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 yet been quantified~~ yet~~, but influencing~~es~~ 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 depending~~ with~~ on the type of bedrock. As yet, no ~~So~~ far studies have investigated~~ing~~ the contribution of GOC derived from different terrestrial sedimentary rocks to soil OC contents~~ are missing~~.

In order to fill this knowledge gap, ~~we analysed 10~~ 10-m long sediment cores ~~at~~ from three sites recovered from Pleistocene Loess, Miocene Sand and Triassic Red Sandstone were analysed and ~~calculated~~ the amount of GOC calculated based on ^{14}C measurements. The ^{14}C ages of bulk sedimentary OC revealed that OC ~~represents a mixture~~ is comprised of both biogenic and geogenic components. The ~~B~~biogenic component ~~refers~~ relates to OC that recently entered the sediments ~~recently~~ from plant sources. All the sediments contained considerable amounts of GOC (median amounts of 0.10 g kg^{-1} ~~at~~ in~~the~~ Miocene Sand, 0.27 g kg^{-1} ~~at the~~in Pleistocene Loess and 0.17 ~~at~~ in Red Sandstone) ~~in comparison~~ compared with~~to~~ subsoil OC contents (between 0.53-15.21 g kg^{-1}). Long-term incubation experiments revealed that ~~this~~ the GOC ~~seemed to be~~appeared comparatively stable against biodegradation. Its possible contribution to subsoil OC stocks (0.3-1.5 m depth) ranged from 1 to 26 %~~is ∼ 2.5 %~~ in soil developed in the Miocene Sand, from 16 to 21 % ~~∼ 8 %~~ in the Loess soil and from 6 to 36 % ~~∼ 12 %~~ at the Red Sandstone site. Thus GOC ~~having~~ with no detectable ^{14}C content~~s~~ influence~~s~~d the ^{14}C ages of subsoil OC, and ~~thus~~ may partly explain the strong increase in ^{14}C ages ~~increase~~ observed in many subsoils. This ~~is~~ could be particularly important in young soils on terrestrial sediments with comparatively low amounts of OC, where GOC can ~~considerably~~ make a large contribution~~e~~ to total OC stocks.

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

1. Introduction

On average, the world's ~~a global average~~ soils store more than 50 % of OC in the subsoil below 30 cm depth (Batjes, 2014). This type of carbon is considered ~~as~~ a highly ~~stabilised~~ stable carbon pool due to its ~~high~~ apparently high ^{14}C ages (Mathieu et al., 2015, Schrumpf et al., 2013).~~ This, h~~ However, another explanation for this could be~~ may also be explained by an~~ the contribution ~~from~~ of 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). Therefore GOC may significantly influence and affect the overall ^{14}C signal, particularly in OC-poo subsoils. Vindušková et al. (2015)~~The~~ investigated the contribution of GOC to soils ~~has been investigated~~ in reclaimed mine soils, and ~~where Vindušková et al. (2015)~~ found GOC contributions to total soil OC of ~~from GOC~~ between 26 and 99 %~~ to total soil OC~~. Furthermore ~~especially OC~~ OC-rich sediments with contents of 2-7 g kg^{-1} (Hemingway et al., 2018) ~~or~~ and 28-105 g kg^{-1} (Frouz et al., 2011) have been investigated with regard to the stability of OC in these sediments, but no conclusion reached about GOC contributions in soils. However, ~~T~~the impact of GOC on soils derived from sediments or sedimentary rocks with lower OC contents~~, however,~~ has not yet 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~~large portion might be derived from recent sedimentation processes. ~~So far~~ T~~t~~here is not yet much literature about sediments ~~with~~ containing only low amounts of OC. There are estimations that assume sandstones to be free of 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 GOC in sediments is needed.

To estimate the possible contribution of GOC to subsoil OC stocks, it is ~~further~~ important to establish ~~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, such as ~~like~~ potential rooting depth or pore distribution~~hydraulic conductivity~~. ~~So far n~~No method ~~could~~ has yet been~~be~~ established ~~that would~~to 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 between both sources is the use of ^{14}C. ~~Because~~ Since deposition of sediments mostly took place > 50,000 ~~yrs.~~years BP, they do not contain ~~any~~ ^{14}C, which has a mean half-~~-~~life time of 5,730 ~~yrs.~~years (Libby, 1952). In addition, the δ^{13}C values of OC in the sediments allow ~~to distinguish~~ carbonaceous sources with δ^{13}C values around 0 ‰ to be distinguished from organic sources with δ^{13}C values < -22 ‰. Thus, ~~using~~ the use of both carbon isotopes ~~can~~ could reveal ~~if~~ whether the OC is a mixture of GOC and OC from ~~the~~ vegetation that is ~~younger~~ less than 50,000 ~~yrs.~~years old. ~~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~~ about the ~~a~~ possible contribution ~~from~~ of GOC in soils is whether~~, if this~~ the GOC ~~will be~~ is mineralised when it becomes part of the soil. ~~Due to the fact that~~As ~~-~~GOC resists degradation ~~since~~ once 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 prevents~~ed~~ microbial accessibility. However, when it becomes part of the subsoil during ~~progressing~~ soil development, ~~the~~ this OC pool could be degraded by the infiltration of water, oxygen, fresh nutrients and microorganisms ~~might cause the degradation of this OC pool~~. ~~The d~~Direct microbial coal degradation has already been observed ~~via~~ in incubation experiments ~~in~~ on 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~~ There has been no study to establish whether GOC is degradable in OC-poor sediments or sedimentary rocks has not been investigated, ~~so far~~ but it could differ~~might be different~~ since the amount of available ~~-~~OC can also drive microbial respiration (Colman and Schimel, 2013). Therefore these sediments might contain fewer microorganisms that can be spatially separated from the GOC, which may hamper its respiration.

To the best of ~~our~~ the author's knowledge, there ~~is~~ has only been one study by van der Voort et al. (2018) ~~investigating~~ that has investigated the amount of GOC in soils. They estimated~~ and estimating~~ that GOC ~~this to~~ makes up ~~about~~ around 80 % of soil OC in a moraine-derived soil, suggesting~~. This reveals~~ that GOC's contribution ~~might considerably contribute~~ to soil OC is large. ~~But~~ However, apart from this study~~beside the study from~~ by van der Voort et al. (2018) on a very specific sediment, there have been no ~~further~~ direct calculations of the amount of GOC in soils~~ are missing~~.

