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Carbonate recrystallization in root-free soil and rhizosphere of *Triticum aestivum* and *Lolium perenne* estimated by ^{14}C labeling

Martina Gocke · Konstantin Pustovoytov · Yakov Kuzyakov

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Abstract Under arid and semiarid conditions, pedogenic (secondary) carbonates are formed in soil by precipitation of Ca^{2+} from soil parent material with dissolved CO_2 originating from root and rhizomicrobial respiration. $\delta^{13}C$ values of secondary $CaCO_3$ record the photosynthetic pathway of former vegetation and is therefore used as a tool for paleoenvironmental studies. The time scale of pedogenic carbonate formation as well as the influence of several environmental factors are crucial, yet poorly known. We estimated the recrystallization rate of pedogenic carbonate by the ^{14}C isotopic exchange method. $^{14}CO_2$ was assimilated by plants, respired into the rhizosphere and subsequently incorporated into secondary carbonate by recrystallization of primary loess carbonate. With ascending number of $^{14}CO_2$ pulses, the amount of rhizosphere ^{14}C recovered in loess $CaCO_3$ increased linearly, leading to recrystallization rates of 3.2×10^{-5} and 2.8×10^{-5} day^{-1} for wheat and ryegrass, respectively. In loess close to roots, recrystallization rates more than twice as high were obtained. Extrapolating these rates we showed that several hundred years are necessary for complete recrystallization of primary loess $CaCO_3$ in root-free substrate, assuming that both primary and secondary carbonate is recrystallized several times. In contrast, the process probably takes only decades in rhizosphere loess if carbonaceous encrustations form around the root, impeding repeated recrystallization. This indicates the importance of rhizosphere processes (e.g. respiration of roots and microorganisms, exudation) for secondary carbonate formation.

Keywords ^{14}C pulse labeling · Loess · Pedogenic $CaCO_3$ · Recrystallization rate · Rhizosphere processes · Soil CO_2

M. Gocke (✉) · Y. Kuzyakov
Department of Agroecosystem Research, BayCEER, University of Bayreuth, 95447 Bayreuth, Germany
e-mail: martina.gocke@uni-bayreuth.de

K. Pustovoytov
Institute of Soil Science and Land Evaluation (310), University of Hohenheim, 70593 Stuttgart, Germany

Introduction

The formation of pedogenic (secondary) carbonates by interaction of Ca^{2+} from soil parent material with dissolved CO_2 of soil air, plays an important role in pedogenesis in soils of semiarid and arid regions like southwest USA (Machette 1985) or Russian steppe (Lebedeva et al. 2002; Lebedeva and Ovechkin 2003). Highest abundance of secondary carbonate accumulations occurs under semiarid conditions with mean annual precipitation of less than approximately 500 mm (Birkeland 1999).

Stable carbon (C) isotope studies demonstrate that C of pedogenic carbonates originates from root and rhizomicrobial respiration (Cerling 1984; Cerling et al.

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1989). C from primary (lithogenic) $CaCO_3$, if the latter is present, is replaced by C from soil CO_2 and thus does not contribute to the C isotopic composition of secondary carbonates (Cerling 1984; Nordt et al. 1996). The isotopic composition ($\delta^{13}C$ and $\Delta^{14}C$) of pedogenic carbonate is thus related to the isotopic composition of soil CO_2; it reflects the former local vegetation with regard to the photosynthetic pathway (Cerling et al. 1989; Amundson et al. 1989; Cerling and Quade 1993). Based on the C exchange during recrystallization, pedogenic carbonates can help reconstruct the paleoclimate and paleovegetation (e.g. Buck and Monger 1999; Deutz et al. 2001; Boguckyi et al. 2006; Achyuthan et al. 2007; Pustovoytov et al. 2007). They can also help estimate former CO_2 concentrations in the Earth's atmosphere (Cerling 1991, 1992; Royer et al. 2001; Tanner et al. 2001) and are useful in chronological studies using radiocarbon dating (e.g. Amundson et al. 1994; Wang et al. 1996; Pustovoytov et al. 2007). Beyond stable carbon isotope composition, also the $^{18}O/^{16}O$ ratio in pedogenic carbonate can provide paleoclimatic information (e.g. Cerling 1984; Dworkin et al. 2005). Royer et al. (2001), however, pointed out that the temporal resolution of stable isotope analysis based on pedogenic $CaCO_3$ is limited by the time scale of secondary carbonate formation.

The high potential of pedogenic carbonate as a proxy is complicated by the fact that carbonate, once formed, theoretically can be recrystallized with time and thus lose its paleonvironmental and chronological value. This potential problem of alteration of carbonate archives by diagenesis or overprint has been recognized in the literature (Cerling 1991; Amundson et al. 1994; Budd et al. 2002). Changes in profile distribution of ^{14}C ages of artificial lime mortar have been demonstrated for a soil on a cultural layer (Pustovoytov and Leisten, 2002).

Few attempts, however, have been made to estimate the recrystallization period of pedogenic $CaCO_3$ in the field, based either on radiocarbon data or on stable carbon isotopic composition. Pendall et al. (1994) estimated the recrystallization rate indirectly by comparing radiocarbon ages of these carbonates with ages determined independently from isotopic methods. Very low recrystallization rates impede assessing the process and rule out applying stable carbon isotope natural abundance. Thus, current methods of geosciences are insufficient to determine the recrystallization rate of secondary carbonates in situ.

A new approach—the estimation of pedogenic carbonate recrystallization rates under controlled conditions by artificial ^{14}C isotopic labeling—was introduced by Kuzyakov et al. (2006). The method enables estimating the amount of root-derived C incorporated into primary $CaCO_3$ by recrystallization by isotopic exchange. It involves exposing plants to an artificially labeled $^{14}CO_2$ atmosphere. After $^{14}CO_2$ assimilation by plants, transport of assimilates belowground, subsequent release into the rhizosphere by root and rhizomicrobial respiration and recrystallization with primary loess carbonate, the ^{14}C label was recovered quantitatively in loess $CaCO_3$.

Our previous study (Gocke et al. 2010) showed that recrystallization of loess carbonate by direct contact with added CO_2 takes place also without plants, but in a smaller scope. The estimated rates of 10^{-7} day^{-1} without plants (Gocke et al. 2010) were approximately two orders of magnitude lower than rates with plants (Kuzyakov et al. 2006). This indicates the importance of biological processes (root respiration and microbial decomposition of root exudates) for the recrystallization of soil carbonate. This calls for considering the effect of living plants on the carbonate recrystallization rate. As no other studies have estimated this rate, we compared the effect of two plants: wheat and ryegrass.

