

Tekninen loppuraportti

Tutkimushankkeen nimi Maanparannusaineiden hiilivarastovaikutusten mallinnus (MAHTAVA)
Tutkimushankkeen nimi englanniksi Modelling the carbon sequestration potential of soil amendments

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Kesto (20xx-20xx) 2016-2019	Loppuraportti xx.xx.20xx 3.6.2019
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Rahoitus	Euroa
· Kokonaiskustannukset	225 621,50
· MMM:ltä saatu kokonaisrahoitus	160 000,00
· Oma rahoitus	65621,50

· Muista julkisista lähteistä saatu rahoitus	0
· Muu ulkopuolinen rahoitus	0

Avainsanat

maaperä, hiilivarasto, maanparannus

Tiivistelmä

Tavoitteet

Ilmastotavoitteiden kiristyessä myös maankäyttösektorilla tulee tarve sisällyttää maaperän hoidon hiilivarastovaikutuksia kasvihuonekaasuraportointiin. Suomen kasvihuonekaasuinventaariossa käytetty maaperän hiilimalli (Yasso07) mahdollistaa erilaisten orgaanisten materiaalien maassa tapahtuvan hajoamisen simuloinnin. Tämän hankkeen tavoitteena oli verifioida mallin soveltuvuus myös muiden kuin tavanomaisten kasvintähteiden hajoamisen ennustamiseen ja siten edistää maanparannustoimien vaikutusten raportointia kansainvälisissä ilmastoraportoinneissa.

Tulokset

Hanke tuotti runsaasti lähtötietoa erilaisten orgaanisten materiaalien kemiallisesta laadusta, jota voidaan käyttää sisällytettäessä esimerkiksi maanparannusaineiden, eri tavoin käsiteltyjen lantojen tai biohiilien vaikutuksia arvioihin maatalousmaiden maaperän hiilivarastojen muutoksista. Osa tutkituista materiaaleista otettiin tarkempiin kokeisiin, joissa tutkittiin niiden hajoamista laboratorio- ja kenttäolosuhteissa. Tulosten mukaan materiaalien vaikutusta maaperän hiilivarastoihin voidaan pääsääntöisesti ennustaa niiden kemiallisen laadun perusteella, joten Yasso-mallin käyttöä voidaan laajentaa nykyisestä. Hanke mahdollistaa kasvihuonekaasuinventaarion parantamisen, esimerkkeinä juurten hitaamman hajoamisen huomioon ottaminen mallinnuksessa sekä tilastoitujen toimien, kuten kerääjäkasvien ja maanparannusaineiden käytön, lisääminen nykyisiin arvioihin.

Tulosten arviointi

Kun ympäristökorvaussitoumuksissa v. 2017 mukana olevien kerääjäkasvien ja maanparannusaineiden vaikutus lisätään kasvihuonekaasuinventariolaskentaan, pienenevät kivennäismaiden hiilidioksidipäästöt 12 % verrattuna nyt vuodelle 2017

raportoituun arvoon. Koko viljelysmaa-kategorian päästöt (ml. turvepellot) pienenevät kuitenkin vain alle yhden prosentin. Joissakin tapauksissa mallinnukseen jää isohko epävarmuus, sillä malli yliarvioi joidenkin materiaalien pysyvyyden maassa. Tämä ei kuitenkaan vaikuta olennaisesti koko viljelysmaa-raportointiluokan päästöarvion epävarmuuteen.

Julkaisut

Jaakko Heikkinen, Elise Ketoja, Leena Seppänen, Sari Luostarinen, Kristiina Regina
Chemical quality and decomposition of typical organic amendments used in agricultural soils. Käsikirjoitus (loppuraportin liitteenä).

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Heikkinen J, Seppänen L, Luostarinen S, Ketoja E, Regina K. Orgaanisten maanparannusaineiden pysyvyys maaperässä. Poster, Maaperätieteen päivät 9.-10.1.2019, Helsinki.

Hankkeen tuloksia esiteltiin myös Soil TAP -verkoston kokouksessa Brysselissä 11.6.2018 otsikolla "Modelling the carbon sequestration potential of soil amendments".

Liite 1 Artikkelikäsitelmä

Chemical quality and decomposition of typical organic amendments used in agricultural soils

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1 Introduction

There is an urgent need to improve the carbon balance of cultivated soils both from the viewpoint of climate (Soussana et al. 2019) and plant productivity (Schjønning et al. 2018). As the role of cultivated soils in climate policies grows, also the methods to report changes in soil carbon stocks will need to be improved. This requires understanding of the decomposition processes of crop residues and different substances added to cultivated soils as well as valid input data for the models used in estimating the effects of cultivation and soil management on cropland carbon stocks.

The decreasing trend in cropland soil organic matter observed in many regions (e.g. Heikkinen et al. 2013; Steinmann et al. 2016) reflects the imbalance between organic matter return to the soils and losses due to decomposition, leaching and erosion. Depending on the crop, around 35-65% of the plant biomass is removed from the field with the harvested yield (calculated based on De Klein et al. 2006), and the collection of harvest residues for bioenergy production and animal bedding further decreases the amount of organic matter returning the soil (Hakala et al. 2016). The current input of carbon as crop residues does not generally maintain the carbon stocks but leads to a decrease in the stock (Yang et al. 2003; Kätterer et al. 2011; Poulton et al. 2018).

Concern for soil degradation has initiated research on the potential to sequester carbon with different soil amendments (Larney and Angers 2011; Poulton et al. 2018). Use of manure improves soil carbon balance (Poulton et al. 2018; Jiang et al. 2018) but manure is commonly concentrated to certain regions and not optimally used from the viewpoint of soil quality (Ylivainio et al. 2014). Novel manure management options do not increase the total carbon input to soils but enable applying manure also outside the animal farms which is a way to improve soil quality in a wider range of fields with the existing biomasses (Flotats et al. 2007). The balance between inputs and losses of carbon can be improved by introducing species with extensive root system or cover crops that can double the carbon input to the system (McDaniel et al. 2014; Poeplau & Don 2015). Roots contribute more to the carbon stocks than above-ground residues as their exudates provide continuous carbon supply to soil and root biomass is generally chemically more resistant in comparison to above-ground biomass (Kätterer et al. 2011; Rasse et al. 2005). Any organic amendments outside the farming system like the by-products of forest and food industry and energy production bring new organic matter to the food production system but their properties and thus effects in soil vary greatly depending on the nature of the biomass (Larney and Angers, 2011; Wang et al. 2016).

