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RESEARCH ARTICLE

Relevance of nonfunctional linear polyacrylic acid for the biodegradation of superabsorbent polymer in soils

Mo Bai · Burkhard Wilske · Franz Buegger · Jürgen Esperschütz · Martin Bach · Hans-Georg Frede · Lutz Breuer

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Abstract Biodegradability is a desired characteristic for synthetic soil amendments. Cross-linked polyacrylic acid (PAA) is a synthetic superabsorbent used to increase the water availability for plant growth in soils. About 4 % within products of cross-linked PAA remains as linear polyacrylic acid (PAA_{linear}). PAA_{linear} has no superabsorbent function but may contribute to the apparent biodegradation of the overall product. This is the first study that shows specifically the biodegradation of PAA_{linear} in agricultural soil. Two ^{13}C-labeled PAA_{linear} of the average molecular weights of 530, 400, and 219,500 g mol^{-1} were incubated in soil. Mineralization of PAA_{linear} was measured directly as the $^{13}CO_2$ efflux from incubation vessels using an automatic system, which is based on ^{13}C-sensitive wavelength-scanned cavity ring-down spectroscopy. After 149 days, the PAA_{linear} with the larger average molecular weight and chain length showed about half of the degradation (0.91 % of the initial weight) of the smaller PAA_{linear} (1.85 %). The difference in biodegradation was confirmed by the $\delta^{13}C$ signature of the microbial biomass ($\delta^{13}C_{mic}$), which was significantly enriched in the samples with short PAA_{linear} (−13‰ against reference Vienna Pee Dee Belemnite,VPDB) as compared to those with long PAA_{linear} (−16‰ VPDB). In agreement with other polymer studies, the results suggest that the biodegradation of PAA_{linear} in soil is determined by the average molecular weight and occurs mainly at terminal sites. Most importantly, the study outlines that the size of PAA that escapes cross-linking can have a significant impact on the overall biodegradability of a PAA-based superabsorbent.

Keywords Polymer mineralization · Polyacrylate · Water superabsorbent polymer (SAP) · $^{13}CO_2$ efflux

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M. Bai · B. Wilske (✉) · M. Bach · H.-G. Frede · L. Breuer
Institute for Landscape Ecology and Resources Management (ILR), Research Centre for BioSystems, Land Use and Nutrition (IFZ), Justus-Liebig-Universität Gießen, Gießen, Germany
e-mail: brkwils@yahoo.com

F. Buegger · J. Esperschütz
Helmholtz Zentrum München, German Research Center for Environmental Health, Institute of Soil Ecology, München, Germany

Introduction

Cross-linked polyacrylic acid (PAA) is used as water superabsorbent and soil amendment. Superabsorbent polymers (SAP) including cross-linked PAA absorb water up to several hundred times of their own weight and are applied in horticulture and in dry regions to avoid soil water deficit and soil erosion (Puoci et al. 2008; Agaba et al. 2010). Many studies confirmed the benefits of SAP products for plant growth (Geesing and Schmidhalter 2004; Orzeszyna et al. 2006; Guiwei et al. 2008; Moslemi et al. 2012).

However, the synthetic soil amendments such as SAP are required to be biodegradable to protect soil and water resources from latent pollution. Therefore, environmental regulations aim at the complete biodegradation of a substance, which essentially means that basically every single monomer of a synthetic polymer should be mineralized to CO_2 and water.

Oligomers of acrylic acid in activated sewage sludge degrade quickly, e.g., 70–80 % within less than 35 days (Larson et al. 1997). With respect to the use of PAA-based SAP as soil conditioner, however, it is important to know the stability of the synthetic product in soil. For example, almost up to 10 % within a product of cross-linked PAA is soluble polyacrylate (Rittmann et al. 1992; Sack et al. 1998). This soluble fraction can potentially leach from the soil amendment into the groundwater. Furthermore, insoluble cross-linked PAA can decompose to water-soluble compounds (Sack et al. 1998; Cameron et al. 2000). A slow degradation of PAA in soil

has been interpreted as a result of high molar mass and cross-linking (Stahl et al. 2000). However, PAA contains up to 4 % linear PAA (Sack et al. 1998). This linear polyacrylic acid (PAA_{linear}) contributes little to the function of the superabsorbent, but it may contribute significantly to the biodegradability of the overall PAA product, in particular because the biodegradability of a product is usually estimated based on relatively short degradation studies. Therefore, it was the first objective of the present study to determine specifically the biodegradation of PAA_{linear} in soil.