This study aims: (1) to demonstrate the methodological sensitivity and reproducibility of the ^{14}C isotopic exchange method for quantifying pedogenic carbonate recrystallization, (2) to estimate initial recrystallization rates of loess $CaCO_3$ under controlled conditions and to extrapolate the periods necessary for complete recrystallization to show the accuracy limit of temporal resolution in paleoenvironmental studies based on $\delta^{13}C$ values of pedogenic carbonates, (3) to uncover possible differences in recrystallization intensities between agricultural cereals and pasture plants, (4) to reveal the influence of root vicinity on $CaCO_3$ recrystallization.

Materials and methods

Plants and growing substrate

To test the effect of plant species on the recrystallization rate of pedogenic carbonate, two species—the agricultural cereal winter wheat [*Triticum aestivum*

(L.)] and pasture grass [perennial ryegrass, *Lolium perenne* (L.)]—were investigated. Both species belong to the family Poaceae, but show differences concerning growth rate, percentage of assimilated C that the plant allocates belowground and invests into rhizosphere processes, and length of the growing season.

The plants were grown on loess originating from a depth of 15 m below the present soil surface. Loess from this depth is not influenced by modern pedogenic processes like humification, leaching or calcification. For our experiment this means that, firstly, CO_2 concentration and fluxes from root and rhizomicrobial respiration are not disturbed by CO_2 produced by microbial decomposition of soil organic matter and, secondly, the loess $CaCO_3$ is primary, i.e. not recrystallized, and shows a uniform spatial distribution and grain size. In summary, we simulated the conditions of initial soil formation in loess.

Experiment layout and plant growing conditions

Wheat and ryegrass were grown on loess from an open cast mine at Nussloch (SW Germany, see Bente and Löscher 1987). The loess contained 29% $CaCO_3$. Many studies about the loess from Nussloch contain sedimentological (e.g. Löscher and Zöller 2001) as well as stratigraphic and paleoclimatic (e.g. Hatté et al. 1999, Moine et al. 2005) information.

As plant pots, we used polycarbonate filtration devices with three inlets in the lid and one main opening for growth of the plant shoots (CombiSart, Sartorius AG, Germany; real volume 340 ml). The devices were described in detail by Kuzyakov and Siniakina (2001). The chamber of the CombiSart device was used as a loess-root compartment, separated from the outlet in the bottom by a perforated filter support overlain by a viscose mesh. The CombiSart devices can be unscrewed, allowing non-destructive sampling of loess and roots.

Seeds from wheat and ryegrass were pre-germinated for 3 and 6 days, respectively. Each plant pot was filled with 450 g of air-dried and sieved loess and planted with 4 seeds of wheat or 6 seeds of ryegrass. For the introduction of microorganisms, 10 ml of soil extract from a Haplic Luvisol (developed from loess) were added. As loess, contrary to soil, does not contain nutrients, the plants were treated with Hoagland nutrient solution (Hoagland and Arnon 1950). The nutrient solution was modified by doubling the amounts of KH_2PO_4 and KNO_3 and omitting the $Ca(NO_3)_2{\cdot}4\ H_2O$ to compensate the huge amount of Ca^{2+} ions available from loess $CaCO_3$. The applied nutrient solution contained 138, 62 and 469 μg ml^{-1} of N, P and K, respectively. The plants were grown at 14/10 h day/night periods, light intensity of 300 μmol m^{-2} s^{-1}, and loess moisture was equal to 70% of water holding capacity (WHC = 28% of loess weight).

The experiment layout included seven treatments for each plant species:

(1) Plants in sealed pots, labeled once
(2) Plants in sealed pots, labeled twice
(3) Plants in sealed pots, labeled three times
(4) Plants in sealed pots, labeled four times
(5) Plants in sealed pots, labeled five times
(6) Plants in open pots, labeled twice
(7) Plants in open pots, labeled five times.

For each of the seven treatments, three replications were made, yielding a total of 42 plant pots (21 pots for each plant). The first pulse labeling of wheat was done 27 days after planting, and of ryegrass 59 days after planting. The subsequent isotopic pulses were applied in intervals of 5 days.

^{14}C labeling and sampling

One day before the first labeling, the openings in the pots were completely closed by plugs and sealed around the plant shoot. For this purpose, every shoot was encased with cellulose, covered by a non-toxic two-component silicone paste (NG 3170, Thauer & Co., Germany). The seal was tested for air leaks. By using sealed plant pots, the air from the root-loess compartment could be separated from the atmospheric air, thus avoiding a loss of ^{14}C labeled and total CO_2. The two treatments with unsealed pots were applied to simulate natural conditions by allowing air exchange between atmosphere and the loess-root compartment. Directly before applying the first ^{14}C pulse label, every pot was flushed with atmospheric air for several hours by a membrane pump (Type SMG4, Gardner Denver Thomas GmbH, Germany). All CO_2 previously released by root and rhizomicrobial respiration and accumulated within the rhizosphere during plant growth was thus

removed from the pots. The moisture in loess was then enhanced to 95% of WHC to bypass dryness during the 5 days until the next ^{14}C pulse.

All pots of one plant species were labeled simultaneously in an airtight chamber. The label, consisting of 407 kBq of ^{14}C as $Na_2^{14}CO_3$ (ARC Inc., USA) per plant pot, was diluted with 10 ml of de-ionized water in a 30 ml vial. Previously, the water was slightly alkalinized to prevent loss of ^{14}C activity by exchange with atmospheric CO_2. After connecting the output of the label solution vial with the label chamber, $^{14}CO_2$ was released by adding 3 ml of 5 M H_2SO_4 to the label solution and pumped through the chamber in a closed cycle for 10 min by a membrane pump. The plants stayed in the chamber for 3 h (wheat) or 4 h (ryegrass) to allow for assimilation of the ^{14}C labeled CO_2. After that time, the air of the chamber was pumped through 15 ml of 1 M NaOH to trap the remaining unassimilated CO_2. The chamber was opened and the plants continued growth under normal conditions.

Prior to the next labeling, the rhizosphere air of every plant pot was pumped through 15 ml of 1 M NaOH for 90 min in a closed cycle to trap CO_2 from root and rhizomicrobial respiration. Three plants were selected for analysis and the remaining plants were labeled again as described above.