~~Our~~ The aim of this study was to quantify GOC in different terrestrial sediments and a sedimentary rock, and investigate its stability in incubation experiments in order to make assumptions about its possible contribution to soil OC stocks in soil profiles at the same site. ~~Our~~ The main research questions were: i) ~~what~~ What is the relationship between sedimentary and subsoil OC contents? ii) ~~i~~Is OC in sediments ^{14}C-free and how much is really geogenic? iii) ~~will~~ Will sedimentary GOC be degraded? and iv) ~~how~~ 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 below as “Red Sandstone”. The soil ~~was~~ is classified as a ~~Cambisol~~ Folic Brunic Arenosol according to the World Reference Base for Soil Resources (WRB, 2006). The sediments were loessic deposits (Weichselian Glacial) that have been under agricultural land use for the past decades, 30 km north of Göttingen (51°48.101 N; 9°58.002’ O), referred to 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”. The respective soils have been classified as a Haplic Luvisol and a Dystric Chromic Arenosol accordingly. The sediments at the Loess site were deposited between the last glacial and interglacial periods between 115,000 and 400,000 years BP, according to Jordan and Schwartau (1993). To the best of ~~our~~ the author’s knowledge, ~~the~~ these forest sites ~~were~~ have never been 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~~according to the nearby weather station ~~including~~ that covers 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 the flushing solution. The replicates per site were drilled ~~in a distance of~~ approximately 10 m apart. ~~We subdivided t~~The sampled cores were subdivided into 1-m increments. For further chemical analysis, ~~we took~~ material was taken from ~~respectively~~ a depth of 85-95 cm ~~depth of~~ for each 1~~-~~-m increment, and ~~removed~~ the outer 5 cm removed to avoid possible contamination~~s~~. ~~This means e.g. for a sample~~Thus the increment from 1-2 m~~,~~, for example, was represented by a sample~~ the sample represents the~~ from a 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 being dr~~ying~~ied and ~~sieving~~ sieved~~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).

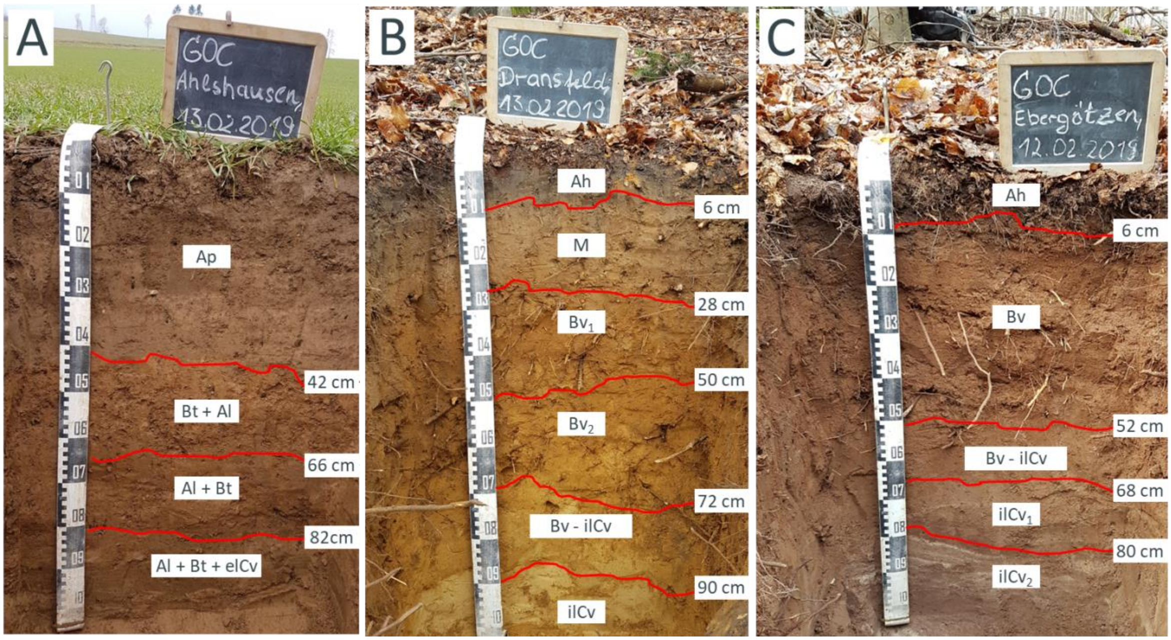

Fig. 1: Respective soil profiles ~~of~~ at the Loess (A), Miocene Sand (B) and Red Sandstone (C) sites. Soil classification was conducted using the German classification system for soil horizons (Eckelmann et al., 2006) and later transferred to the WRB (2006). Depth transitions to the ~~beginning~~ starting 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 1 M 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~~ were 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 was ignited for 16 h in a muffle kiln at 450 °C ~~for 16 h in a muffle kiln to remove the organic part of total C~~according to Nelson and Summers (1983), 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 removal 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 1% HCl ~~acid~~ to remove inorganic C, and ~~where~~ then transferred into pre-combusted quartz ampoules containing~~together with~~ copper oxide 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). The ^{14}C contents were measured with the MICADAS accelerator mass spectrometry (AMS) system at ~~the~~ ETH Zürich, Switzerland. ~~If~~ Where 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~~ it was decided to set the bo~~a~~rders between the topsoils- and subsoils ~~to~~ at 0.3 m and the transition from subsoils to the sediments ~~to~~ at 1.5 m. According to Richter and Markewitz (1995) this represents a common bo~~a~~rder for the transition from soil to sediment. ~~We further subdivided the~~ The sediments where further subdivided into an upper and a lower part at a ~~4 m~~ depth of 4 m.

In a second step, ~~we calculated~~ the amount of GOC and biogenic OC in the sediments was calculated, considering GOC as one carbon pool free of ^{14}C. For the sediments, ~~we calculated~~ the proportion of biogenic OC ($f_{biogenic}$) ~~on~~ of the total amount of OC was calculated ~~with~~ in 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 the fraction modern carbon (F^{14}C) from a source compared ~~to~~ with the ^{14}C content of an oxalic standard (Stuiver and Polach, 1977, Torn et al., 2009). The ~~S~~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~~ could 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.~~years BP was assumed,~~.~~ ~~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.~~years BP, and were therefore even younger than ~~in~~ at 74 cm depth (4,413 ~~yrs.~~years BP). Thus, they were treated like the soil part for the calculation below of a GOC fraction~~ in the following~~. Respective times were converted into ^{14}C contents ($F_{biogenic\ OC}$) according to Torn et al. (2009):