Different methods were used to determine the stability or, vice versa, the degradation of PAA and related SAPs. Phang et al. (2011) applied thermogravimetric analysis to determine the degradation of PAA-containing copolymers in soil. Another often used method involves liquid cultures or soil incubations of ^{14}C-labeled polymers, whereby the mineralization of cross-linked PAA, polyamide/polyacrylate copolymers, or soluble PAA was measured by means of the $^{14}CO_2$ evolution (Rittmann et al. 1992; Mai et al. 2004; Stahl et al. 2000; Wolter et al. 2010). However, ^{14}C isotope labeling may not be environmentally safe, and hence, it is subjected to special laboratory conditions. In contrast, the use of the stable ^{13}C isotope for labeling is safe and free of environmental concerns. Basically, the isotopic signature of $\delta^{13}C$ can be used to determine the SAP degradation, although this method can fail in soils with high soil organic carbon (Entry et al. 2008). In the present study, the biodegradation of PAA_{linear} was measured by means of a novel system, which automatically couples the gas sampling from a series of dynamic chambers to $^{13}CO_2$-sensitive wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) (Bai et al. 2011, 2013; Wilske et al. 2013). Thus, biodegradation was measured directly as the $^{13}CO_2$ efflux from incubations including ^{13}C-labeled PAA_{linear} in soil.

Biodegradation occurs when microorganisms use polymer as an energy and/or carbon source, which includes the enzymatic oxidation of the compound. Mainly fungi but also some bacteria contribute to the degradation of PAA (Sutherland et al. 1997; Cameron et al. 2000; Matsuoka et al. 2002; Mai et al. 2004). With respect to the diverse polymers compiled by Schnabel (1981) and Gross and Kalra (2002), biodegradation generally increases from cross-linked to linear polymers, from large to small chain lengths and/or molecular weights, and it often occurs at the terminal base or chain ends only. Based on the same understanding, a test system was used consisting of two variants of ^{13}C-labeled PAA_{linear}, whereby one variant of linear polymer was about half the size of the other. The ratio in biodegradation of short to long polymer was expected to be reciprocally proportional to the increment in chain length, if the two working hypotheses were to be confirmed that the biodegradation of PAA_{linear} (1) increases with decreasing average molecular weight (MW_a) and (2) occurs mainly at the end of chains. With respect to the small percentage of PAA_{linear} in SAP, the second objective was to examine whether reasonable increments in biodegradability of PAA_{linear} of decreasing size may attain amounts that can significantly contribute to the overall biodegradation, which is observed with SAP products.

To mathematically describe the degradation of PAA_{linear} in soil, the study reverted to a first-order decay model (FODM) and a double-exponential model (DEM). Both models performed well in reflecting the decomposition of native soil organic matter (Wider and Lang 1982), pyrolized organic matter (Bai et al. 2013), and the degradation of synthetic organic material in soil (Alexander 1994).

Material and methods

Polyacrylic acids and soil incubation

Four PAA_{linear} were obtained from the Institute for Organic and Macromolecular Chemistry, Heinrich Heine University, Düsseldorf, Germany. Two PAA_{linear} of different molar mass contained 9 % (weight to weight) of acrylic acid monomers that were ^{13}C single-labeled, i.e., only the carboxyl-C was ^{13}C (Table 1, $PAA_{linear}1$* and $PAA_{linear}2$*). Two further PAA_{linear} of corresponding molar masses were synthesized from unlabeled monomers only. Both labeled and unlabeled monomers were from Sigma-Aldrich (Taufkirchen, Germany). Soil incubations of PAA_{linear} without ^{13}C labeling served as reference samples, which also eliminated potential effects of priming. Unlabeled and carboxyl-labeled PAA_{linear} were applied on the same weight basis. Thus, the experiments accounted for different average molecular weights (MW_a) and different number of individual molecules, i.e., different number of chain ends. The number average molecular weight (M_n), i.e., the molecular weight reflecting the polymerization-immanent variability, included a reduction of 59 %. Hence, the ratio of average chain length from long ($PAA_{linear}2$*) to short chain polymer ($PAA_{linear}2$*) was 1:0.41 (Table 1). However, soil incubations tested on an equal weight basis contained an equal total of labeled carboxyl groups. Accordingly, a terminal degradation could be inferred, if the measurements resulted in a

Table 1 Parameters of the labeled and unlabeled linear polyacrylic acids: labeled short-chained $PAA_{linear}1$* and long-chained $PAA_{linear}2$* and corresponding unlabeled linear polyacrylate

Polyacrylic acid	M_n (g mol^{-1})	C (%)	$\delta^{13}C$ (‰)	^{13}C (%)
$PAA_{linear}1$*	219,500	32.37	1548	0.90
$PAA_{linear}1$	255,600	35.10	−26.07	0.38
$PAA_{linear}2$*	530,400	32.16	1510	0.88
$PAA_{linear}2$	490,200	33.02	−25.23	0.36

M_n number average molecular weight

degradation ratio of 2.4:1 ($PAA_{linear}1^*/PAA_{linear}2^*$) of short to long PAA_{linear}. A ratio much larger than 2.4:1 would indicate that the degradation is not restricted to terminal sites only.

The soil for the incubation of PAA_{linear} was obtained from the field experiment station Rauischholzhausen of the Justus Liebig University, Giessen, Germany. The soil was a silt loam (texture 72.2 % silt, 20.1 % clay, 7.7 % sand) with a pH of 5.3 (0.01 M $CaCl_2$) and a C/N ratio of 4.64 (1.35 % organic C and 0.29 % N). The ^{13}C content and the $\delta^{13}C$ of the soil were 0.014 % and −26.86‰, respectively. Prior to experimental use, the soil was air-dried, and subsequently, a part of the soil was preincubated at a moisture content of 50 % water-holding capacity for 14 days.