From the harvested replications, shoots were cut and roots were separated from loess ("non-rhizosphere loess") with tweezers. The roots, together with adhering loess (in the following termed "rhizosphere loess"), were washed with 60 ml of slightly alkalinized de-ionized water to remove loess and dissolved inorganic and organic carbon (DIC and DOC). Both shoots and roots were dried at 60°C and grinded in a ball mill (MM200, Retsch, Germany). The solution obtained from root washing, containing loess directly adjoining the roots, was filtrated by a stainless steel pressure filter holder (SM 16249, Sartorius, Germany). Three grams from mixed non-rhizosphere loess were washed with 10 ml of slightly alkalinized de-ionized water. All loess samples were dried at 90°C.

^{14}C sample analysis

After the labeling, ^{14}C activities of the residue of the label $Na_2^{14}CO_3$ solution and of unassimilated CO_2 trapped in NaOH were measured on 1 ml aliquots mixed with 2 ml of scintillation cocktail (Rotiszint EcoPlus, Carl Roth, Germany) after decay of chemiluminescence (for NaOH). The ^{14}C measurements were done using a 1450 LSC & Luminescence Counter (MicroBeta TriLux, Perkin Elmer Inc., USA). The ^{14}C counting efficiency was at least 70%, the measurement error did not exceed 3.5%. The absolute ^{14}C activity was standardized by SQP(E) by adding increasing amounts of NaOH as a quencher. ^{14}C activity of respired CO_2 trapped in 15 ml of NaOH was measured on 1 ml aliquots in the same way.

To analyze ^{14}C incorporated into plant biomass, small amounts of plant material (35 mg from shoots and 45 mg from roots) were combusted in an oven ("Feststoffmodul 1300", AnalytikJena, Germany). The CO_2 released by combustion was trapped in 8 ml of 1 M NaOH. ^{14}C activity of the NaOH was measured on 1 ml aliquots as described above.

^{14}C activities of loess carbonate, DIC and DOC were measured on larger aliquots because we expected comparatively low ^{14}C activities in these samples. The ^{14}C counting efficiency of the scintillation spectrometer (LS 6500 Multi-Purpose Scintillation Counter, Beckman, USA) was at least 90% and the measurement error did not exceed 4%. The absolute ^{14}C activity was standardized by the H number method, using a ^{137}Cs external standard.

^{14}C activity of the washing water from the rhizosphere and non-rhizosphere loess was measured on 4 ml aliquots for total dissolved carbon and for DOC after release of CO_2 from DIC by adding 0.2 ml of 1 M HCl. ^{14}C activity of DIC was calculated by subtracting the ^{14}C in washing water before and after DIC release.

To measure ^{14}C incorporated into loess carbonate, we did not combust the loess samples (the usual method for soil samples) but rather dissolved the samples by acid, as combustion would lead to CO_2 release not only from carbonate but also from organic matter accumulated in loess by plant growth. Two grams of every dried loess sample (rhizosphere and non-rhizosphere) were treated with 15 ml of 3 M H_3PO_4, and the CO_2 evolving from $CaCO_3$ was trapped in 12 ml of 2 M NaOH during 4 h to assure complete CO_2 absorption. ^{14}C activity of loess carbonate was measured on 6 ml aliquots of NaOH added to 12 ml of scintillation cocktail. Prior to ^{14}C analyses in loess carbonate, this method was tested

for reliability by treating a sample of strongly ^{14}C enriched ryegrass shoot biomass with 3 M H_3PO_4 in the same way as described above. Subsequent ^{14}C analyses revealed a lack of ^{14}C in NaOH, showing that no organic C was released from shoot biomass by phosphoric acid.

Total inorganic and organic carbon contents in washing water were measured using a N/C analyzer ("Multi N/C 2100", AnalytikJena, Germany). Total carbon content of respired CO_2 trapped in NaOH was measured by titrating 0.1 ml aliquots with 0.01 M HCl against phenolphthalein after adding 1 M $BaCl_2$ solution (Zibilske 1994).

Calculations of carbonate recrystallization rate and statistical analysis

The ^{14}C results are presented as percentages of total assimilated ^{14}C ($^{14}C_{ass}$), which was calculated by subtracting the ^{14}C activities of the label residue ($^{14}C_{res}$) and of unassimilated CO_2 trapped in NaOH ($^{14}C_{NaOH}$) from the input ^{14}C activity ($^{14}C_{input}$).

$$^{14}C_{ass} = {}^{14}C_{input} - {}^{14}C_{res} - {}^{14}C_{NaOH} \quad (1)$$

The ^{14}C specific activity ($^{14}C_{SA}^{CO_2}$) of CO_2 respired by roots and rhizomicrobial microorganisms was calculated as the ratio of ^{14}C activity ($^{14}C^{CO_2}$) and total C content in respired CO_2 ($C_t^{CO_2}$):

$$^{14}C_{SA}^{CO_2} = \frac{^{14}C^{CO_2}}{C_t^{CO_2}} \quad (2)$$

We assume that the ^{14}C specific activities of respired CO_2 and of C that was incorporated into the loess carbonate by recrystallization and formation of secondary $CaCO_3$ are equal. Therefore, the amount of recrystallized $CaCO_3$ ($C_{t_{recryst}}^{CaCO_3}$) was calculated according to Eq. 3, based on ^{14}C activity of loess $CaCO_3$ ($^{14}C^{CaCO_3}$). The open pots were not sealed to allow an undisturbed exchange of air inside and outside of the pots. Therefore, the carbonate recrystallization in these pots better reflect the natural conditions. However, the ^{14}C specific activity in the pots was diluted by atmospheric CO_2. Thus, to calculate the amount of recrystallized $CaCO_3$ (Eq. 3), we used the average ^{14}C specific activity of respired CO_2 in sealed pots with the respective number of applied isotopic pulses, as the CO_2 respired by roots and rhizosphere microorganisms is identical in open and closed pots:

$$C_{t_{recryst}}^{CaCO_3} = \frac{^{14}C^{CaCO_3}}{^{14}C_{SA}^{CO_2}} \quad (3)$$

Finally, the recrystallization rate of the secondary $CaCO_3$ was calculated as the amount of recrystallized $CaCO_3$-C divided by the amount of total C content of the loess carbonate ($C_t^{CaCO_3}$) and by the time (t) between the first labeling and the respective sampling (25 days at maximum).

$$CaCO_3 \text{ recrystallization rate} = \frac{C_{t_{recryst}}^{CaCO_3}}{C_t^{CaCO_3} \cdot t} \quad (4)$$

Standard errors of means are presented in figures. Significance of differences between the treatments was analyzed by one-way ANOVA with $\alpha = 5\%$ significance level.