Soil organic matter is formed from degraded crop residues and other organic material as a result of microbial and geochemical processes the main constituents being plant litter and microbial necromass (Kögel-Knabner 2002). The major organic compounds taking part in this process include cellulose, hemicellulose, lignin, proteins, polysaccharides, tannins, lipids, cutin, suberin, chitin and acids that have different rates of decomposition when mixed with soil. However, the variables used to describe the chemical quality of organic amendments, typically proportions of the above-mentioned compounds or the C:N ratio, are always simplifications. The study by Kätterer et al. (2011) illustrated the significance of the chemical quality of the carbon input: when the input to a long-term experiment was adjusted using a factor describing the chemical quality, it greatly improved the linear dependence between the change in the soil carbon stock and the carbon input. Processing of organic materials prior to field application e.g. by composting, anaerobic digestion or pyrolysis leaves more recalcitrant residue for the soil organisms to decompose. Persistence of organic amendments and its significance for soil carbon stocks have been studied e.g. for sewage sludges (Börjesson & Kätterer 2018), cover crops (Poeplau & Don 2015), biochar (Wang et al. 2016; Rasse et al. 2017) and manure (Maillard & Angers 2014).

The current soil carbon models usually simulate humus formation based on the chemical quality of carbon input to soil and environmental variables (Andrén et al. 2004; Tuomi et al. 2011; Coleman and Jenkinson 1999). However, the development of the models is based on the most common types of carbon input like crop residues and manure, and thus their results for application of more recalcitrant materials are generally not verified with field results. Future models will likely be less simplified and will include a more complex understanding of the continuum of organic compound transformations and more variables like the effects of microbial populations or the protective capacity of soils (Kleber 2010; Lehmann & Kleber 2015).

Quantitative estimates of the impacts of different soil amendments on soil carbon stocks are needed e.g. to report the effects of improved soil management under the climate commitments. Long-term experiments provide data to support that but only for the most common types of amendments. The aims of this study were to assess the potential to increase soil carbon stocks by various organic amendments including plant materials, manures, composts, industrial side streams and biochars and to find out to what extent the initial chemical quality of the amendments explains their resistance in soil. A set of experiments was designed to answer this question. We hypothesized that by measuring the chemical quality of a large variety of materials and verifying soil carbon model results of decomposition rates by measurements, it would be possible to estimate the rate of soil organic carbon sequestration by these amendments using e.g. Yasso07 soil carbon model.

2 Materials and methods

2.1 Chemical fractionation

The studied materials were selected to represent plants used as cover crops or in composts, differently treated manures and sewage sludges, side products of forest industry and biochars (Table 1). Samples were shredded and sieved through a 1 mm size sieve. Carbon and nitrogen contents of the samples were analysed using a dry combustion instrument (LECO, St Joseph, MI, USA) and were used to calculate the C:N ratios. Dry matter content of the samples was determined by drying one gram of each material overnight at 105 °C. Ash content was determined using the loss on ignition method (550 °C for 4 hours). Prior to weighting, the samples were cooled in an exicator.

A method modified from Berg et al. 1991 was used for determining the chemical quality of the organic amendments. Half a gram of each material (two replicates) was weighed into 30 ml centrifuge tubes and 20 ml ethanol was added. The samples were placed in an ultrasonic bath for 45 minutes followed by centrifugation (2500 rpm for 10 minutes). The supernatant was removed with pipette and the treatment was repeated with 20 ml ethanol and 45 minutes sonication. Then the samples were moved to crucibles with integral glass sintered disc (grade 4 porosity) and the samples were rinsed with 30 ml ethanol using pressure assisted filtration. Samples were dried overnight at 105 °C and weighted. The weight loss represented the ethanol soluble fraction. Thereafter the remaining fraction of samples was moved into 30 ml centrifuge tubes. The tube was filled with 20 ml ultrapure water and sonicated for 90 minutes. The samples were filtered as described above with the exception that they were rinsed with 30 ml of hot ultrapure water. The samples were dried overnight at 105 °C and weighted and the weight loss was taken as the water soluble fraction.

For the acid extraction, a subsample of 0.3 g was taken from each sample and moved into 30 ml centrifuge tube with a screw cap. Further, 3 ml of 72% sulfuric acid was added and the samples were hydrolyzed in ultrasonic bath for 60 minutes. The samples were moved to autoclavable reagent bottles using 80 ml of ultrapure water and the hydrolysis was continued by placing the bottles into an autoclave (121 °C/1.3 bar) for 60 minutes. The solid fraction of each sample was separated from the liquid using sintered glasses with pressure assisted filtration. Samples were rinsed three times using 10 ml ultrapure water, dried at 105 C overnight and weighted.

Chemical composition of each material was calculated based on the mass loss due to ethanol (E), water (W) and acid (A) extraction. The results were corrected with the ash content of the sample.

In order to study the dependence of the decomposition on the initial chemical quality of the organic amendments, the AWEN fractions were converted to scaled chemical quality (CQ) as follows:

$$CQ = (w_A \times \alpha_A) + (w_W \times \alpha_W) + (w_E \times \alpha_E) + (w_N \times \alpha_N)$$

where w_A , w_W , w_E and w_N indicate the mass fractions of the A, W, E and N fractions, respectively, and α indicates the decomposition rate of each fraction as defined in Yasso07 soil carbon model (see chapter 2.4). The four mass fractions sum up to one.

2.2 Laboratory incubation

Soil for the incubation experiment was collected from a long-term field experiment of Natural Resources Institute Luke (Turtola & Paajanen, 1995) located in Jokioinen in southern Finland. According to the WRB classification the soil type is Protovertic Luvisol (FAO, 2014). The study material was collected from the topmost 10 cm layer of an annually ploughed plot. Sand, silt and clay contents of the soil were 4.7%, 30.5% and 64.8%, respectively. Carbon content of the soil was 2.9% and pH 6.3.

Field moist soil was air-dried and sieved through a 2 mm mesh sieve. Incubated materials were prepared by mixing 30 g of soil and 1 g of each biomass in addition to control with no added biomass. Three replicates of each amendment type and control were prepared. The incubation was conducted in 120 ml glass flasks at constant temperature (21 °C) and moisture conditions. The

flasks were closed with perforated parafilm. Water content was set to 40% of the maximum water holding capacity of the soil and was kept constant by weighting samples weekly and adding deionized water with a pipette.