The ^{13}C-labeled PAA_{linear} was mixed in a proportion of 0.1 % (*w*/*w*) with 250 g soil (50 g dry soil and 200 g preincubated soil) and transferred to 1-L incubation vessels. For reference samples, unlabeled PAA_{linear} was mixed in a similar proportion. Continuous microbial activity was checked by means of the total CO_2 efflux ($^{12}CO_2+^{13}CO_2$) from soil samples, which were incubated without polymer application. The moisture of the samples was adjusted to 40 % soil water-holding capacity. Each sample, reference sample, and soil-only sample was tested in four replicates (i.e., 4×($PAA_{linear}1^*$ and $PAA_{linear}2^*$, $PAA_{linear}1$ and $PAA_{linear}2$, and soil-only)=20 samples in total). All samples were incubated at 25 °C for 149 days.

Measurement of biodegradation

The novel method to measure the biodegradation of recalcitrant carbon compounds including PAA has been explained in previous publications (Bai et al. 2011, 2013; Wilske et al. 2013). Briefly, the $^{13}CO_2$ efflux from ^{13}C-labeled compounds was determined using an automated system that couples a batch of open dynamic chambers to WS-CRDS. The coupling between incubation vessels and analyzer was facilitated by three levels of microprocessor-controlled valves. The analyzer at the core of the system provided direct quantification of both the ^{13}C and the ^{12}C stabile isotope in CO_2 of sample gas (i.e., the separate mixing ratios of $^{13}CO_2$ and $^{13}CO_2$ in μmol mol^{-1}; WS-CRDS model G1101-i, Picarro, Sunnyvale, CA, USA). One sample after the other is connected through to the WS-CRDS, while the other samples are flushed with ambient air at the same rate using an external pump. After a sample is connected to the analyzer, carryover effects are flushed out during the first 180 s, while the $^{13}CO_2$ efflux is averaged over the following six records (60 s). Subsequently, the $^{13}CO_2$ concentration of the ambient air is measured for 180 s to enable elimination of fluctuations in $^{13}CO_2$ at the inlet of the incubation vessels. Calibration of the measurements was checked regularly using at least two $^{13}CO_2$ isotope standards enclosing the target mixing ratios (e.g., −20‰ V-PDB in CO_2 totals of 200 and 1,000 μmol mol^{-1}; Deuste-Steininger GmbH, Mühlhausen, Germany).

Apparent recovery of polyacrylic acid

In addition to the PAA_{linear}/soil samples, incubations of pure soil, i.e., without PAA treatment, were measured along with the other samples. After the experiments, the pure soil samples were used as reference samples to calculate the apparent recovery of PAA_{linear}. One gram of soil was sampled from each incubation vessel, and the $\delta^{13}C$ of the soils, the ^{13}C-labeled PAA_{linear}, and the nonlabeled PAA_{linear} treatment were determined by isotope ratio mass spectrometry (IR-MS). This $\delta^{13}C$ analysis was conducted at the Helmholtz Centre Munich using an IR mass spectrometer (delta V Advantage, Thermo Finnigan, Bremen, Germany) coupled with an elemental analyzer (Euro EA, Eurovector, Milan, Italy).

The $\delta^{13}C$ in microbial biomass (C_{mic})

In order to assess the total amount of PAA_{linear}-carbon that was metabolized and introduced into microbial biomass at the end of experiments, the soil samples were analyzed for $\delta^{13}C_{mic}$ following chloroform-fumigation extraction (Vance et al. 1987; Esperschütz et al. 2009). The samples were extracted in triplicate using 0.5 M K_2SO_4 solution. Total organic C content in the extracts as well as the $\delta^{13}C$ in total organic carbon was measured by on-line coupling of liquid chromatography and stable isotope ratio mass spectrometry (LC IsoLink, Thermo Electron, Bremen, Germany). Microbial biomass was calculated using a kEC factor of 0.45 (Wu et al. 1990).

Calculation and statistics

The $^{13}CO_2$ efflux F (μg g^{-1} soil day^{-1}) from samples was calculated based on Bai et al. (2013) as

$$F = \frac{U \times 10^{-6} \times (C_{out} - C_{in}) \times b}{MV \times W} \times 60 \times 24 \quad (1)$$

where U represents the gas flow rate (22 mL min^{-1}), C_{out} (μmol mol^{-1}) the $^{13}CO_2$ concentration in the chamber, C_{in} (μmol mol^{-1}) the $^{13}CO_2$ concentration in ambient air (μmol mol^{-1}), b the molar mass of ^{13}C (g mol^{-1}), MV the temperature- and pressure-adjusted molar volume (m^3 mol^{-1}), and W the weight of soil (g).