Results

Budget of assimilated ^{14}C

Throughout the experiment, the largest percentage of assimilated ^{14}C was allocated in plant biomass. ^{14}C activities in shoots and roots of wheat plants remained approximately constant during the experiment, with shoot values fluctuating between 84.9 and 86.4% of recovered ^{14}C, and root values between 8.6 and 10.6% (Fig. 1). In contrast, ryegrass plants showed a distinct decrease of ^{14}C activity in shoots from 92.7 to 74.8% and an increase in roots from 4.5 to 16.2%. Accordingly, the total living plant biomass comprised up to 97% of recovered ^{14}C. These values do not include the treatments with plant pots open for air exchange (shaded columns in Fig. 1). Due to $^{14}CO_2$ gas losses, the distribution patterns of recovered ^{14}C in these treatments are not in-line with the temporal changes observed in those treatments of sealed pots.

^{14}C activities in respired CO_2 reflect accumulated ^{14}C from the 1st pulse label to the respective sampling date. The part of assimilated ^{14}C found in respired CO_2 increased from 1.3 to 2.1% for wheat, and from 0.9 to 3.2% for ryegrass. In open plant pots these values remained low (0.7% at maximum) and did not increase as much as in sealed pots due to CO_2 and $^{14}CO_2$ losses to atmospheric air.

The most obvious differences between both plant species, concerning the balance of incorporated ^{14}C,

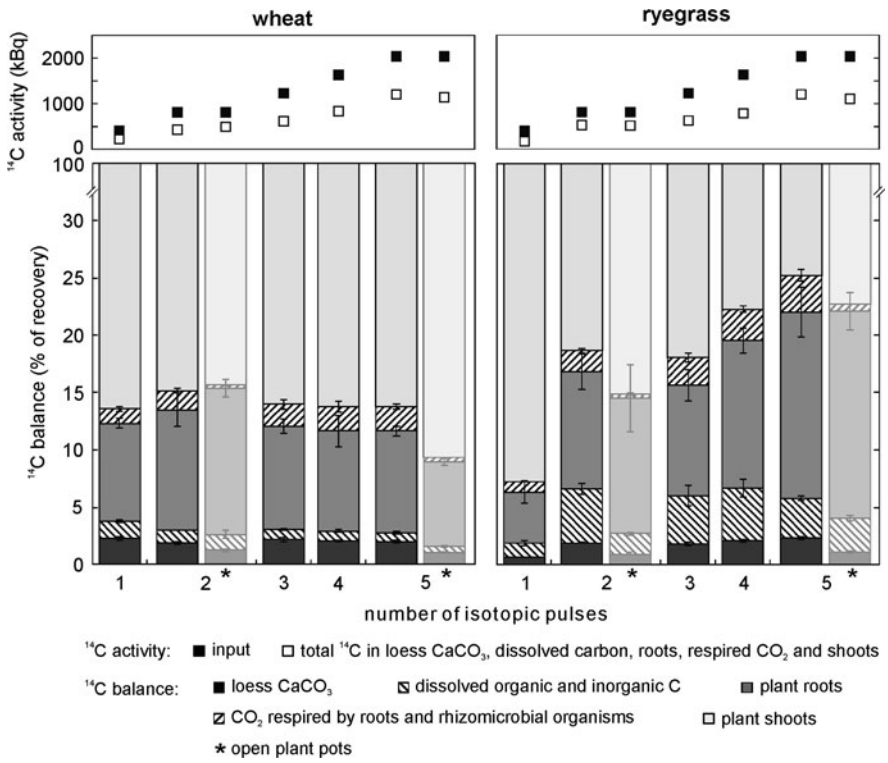

Fig. 1 Overview of ^{14}C dynamics for wheat and ryegrass. The upper diagrams show the totally recovered ^{14}C activities compared to the added ^{14}C label (summed up). A loss of up to 40% of the ^{14}C label by shoot respiration agrees with literature data (Kuzyakov et al. 2001). The lower diagrams show the distribution of recovered ^{14}C between above- and belowground C pools. Shaded columns represent the distribution patterns of unsealed plant pots

were evident in loess carbonate and in dissolved C. In wheat, ^{14}C activity in loess carbonate varied slightly between 1.8 and 2.2%, and ^{14}C activity in dissolved C decreased from 1.5 to 0.8% from 1st to last sampling date. In ryegrass, the corresponding values were an increase from 0.7 to 2.3% and an increase from 1.2% to values between 3.5 and 4.7%.

A closer look at ^{14}C recoveries in loess carbonate, DIC and DOC from rhizosphere and non-rhizosphere substrate shows that, for wheat, the recovery in both non-rhizosphere and rhizosphere loess $CaCO_3$ remained approximately constant (Fig. 2). The latter is approximately 10–14% of total ^{14}C activity recovered in loess carbonate. In non-rhizosphere loess, the percentage of recovered ^{14}C activity in DIC was initially higher than in DOC, decreased permanently, and was lower than DOC from the 4th sampling on. In rhizosphere loess, the percentage of DIC-^{14}C was much lower than DOC-^{14}C and decreased down to zero whereas DOC remained constant (Fig. 2, left).

In ryegrass, ^{14}C recovery increased more consistently in non-rhizosphere versus rhizosphere loess carbonate, the latter containing between 6 and 16% of total loess carbonate ^{14}C activity. In non-rhizosphere loess, the percentage of ^{14}C recovered in DIC remained constant and was lower than DOC from the onset, while ^{14}C in DOC increased strongly between 1st and 2nd sampling. In rhizosphere loess, the percentage of ^{14}C in DIC remained low with little variation, while in DOC it first showed an increase, then slightly decreased (Fig. 2, right).

Dissolved inorganic carbon (DIC) consists of CO_2(aq), HCO_3^- and CO_3^{2-}. Dissolved organic carbon (DOC) comprises root exudates and microbial decomposition products. The absolute recovery of ^{14}C activity increased in both of these C pools during the experiment in non-rhizosphere loess. However, the steeper incline of ^{14}C activity in DOC, leading to a decreasing $^{14}C_{DIC}/^{14}C_{DOC}$ ratio, reflects increasing amounts of root exudates remaining in the loess during plant growth. At the same time, the ^{14}C in inorganic carbon in solution (DIC) cannot be accumulated because it undergoes recrystallization with and incorporation into $CaCO_3$. In loess adjacent to roots (rhizosphere loess), equal (wheat) or even higher (ryegrass) percentages of ^{14}C were recovered in DOC versus loess $CaCO_3$ due to root exudation.

