Eusterhues, K. and Leinweber, P.: Organo-mineral associations in temperate soils: Integrating biology, mineralogy, and organic matter chemistry, Journal of Plant Nutrition and Soil Science, 171, 61-82, 2008

Libby, W. F.: Radiocarbon Dating, The Society for American Archaeology, 132, 1952

Litt, T., Behre, K.-E., Meyer, K.-D., Stephan, H.-J. and Wansa, S.: Stratigraphische Begriffe für das Quartär des norddeutschen Vereisungsgebietes, Quaternary Science Journal, 56, 7-65, 2007

Magnabosco, C., Lin, L.-H., Dong, H., Bomberg, M., Ghiorse, W., Stan-Lotter, H., Pedersen, K., Kieft, T., Van Heerden, E. and Onstott, T. C.: The biomass and biodiversity of the continental subsurface, Nature Geoscience, 11, 707-717, 2018

Krumholz, L.R., McKinley, J. P., Ulrich, G.A., Suflita, J.M., Confined subsurface microbial communities in Cretaceous rock, Nature, 386, 64-66, 1997

Marin-Spiotta, E., Chaopricha, N. T., Plante, A. F., Diefendorf, A. F., Mueller, C. W., Grandy, A. S. and Mason, J. A.: Long-term stabilization of deep soil carbon by fire and burial during early Holocene climate change, Nature Geoscience, 7, 428-432, 2014

Mathieu, J. A., Hatté, C., Balesdent, J. and Parent, É.: Deep soil carbon dynamics are driven more by soil type than by climate: a worldwide meta-analysis of radiocarbon profiles, Global change biology, 21, 4278-4292, 2015

Murton, J. B., Goslar, T., Edwards, M. E., Bateman, M. D., Danilov, P. P., Savvinov, G. N., Gubin, S. V., Ghaleb, B., Haile, J. and Kanevskiy, M.: Palaeoenvironmental Interpretation of Yedoma Silt (Ice Complex) Deposition as Cold-Climate Loess, Duvanny Yar, Northeast Siberia, Permafrost Periglacial Processes, 26, 208-288, 2015

Paul, E., Collins, H. and Leavitt, S.: Dynamics of resistant soil carbon of Midwestern agricultural soils measured by naturally occurring 14C abundance, Geoderma, 104, 239-256, 2001

Petsch, S., Berner, R. and Eglinton, T.: A field study of the chemical weathering of ancient sedimentary organic matter, Org Geochem, 31, 475-487, 2000

Purkamo, L., Kietäväinen, R., Nuppunen-Puputti, M., Blomberg, M.: Ultradeep microbial communities at 4.4 km within crystalline bedrock: implications for habitability in a planetary context, Life, 10, 1, 2020

Qualls, R. G. and Haines, B. L.: Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water, Soil Science Society of America Journal, 56, 578-586, 1992

R Core Team: R: A language and environment for statistical computing, 2018

Rasmussen, C., Southard, R. J. and Horwath, W. R.: Mineral control of organic carbon mineralization in a range of temperate conifer forest soils, Global Change Biology, 12, 834-847, 2006

Rethemeyer, J., Gierga, M., Heinze, S., Stolz, A., Wotte, A., Wischhöfer, P., Berg, S., Melchert, J. and Dewald, A.: Current sample preparation and analytical capabilities of the radiocarbon laboratory at CologneAMS, Radiocarbon, 61, 1449-1460, 2019

Richter, D. D. and Markewitz, D.: How deep is soil?, BioScience, 45, 600-609, 1995

Rumpel, C. and Kögel-Knabner, I.: The role of lignite in the carbon cycle of lignite-containing mine soils: evidence from carbon mineralisation and humic acid extractions, Org Geochem, 33, 393-399, 2002

Rumpel, C., Kögel-Knabner, I. and Bruhn, F.: Vertical distribution, age, and chemical composition of organic carbon in two forest soils of different pedogenesis, Org Geochem, 33, 1131-1142, 2002

Saidy, A. R., Smernik, R. J., Baldock, J. A., Kaiser, K., Sanderman, J. and Macdonald, L. M.: Effects of clay mineralogy and hydrous iron oxides on labile organic carbon stabilisation, Geoderma, 173, 104-110, 2012

Santos, F., Torn, M. S. and Bird, J. A.: Biological degradation of pyrogenic organic matter in temperate forest soils, Soil Biol Biochem, 51, 115-124, 2012

Saxton, K. E. and Rawls, W. J.: Soil water characteristic estimates by texture and organic matter for hydrologic solutions, Soil Science Society of America Journal, 70, 1569-1578, 2006

Schenk, H. J., Jackson, R.B.: Mapping the global distribution of deep roots in relation to climate and soil characteristics, Geoderma, 126, 129-140, 2005