The ^{13}C mineralization (μg μg^{-1} applied ^{13}C day^{-1}) due to PAA_{linear} degradation was calculated as

$$^{13}C_{min} = \frac{F_{labeled} - F_{non-labeled}}{A} \quad (2)$$

where $^{13}C_{min}$ (μg μg^{-1} applied ^{13}C day^{-1}) was referenced to the initial ^{13}C application A (μg g^{-1} soil). $F_{labeled}$ and $F_{nonlabeled}$ are the ^{13}C efflux from ^{13}C-labeled and nonlabeled PAA_{linear} treatment, respectively. The remaining ^{13}C in initial weight $^{13}C_{rem}$ (μg μg^{-1} applied ^{13}C) was calculated as

$$^{13}C_{rem} = 1 - \Sigma^{13}C_{min} \quad (3)$$

where $\sum^{13}C_{min}$ (μg μg^{-1} applied ^{13}C) is the cumulative ^{13}C mineralization after a definite number of days. Two models were applied to describe the underlying kinetic of the degradation based on the course of remaining ^{13}C in initial weight (μg μg^{-1} applied ^{13}C). The basic difference between the models lies with the pool of carbon compounds that are subjected to degradation. The FODM implicates a uniform carbon pool. In contrast, a DEM is often used to reflect the mineralization of a more heterogeneous carbon pool of (yet) undefined fractions (Lehmann et al. 2009). As a first approximation, the DEM considers the overall carbon pool being composed of easier degradable carbon compounds (C_1) and a more recalcitrant pool of carbon compounds (C_2). The FODM model is

$$^{13}C_{rem} = {}^{13}C0 \times e^{-k \cdot t} \quad (4)$$

The DEM is

$$^{13}C_{rem} = {}^{13}C1 \times e^{-k_1 \cdot t} + {}^{13}C2 \times e^{-k_2 \cdot t} \quad (5)$$

where $^{13}C_{rem}$ is the ^{13}C weight remaining from the initial weight after a certain number of incubation days, $^{13}C_0$ is the initial carbon applied at the start of experiment is required, and k, k_1, and k_2 are the rate constants of decrease (day^{-1}), respectively. Note that in the present case, C_2 is equal 1 minus C_1. The apparent recovery of PAA was then calculated as

$$AR = \frac{^{13}C_p + {}^{13}C_s - {}^{13}C_{end}}{^{13}C13} \times 100\% \quad (6)$$

where AR (%) is the apparent recovery of PAA_{linear}. The $^{13}C_p$ is the amount of ^{13}C application of labeled PAA_{linear} in the soil, and the $^{13}C_s$ is ^{13}C content of the soil at the start of the experiment (both in μg μg^{-1}soil). $^{13}C_{end}$ is the total ^{13}C content of labeled PAA_{linear} treatment at the end of experiment. Note that within the 149 incubation days, the loss of ^{13}C from native soil organic carbon was negligibly small as compared to the ^{13}C applied with the polymer.

The δ^{13}C in microbial biomass ($\delta^{13}C_{mic}$) was calculated according to Marx et al. (2007) and Esperschütz et al. (2009) as

$$\delta^{13}C_{mic}(‰) = \frac{\delta^{13}C_{fum} \times C_{fum} - \delta^{13}C_{n.fum} \times C_{n.fum}}{C_{bio}} \quad (7)$$

where $\delta^{13}C_{fum}$ and $\delta^{13}C_{n\text{-}fum}$ are δ^{13}C in fumigated and nonfumigated extracts, respectively. C_{fum} and $C_{n\text{-}fum}$ are C concentrations (mg C L^{-1}) of fumigated and nonfumigated extracts, and C_{bio} is the microbial C concentration (mg C L^{-1}).

The $^{13}CO_2$ efflux rates from samples and reference samples were tested for significant differences (p=0.05) using univariate analysis of variance (ANOVA, IBM SPSS version 20, NY, USA). The significance of the means of the accumulated net degradation rates of PAA_{linear} was checked using repeated measure analysis of variance (RM-ANOVA; ditto), whereby treatment and time were used as fixed factors. Nonlinear regression and linear regression analyses were used to calculate the parameters k, and k_1 and k_2 for the FODM and DEM, respectively (IBM SPSS version 20, NY, USA). The corrected Akaike information criterion (AIC_C) was used to indicate the goodness of fit of the two models for each treatment (Akaike 1981; Burnham and Anderson 2004). AIC_C values provide a mean for model selection by weighing the goodness of fit versus the number of parameters included in a model, thereby penalizing overfitting.

Results

Parallel measurements of soil samples without PAA corroborated a continuous soil microbial activity over the entire test period. The initial burst of soil respiration (mean±SD) decreased rapidly from 10.36±0.09 μg C g^{-1} day^{-1} on day 1 to 2.98±0.17 μg C g^{-1} day^{-1} on day 14. Thereinafter, base respiration decreased only moderately, i.e., to 1.41±0.13 μg C g^{-1} day^{-1} on day 149.

