Modelling Dissolved Organic Carbon Production in Coniferous Forest Soils

The production of dissolved carbon (DOC) in forest soils is still not well understood as a result of difficulties in isolating co-occurring processes. We have used an extension of the continuous-quality theory to analyze the consequences of three modes for DOC production in coniferous forest soils: Model A, the production of DOC occurs through physical leaching of soil organic carbon (SOC) and the composition of DOC is proportional to the composition of SOC with respect to carbon (C) qualities; Model B, the production of DOC occurs when the decomposers use SOC and the composition of DOC will be proportional to the composition of SOC that decomposers extract; and Model C, the production of DOC is associated with mortality of decomposers and the composition of DOC reflects the composition of decomposer biomass. The results from Models B and C resemble each other but differ from Model A. Models B and C lead to a larger fraction of C being lost through leaching, a higher quality of the C leached, and a lower 14C age of the leached C than Model A. Models B and C differ with respect to properties of DOC leached from a horizon. All three models were found capable of describing stores of C in and leaching of DOC from an organic horizon and an underlying mineral soil in three temperate/boreal Norway spruce [Picea abies (L.) Karst.] forests. Microbial activity should always be an important agent for DOC production. Model B and, in particular, Model C suggest a larger contribution of microbially processed C in DOC than Model A.

Abbreviations: DOC, dissolved organic C; SOC, soil organic C; SOM, soil organic matter.

Core Ideas

- Mechanisms of DOC production affect the quantities and qualities of SOC and DOC.
- Three models with different physical and microbial processes were analyzed.
- Comparisons with experimental data provides no strong discrimination between models.
Quality of DOC and how the quality is related to parent soil organic matter (SOM) is another contentious issue. As stated by Michel et al. (2006), “Overall, the importance of SOM quality for DOM composition is largely unknown.” However, it is clear that the source material for DOC is important (e.g., Yano et al., 2005; Michel et al., 2006) but DOC will differ from the source material due to microbial processing. Kalbitz et al. (2000) found that carbohydrates in DOC are hexose-dominated, indicating microbial origin. The concentrations of O-alkyls and aromatics are sometimes used as indicators of microbial modification of SOM, but NMR studies are contradictory with respect to how these classes are related in SOM and DOC (Michel et al., 2006; Fröberg et al., 2003). There is also a decrease in the degradability of DOC with the age of the source material (Don and Kalbitz 2005; Bourbonniere and Creed, 2006).

We believe that part of the confusion over DOC production and properties stems from definitions of systems that are not compatible among investigations. To clarify some of the issues we will take a theoretical approach to relate DOC chemistry and production to SOM source quality. The approach we will use is an application and extension of the Q-model (Ågren and Bosatta, 1998), which will give us analytical solutions that will help us identify which system properties control which result. Our model differs from others (e.g., DyDOC, Michalzik et al., 2003, or the model by Neff and Asner, 2001) by using analytical solutions, making it easier to see how model properties control model results. It has structural similarities to models by Qualls (2000), Campbell et al. (2016), and Moore et al. (2008), but is simpler by not including vertical transport explicitly and sorption–desorption processes. We want instead to focus on the consequences of the mechanisms by which DOC is released from SOM. It is, also, more constrained than other models by being based on fewer assumptions about processes involved and has a considerably lower number of free parameters to be estimated for a particular application. We have tested the model on three temperate/boreal Norway spruce ecosystems.

### THEORY

We will use a model that describes the soil organic C (SOC) dynamics in a forest soil horizon, a typical case would be the organic (O) horizon of a Podzol soil. Litter input, respiration and DOC losses are the processes that determine the C stock in the horizon. For such a horizon we will use the continuous-quality theory (Bosatta and Ågren, 1991; Ågren and Bosatta, 1998) to calculate its C stock, as well as its $^{14}$C age, as a function of quantity and quality of litter input. Rates of DOC leaching and quality and $^{14}$C age of DOC will also be derived. Since we want to focus on analytical results and qualitative differences between modes of DOC production, we will only consider steady state situations. The “bomb carbon” effect (e.g., Levin and Heshlamier, 2000) will, therefore not be considered in this paper but there is in principle no problems of doing the (numerical) calculations associated with “bomb carbon” (see Franklin et al., 2003).