Decomposition of the organic amendments was monitored by measuring the formation of CO₂ in the flasks. Samples were taken 14 times during the 42-day incubation experiment. The flasks were closed tightly with rubber septa and 1 ml of the headspace air was sampled with a syringe equipped with a needle 1, 3 and 5 hours after closing the flasks. The gas samples were analysed for CO₂ concentration with the Agilent 7890A gas chromatograph equipped with a Gilson autosampler (Nieminen et al., 2015). The production rate of CO₂ (g m⁻² h⁻¹) was calculated from the increase in gas concentration over time using linear regression. Finally, the C loss of the control samples was subtracted from those of the other treatments and the formation of CO₂ was converted to dry matter loss.

2.3 Litterbag experiment

In addition to the incubation experiment, the decomposition of the same materials was studied using litterbags buried in soil. The experiment was conducted in clay soil in Jokioinen, southern Finland (N 60.82°, E 23.51°). Polyester mesh fabric with 1 mm mesh size was used to prepare 10 × 10 cm litterbags. Sides of the bags were closed using a serger. Litterbags were filled with 5 g of each material and dried at 60 °C. For each material, 20 litterbags were prepared with the exception of clover shoots and roots for which there was material only for 16 bags. The site was divided in three blocks and the litterbags were randomly placed to the blocks at the depth of 10 cm in October 2016. Two of the blocks included four litterbags for each organic material and those were collected from the soil in April and July 2017. To assure enough sample for the analysis after a 1-year decomposition period in October 2017, the number of litterbags in the third block was 8 for both clover shoots and roots and 12 for other materials.

The collected litterbags were first air-dried and then the material was carefully removed from the polyester bags and analysed for mass loss. Due to the 1 mm mesh size, a variable amount of surrounding soil was incorporated into the bags. The mixture of residue and soil from the bags was ground and about 0.5 g of the ground sample was taken for the loss on ignition (LOI) analysis. The samples were incinerated at 550 °C for 5 h in a high temperature muffle furnace. This enables calculating the content of organic matter in the samples as the ignition leaves the mineral part of the soil as ash while organic matter is lost. The results from the separate LOI analysis from the original material, and the surrounding soil samples, were used in determining ash free dry weight. Organic matter loss of the materials for all three collection dates was expressed as a proportion of ash free dry weight of the initial dry weight.

Organic matter loss was modelled as a function of climate scaled time as there was great seasonal variation in climate during the experiment. Climate scaled time was calculated as a cumulative sum of the monthly decomposition coefficients (k) as described in Yasso07 model (see chapter 2.4 and Fig. 1). Weather data were taken from monthly 1×1 km gridded data (Finnish meteorological institute) by selecting the nearest grid point to the study site.

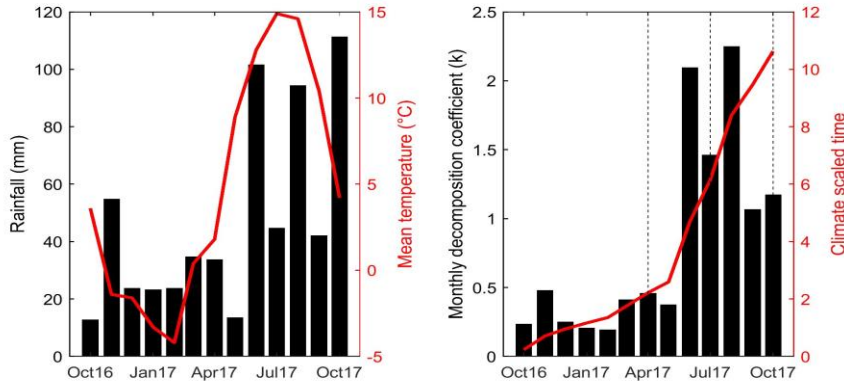


Figure 1 Mean monthly temperature (curve) and rainfall (bars) from October 2016 to October 2017 (left panel). Climate scaled time (right panel) was calculated as a cumulative sum of monthly decomposition coefficients (k). The three dashed vertical lines in the right panel indicate the collection dates of the litterbags in the litterbag experiment.

Decomposition of the organic amendments was modelled using an exponential decay function of the following form:

$$E(Y_{ijk}) = (1 - b_j)\exp(a_j t_k) + b_j$$

where $E(Y_{ijk})$ is the average organic matter proportion for the i -th litterbag of organic amendment j at the k -th time, t_k is climate scaled time, b_j is the asymptote of organic amendment j as t goes to infinity, and a_j (constrained to be less than zero) is the rate of exponential decay which describes how quickly the process decays from the initial value to the asymptote. Due to higher variation in the observations and absence of an asymptote, the data of fiber sludge were modelled using a simpler function:

$$E(Y_{ik}) = \exp(at_k)$$

In the models, organic matter proportions were assumed to be distributed according to a beta distribution which is a common distribution for proportions (Gbur et al. 2012). The parameters of the models were estimated using the method of maximum likelihood and standard errors of the estimates were obtained by the delta method (Cox 1998). The data included seven outlying values whose influence on the results was examined by fitting the models with and without the outliers. The modelling was implemented by the NL MIXED procedure of the SAS/STAT software (version 14.2; SAS Institute 2016).

2.4 Modelling decomposition with Yasso07-model

Yasso07 soil carbon model is widely applied in various agricultural, forestry and land-use change applications, e.g. in the national greenhouse gas inventories of several countries. Yasso07 is a dynamic soil carbon model in which soil carbon is divided in five different pools: acid (A), water (W) and ethanol (E) soluble, non-soluble (N) and humus (H) pools (Tuomi et al. 2011; Fig. 2). Carbon input is given to the model as measurable fractions of the AWEN fractions which roughly represent the content of cellulose (A), sugars (W), waxes (E) and lignin (N) in the residues. Decomposition rates of the pools range in three orders of magnitude being the highest for the water-soluble

fraction and lowest for humus. Decomposition results not only in CO₂ emissions to atmosphere but also in mass flow between compartments.