Biodegradation rates of two PAA_{linear} in the same soil were obtained from the difference in daily ^{13}C efflux of labeled samples and unlabeled reference samples (Fig. 1). Past the initial burst of $^{13}CO_2$ efflux owing to sample preparation, the daily $^{13}CO_2$ efflux rates were—with few exceptions—not significantly different between the reference samples containing the unlabeled long and short PAA_{linear} (Fig. 1a). In contrast, the $^{13}CO_2$ efflux was mostly significantly larger from the labeled variants than the unlabeled variants of short and long PAA_{linear} (Fig. 1b, c).

Beyond the quality checks shown above, the overall 149-day degradation rates were significantly different between the PAA_{linear} of lower and larger molecular weight (p<0.0001). The PAA_{linear} of lower molecular weight ($PAA_{linear}1$) degraded by approximately 1.85 %, whereas the PAA_{linear} of larger molecular weight ($PAA_{linear}2$) showed a degradation of almost

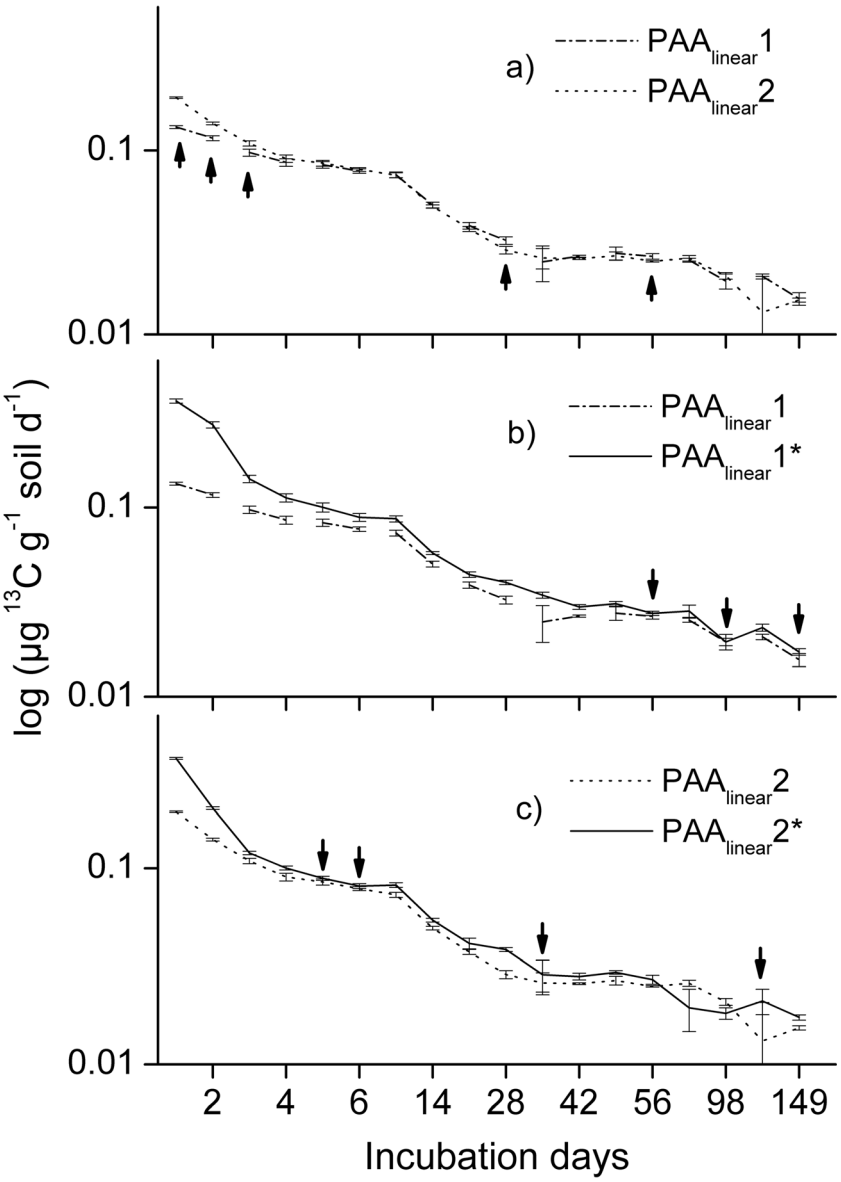

Fig. 1 Daily $^{13}CO_2$ efflux (mean ±SD, n=4) from the biodegradation of two size variants of linear polyacrylic acid incubated in soil: efflux **a** from unlabeled short ($PAA_{linear}1$) and long ($PAA_{linear}2$) reference samples, **b** from labeled short $PAA_{linear}1$* and the corresponding unlabeled reference, and **c** from labeled long $PAA_{linear}2$* and its unlabeled reference. *Arrows pointing up* (**a**) and *down* (**b**, **c**) indicate means that were significantly different and not significantly different, respectively (significance level p=0.05)

0.91 % within 149 days (Fig. 2, Table 2). Thus, the ratio of degradation of $PAA_{linear}1$ to $PAA_{linear}2$ was 2.03:1. About half of the total degradation of both polymers was measured within the first 2 weeks. A virtual increase of remaining ^{13}C of labeled $PAA_{linear}2$ samples on day 98 was the result of mean $^{13}CO_2$ efflux rates from unlabeled reference samples being intermittently larger than from labeled samples (see Fig. 1c, days 70 and 98, and Fig. 2b, day 98). Although this displays as a slight recovery of initial weight, the difference between the mean efflux from four $PAA_{linear}2$ and four reference samples was not significantly different from zero.