During plant growth, assimilated ^{14}C was incorporated also in solid organic compounds in loess

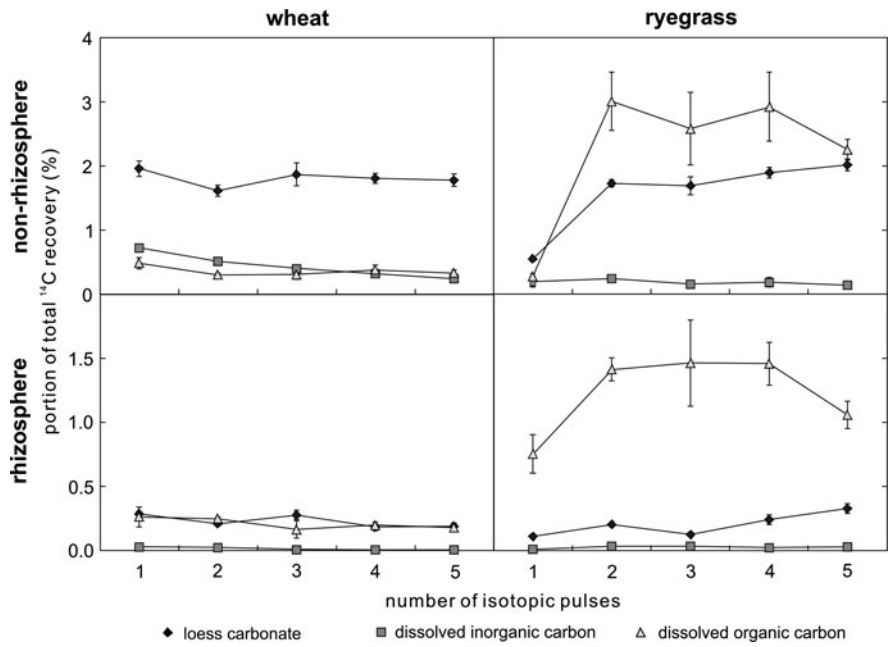

Fig. 2 ^{14}C activities recovered in loess carbonate, DIC and DOC of non-rhizosphere and rhizosphere loess as percentage of total ^{14}C recovery

(e.g. lipids), released either by plant roots or by rhizomicrobial organisms decomposing plant remains. The above-described ^{14}C distribution patterns neglect this organic C pool in loess. Lipid extraction from ryegrass loess samples showed that in non-rhizosphere and rhizosphere loess, extractable lipids contribute merely 0.08–0.15% and 0.01–0.02% to the totally recovered ^{14}C, respectively (Gocke et al., unpublished data).

Calculated recrystallization rates in rhizosphere and root-free loess

The amount of recrystallized loess $CaCO_3$ as a portion of total loess carbonate was calculated for each of the five sampling dates in sealed and in open plant pots. The calculation is based on ^{14}C activity in loess $CaCO_3$ and ^{14}C specific activity of CO_2 evolved by root and rhizomicrobial respiration. As ^{14}C specific activities of $^{14}CO_2$ in open pots was low due to losses to atmospheric air, the amounts of recrystallized carbonate in open pots were calculated using the average ^{14}C specific activities of $^{14}CO_2$ in sealed pots from the same sampling date, and the ^{14}C activity recovered in loess.

Although the percentage of ^{14}C recovered in loess carbonate did not change significantly during the experiment (Fig. 1; for ryegrass from 2nd sampling on), calculated amounts of recrystallized carbonate increased from the first to the last sampling date (Fig. 3). The absolute ^{14}C activity in loess $CaCO_3$ as well as the total ^{14}C recovery increased from 1st to 5th sampling due to addition of equal ^{14}C pulses at every labeling (see upper diagrams in Fig. 1).

Wheat as well as ryegrass showed linearly increasing amounts of recrystallized carbonate up to day 25 of the labeling (Fig. 3). In the *non-rhizosphere loess* samples, the recrystallized portion of loess $CaCO_3$ in sealed plant pots rose from 0.06 to 0.15% (wheat) and from 0.02 to 0.16% (ryegrass). As the graph of the trend curves intersected the time axis approximately at the date of the 1st pulse label, we set the intersection at zero and recalculated the slopes. The slopes then corresponded to recrystallization rates of 6.2×10^{-5} day^{-1} (wheat) and 6.1×10^{-5} day^{-1} (ryegrass). At average, the recrystallization in open plant pots was approximately half as fast as in sealed pots despite similar ^{14}C distribution patterns in both treatments (see Fig. 1). The CO_2 concentration in the open plant pots reflected more likely the natural conditions in soil. For this reason, the slope of the recrystallization lines for the open plant pots (Fig. 3) expresses the actual $CaCO_3$ recrystallization rates under laboratory conditions of 3.2×10^{-5} day^{-1} for wheat and 2.8×10^{-5} day^{-1} for ryegrass (Table 1).

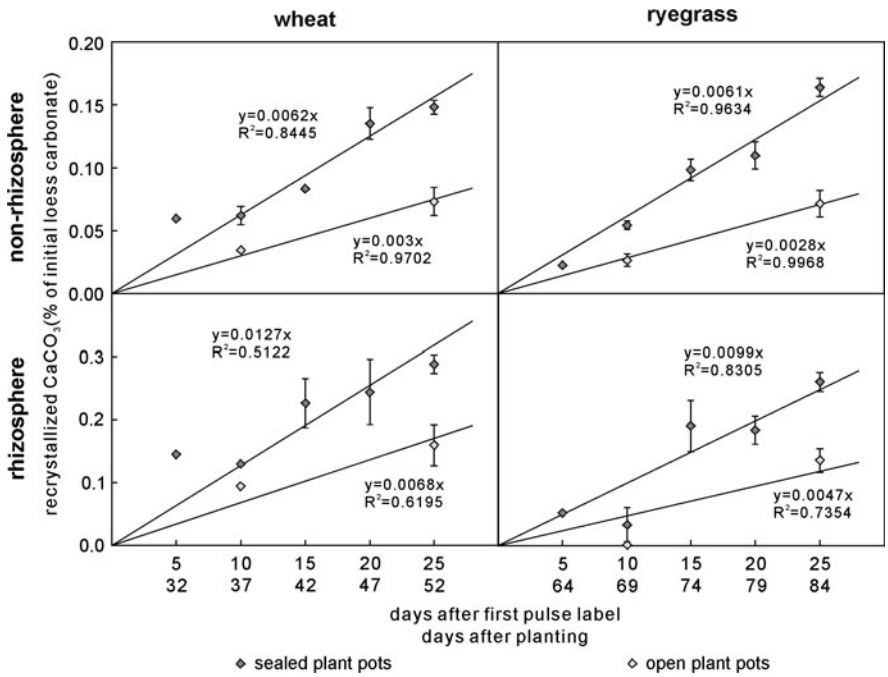

Fig. 3 Percentage of loess $CaCO_3$ recrystallized since the first pulse label in "root-free" loess samples (non-rhizosphere loess) and in loess adjacent to roots (rhizosphere loess) for wheat (left) and ryegrass (right). The linear trends reflect the recrystallization rates as % of initial $CaCO_3$ day^{-1}