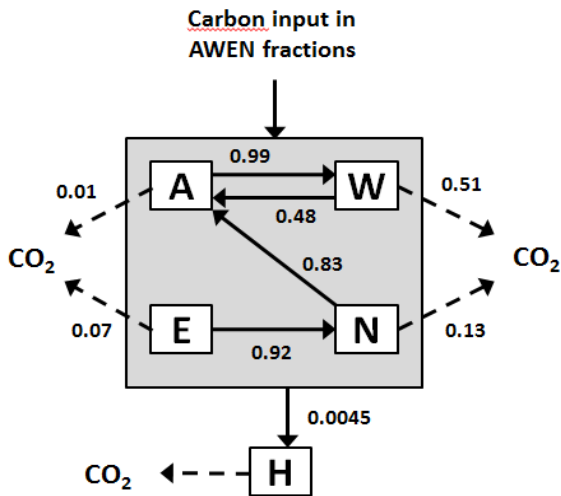


Figure 2 Flow chart of Yasso07 soil carbon model. The boxes represent soil carbon as acid (A), water (W) and ethanol (E) soluble, non-soluble (N) and humus (H) fractions. The solid arrows indicate mass flow between compartments, the dashed arrows mass flow to the atmosphere and the numbers the mass flow fraction.

Mean annual temperature and rainfall control the monthly decomposition rate (R_i) as follows:

$$R_i = \alpha_i * k = \alpha_i * \exp(0.096 * MT - 0.0014 * MT^2) * (1 - \exp(-1.21 * PR * 12)),$$

where α_i is decomposition rate of A, W, E, N and H pools ($\alpha_A = 0.73$, $\alpha_W = 5.8$, $\alpha_E = 0.29$ and $\alpha_N = 0.031$), k is the monthly decomposition coefficient, MT is the mean monthly temperature (°C) and PR is the monthly rainfall (mm).

Decomposition during the litterbag incubation of the 10 materials selected for detailed analysis was modelled with Yasso07 model using monthly timesteps. The temperature and rainfall data used in the modelling was taken from monthly 1x1 km gridded data (Finnish meteorological institute; Fig. 1). Initial mass of the materials was assumed to equal to one and therefore the modelling results represent the remaining share of the organic matter in the end of the experiment. Chemical qualities determined in this study were used to define the carbon input to soil (see 2.1). The model results were compared to observed decomposition in the litterbag experiment.

3 Results

3.1 Chemical quality of the soil amendments

Carbon to nitrogen ratio of the soil amendment types ranged from 6 to 833 with that of fiber sludge from forest industry being the highest of the studied materials (Table 1). Biochars were among the materials with high C:N ratios and the materials with high N content like manures had the lowest values. Ash content of the materials varied from 2 to 66%.

With the exception of most biochars, the acid soluble fraction was the main component of the studied materials (Table 1). The acid soluble fraction ranged from 1% in the biochar made of willow to nearly 94% in fiber sludge. The water soluble fraction varied from close to zero in the biochars to almost 40% in clover shoots. The fraction soluble to ethanol was 25% at the highest. The non-soluble fraction ranged from zero to 100%.

Table 1 Mean (\pm standard deviation) of the chemical quality as acid (A), water (W) and ethanol (E) soluble and non-soluble (N) fractions, ash content and C:N ratio of the studied materials (n=2)

Material	Description	A (%)	W (%)	E (%)	N (%)	Ash (%)	C:N
Clover shoots	Red clover	50.0 \pm 1.6	39.7 \pm 0.5	10.3 \pm 1.0	0.0 \pm 0.0	12.8 \pm 0.2	13.6
Clover roots	Red clover	73.6 \pm 0.1	16.3 \pm 1.5	10.1 \pm 1.4	0.0 \pm 0.0	16.6 \pm 0.2	18.6
Ryegrass shoots	Italian ryegrass	60.0 \pm 0.8	31.0 \pm 0.2	9.0 \pm 0.6	0.0 \pm 0.0	17.3 \pm 1.0	17.3
Ryegrass roots	Italian ryegrass	82.0 \pm 2.1	12.9 \pm 1.5	5.1 \pm 0.7	0.0 \pm 0.0	29.3 \pm 1.4	35.4
Straw	Barley	83.2 \pm 0.4	10.5 \pm 0.3	6.3 \pm 0.1	0.0 \pm 0.0	8.9 \pm 0.0	70.1
Hemp shoots		84.0 \pm 0.2	4.1 \pm 0.2	1.7 \pm 0.3	10.2 \pm 0.2	1.7 \pm 0.1	80.0
Common reed	Composted for 1 yr	78.4 \pm 1.8	3.8 \pm 0.4	5.3 \pm 0.3	12.6 \pm 2.6	13.8 \pm 0.5	38.9
Vegetable residues	Composted for 2 yrs, salad+other vegetables, 30% peat litter	81.8 \pm 1.4	8.7 \pm 1.3	4.5 \pm 0.9	5.0 \pm 1.0	35.5 \pm 1.0	23.3
Manure, horse	Raw	77.1 \pm 0.3	10.5 \pm 0.6	4.9 \pm 0.6	7.6 \pm 1.5	7.2 \pm 0.3	33.3
Manure, horse	Composted, peat litter	64.6 \pm 5.9	8.3 \pm 0.4	1.7 \pm 0.2	25.4 \pm 6.5	18.1 \pm 1.9	18.9
Manure, horse	Composted, straw litter	83.1 \pm 0.3	9.8 \pm 0.3	2.5 \pm 0.6	4.7 \pm 1.2	6.7 \pm 0.4	48.9
Manure, broiler		58.0 \pm 0.4	32.7 \pm 0.6	9.3 \pm 1.0	0.0 \pm 0.0	14.7 \pm 0.3	10.0
Manure, fox		76.7 \pm 2.8	15.8 \pm 1.5	7.4 \pm 1.2	0.0 \pm 0.0	41.4 \pm 0.1	7.0
Manure, mink		51.3 \pm 0.4	38.2 \pm 0.8	10.5 \pm 0.3	0.0 \pm 0.0	25.7 \pm 0.2	5.7
Slurry, dairy cattle	Raw slurry	74.0 \pm 0.6	17.8 \pm 0.2	8.2 \pm 0.4	0.0 \pm 0.0	19.6 \pm 0.3	16.8
Slurry, dairy cattle	Digested, grass silage as additional material	74.8 \pm 1.1	19.2 \pm 1.0	6.0 \pm 0.0	0.0 \pm 0.0	22.5 \pm 0.1	16.8
Slurry, dairy cattle	Digested, separated solid fraction	74.5 \pm 0.1	5.2 \pm 0.3	2.6 \pm 0.3	17.6 \pm 0.1	9.3 \pm 0.3	32.3
Slurry, pig	Raw slurry	53.9 \pm 0.5	27.9 \pm 0.0	18.2 \pm 0.4	0.0 \pm 0.0	25.5 \pm 0.1	11.5
Slurry, mixed	Pig slurry:side streams from food industry 25:75), digested, separated dry fraction	67.2 \pm 3.4	15.7 \pm 1.3	17.1 \pm 2.1	0.0 \pm 0.0	65.7 \pm 0.0	9.2
Sewage sludge	Raw	80.6 \pm 1.3	10.2 \pm 0.6	9.1 \pm 0.7	0.0 \pm 0.0	49.3 \pm 0.0	7.7
Sewage sludge	Composted, 30% peat litter	87.3 \pm 1.0	8.8 \pm 0.9	3.9 \pm 0.0	0.0 \pm 0.0	41.8 \pm 0.5	11.4
Sewage sludge	Digested	87.7 \pm 0.1	4.6 \pm 0.6	7.7 \pm 0.5	0.0 \pm 0.0	47.0 \pm 0.1	9.6
Fiber sludge	Side stream of forest industry	93.6 \pm 2.9	4.4 \pm 1.0	1.9 \pm 1.9	0.0 \pm 0.0	31.6 \pm 0.2	832.8
Pulp mill sludge	Lime-stabilized	89.5 \pm 0.6	7.4 \pm 1.7	3.1 \pm 1.1	0.0 \pm 0.0	36.2 \pm 0.2	34.3
Pulp mill sludge	Composted	80.3 \pm 6.3	5.1 \pm 0.6	3.4 \pm 0.5	11.3 \pm 7.4	18.4 \pm 0.2	42.9
Pine bark biochar	Slow pyrolysis at 375°C	2.1 \pm 0.0	0.4 \pm 0.0	0.1 \pm 0.0	97.4 \pm 0.0	3.8 \pm 0.1	164.7
Willow biochar	Hydrothermally carbonised at 260 °C	1.3 \pm 0.5	0.6 \pm 0.4	25.8 \pm 0.4	72.3 \pm 0.4	0.7 \pm 0.1	110.0
Spruce biochar	Torrefaction at 280 °C	63.4 \pm 0.4	2.3 \pm 0.2	1.1 \pm 0.3	33.2 \pm 0.1	0.6 \pm 0.1	737.6
Straw biochar	Barley, pyrolysed at 460 °C	7.6 \pm 0.7	5.8 \pm 0.6	4.6 \pm 0.4	82.0 \pm 1.6	23.5 \pm 0.3	71.8