Fitting the biodegradation of PAA_{linear} with the double-exponential model and the first-order decay rate model resulted in a much better data correlation for the DEM ($R^2 \geq 0.80$) than the FODM (R^2=0.00) (Fig. 2). In case of the FODM, the rate constants were so small that they resulted in almost no curvature (Fig. 2a, k=−0.000175; Fig. 2b, k=−0.0000859). Also, the AIC_C values for DEM ($PAA_{linear}1$, −177.61; PAA_{linear} 2, −199.59) were lower than those for the FODM (PAA_{linear} 1, −160.68; PAA_{linear} 2, −184.85), thus confirming the better fit of the DEM as compared to the FODM. Note that the lower AIC_C points to the better model.

The initial $\delta^{13}C$ of the microbial biomass in pure soil was −25‰, and the $\delta^{13}C$ did not change until the end of experiments (Fig. 3). Also, the $\delta^{13}C$ of the microbial biomass of unlabeled PAA_{linear} treatments was not significantly different from the pure soil value at day 149. However, the microbial biomass of short ($PAA_{linear}1$) and long ($PAA_{linear}2$) treatments showed significantly different final enrichments to −13 and −16‰, respectively.

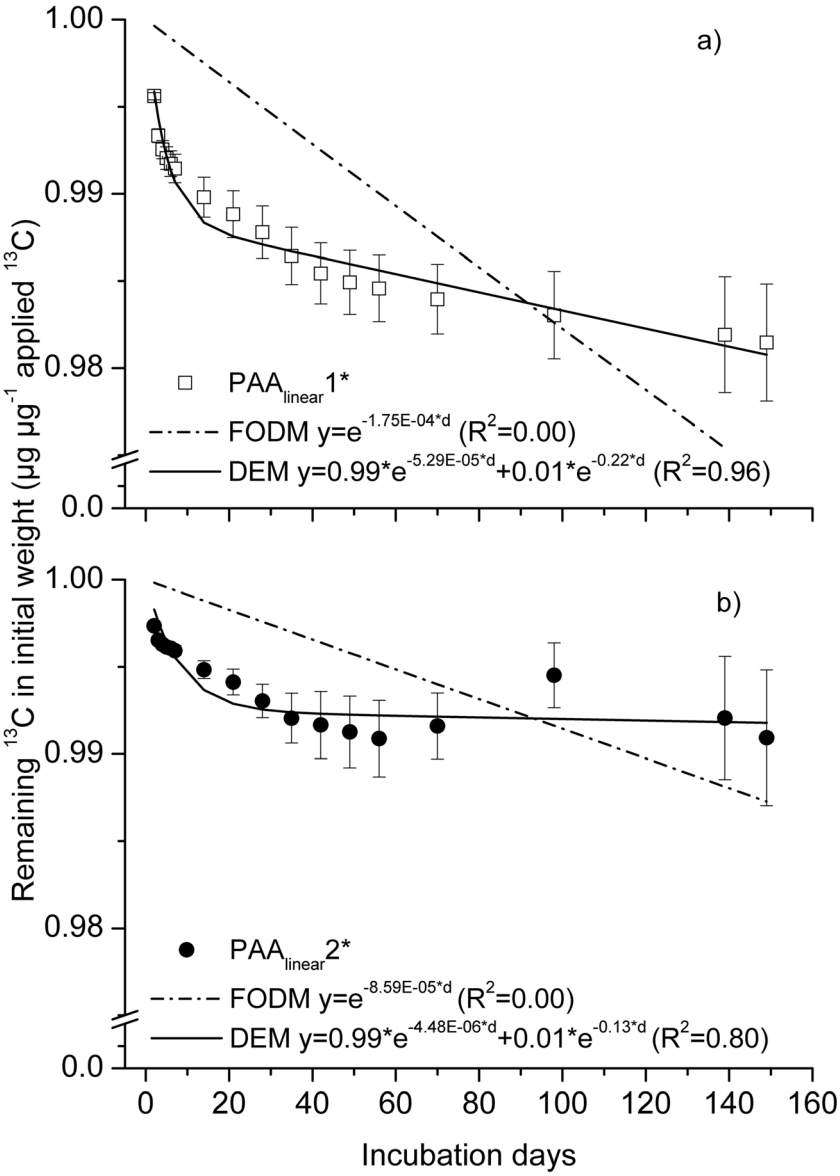

Fig. 2 Measured and modeled biodegradation of two linear polyacrylic acids over a period of 149 incubation days. Measured values show means±SD (n=4) of the remaining ^{13}C based on the initially applied weight of PAA$_{linear}$1 (**a**, lower molecular weight) and PAA$_{linear}$2 (**b**, larger M_n). Model results present the biodegradation of PAA$_{linear}$ based on the fitted first-order degradation model (FODM) and the double-exponential model (DEM). Note that in both cases, the k-values obtained with the FODM were so small that curvature was virtually absent

The apparent recovery (AR) rates of the short and long PAA$_{linear}$ were 96.34 and 97.54 %, respectively (Table 2). The remaining ^{13}C of the PAA$_{linear}$, which were calculated based on the ^{13}C mineralization, were 98.15 and 99.09 % for short and long PAA$_{linear}$ treatment, respectively, and thus higher than the AR. While the difference between the AR and the remaining ^{13}C was not significant (p=0.267) in case of the short PAA$_{linear}$1, the same difference was significant (p=0.001) for the long PAA$_{linear}$2.