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

where *t* represents the ^{14}C age (1,000 or 4,000 ~~yrs.~~years BP respectively) and 8033 ~~yrs.~~represents the mean life of radiocarbon in years. The proportion of GOC in the sediments (f_{GOC}) ~~consequently~~ is therefore the ~~remaining~~ portion left (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 were linearly interpolated with measured ^{14}C ages from ~~over- and underlying~~ samples above and below. 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 was first calculated by multiplying its fraction (f_{GOC}) ~~with~~ by the respective OC content (in g OC per kg^{-1} dry mass). ~~We then took t~~The median amount of GOC (g GOC per kg^{-1} dry mass) of these sedimentary values was then taken and ~~calculated~~ its proportion ~~on~~ of~~the~~ soil OC content calculated (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~~ It was assumed that the GOC fraction resisted degradation during soil formation. Therefore, this proportion represents the ~~highest~~ largest possible amount of GOC that ~~may~~ could contribute to soil OC stocks. ~~Under~~ On this assumption, it was also possible~~ 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 were expected at lower temperatures. The first, 50~~-~~-day~~s~~ ~~lasting~~ experiment was conducted with intact Red Sandstone core samples, while the second experiment was performed after ~~crushing~~ the Red Sandstone was crushed to ~~sizes~~ pieces < 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~~ of 1,340-6,890 g per sample from different depth intervals were used. The sample material was stored at room temperature until the start of the incubation experiment~~ started~~. ~~We took f~~Four samples were taken 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 w~~Water content was adjusted to correspond~~ing~~ to 40 % of ~~the~~ water~~-~~holding capacity based on the poured bulk density, determined by filling the loose material into a defined volume and measuring its weight. ~~was adjusted.~~ The material for the four repetitions was mixed in ~~big~~ large plastic vats and water ~~was~~ added before the respective four subsamples were transferred ~~in~~to incubation vessels. There were also ~~Additionally~~ four blank samples with no material~~ were installed~~. Based on preliminary tests and ~~its~~ their 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 cm^3 and ~~closed~~ made 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 start of 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. The c~~C~~orresponding pressure was measured ~~at~~ on 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 no~~t~~ longer be ruled out~~ be excluded~~. This happened for ~~one~~ a third of all the samples.

The amount of respired CO_2-C (mg CO_2-C d^{-1}) was calculated ~~with~~ using 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~~in CO_2 concentration between the samplings (ppm), M is the molar mass of C (g mol^{-1}), V is the air volume of the sample (m^3), 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 where necessary 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 being divid~~ing~~ed ~~it~~ by the total amount of OC in g in the sample.

Since we observed an almost ~~nearly~~ linear respiration behaviour was observed in both incubation experiments, ~~we fitted~~ a simple linear regression model was fitted 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 the function “*lm*” to fit linear models and the package *ggplot2* (Wickham, 2016) for graphical presentation. The ~~M~~models were tested for deviations from homoscedasticity, normality of residuals and absence of collinearity. The tests revealed heteroscedasticity of the residuals, which~~. This~~ can be explained by an increasing standard deviation with time. It subsequently became apparent that the residuals were not ~~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~~ Bearing this in mind, the results ~~have~~ should ~~to~~ be treated as an indicator ~~for~~ of~~the~~ differences between the samples and a scale for the mineralisation of ~~a~~ the OC pool. ~~We t~~Therefore ~~also omitted~~ calculations of standard errors and significance of the parameters were omitted since this would not ~~lead to~~ produce reasonable results with the ~~used~~ model used.

3. Results

3.1 ~~Relation~~ Relationship between sedimentary and subsoil organic carbon

Organic carbon was detectable in all the sediments analysed using three laboratory replicates per sample and comparing them with the muffled samples, measurable. ~~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~~g C kg^{-1} soil) showed values between 0.00 and 0.01 ~~mg C g~~g C kg^{-1} soil after removal of OC ~~was removed~~ at 450 °C. Thus the range ~~from~~ of 0.00 to 0.01 ~~mg C g~~g C kg^{-1} soil was assumed to be the ~~random~~ mean standard error ~~noise~~ from the measurement. Despite having the same material down to 10 m depth at each site, there were still some inhomogeneities that were visible and measurable. This was especially true for Loess and Red Sandstone. 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), while much~~. Considerably~~ higher OC contents of 0.21-9.71 g C kg^{-1} were found in ~~the~~ Loess (Fig. ~~1~~ 2 a). The median OC content of the sediments was within a range comparable to ~~those~~ that ~~in~~ of the respective deepest subsoil horizon. This deepest horizon was a Cv horizon ~~in~~ at 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~~ with 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~~ At 4-5 m depth, the OC contents of ~~the~~ Loess were even higher (9.7 g kg^{-1}) than in the subsoil (3 g kg^{-1}). This was not an outlier because the high OC content could be visually confirmed by the very dark colour of the sample. In ~~the~~ Miocene Sand and ~~the~~ Red Sandstone, no clear depth gradient of OC was found ~~in~~ at 2-10 m depth (Fig. ~~1~~ 2 a). Even though the OC content in the sediments ~~are~~ were low, the OC stocks ~~can~~ could be ~~considerable~~ very 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 δ^{13}C values of OC in the soil and sediment profiles showed an increase ~~of~~ in δ^{13}C with ~~increasing~~ depth in the soil down to 1 m ~~depth~~ (Fig. ~~1~~ 2 b). In c~~C~~ontrast~~ingly~~, the δ^{13}C values of OC in the sediments showed no clear trend with increasing depth, but they all were within the range of C$_3$ plant material. A value above -25 ‰ for ~~the~~ Red Sandstone ~~in~~ at 4 m depth ~~can~~ could be explained by ~~corresponding~~ the high values of inorganic carbon (IC) ~~in~~ at 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~~ 2 c). The Loess also included~~s~~ some distinct calcareous layers ~~in~~ at 5 and 10 m depth, while there were only small amounts of around 0.1 mg IC g^{-1} soil ~~in~~ at the other depths. This could be due to the fact that the investigated loess deposits belong~~s~~ 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 n~~No IC was present in ~~the~~ Miocene Sand.