The materials that were selected for detailed analysis also represented a variety of chemical qualities (Fig. 3). The slow-pyrolysed biochar consisted almost entirely of the non-soluble fraction (97%). In addition to biochar, the non-soluble fraction was only found in composted horse manure, common reed and pulp mill sludge. Highest shares of the easily decaying water and ethanol solubles were found in fresh plant litter and dairy cattle slurry. Digestion of the cattle slurry affected the AWEN fractions only slightly, however, the difference is not only due to digestion but also the addition of grass silage to the slurry during processing.

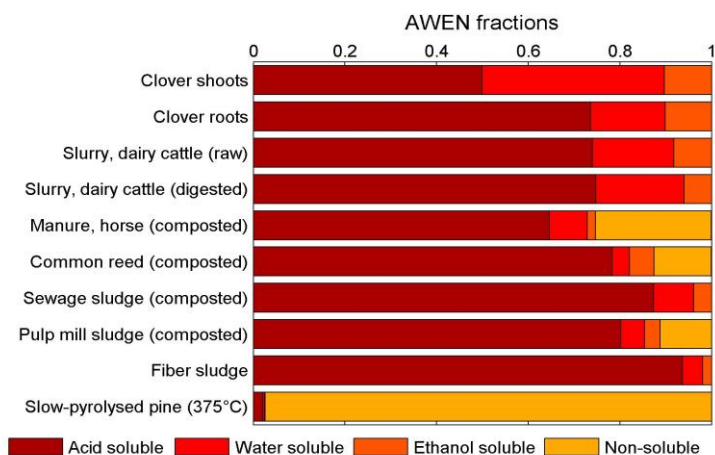


Figure 3 Chemical quality of the materials selected for detailed analysis.

3.2 Decomposition of the biomasses

3.2.1 Laboratory incubation

Proportion of the remaining organic matter after the incubation with soil in laboratory conditions ranged between 31% and 100% depending on the material (Fig. 4). Fresh plant litter and especially its above ground parts lost highest proportion of organic matter during incubation whereas there was practically no detectable organic matter loss with pyrolyzed pine bark, composted sewage sludge and horse manure. Anaerobic digestion increased the persistence of the dairy cattle slurry.

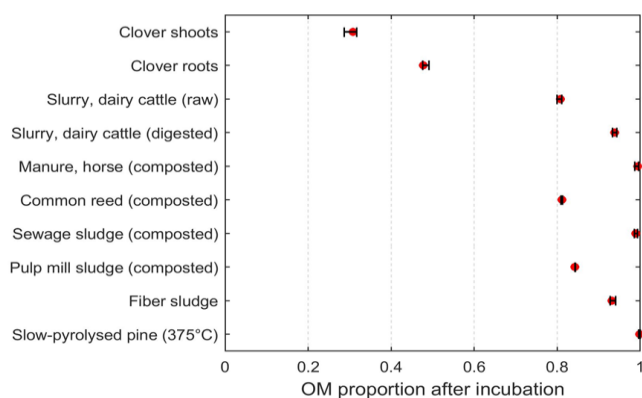


Figure 4 Organic matter (OM) proportion after 6-week incubation with soil in the laboratory. Bars indicate minimum and maximum values and the circles the median value for three replicates.

3.2.2 Litterbag experiment and Yasso modelling

Decomposition of the soil amendments in litterbags buried in soil for one year varied from no detectable decomposition in the pine biochar to 90% loss of clover shoots (Table 2, Fig. 5). For most materials, the rate of decomposition was higher at the beginning but slowed down over time. The variation among replicates was relatively low except the outliers in the case of cattle slurry, horse manure and fiber sludge. Ignoring the outliers, however, had a minor effect on the shape of the curves.

The resistant proportion of organic matter of the studied organic amendments varied between 10% and 100% depending on the material (Table 2, Fig. 5). The most resistant material was the slow pyrolyzed pine for which no mass loss was detected during the litterbag experiment. Horse manure, composted sewage sludge and digested slurry were the next resistant of the studied materials. Digested cattle slurry thus decomposed more slowly than raw slurry. Horse manure and sewage sludge were both composted with peat as additional material. Common reed harvested from the lakeside and composted for soil improvement showed to be quite resistant in soil. The lowest persistent proportions of organic matter were found with clover shoots and roots. The red clover shoots decomposed clearly faster than roots. Yasso07 model predicted relatively well the decomposition of the resistant materials whereas decomposition of the easily decaying materials, fresh plant litter and fiber sludge, was underestimated (Fig. 5).