Table 2 Apparent recovery (AR) of labeled PAA$_{linear}$1* (short-chained) and PAA$_{linear}$ 2* (long-chained) compared to the remaining C based on the $^{13}CO_2$ efflux accumulated over 149 incubation days (both mean±SD, n=4)

Treatment	AR (%)	SD (%)	Measurement (%)	SD (%)
PAA$_{linear}$1*	96.34	2.95	98.15	0.34
PAA$_{linear}$2*	97.31	0.45	99.09	0.39

Discussion

A study by Wolter et al. (2010) presented a degradation of 0.3 % for a cross-linked acrylic acid acrylamid copolymer in agricultural soil within 196 days. Recently, we reported the 6-month biodegradation of a single-labeled, cross-linked acrylic acid polymer to range between 0.45 and 0.82 % depending on soil type (Wilske et al. 2013). The present study, which was conducted using the same measurement system, showed a degradation of 1.85 and 0.91 % for a short- and long-chained PAA$_{linear}$, respectively. The results of δ^{13}C in

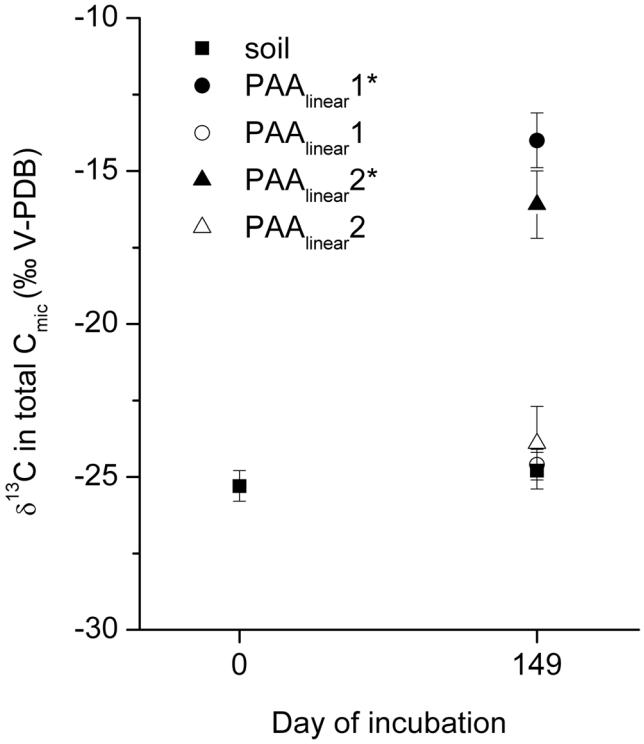

Fig. 3 The $\delta^{13}C$ in microbial biomass at the start and end of the experiment. $PAA_{linear}1$* and $PAA_{linear}2$* are ^{13}C-labeled linear polyacrylic acids; $PAA_{linear}1$ and $PAA_{linear}2$ are nonlabeled PAA_{linear} and serve as references for $PAA_{linear}1$* and $PAA_{linear}2$*, respectively

microbial biomass confirmed that the shorter PAA_{linear} was subjected to a stronger biodegradation than the longer PAA_{linear}. Thus basically, the biodegradation of PAA_{linear} increased with decreasing molecular weight.

We set out from the working hypothesis that degradation will occur mainly at terminal ends. The ratio of biodegradation between the two linear PAA was expected to follow the ratio of their molecular weights, if degradation occurred strictly at terminal ends. Based on the different molecular weights and chain lengths of short and long PAA_{linear} in our experiment, the expected result for a ratio confirming terminal degradation would be 2.4:1. The factual ratio between the results of $PAA_{linear}1$ and $PAA_{linear}2$ was 15 % lower (2.03:1), but still points to the double amount of terminal ends contributing the main increment in biodegradation from the longer to the shorter PAA_{linear}.