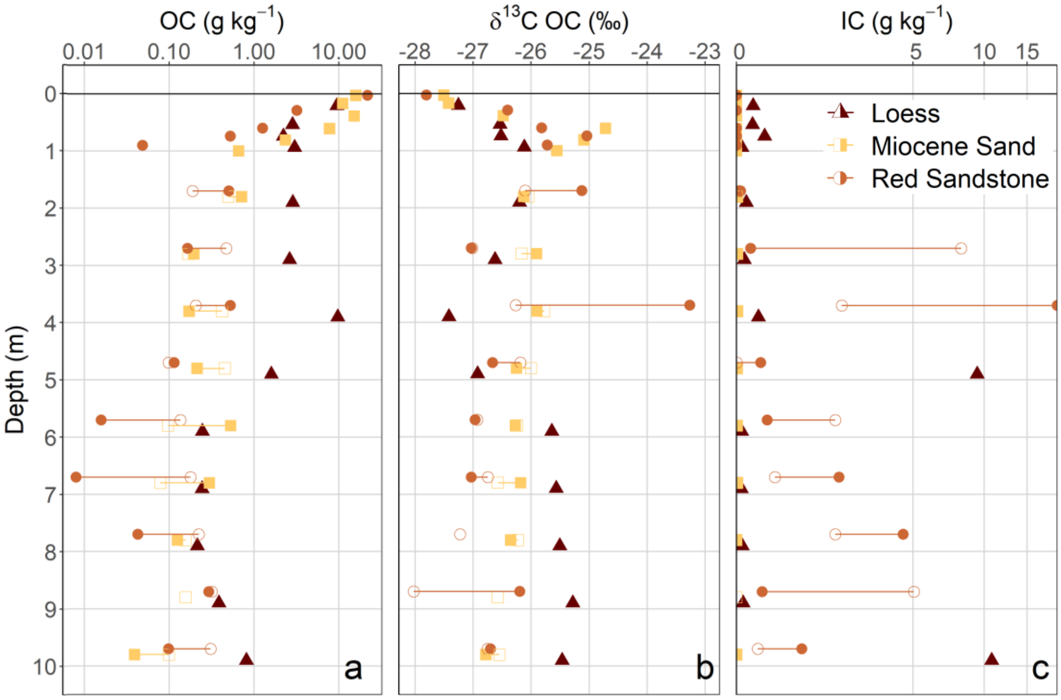

Fig. 2: Depth distribution of different bulk properties of the soil profiles and ~~the~~ deep drilling cores. Presented parameters include the log scale organic carbon (OC) and inorganic carbon (IC) content (a and c) and the δ^{13}C values of the organic carbon (b) related to the amount of fine soil 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.

Substrate	Layer	Depth (m)	TOC (Mg·ha^{-1})	TOC (%)^a	OC stocks (Mg ha^{-1}) geogenic 4,000 yrs.	OC stocks geogenic 1,000 yrs.	OC stocks biogenic 1,000 yrs.	OC stocks biogenic 4,000 yrs.	Proportion of OC (%)^b geogenic 4,000 yrs.	Proportion geogenic 1,000 yrs.	Proportion biogenic 1,000 yrs.	Proportion biogenic 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 Sandstone	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.~~years BP) ~~in~~ at 0.3 m depth, with a sharp increase up to 4,413 ± 51 ~~yrs.~~years BP ~~in~~ at 0.7 m depth (Fig. 3~~2~~ a). For the Red Sandstone soil profile there was only an increase in the ages from a modern ~~like~~ signature ~~in~~ at 0.04 m to 532 ± 41 ~~yrs.~~years BP ~~in~~ at 0.3 m depth. The Miocene Sand soil profile ~~in~~ at 0.4 m depth showed an increase from 1,277 ± 41 to 1,771 ± 44 ~~yrs.~~years BP ~~in~~ at 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~~In contrast, ~~the~~ Loess had~~s~~ a modern ~~like~~ signature ~~in~~ at 0.3 m, while the soil developed in Red Sandstone showed an average age of 532 ± 41 ~~yrs.~~years BP ~~in~~ at 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.~~years BP, with respective mean ages of 9,077 ± 3,234 ~~yrs.~~years BP for ~~the~~ Miocene Sand, 13,674 ± 9,632 ~~yrs.~~years BP for ~~the~~ Loess, and 14,463 ± 1,992 ~~yrs.~~years BP for ~~the~~ Red Sandstone. For all sediments, 11 out of 16 samples ~~contained~~ had a ^{14}C content that led to an ~~apparent~~ ^{14}C age older than ~~the soil age of~~ 11,600 ~~yrs.~~years BP, which we assumed to be the time ~~assuming that soil development started~~ after the latest glacial period when soil development started~~at this time~~ (Litt et al., 2007). Therefore the sediments contained 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.~~years BP (Fig. ~~2~~ 3 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.~~years BP and from 6,750 ± 86 to 12,770 ± 151 ~~yrs.~~years BP~~,~~ respectively, revealing no depth trend with ~~higher~~ age~~s~~ 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~~ 3 b). For the three ~~samples of the~~ Miocene Sand samples, the GOC fraction ranged~~s~~ 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~~ rising to between ~~up to~~ 71 to 98 % while it was only 5 to 19 % at the~~in~~ 2 to 4 m depth.

The calculated weight~~-~~-based content of GOC in the sediment revealed a comparatively uniform distribution for all the sediments with depth, except the extremely high contents of ~~the~~ Loess ~~in~~ at 5 m depth (Fig. ~~2~~ 3 c). The investigated sediment depths revealed ~~a~~ quite a 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.