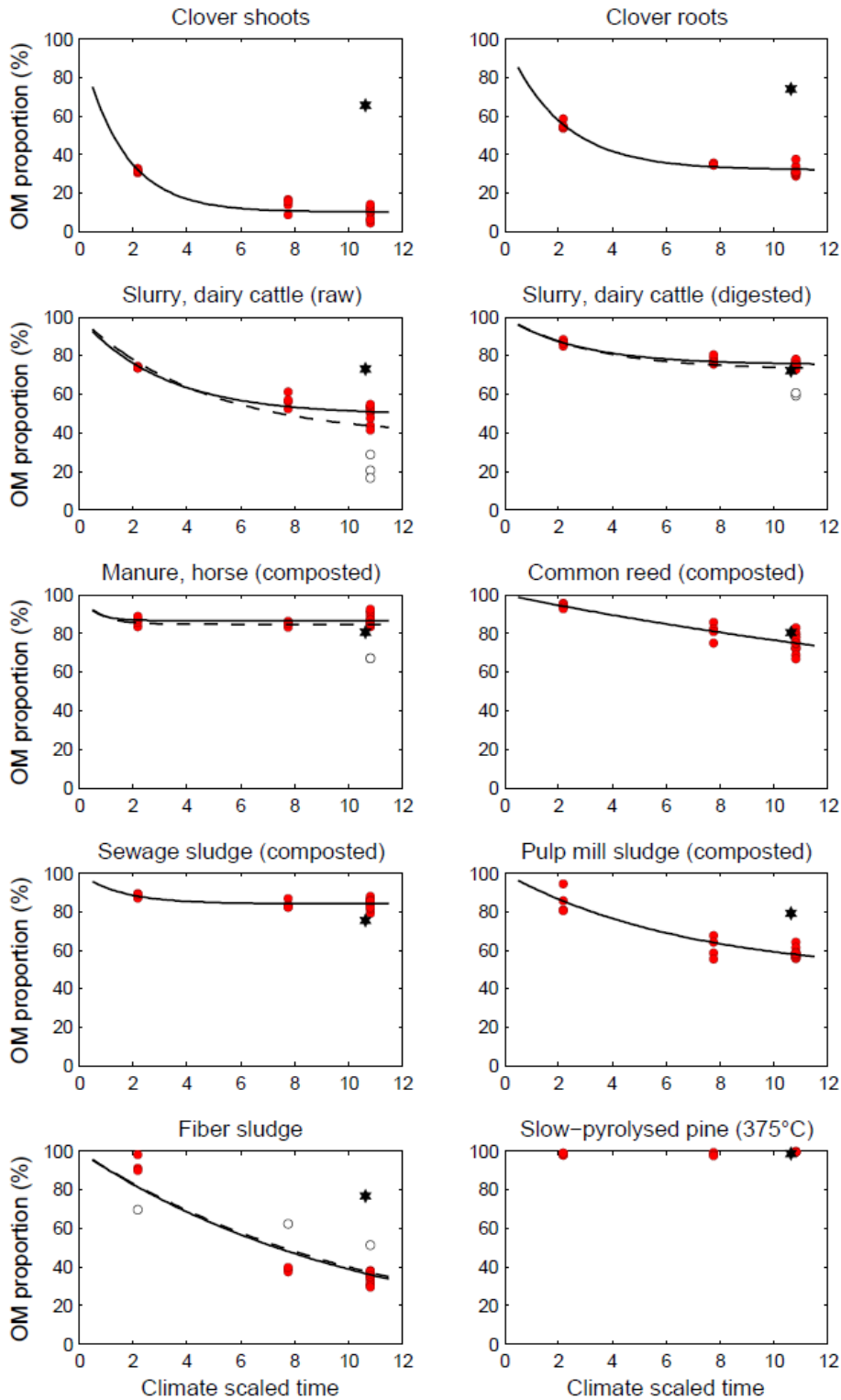


Figure 5 Measured amount of organic matter (OM) of the initial amount in litter bags (circles) and decomposition according to exponential decay models fitted to the data with (dashed line) and without (solid line) outlying values (open circles). Modelled OM content in the end of the experiment using Yasso07 model is marked with a hexagram. Climate scaled time in the X-axis is defined as in Fig. 1.

Table 2 Estimates for the rate of decay and proportion of resistant organic matter (asymptote) in the models fitted to the data of from the litter bag experiment

Material	n	Rate of decay	SE	Resistant proportion	SE
1. Clover shoot	16	-0.65	0.04	0.1	0.01
2. Clover root	16	-0.49	0.05	0.32	0.01
3. Cattle slurry, raw	17	-0.32	0.04	0.49	0.02
4. Cattle slurry, digested	18	-0.36	0.07	0.75	0.01
5. Manure, horse (composted)	18	-1.82	1.39	0.87	0.01
6. Common reed	20	-0.04	0.03	0.25	0.54
7. Sewage sludge, composted	20	-0.64	0.17	0.84	0.01
8. Pulp mill sludge, composted	20	-0.15	0.03	0.47	0.05
9. Fiber sludge ^a	17	-0.09	0.01	-	-
10. Slow-pyrolyzed pine (375°) ^b	20	-	-	1	-

Calculated without the outliers (see Fig. 5); SE = standard error; n = number of observations

^aThe data of fiber sludge were modelled separately from the data of the other organic amendments due to higher variation in the observations and absence of asymptote.

^bThe data of the slow-pyrolysed pine were not modelled as the material did not decompose during the experiment.

3.3 Dependency of the proportion of resistant organic matter on the initial chemical quality of the amendment

Decomposition rates of the organic amendments based on the litterbag experiment were moderately correlated with their initial AWEN composition (Fig. 6a). However, the digested slurry (4) and sewage sludge (7) showed notably higher resistance against decomposition than expected based on their AWEN composition. In contrary, the common reed (6) tended to decompose faster than expected on the basis of the incubation experiment (Fig. 6c). However, the result should be treated cautiously due to large standard error (uncertainty) of the estimated resistant proportion for the common reed in the litterbag experiment. Results of the litterbag and incubation experiments were quite similar with respect to the resistance of the studied organic amendments (Fig. 6c). Resistant proportions and C:N ratios were positively but weakly correlated (Fig. 6b).