Table 1 Recrystallization rates calculated based on ^{14}C incorporated into loess $CaCO_3$ in different treatments

Recrystallization rates (day^{-1})	Wheat		Ryegrass	
	Root-free	Rhizosphere	Root-free	Rhizosphere
Sealed pots	6.2×10^{-5}	12.7×10^{-5}	6.1×10^{-5}	9.9×10^{-5}
Open pots	3.2×10^{-5}	6.8×10^{-5}	2.8×10^{-5}	4.7×10^{-5}

The sampled *rhizosphere loess* comprised only 6 mass% of the total amount of loess (average of all sampling dates). However, 12.5% of ^{14}C recovered in loess carbonate was allocated in the rhizosphere. This suggested higher recrystallization intensity near plant roots, which was confirmed by the calculated amounts of recrystallized $CaCO_3$: At the last sampling date, recrystallized portions of loess carbonate in open plant pots with wheat were 0.07% and 0.16% in root-free and rhizosphere loess, reflecting recrystallizaton rates of 3.2×10^{-5} day^{-1} and 6.8×10^{-5} day^{-1}, respectively (Fig. 3). In contrast to non-rhizosphere loess samples, the calculated amounts in rhizosphere loess show rather high standard errors of the mean and, in the case of ryegrass, a rather high deviation from the linear trend (Fig. 3). The reason is a sampling-related irregular distinction between rhizosphere and non-rhizosphere material, leading to different portions of non-rhizosphere material in the rhizosphere samples. Nevertheless, in the case of wheat, the rates in the rhizosphere and root-free loess differed significantly from each other.

Discussion

Estimation of $CaCO_3$ recrystallization rates using the ^{14}C isotopic exchange approach

Based on the exchange of primary loess $CaCO_3$-C with C from root and rhizomicrobial respiration, we applied the isotopic exchange approach with ^{14}C as tracer to estimate the recrystallization rate of loess $CaCO_3$. Despite removal of root and rhizomicrobial respired CO_2 prior to each subsequent labeling, an

artificial effect of the method on carbonate recrystallization can be excluded for the following reasons. First, we assume that CO_2 concentrations equal to the situation before CO_2 removal were reached within few hours because of permanent CO_2 supply over the time period of the experiment. Second, even if the removal of CO_2 prior to each labeling has entailed artificial precipitation of secondary carbonate, this presumably small portion of the total amount of secondary carbonate formed with ^{12}C and ^{13}C instead of ^{14}C and therefore was not included in the calculations based on ^{14}C activities in secondary carbonate. Therefore, the ^{14}C isotopic exchange approach yields reliable results and does not lead to artificially high recrystallization rates despite CO_2 removal from loess air prior to each labeling.

The method was first used to estimate pedogenic carbonate recrystallization by Kuzyakov et al. (2006). Their results as well as our current study show that the methodological sensitivity is high enough to detect the very low $CaCO_3$ recrystallization rates. Both studies yielded similar initial recrystallization rates of about 3×10^{-5} day^{-1} in loess not adjacent to roots (non-rhizosphere loess), although growing conditions (nutrient supply) and experimental layout (plant species and age at the day of the first isotopic pulse) were not identical. This shows the good reproducibility of the ^{14}C isotopic exchange approach. Despite the very slow process, we were able to reproduce the former estimate, even with a modified experimental design. Nonetheless, our understanding of carbonate recrystallization in soils remains limited by the artificial conditions of the experiment. Especially the restricted space for root growth hinders direct extrapolation to field conditions.

Influence of plant species on ^{14}C dynamics and $CaCO_3$ recrystallization

We chose two plant species: (1) wheat (*Triticum aestivum*) to represent a typical agricultural cereal, and (2) ryegrass (*Lolium perenne*) to represent pasture grasses. The stage of plant development at the date of the first ^{14}C pulse differed for these species because ryegrass grows much slower than wheat.

The root biomass of wheat remained constant during the experiment, while root amounts in ryegrass increased from the first to the last sampling date. It is common for perennial plants that they increase C allocation belowground during the first year. Similar patterns were shown by the ^{14}C distribution: constant or even decreasing percentage of assimilated ^{14}C were recovered in belowground C pools of wheat, while strongly increasing percentages of ^{14}C were found in belowground C pools of ryegrass (Fig. 1, 4).

Throughout the experiment and for both species, shoots comprised a much higher percentage of incorporated ^{14}C than roots. The distribution of total labeled and unlabeled C in plant biomass cannot be concluded directly from the distribution of the ^{14}C label (Kuzyakov and Domanski 2000). However, the recorded temporal changes in ^{14}C distribution patterns (Fig. 1) roughly represent the natural situation: during plant growth, the percentage of belowground translocated assimilated C decreases for cereals (e.g. Palta and Gregory 1998), while it increases for pasture

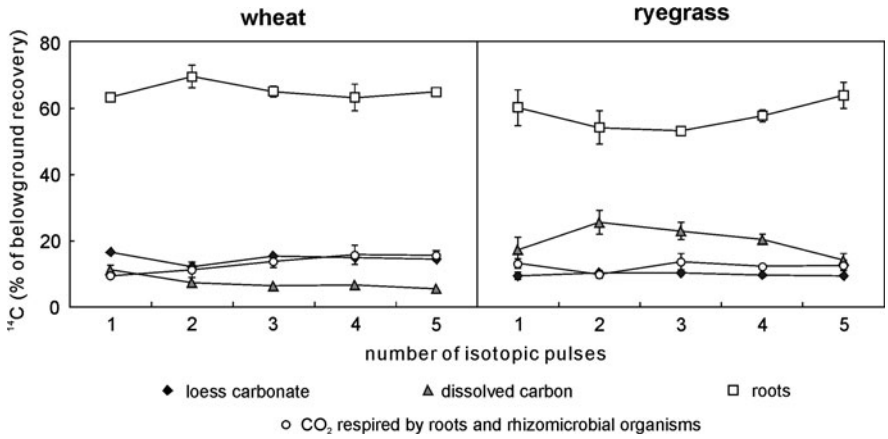

Fig. 4 Distribution of recovered ^{14}C between belowground C pools as percentage of total belowground ^{14}C activity

grasses (Kuzyakov et al. 2001). The increasing part of ^{14}C recovered in ryegrass roots (from 4.5 to 16.2%) demonstrates the ascending C allocation to belowground pools by the pasture grass.