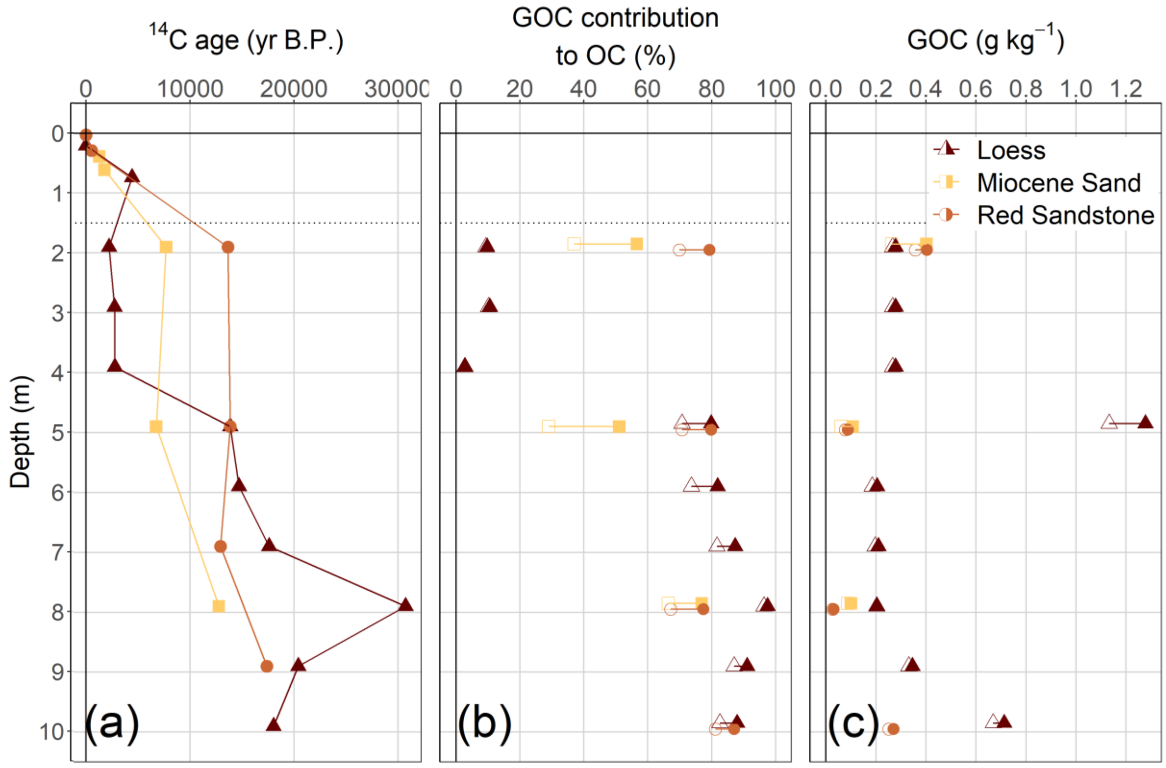

Fig. 3: Depth distribution of apparent ^{14}C ages (in ~~yrs.~~years BP) (a), GOC contribution to OC contents in the sediments (b) and resulting weight based amounts of GOC (c) in the sediments. The range in the contribution from GOC is due to the assumption of an average biogenic OC age of 4,000 (empty 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~~4). To compare the effect of crushing on the respiration of Red Sandstone samples, ~~we compared~~ the mineralisation rates from the first incubation experiment were compared with ~~the mineralisation rates~~those of the second incubation experiment (Table ~~3~~2). 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~~ In a comparison of~~the~~ Loess and ~~the~~ Miocene Sand, both revealed ~~high~~ large differences between samples with the 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~~ have up to 6.8 times lower respiration rate constants ~~compared~~ than ~~to~~ samples from the 2 and 4 m depth. ~~Additionally, t~~There was also a ~~-~~very ~~high~~ wide variation between samples from the same depth (see Fig. A1) as revealed by the high standard deviations. Assuming a constant mineralisation rate ~~constant~~ over time, the results of the incubation experiment would result in mean residence times of between 29 and 135 ~~yrs.~~years for the Loess, 83 and 556 ~~yrs.~~years for the Miocene Sand and between 476 and 1,000 ~~yrs.~~years for the crushed Red Sandstone. Since the CH_4~~-~~

levels of the samples remained ~~on~~ at a low level (Fig. A3) there were no indications ~~for~~ of oxygen-limited conditions during the incubation.

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

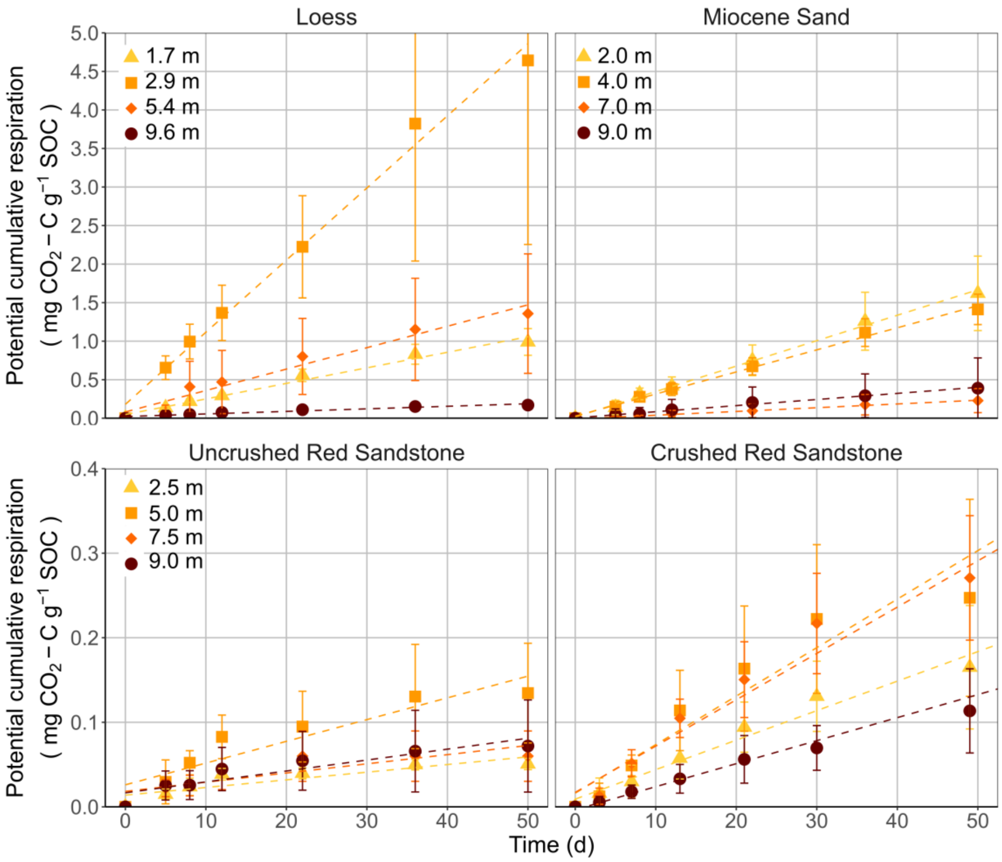

Fig. 4: Potential degradability of sedimentary OC from three sites. Results represent cumulative respiration from Loeses and Miocene Sand samples and both Red Sandstone incubation experiments with uncrushed and crushed samples, with respective standard deviations (n = 4). Dashed lines represent a fitted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

3.4 Possible contribution from geogenic organic carbon to soil organic carbon

~~When the~~As bedrock ~~is~~ weathers~~ing~~, it becomes part of the soil and ~~also~~ GOC also becomes soil OC. The potential amount of GOC in the subsoil was dependent on the sedimentary bedrock (Fig. ~~4~~5). In the subsoil of ~~the~~ Miocene Sand ~~it~~ the proportion of GOC amounted~~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 possible contribution of GOC to soil OC was also calculated under the assumption that the biogenic fraction had an unrealistically high average age of 10,000 years (Fig. A5). This resulted in the GOC fraction falling to 0 for Miocene Sand. For Loess the geogenic fraction fell by ~ 25 %, and for Red Sandstone by ~ 16 %.~~.~~

The presence of ^{14}C-free GOC ~~to~~in soil OC reduced~~s~~ the mean bulk soil OC ^{14}C ages, depending on its proportion ~~on~~ in 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~~ Due to~~of~~ the large proportion of biogenic OC, ~~an~~ no influence of a geogenic fraction ~~is not~~ was detected ~~detectable~~ in the topsoil of these sites. No ^{14}C data ~~are~~ were available for the topsoil of ~~the~~ Miocene