To assess the relevance of nonfunctional PAA_{linear} for the biodegradation of PAA-based SAP in soils, we started from the following basis: (1) Revisiting the data published by Wilske et al. (2013), the mean biodegradation of a superabsorbent of cross-linked PAA is 0.64 % within 169 days. The increment from day 149 to 169 was negligibly small, and all following considerations are based on a biodegradation period of 149 days. (2) The weight contribution of PAA_{linear} within a superabsorbent product is 4 % irrespective of the particular chain length. Accordingly, if a superabsorbent would only contain linear contributions the size of $PAA_{linear}1$, these 4 % PAA_{linear} would contribute 0.074 % to the total biodegradation of 0.64 %. (3) With respect to the current results, there is a twofold increase in degradation of linear (non-cross-linked) contributions in PAA with every reduction of 59 % in the average chain length. Thus, we can calculate the increasing relevance of nonfunctional PAA_{linear} for the total observed biodegradation of a SAP by varying the chain length of PAA_{linear}. For example, if we simply bisect the size of the current PAAlinear1 two and three times, the resulting average molecular weights of PAA_{linear} of about 36,900 and 15,100 g mol^{-1} would contribute a degradation of 0.296 and 0.592 %, respectively. In other words, they would explain 46 and 92 % of the total 0.64 % biodegradation of a PAA-based superabsorbent product.

Higher CO_2 efflux from the reference than the samples was observed within the measurement sequence of the longer $PAA_{linear}2$. A negative net degradation points to the effect of negative priming exerted by polymer on native soil organic carbon. The most obvious mechanism of negative priming is found in the inhibition of microbial activity or their enzymes by the treatment (Kuzyakov et al. 2000). Such inhibition could be caused primarily by toxicity, deprivation of oxygen or water. The cause for the negative priming as a result of PAA_{linear} treatment was not clearly identified. Although considering the small differences required resulting in the observed effect, it may have just been that the PAA_{linear} reduced the connectivity among pore spaces in the soil and involved a reduction in oxygen diffusion.

The AR rates confirmed that the $^{13}CO_2$ efflux reflected the majority of the PAA_{linear} degradation in soil. The remaining PAA_{linear} was only slightly higher based on the $^{13}CO_2$ efflux than with respect to the calculated recovery rate. At the end of the experiment, the PAA_{linear} cannot be isolated from the soil, and hence, the ^{13}C value reflects the contents of both the PAA_{linear} and the soil. Thus, the AR would be expected to be rather higher than lower than the remaining ^{13}C value. There are two causes for the missing consistency between AR and remaining ^{13}C: (1) The small amount of samples from the PAA_{linear}/soil mixtures analyzed for AR (i.e., 1 g of the mixture was sampled) underrepresented the PAA_{linear} content. This could be possible if PAA_{linear} is leaching to the bottom of the experimental vessel and is not captured when taking the samples. (2) In cases, where the calculation of the remaining ^{13}C has to reflect negative degradation rates (e.g., in Fig. 1 $PAA_{linear}2$), it results in a slightly higher remaining ^{13}C as compared to calculating a negative value as zero degradation.

The DEM adjusted well to the degradation of PAA_{linear}, outperforming the simpler FODM approach as confirmed by the AICc. The DEM reflects the general existence of slower and faster degradable pools of compounds. If a FODM is used, the rapid degradation in the first couple of days can superimpose the generally slow degradation as shown in this

study. While this result reminds us that the course of SAP degradation will always reflect certain nonuniformity in polymerization products, our extrapolation of the biodegradation of differently sized PAA_{linear} shows that minor contributions may even dominate the biodegradability of a whole product. Thus, reports on the degradation of polymer-based superabsorbent need to be carefully looked at. It is likely that the degradation of complex polymer structures is masked by the quick degradation of nonfunctional components.

At the end, we like to underline that using ^{13}C rather than ^{14}C labeling to determine the biodegradation of synthetic polymers can be not only safer but also cheaper. Measurements on the biodegradation of SAP s need to cover longer observation periods as compared to most tests described in OECD guidelines (0 to 28 days). Especially, considering the required month-long measurements, our newly developed system facilitates user-friendly and simple but accurate examination of polymer biodegradation.

Conclusions

SAP of cross-linked PAA improve water retention in the rooting zone and achieve better plant growth but need to be completely biodegradable to protect soil and groundwater resources. As fractions of the polymerization products escape cross-linking, they remain as PAA_{linear} within the SAP. By means of ^{13}C-labeled PAA_{linear}, the study showed that (1) their biodegradation was much larger than as determined previously for cross-linked PAA, and (2) among two PAA_{linear}, the degradation rate almost doubled with half the average molecular weight (MW_a). The latter result was generally confirmed by the $\delta^{13}C$ in microbial biomass and the apparent recovery rate. The specific ratio between chain lengths and degradation rates suggests that biodegradation occurs mainly at the terminal sites. Hence, we estimated roughly (a) the increment of degradation rate with every 50 % reduction in MW_a and (b) at which size small quantities of PAA_{linear} contribute significantly to the overall SAP biodegradation. Polymerization usually provides an array of molecule sizes around the target size, which explains why a two-pool model performed better than the first-order decay rate model in simulating the observed degradation rates. Conditions during SAP production determine the MW_a of the polymer fraction, which remains as PAA_{linear}. We conclude that (1) the apparent biodegradation measured with SAP products can include significant contributions from the biodegradation of the nonfunctional PAA_{linear}, and (2) the amount and MW_a of PAA_{linear} must be determined when investigating SAP biodegradability.

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