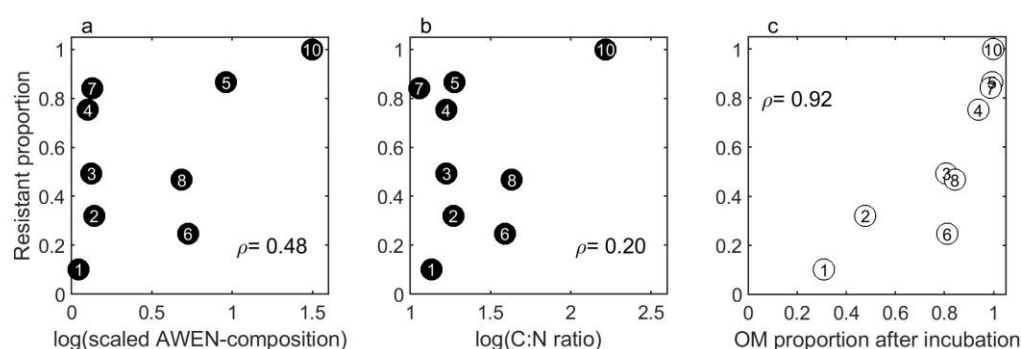


Figure 6 Pairwise associations between the resistant proportion of organic amendments in the litterbag experiment and the chemical quality as log-transformed AWEN composition (a), log C:N ratio (b) and OM proportion after the laboratory incubation (c). Numbers inside the symbols indicate the material as presented in Table 2. Spearman rank correlation coefficient (ρ) is also shown.

3.4 Potential of organic amendments to increase soil organic matter content

Based on the litterbag experiment, the studied organic amendments can increase soil organic matter content by 88-962 kg per applied 1000 kg (DM) of the material (Table 3). Biochar had the highest potential to increase soil organic matter content but also the application of raw manure turned out to have a relatively high impact. Although the resistant proportion of sewage sludge is comparatively high (0.84, see Table 2), it did not increase soil organic matter content at the same rate due to its high initial ash content. The increase for composted common reed should be treated cautiously due to uncertainty of its estimated resistant proportion (Table 2).

Table 3 Increase in soil organic matter by organic amendments, the annual application rate required to reach the goal of the 4/1000 initiative^a and typical application rates.

Material	Effect on soil organic matter content (kg 1000 kg DM ⁻¹)	Rate ^b (kg DM ha ⁻¹) required for 4‰ increase	Typical rate (kg DM ha ⁻¹ yr ⁻¹)
Clover shoots	88	2450	670
Clover roots	267	809	1240
Slurry, dairy cattle (raw)	396	545	2200
Slurry, dairy cattle (digested)	583	370	2200
Manure, horse (composted)	709	305	7400
Common reed (composted)	213	1015	7000
Sewage sludge (composted)	490	441	7500
Pulp mill sludge (composted)	381	566	225
Fiber sludge	-	-	-
Slow-pyrolysed pine (375°C)	962	225	-

^aBased on the estimated resistant proportions in the litterbag experiment (Table 2) and on the organic matter contents of the amendments (Table 1)

^bCalculated using the mean soil carbon stock of 54 Mg C ha in the 0-15 cm layer in Finnish cropland soils (Heikkinen et al. 2013).

For some treatments, it was possible to estimate the climate impact of the treatment compared to the conventional management. Cover crops bring additional carbon to the system compared to conventional annual field crop production. It is estimated that in boreal climatic conditions the biomass of Italian ryegrass, red clover and white clover is 2000, 1600 and 1200 kg DM ha⁻¹, respectively, of which about half of the biomass is in the root system (Känkänen et al., manuscript). Roughly estimated, based on the dry matter biomasses, 50% carbon content and the resistant fraction of 10% for clover shoots and 32% for roots, the cultivation of cover crops increases soil carbon stock by 131 kg C ha⁻¹ annually (Fig. 7a).

In the case of cattle slurry, a typical 28 t annual application of slurry (8% DM) means soil carbon stock increase by 196 kg C ha⁻¹. When the same slurry is first digested, 40% of the carbon is removed as biogas but digestion increases the share of the resistant fraction from 49% to 75%. As a result, the potential of the digested slurry to sequester carbon to the soil is close to that of raw slurry (Fig. 7b).

The effect of biochar in croplands can be compared to the fate of the raw material in the system where they are derived from. In the case of biochar made of forest residues the result can thus be compared to the situation that the residues are left in the forest (Fig. 7c). Based on modelling using the Yasso07 model, only 14% of the untreated residue carbon remains in forest after 100 years, whereas 100% of the biochar can be sequestered in cropland soil. Even though 46% of the mass may be lost in the pyrolysis process, the increase in soil carbon stock would be 210 kg larger with biochar compared to leaving the bark in forest.

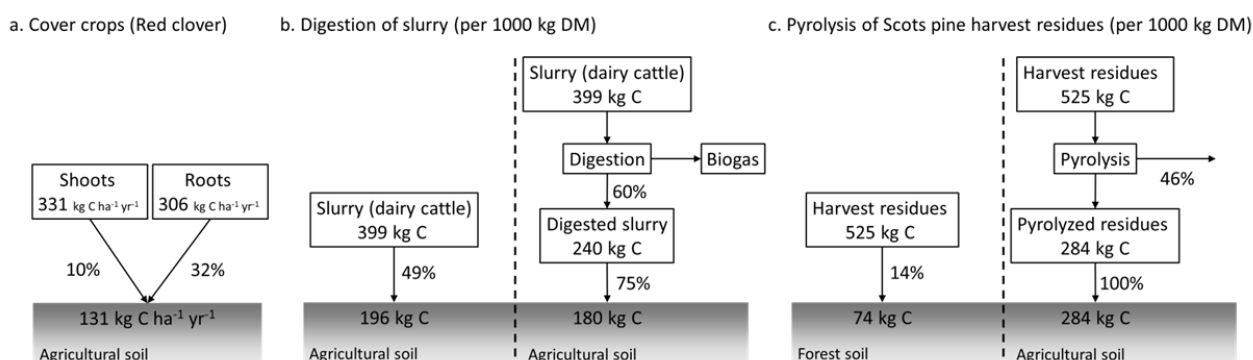


Figure 7 Estimated climate impact of selected soil amendments

4 Discussion

Based on the estimated decomposition rates, fresh plant residues decomposed fastest of the studied materials. Results on the chemical quality and decomposition confirmed some earlier observations that roots decompose more slowly than above-ground residues (Rasse et al. 2005; Kätterer et al. 2011). This may have some significance for developing methods to report the effects of soil management e.g. in greenhouse gas inventories as deep-rooted crops are seen as a way to mitigate climate change. As the pool of data on the chemical quality of root litter and amounts of root biomass grows, it enables taking roots into account when estimating carbon stock changes in soil under management types with increased carbon input through plant biomass.