Sand. For all subsoils, the influence of GOC on bulk soil OC ^{14}C contents depend~~s~~ed ~~strongly~~ greatly on the depth and ~~the~~ corresponding OC contents. For ~~the~~ Loess, the possible influence on ^{14}C ages in the subsoils ~~would be~~was quite high, with an average of 10 % reduction in mean apparent ^{14}C ages in the subsoil. Thus it~~It~~ would ~~therefore~~ reduce the measured age ~~from~~ of 4,413 ~~yrs.~~years BP in 74 cm depth by 532-555 ~~yrs.~~years BP. Geogenic OC potentially reduced~~s~~ the mean apparent radiocarbon age of 1,277 ~~yrs.~~years BP ~~in~~ at 0.39 m depth in ~~the~~ Miocene Sand by about 7-9 ~~yrs~~ years, and the radiocarbon age of 1,771 ~~yrs.~~years BP ~~in~~ at 0.61 m depth by 20-24 ~~yrs.~~years. ~~This~~ These reductions are ~~reduction is~~ below the respective standard deviations of the measurement. Nevertheless, ~~in~~ at 1 m depth a given possible proportion of 13.1-16.3 % would reduce an interpolated ^{14}C age of 3,053 ~~yrs.~~years BP by 399-497 ~~yrs.~~years For ~~the~~ Red Sandstone the influence of GOC on ^{14}C ages would be highest in the subsoil. ~~In~~ At 74 cm depth it would ~~influence~~ increase an age of 1,453 ~~yrs.~~years BP by 451-490 ~~yrs.~~years BP. Due to the low amounts of soil OC ~~in~~ at 90 cm depth at the Red Sandstone site, the weight-based median amount of GOC in the sediments ~~is~~ was ~~even~~ four times higher than the biogenic amount of soil OC.

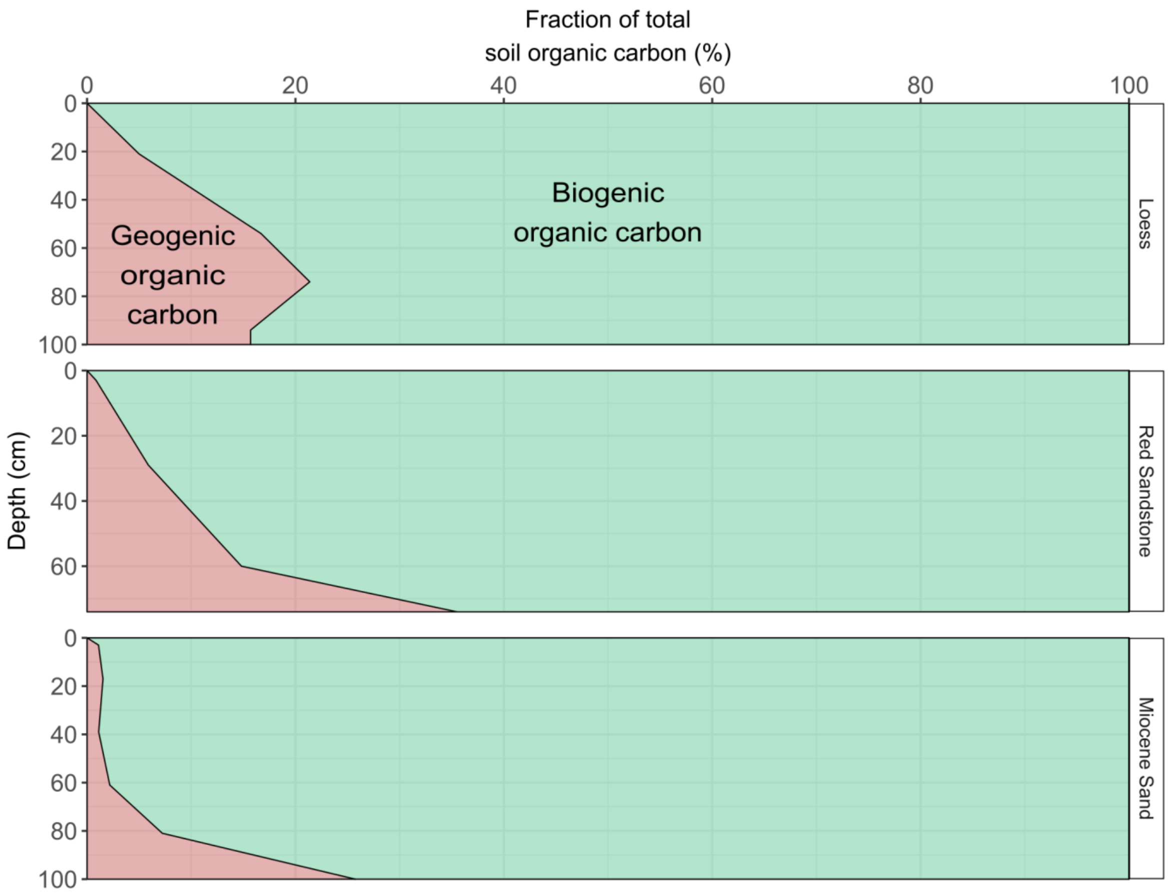

Fig. 5: ~~Highest~~ Largest possible contribution ~~from~~ of GOC to OC (red area) in relation to ~~the~~ bulk OC content, taking into account~~. Here~~ the median GOC contents of the sediments ~~were taken into account~~ for the respective horizontal weight based OC contents. The contribution ~~from~~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

4. Discussion

4.1 Geogenic OC in the sediments

Generally, our calculations on the GOC fraction in the sediments are based on the assumption that biogenic OC in the sediments is not older than 4,000 yrs BP on average. And we also excluded the influence of a biogenic OC fraction that derives from soils that developed before the latest glacial period. Thus, there is uncertainty of a biogenic OC fraction in the sediments since it is unknown when biogenic OC entered the sediments. We assumed a mean age of 1000 to 4000 years based on DO^{14}C data that was leached from the soil. Nevertheless, even with an assumed age of 10,000 years for the biogenic OC fraction, the highest possible contribution was 15 % for the Loss (94 cm depth) and 22 % for the Red Sandstone (74 cm depth) (Fig. A5). A mean age of 10.000 years is an unrealistic assumption since sediments are open systems and may receive OC input throughout the pedogenic period if vegetation is present and not only at the start of pedogenesis.

4.1.1 Site dependent contents of GOC

Regarding ~~our~~ the calculated contribution ~~from~~ of GOC to OC in the sediments, the assumed range of biogenic ^{14}C ages from 1,000-4,000 ~~yrs.~~years BP ~~is~~ was within the typical range for ages of dissolved OC leaching from soils (Artinger et al., 1996, Jia et al., 2019). ~~Despite this~~Nevertheless, the range ~~from~~ of 1,000-4,000 ~~yrs.~~years 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~~ with the contribution for ~~the~~ Red Sandstone and ~~the~~ Loess, especially ~~in~~ at 5 m depth. Compared ~~to~~ with the Red Sandstone, this could be due to deep biogenic carbon inputs, such ~~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~~ with the Red Sandstone site with its shallow bedrock as a root~~-~~-restricting layer (Schneider and Don, 2019). Although ~~we could not~~it was not possible to define the exact rooting depth for ~~the~~ Miocene Sand, this depth probably does not exceed 4 m, according to ~~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~~ at 8 m depth.