Despite different ^{14}C distribution patterns, both species showed similar recrystallization rates of approximately 3×10^{-5} day^{-1} for non-rhizosphere loess. The replicates showed no significant difference between the rate in wheat and that in ryegrass. This was surprising because we expected different rooting properties of agricultural and pasture plants to result in differing carbonate recrystallization rates: In our study, more belowground plant biomass and thinner roots of ryegrass versus wheat provided more root surface for rhizosphere processes (respiration, exudation). This situation is reflected by higher percentages of recovered ^{14}C in ryegrass dissolved organic carbon (DOC) than in wheat DOC (Fig. 2). Several reports show that pasture plants translocate approximately 30–50% of assimilated C into the soil (e.g. Swinnen 1994), compared with only 20–30% for cereals (e.g. Meharg and Killham 1990, 1991) as a result of breeding. This discrepancy, also found in field studies (Mensah et al. 2003), may be compensated by higher total CO_2 assimilation of cereals because of higher productivity (Kuzyakov and Domanski 2000), resulting in nearly equal C input of pasture and agricultural plants (1,500 kg C ha^{-1} year^{-1}) if the same time periods of growth are considered (Whipps 1990; Martin and Merckx 1992; van Ginkel et al. 1997).

In a study without living plants, the recrystallization rate strongly depended on the CO_2 concentration in soil air, with the graph describing a saturation curve where maximum amounts of recrystallized $CaCO_3$ were obtained at a CO_2 concentration of 5% (Gocke et al. 2010). For wheat and ryegrass, the CO_2 concentration in soil air of open plant pots averaged $6.7 \pm 0.5\%$ and $6.3 \pm 0.5\%$. This probably explains the similar recrystallization rates.

Greater differences in plant characteristics (e.g. part of assimilated C used for belowground processes, respiration rates, exudation rates, growth rates, amount of fine roots, etc.) could lead to more widely diverging rates.

Effect of root vicinity on recrystallization rates

The carbonate recrystallization rates calculated in loess adjacent to roots were approximately twice as high as in "root-free" loess (Table 1). This shows the importance of vegetation for the rates of secondary $CaCO_3$ formation. The three main factors controlling dissolution and precipitation of $CaCO_3$ are: (1) CO_2 partial pressure in pore space, (2) pH of soil solution, and (3) mass flow of dissolved carbon species.

According to the Henry Law, the solubility of CO_2 increases directly proportional to CO_2 partial pressure. This means that high CO_2 concentration in soil air should lead to a higher concentration of H^+ in soil solution by dissociation of carbonic acid, and thus to a decreasing pH. High $CaCO_3$ content in loess buffers these pH variations. Nevertheless, the dependence of $CaCO_3$ recrystallization on CO_2 concentration is evident when comparing sealed and open plant pots: In sealed pots, both CO_2 concentrations (11.1% for wheat, 17.7% for ryegrass) and recrystallization rates were twice or three times as high as in open pots allowing air exchange with the atmosphere. Independent of plant species, accumulation of respired CO_2 leads to enhanced dissolution and recrystallization of primary $CaCO_3$. This is supported by a previous study without living plants (Gocke et al. 2010) which showed that the recrystallization intensity increases with ascending CO_2 concentration in a range between 380 and 50,000 ppm CO_2. Under field conditions, soil CO_2 concentrations typically vary between the atmospheric value (around 0.04%) and 100 times the atmospheric value (Davidson 1995). However, only few studies distinguish between CO_2 concentrations in the rhizosphere and those in root-free soil. Gollany et al. (1993) showed that pCO_2 decreases smoothly with increasing distance to the root surface of sorghum plants within the first few millimeters. Hinsinger et al. (2003) suggest that the effect of CO_2 released by root and rhizomicrobial respiration is locally limited because of the higher diffusivity of CO_2 when compared to dissolved inorganic C species. That means that high CO_2 concentration occurs only locally, adjacent to the plant roots where CO_2 supply is constant. Our present data confirm this: recrystallization rates were significantly higher in the rhizosphere versus "root-free" loess of wheat and ryegrass.

The pH in soil and especially in rhizosphere of living plants is affected by several interacting factors. These were listed by Hinsinger et al. (2003) as (1) bulk soil pH and pH buffering capacity, (2) H^+ or OH^- release by roots for a neutral anion/cation

balance, (3) release of organic anions from fatty acids, (4) root exudation and respiration, (5) redox-coupled processes, (6) environmental and nutritional factors. Moreover, as revealed by Gras (1974) and Nye (1981), the effect of increased root and rhizomicrobial respiration on rhizosphere pH becomes much more noticeable in calcareous than in acidic soils. Some of these factors were affected in our study by using a nutrient solution that contained nitrogen (N) solely as NO_3^-, resulting in OH^- release by plant roots, and by applying loess as a growth medium (pH (H_2O) $\approx$ 8.4, $CaCO_3$ content 29%).

CO_2 release by roots and rhizosphere microorganisms is at least 1 order of magnitude higher compared to H^+ or OH^- release by roots (Lambers et al. 1996; Durand and Bellon 1993; Durand et al. 2001). Thus, high CO_2 concentrations (also in the open plant pots) were one of the main factors promoting and accelerating loess $CaCO_3$ recrystallization in general, and especially in the rhizosphere. In arable soils, however, the rhizosphere pH and $CaCO_3$ recrystallization intensity could also be affected by fertilizer composition (type of added N as anions or cations, amount of PO_4^{3-}). Yongliang et al. (2001) measured a remarkable decrease of rhizosphere pH compared with bulk soil after applying NH_4^+ fertilizer to pines. Moreover, soil fertility management can increase the recrystallization rate by increasing the belowground biomass, promoting CO_2 flux (Lal and Kimble 2000).