Schiff, S., Aravena, R., Trumbore, S. E., Hinton, M., Elgood, R. and Dillon, P.: Export of DOC from forested catchments on the Precambrian Shield of Central Ontario: clues from 13 C and 14 C, Biogeochemistry, 36, 43-65, 1997

Schneider, F. and Don, A.: Root-restricting layers in German agricultural soils. Part I: extent and cause, Plant Soil, 442, 433-451, 2019

Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I. and Schulze, E.-D.: Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and attachment to minerals, Biogeosciences, 10, 1675-1691, 2013

Schwab, V. F., Nowak, M.E., Elder, C.D., Trumbore, S.E., Xu, X., Gleixner, G., Lehmann, R., Pohnert, G., Muhr, J., Küsel, K., Totsche, K.U.: 14C-Free Carbon Is a Major Contributor to Cellular Biomass in Geochemically Distinct Groundwater of Shallow Sedimentary Bedrock Aquifers, Water Resources Research, 55, 2104-2121, 2019

Seifert, A.-G., Trumbore, S., Xu, X., Zhang, D., Kothe, E., Gleixner, G.: Variable effects of labile carbon on the carbon use of different microbial groups in black slate degradation, Geochimica et Cosmochimica Acta, 75, 2557-2570, 2011

Soucemarianadin, L. N., Cecillon, L., Guenet, B., Chenu, C., Baudin, F., Nicolas, M., Girardin, C. and Barre, P.: Environmental factors controlling soil organic carbon stability in French forest soils, Plant Soil, 426, 267-286, 2018

Soulet, G., Hilton, R. G., Garnett, M. H., Dellinger, M., Croissant, T., Ogrič, M. and Klotz, S.: in situ measurement of flux and isotopic composition of CO2 released during oxidative weathering of sedimentary rocks, Biogeosciences, 2017

Strauss, J., Schirrmeister, L., Wetterich, S., Borchers, A. and Davydov, S.: Grain-size properties and organic-carbon stock of Yedoma Ice Complex permafrost from the Kolyma lowland, northeastern Siberia, Global biogeochemical cycles, 26, 2012

Stuiver, M. and Polach, H. A.: Reporting of C-14 data-Discussion, Radiocarbon, 19, 355-363, 1977

Swanson, S. K., Bahr, J. M., Bradbury, K. R. and Anderson, K. M. J. S. G.: Evidence for preferential flow through sandstone aquifers in Southern Wisconsin, 184, 331-342, 2006

Torn, M., Swanston, C., Castanha, C. and Trumbore, S., Wiley, Hoboken, 2009

Trumbore, S.: Radiocarbon and soil carbon dynamics, Annual Review of Earth Planetary Sciences, 37, 47-66, 2009

Tückmantel, T., Leuschner, C., Preusser, S., Kandeler, E., Angst, G., Mueller, C. W. and Meier, I. C.: Root exudation patterns in a beech forest: dependence on soil depth, root morphology, and environment, Soil Biology Biochemistry, 107, 188-197, 2017 van der Voort, T., Mannu, U., Hagedorn, F., McIntyre, C., Walthert, L., Schleppi, P., Haghipour, N. and Eglinton, T.: Dynamics of deep soil carbon - insights from 14C time series across a climatic gradient, Biogeosciences, 2018

Vindušková, O., Sebag, D., Cailleau, G., Brus, J. and Frouz, J.: Methodological comparison for quantitative analysis of fossil and recently derived carbon in mine soils with high content of aliphatic kerogen, Org Geochem, 89, 14-22, 2015

Wagner, B.: Spatial analysis of loess and loess-like sediments in the Weser-Aller catchment (Lower Saxony and Northern Hesse, NW Germany), Quarternary Science Journal, 60, 27-46, 2011

Wang, X., Cammeraat, L. H., Wang, Z., Zhou, J., Govers, G. and Kalbitz, K.: Stability of organic matter in soils of the Belgian Loess Belt upon erosion and deposition, Eur J Soil Sci, 64, 219-228, 2013

Wang, Y., Amundson, R. and Trumbore, S.: Radiocarbon dating of soil organic matter, Quaternary Research, 45, 282-288, 1996

Waschkies, C. and Huttl, R. F.: Microbial degradation of geogenic organic C and N in mine spoils, Plant Soil, 213, 221-230, 1999

Wordell-Dietrich, P., Don, A. and Helfrich, M.: Controlling factors for the stability of subsoil carbon in a Dystric Cambisol, Geoderma, 304, 40-48, 2017

WRB, I. W. G., Food and Agriculture Organization of the United Nations, Rome, 2006

Zethof, J. H. T., Leue, M., Vogel, C., Stoner, S. W. and Kalbitz, K.: Identifying and quantifying geogenic organic carbon in soils – the case of graphite, SOIL, 5, 383-398, 2019