In ~~the~~ Loess, the low ^{14}C ages ~~in~~ at 2-4 m depth (2,200-2,770 ~~yrs.~~years BP) in contrast to a ^{14}C age of 4,413 ~~yrs.~~years BP ~~in~~ at 0.74 m depth were surprising. This might indicate past anthropogenic activities or erosion~~-~~-driven material movement that might have led to a mixing of ~~mixed up~~ the upper part of the profile. Furthermore, the modern ^{14}C signature at 21 cm depth could be due to the plough layer at the Loess site mixing the upper 30 cm.~~-~~ 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 can be expected due to the presence of completely different material in the cores in terms of colour and measured OC contents. For example, the very dark Loess at 4 m depth with its high OC content support the assumption of sedimentation circumstances that favoured the accumulation and preservation of OC. This is in accordance ~~to~~ with Jordan and Schwartau (1993) who investigated the same site and assigned the different layers to specific Pleistocene sedimentation periods.

In summary, the contribution ~~from~~ of GOC to sedimentary OC was substrate dependent. A loosely bedded sediment like ~~the~~ Miocene Sand with extremely low concentrations of OC ~~is~~ could be more prone ~~for~~ to infiltration of biogenic OC and dilution of GOC. 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 t~~The GOC contribution within the sediments ~~did not~~was not found to increase with ~~increasing~~ soil depth. This is in contrast to the results of Frouz et al. (2011) ~~showing~~ which showed that different sediment types from a Miocene clay sediment had higher weight~~-~~-based carbon contents ~~in~~ at 150 m compared ~~to~~ with 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~~-~~s, and OC contents were ~~by far~~much higher (28-112 g kg^{-1} dry mass compared to 0.008-10 g kg^{-1} dry mass in our results). However, ~~But~~ it~~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~~ with other studies

It is hard to compare ~~A comparison of~~ the weight~~-~~-based amounts of GOC in terrestrial sediments ~~is difficult,~~ since most studies in ~~that~~ this field rarely determine the amounts of OC in terrestrial sediments, or pre~~-as~~sume that ~~e.g.~~ sandy sediments, for example, do not contain ~~no considerable~~ large amounts of OC (Artinger et al., 1996). Quite high amounts of OC ~~were~~ have been 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~~ strong influence of organic substances from the soil solution without quantifying it, and ~~they~~ did not directly investigate~~d~~ 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~~ with the amounts of around 1 and 5 mg OC g^{-1} found by Krummholz et al. (1997) for Dakota sandstone layers ~~in~~ at > 180 m depth, but is much ~~higher~~ greater than the median GOC amount in ~~the~~ Red Sandstone (0.2 g kg^{-1}) and ~~the~~ Miocene Sand (0.1 g kg^{-1}) in the present study. ~~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~~ with other studies

Loess deposits are ~~comparably~~ relatively well investigated because they provide a record of ~~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~~ the present study ~~is~~ was low compared with studies ~~from~~ by Hatté et al. (1998), Wang et al. (1996) and Strauss et al. (2012). Hatté et al. (1998) investigated 20~~-~~-m ~~depth~~ deep 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~~ deep 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~~ the ~~investigated~~ site in the present study stored comparatively low GOC contents, although most of the ~~studies~~ above-mentioned studies ~~above did~~ do not distinguish between a biogenic and ~~a~~ geogenic OC pool. Nevertheless, as also shown in the present study, Loess had a high OC content compared with other sediments.~~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 t~~The incubation temperature of 20 °C is above the typical mean temperatures in the subsoils underlining incubation derived mineralisation rates to be potential rates.~~ at the investigated sites having a mean annual temperature of 9.2°C~~. For subsoils with comparable climatic conditions, Wordell-Dietrich et al. (2019) found temperatures at 150 cm depth ranging from 4 to 14.4°C over a two-year period. Assuming a Q_{10} value of around two~~2~~ for the assumable difference (Hamdi et al., 2013), the respiration rate at typical subsoil temperatures would be roughly half ~~as high~~that. A direct mineralisation of OC from sediments is in ~~accordance~~ agreement 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~~ the present study is, that ~~these~~ those studies observed this mineralisation when the sediments were directly exposed to the surface or/and were part of a very ~~fast~~ rapidly eroding area~~. Thus~~ with GOC from the sediments ~~already is already~~being ~~in touch with the atmosphere and~~to inputs of ~~the~~ recent vegetation. However, Frouz et al. (2011) conducted an incubation experiment with sedimentary samples from OC~~-~~-rich Miocene clay sediments and~~. They~~ found quite high respiration rate~~ constants~~, with values between ~~3.5-12.3 mg CO_2-C g^{-1} OC y^{-1}~~0.4-1.2 % OC loss per year ~~within~~ during 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) also found high respiration rates of sedimentary samples, with values between ~~0.9-9.5~~0.1-1 % ~~mg CO_2-C g^{-1}~~ OC loss per year~~y^{-1};~~, ~~which they primarily attributed to the physiological status of the soil microbial community expressed as adenylate energy charge~~. Those results are in fairly good agreement with the respiration rate constants observed in the present study ~~These results fit quite well to our observed respiration rate constants (1 – 34.2 mg CO_2-C g^{-1} OC y^{-1})~~. ~~Meanwhile, c~~Compared ~~to~~ with ~~the~~ subsoil incubation experiments, the mineralisation we found ~~in our the present incubation experiment~~for sediments was quite low. For example, in a 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) report~~ed~~ values between 5-15 mg CO_2-C g^{-1} OC ~~of~~ after 28 days, and Soucemarianadin et al. (2018) report~~ed~~ values between 10- and 12.5 mg CO_2-C g^{-1} OC after 70 days. The difference between the ~~observed~~ respiration rates observed in ~~our~~ the present incubation experiment and the results from sedimentary and subsoil incubation experiments ~~might~~ could be due to ~~a result from~~ different microbial communities, ~~quality of~~ OC quality and the physical disconnection 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 theof extreme differences in respiration rates even within the same substrate and sample.~~