Our sampling design did not permit determining the extent of the rhizosphere effect on loess carbonate recrystallization as a function of distance to the root surface. We suggest, however, that considerably higher rates are limited to the first few millimeters adjacent to the roots. A more detailed view on this relation is desirable and might be possible by applying special sampling approaches: e.g. platy plant boxes (rhizotrons), or separation of soil layers with increasing proximity to the root surface (Kuzyakov et al. 2003). Regarding longer time scales than in our study (years to centuries), the effects of CO_2 partial pressure and rhizosphere pH might be minor compared with the effect of water movement and soil moisture changes. Transport of dissolved Ca^{2+} and HCO_3^- towards the root might enhance $CaCO_3$ precipitation in a diameter of up to several centimeters around the roots. This is possible in calcareous sediments, where high amounts of Ca^{2+} in the rhizosphere can lead to the formation of encrustations around roots termed rhizoliths (Klappa 1980). A high $CaCO_3$ content together with homogeneity and high porosity in loess or calcareous sands (e.g. dune sands) as well as active, long-living roots provide a high potential for such rhizolith formation (Gocke et al. unpublished data).

Extrapolation of $CaCO_3$ recrystallization rates over longer periods

Two approaches for extrapolating the initial recrystallization rate over longer time periods can be considered. In the first approach, the precondition is that every molecule of primary $CaCO_3$ is affected by recrystallization once, and thereafter removed from recrystallization, e.g. by formation of concretions. This corresponds to a linear decrease of the remaining primary $CaCO_3$ with the slope of obtained recrystallization rates. Such a linear decrease translates into complete recrystallization after 100 years at maximum (Fig. 5a, b). The second approach assumes repeated recrystallization of the calcium carbonate. This assumption results in an exponential decrease of remaining primary carbonate with recrystallization

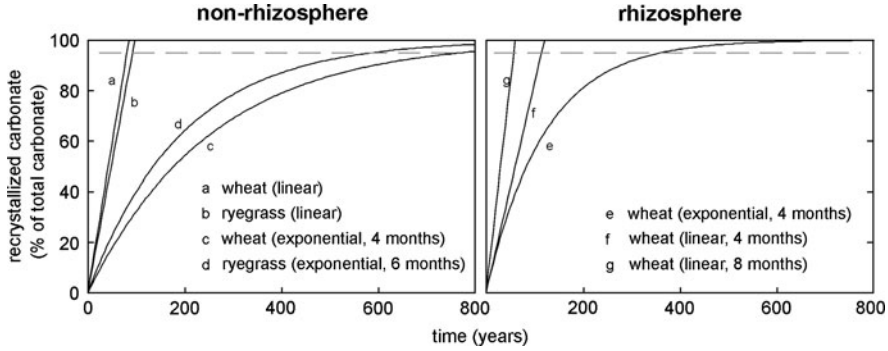

Fig. 5 Recrystallization periods extrapolated by linear and exponential models as depending on the root vicinity and growth season

periods between several hundreds of years and more than 1000 years, depending on the length of the growing season (see Kuzyakov et al. 2006). The amount of recrystallized carbonate ($CaCO_3(t)$) is calculated as follows:

$$CaCO_3(t) = 100 \cdot \left(1 - e^{-t \cdot rate \frac{GS}{365}}\right) \quad (5)$$

with t: time in days, rate: recrystallization rate in day^{-1}, GS: growing season in days. In the following, if the exponential approach is considered, the term recrystallization period means the time necessary for recrystallization of 95% of the $CaCO_3$ initially present in loess. A remaining percentage of 5% of primary carbonate is too small to be detected by mass spectrometric analysis of the natural abundances of stable C isotopes ($\delta^{13}C$).

We modeled the recrystallization periods with typical growing seasons, i.e. 4 months for wheat and 6 months for ryegrass, and calculated the periods necessary for the recrystallization of 95% of primary loess carbonate (Fig. 5c, d). The result was about 800 years for wheat and 600 years for ryegrass. In contrast, only 360 years would be necessary for 95% recrystallization of $CaCO_3$ in rhizosphere of wheat (Fig. 5e). Clearly, the formation of secondary carbonate in soil may be faster directly on the root surface. An extreme case of such a root-mediated process is rhizoliths (Klappa 1980; Gocke et al. unpublished data) and calcified root cells (Pustovoytov and Terhost 2004; Wang and Greenberg 2007). After the formation of initial secondary $CaCO_3$ portions, the root may die. The secondary carbonate crystals, however, may grow further because they have much smaller volume to mass ratio compared to dispersed (primary or secondary) $CaCO_3$ in loess. In case of rhizolith formation, secondary carbonate is removed immediately and will not be affected by recrystallization again. Recrystallization should thus lead to a linear decrease of the amount of remaining primary carbonate. Applying the linear approach to the rate of wheat (growing season 4 months), we extrapolated a recrystallization period of 120 years for recrystallization of 95% of primary $CaCO_3$ (Fig. 5f). However, due to a relatively low nutrient content of loess, plants growing on this sediment are predominantly evergreen plants with growing seasons of up to 8 months. This would potentially lead to a complete (95%) recrystallization within about 60 years (Fig. 5g). These periods are just a rough approximation because they were extrapolated with rhizosphere recrystallization rates of wheat. Rhizoliths, however, more likely were formed by bush or tree vegetation (Gocke et al. unpublished data), whose initial recrystallization rates are unknown. Nevertheless, our modeled data agree with the assumption that rhizoliths form rather fast (decades or even years) during the plant's life time and/or beginning decay (e.g. Wang and Greenberg 2007; Klappa 1980).

As mentioned above, the chronological resolution of paleoenvironmental studies based on pedogenic carbonates is limited not by the analytical precision of the instruments (IRMS for $\delta^{13}C$ or AMS for $\Delta^{14}C$), but by the period necessary for secondary carbonate formation. This should be considered when carbonates are used for high-resolution paleoclimatic and paleoecological studies (e.g. Wang and Greenberg 2007).

Conclusions

The ^{14}C isotopic exchange approach is a very sensitive and reliable tool for estimating low $CaCO_3$ recrystallization rates. It is currently the only approach to estimate recrystallization rates of carbonates in soil based on isotopic exchange with $^{14}CO_2$ released in the rhizosphere after plant labeling. Using this approach, we calculated a very low initial loess $CaCO_3$ recrystallization rate of 3×10^{-5} day^{-1}, which is in accordance with literature data. Similar rates were calculated in root-free loess from wheat and ryegrass, but loess adjacent to roots showed rates that were more than twice as high. This reflects the importance of root respiration and microbial respiration by decomposition of root exudates for $CaCO_3$ recrystallization and becomes relevant especially for exponential extrapolation of rates on recrystallization periods: In non-rhizosphere loess, primary $CaCO_3$ would be completely recrystallized after hundreds of years, depending on the plant's growing season, while the process would be considerably shorter within the rhizosphere. The relation between the carbonate recrystallization rate and the distance to roots is a very important aspect determining the process duration. Therefore, it merits further investigation.

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