Composted materials were relatively resistant in soil as the treatment has already consumed the easily degradable organic matter. The resistant proportion of composts ranged from 25 to 90% which was similar to the range 20 to 70% reported in the literature (Li and Evanylo 2013; Noiro-Cosson et al. 2016).

Unlike for most of the studied materials, for manures there are long-term experiments that allow comparison of the estimates with results in long-term experiments. The resistant proportion of cattle slurry based on the decomposition of slurry in litterbags was close to 50% which is high compared to carbon sequestration rates determined on the basis of long-term field experiments. Such manure retention coefficients reported in the literature range from 9 to 37% (Hua et al. 2014; Maillard and Angers 2014). Estimates from one-year incubation in litterbags should not be taken as to represent carbon sequestration rates as such since the organic matter is subject to continuous transformations in the soil. It is also to be noted that some studied amendments are mixtures of materials which is reflected in the results. For example, the horse manure and sewage sludge were amended with peat litter in the process and this increases the resistant proportion in the material when used as soil amendment. However, our aim was to study the materials as they are applied to soils, not to study the effects of production processes.

As expected, the decomposition of slow pyrolysed biochar was too low to be detected in a short-term incubation or litter bag experiment. Results are in line with the review by Wang et al. (2016) indicating that 97% of biochar carbon contributes directly to long-term C sequestration in soil. The properties of biochars differ widely depending both on the origin of the material and the production process (Cha et al. 2016).

Based on the estimate on the required application rate to reach the goal of the 4/1000 initiative and typical rates, the biomass of cover crops is probably not sufficient for net increase in soil carbon (Table 3). The estimated rate of carbon sequestration by cover crops was less than half of the global estimate ($320 \text{ kg C ha yr}^{-1}$) of Poeplau and Don (2015). The difference is understandable as the biomass of cover crops is relatively small in boreal conditions. However, the potential of a typical yield of cover crops to compensate the observed mean loss of soil carbon in Finnish agricultural soils ($220 \text{ kg C ha}^{-1} \text{ yr}^{-1}$; Heikkinen et al. 2013) is still relatively high and adding cover crops to rotations can be recommended in boreal climate that restricts the length of the vegetated period on croplands.

Typical manure application rates, on the other hand, might lead to carbon sequestration. There are some signs of that in the soil survey of croplands in Finland as even coarse soils were able to sequester carbon in the animal-intensive western regions in 1998-2009 while most soil types and regions lose carbon (Heikkinen et al. 2013). Interestingly, it was found in Sweden that increase in number of horses was related to an increase in soil carbon stocks of croplands (Poeplau et al. 2015). In their study it was the ley area more than manure that explained this trend. However, horse manure typically contains litter bedding that may have a role in carbon sequestration especially if it is peat. This may have implications on the climatic impact of manure use as peat mining decreases carbon stocks elsewhere.

Assessing the climatic impact of many materials is not straightforward and would require life cycle assessment. Without human action, the common reed and forest residues are left in their natural ecosystem and thus they return to soil, while manures and sewage sludge are already currently used extensively in soil improvement, the former in food production and the latter mainly in landscaping, thus the climate impact should be compared to the alternative use of the material.

Energy production during processing may add significant benefits in the climate impact considerations. These results encourage developing the energy use of manures as the loss of carbon in the biogas process does not necessarily reduce the potential for carbon sequestration. The same applies for biochar, it is likely beneficial to utilize the energy of materials first in pyrolysis instead of applying residues like straw or manure as such to soil. However, the final result depends also on the energy yield and on which kind of energy use is replaced which are out of the scope of this paper.

In this study we tested two methods of determining the resistant proportion of organic matter, one simple laboratory incubation method and one performed in more realistic field conditions. The laboratory incubation resulted in considerably higher values for the resistant proportion suggesting that the “traditional” litterbag method cannot be replaced by the simpler one. Of course, also the litterbag method has its downsides. Although for most studied materials one year litter bag experiment seems to be long enough, there was high uncertainty in resistant fractions of composted common reed and pulp mill sludge due to short duration of experiment and low number of sampling over time. Further, the contact of the material in the bag with soil and especially soil macrofauna is restricted, and part of the sample is lost from the bag for example due to leaching.

Most soil carbon models (e.g. Yasso07, RothC, ICBM) are based on the assumption that litter decomposition is controlled mainly by litter quality and climate. Dependence between litter chemical composition and decomposition is well established in previous studies and the results of this study are generally in agreement with them. The resistant proportion in litterbags was better correlated with the AWEN composition than with C:N ratio that has been found to correlate negatively with mineralization of organic amendments (Zhang et al. 2017). However, the association between litter quality and decomposition of the studied organic amendments was not especially strong neither in litterbag nor in incubation experiment indicating that other factors, such as accessibility of organic matter for microbes and decomposer populations, have an impact on the decomposition of organic amendments as well (Dungait et al. 2012).

Absence of non-soluble fraction in many of the studied materials raises the concern that acid treatment dissolves not only organic matter but also mineral compounds. This finding urges the development of better methods for organic matter fractionation. Alternatively, the reliability of the fractionation results could be improved by measuring the ash content prior and after the acid extraction. However, in this study we decided to rely on the method that has been used in the development of the Yasso model in order to have applicable results with respect to model verification.

Conclusions

The results indicate that decomposition of organic amendments depends on their initial chemical composition, and the fractionation scheme in water, ethanol, acid and non-soluble fractions predicts the persistence of the materials more reliably than the simple C:N ratio. Yasso07 model can be used with relatively high confidence to estimate the effects of various types of carbon input on soil carbon sequestration. This enables assessing the efficiency of measures under different agri-environmental programmes and also reporting a variety of soil management measures e.g. in greenhouse gas inventories. Use of the data on the chemical quality of organic amendments is not restricted to Yasso model as parts of them can also be used in other soil carbon models or calculation tools. The examples of the climate impacts of the studied materials showed that it is

more beneficial from soil carbon stock point of view to introduce new carbon input to agricultural systems than to change the processing of the materials already applied on fields. Increasing carbon input is always beneficial for the soil quality of croplands but the climate impact of soil management is a more complicated issue as the life cycles of the materials and effects on e.g. other land use classes should also be considered.

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