~~Our The results of the present~~Our study indicated that there ~~is~~ was a considerable portion of biogenic OC in the sediments. ~~Therefore it could be the case that t~~The observed mineralisation could therefore be ~~is primarily~~ mainly due ~~primarily~~ 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~~A1) promoted~~s~~ 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, t~~The low mineralisation rates of the OC in the sediments might be ~~driven~~ caused by a lack of fresh substrates and/or microorganisms that could enhance the degradation of OC (Fontaine et al., 2007). ~~since~~ Seifert et al. (2011) ~~showed~~ have shown that microorganisms are able to degrade sedimentary OC after the addition of glucose in black slate outcrops. Nevertheless, ~~a~~ mineralisation of OC could only be observed ~~only by~~with the addition of~~adding~~ water, which indicates the widely recognised ~~assumption~~fact of the presence of an active microbial community in the sediments~~, which is a largely recognised assumption~~ (Bomberg et al., 2017, Joergensen and Wichern, 2018, Magnabosco et al., 2018). ~~Since we did not add fresh substrates were not added during the incubation, it has to be taken into account that respiration rates could be even 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 Thus 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 experiment ~~cannot~~ was unable to answer the question ~~if~~ of whether GOC ~~will be~~ is mineralised when it becomes part of the (sub-)soil. Assuming that a large part of the biogenic OC

~~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~~ with the ~~an~~ indirect approach taken by Graz et al. (2010) 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 resists~~ed~~ degradation when it becomes part of the soil due to the results ~~from~~ of 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, also leading to~~ a~~ ~~resistant part~~around 30 % of GOC remaining in the soil~~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~~ no distinction was made between ~~a~~ biogenic and ~~a~~ geogenic OC fractions. 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~~ did not increase with depth, but there were ~~shows~~ clear differences. ~~On the one hand, t~~This ~~represents~~ reflects the sedimentation history with different initial amounts of OC and degradation during sedimentation,~~.~~ which ~~This~~ is particularly evident ~~by~~ in the high amounts of GOC ~~in~~ at 5 m depth ~~of~~ in ~~the~~ Loess. ~~Meanwhile~~However, the contents of GOC, especially in ~~the~~ Red Sandstone and Miocene Sand, were ~~are~~ within the same range ~~over~~ for the whole depth. This might indicate that degradation of GOC is not depth~~-~~-dependen~~d~~t within the sediments. If there ~~would be~~were a stronger degradation of GOC with decreasing depth, ~~one would expect~~ a decreasing amount of GOC could be expected due to the input of water, microorganisms and fresh nutrients from above. Furthermore, there ~~is~~ was a relatively constant contribution ~~from~~ of biogenic OC within the sediments, meaning~~. This means~~ that~~,~~ if biogenic OC enters the sediments~~, together~~ with possibly degrading microorganisms, this biogenic OC might also be ~~preferably~~ largely mineralised. A study by Heitkötter et al. (2018) demonstrate effectively ~~T~~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~~ in sediments, ~~-~~Krummholz et al. (1997) show~~ed~~ that microbial communities ~~are especially present~~can particularly be found in spatially discrete areas. Nevertheless, Heitkötter et al. (2018) also show~~ed~~ 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, for example, are less abundant and stable in sandy soils (Schneider and Don, 2019). ~~-~~With regard to ~~our~~ the ~~investigated~~ sites investigated here, 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 soils, 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~~ often than for~~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).

The conclusion can be drawn ~~This leads to the conclusion~~ that ~~GOC~~ sediment derived OC can and will be degraded when it becomes part of the subsoil but probably to a comparatively ~~low~~ limited extent and low rates with dominant mineralisation of biogenic OC. ~~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 does GOC contributes to soil organic carbon?

The contribution of GOC to soil OC stocks in ~~our~~ this study was~~is~~ driven by the amount of OC in the soil, the amount of GOC in the respective sediment and also ~~its assumed~~the turnover of GOC when it becomes part of the soil. Our results revealed that despite ~~differences~~ differing 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, the greatest~~highest~~ possible contributions to total subsoil OC were found for ~~the~~ Red Sandstone (~30 %) and the 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~~ the investigated soils, the OC contents of 3 g kg^{-1} soil allowed for possible GOC contributions of between 5- and 10 %. For OC contents around 1 g kg^{-1} soil, a GOC contribution of between 10- and 20 % seemed~~s to be~~ possible. ~~Thereby~~ Thus, greater ~~higher~~ contributions were made by~~came from~~ GOC rich sediments ~~like~~ such as~~the~~ Loess, while smaller ~~and lower~~ contributions from sandy sediments. In comparison, van der Voort et al. (2018) estimated the contribution ~~from~~ of GOC ~~of~~ in a soil derived from glacial deposits (flysch) at between 80-100 cm depth to be around 40 %. For a soil developed from a poorly consolidated sedimentary rock (calcareous and shaly moraine), they calculate~~d~~ the contribution ~~from~~ of GOC to range from 20 % ~~in~~ at 145 cm depth to 80 % ~~in~~ at 310 cm depth. ~~There has further been a~~An attempt has also been made to fractionate subsoils to extract the most stable OC that may be derived from GOC. Paul et al. (2001) investigated a soil developed on loess over till with ~~this~~30 % of subsoil OC as a non-hydrolysable fraction ~~non-hydrolysable fraction~~ showing a ^{14}C age of 13,000 ~~yrs.~~years BP.~~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.~~years~~BP.~~ They also concluded that this high ^{14}C age can partly be explained by a GOC fraction. These results indicate that ~~especially~~ deposits from the past glacial periods, such as ~~like~~ flysch or till in particular, have ~~a~~ much ~~higher~~ greater potential for OC contributions from GOC, possibly due to the~~ir~~ higher amounts of GOC in their sediments. Since ~~we~~ only ~~investigated~~ terrestrial sediments were investigated in the present study, it should be noted ~~it has to be taken into account~~ that ~~also~~ marine sediments or shales also contain much higher amounts of OC, up to 250 g kg^{-1} (Hemingway et al., 2018, Petsch et al., 2000). Thus, the ~~Their~~ amount of GOC they conatin and their possible contribution to subsoil OC stocks might therefore be much higher.

Nevertheless, the ^{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, the ^{14}C ages of soil OC are primarily driven by climatic conditions, clay content and age of the soil~~, since soil development started~~ (Mathieu et al., 2015). However, ~~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~~ of possible contributions could be obtained when the amount of OC is known. Thus, ~~at~~ on a global scale, the high ^{14}C age of subsoils is not ~~only~~ driven just by the GOC fraction but the presence of GOC may ~~considerable~~ greatly influence subsoil ^{14}C.

5. Conclusions

~~With our~~This approach of estimating the GOC contribution to soil OC~~, we could show~~ showed that common and abundant terrestrial sediments~~,~~ with low amounts of sedimentary OC~~,~~ can make a considerable contribution~~e~~ ~~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~~ particularly 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 properties may partly be derived from the GOC in the subsoil. The sediments at the investigated sites contained OC in a range ~~from~~ of 0.1-0.3 g kg^{-1}, allowing for contributions from GOC of between 10-30 % in subsoils. Incubation of sediments ~~seem to~~ indicated that this geogenic contribution presents a quite stable OC pool, especially for subsoils. Thus, ~~also~~ even sediments with comparatively low amounts of OC were also able to demonstrate the large contribution of GOC~~, 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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