We start with the continuous-quality theory without DOC losses. The theory has been described extensively elsewhere (Bosatta and Ågren, 1991; Ågren and Bosatta, 1998), and only a brief summary will be given here. The organic matter in the soil of an ecosystem is composed of a large number of chemical components of different qualities. By quality we mean in this context a measure at the molecular scale of the accessibility of a C atom to the decomposers (Bosatta and Ågren, 1999; Joffre et al., 2001); it is represented by the real, continuous variable $q$, where $q > 0$ and high values represent easily degradable C and low values recalcitrant C. Consider a C atom of quality $q$ in the SOC. Decomposers assimilate this atom and utilize it to produce in their biomass a compound of different quality $q'$. This conversion is described by a transition rate, $D(q,q')u(q')$, which is proportional to the microbial rate of C uptake $u(q') \leq 0$ and to the probability distribution $D(q,q')$ describing the fraction of atoms of initial quality $q$ that are converted to atoms of quality $q'$ in the microbial biomass. In addition, the decomposers respire C as carbon dioxide, which we describe by the function $e(q)$, which is the efficiency of converting SOC to microbial biomass C $[0 < e(q) < 1]$, and respiration being the fraction $1 - e(q)$. There is also an influx of C of different qualities, $I(q)$, which we will treat as constant in time. Let $p(q,t)$ denote the distribution over qualities at time $t$ of C in SOC [amount of C of quality $q$ in the quality interval $(q,q + dq)$]; the dynamics of $p$ is then described with the following integro-differential equation for the mass balance of C (Bosatta and Ågren, 1991; Ågren and Bosatta, 1998):

$$
\frac{\partial p(q,t)}{\partial t} = - \int D(q,q')u(q')p(q',t)dq' - \frac{u(q)}{e(q)}p(q,t) + \frac{I(q)}{e(q)}
$$

The integral term in Eq. [1] specifies the inputs of C to quality $q$ from the range of materials of qualities $q'$ coming from microbial transformations (metabolism, mortality). We call the C originating from this term recycled C; it has been cycled from SOC via decomposers back to SOC. The second term specifies the microbial uptake of C from SOC of quality $q$ and includes C going to decomposer biomass and respired C. The integral in Eq. [1] is the sum of all conversions to state $q$, and the last term is the sum of all uses of C or quality $q$. When $I(q) = 0$, Eq. [1] describes the decomposition of a single litter cohort and can be used to describe typical litter decomposition experiments. Another way of understanding $p(q,t)$ is therefore to think of it as the sum of the remainders of a large number of litter cohorts of different ages. A summary of symbols is given in Table 1.

Since $D$ defines the fraction of C of quality $q'$ that is converted into other qualities, the sum of all fractions must be equal to 1:
\[ \int_0^\infty D(q,q')dq=1 \]  

To be specific, consider the organic horizon of a forest soil. The distribution \( \rho(q,t) \) is then the amount of C of quality \( q \) at time \( t \) in this horizon. The total amount of C in the horizon is:

\[ C(t)=\int_0^{q_0} \rho(q,t)dq \]

where \( q_0 \) is the upper limit of qualities, which also is the quality of fresh litter (initial quality).

Equation [1] can be modified in different ways to represent different mechanisms of DOC production. These processes are present in virtually all DOC models, but their relative importance is obscured by the inclusion of many other processes. Here we want to emphasize the importance by which DOC is released from SOM. We will here consider four special cases (Fig. 1). The four cases are:

**Model 0. No leaching.** All carbon losses from the soil are through microbial respiration. This case will serve as a baseline and is described by Eq. [1] without modification.

**Model A. Physical leaching.** The production of DOC occurs through physical leaching of SOC and the composition of DOC is proportional to the composition of SOC with respect to carbon qualities. We assume that all qualities of carbon are leached just in proportion to their abundances with a rate \( \lambda_A \), that is, the leaching losses are \( \lambda_A \rho(q,t) \). Equation [1] is then modified to:

\[
\frac{\partial \rho(q,t)}{\partial t} = \int_0^{q_0} D(q,q')u(q')\rho(q',t)dq' - \left[ \frac{u(q)}{e(q)} + \lambda_A \right] \rho(q,t) + I(q) \]

**Model B. Decomposer growth.** The production of DOC occurs when the decomposers attack SOC and the composition of DOC will be proportional to the composition of SOC that decomposers extract such that a fraction \( \lambda_C \) of the carbon becomes DOC, that is, the leaching losses are \( \lambda_C \rho(q,t) \). Equation [1] is then modified to:

\[
\frac{\partial \rho(q,t)}{\partial t} = \int_0^{q_0} D(q,q')u(q')\rho(q',t)dq' - \left[ \frac{u(q)}{e(q)} + \lambda_B \right] \rho(q,t) + I(q) \]

**Model C. Decomposer mortality.** The production of DOC is associated with the mortality of the decomposers and lysis of microbial cells. The composition of DOC reflects the composition of decomposer biomass such that when decomposers die, a fraction \( \lambda_C \) of the decomposer biomass becomes DOC, that is, the leaching losses are \( \lambda_C \rho(q,t) \). In Model C, DOC is produced when decomposers die, a fraction \( \lambda_C \) of the carbon becomes DOC, that is, the leaching losses are \( \lambda_C \rho(q,t) \). Equation [1] is then modified to:

\[
\frac{\partial \rho(q,t)}{\partial t} = \int_0^{q_0} D(q,q')u(q')\rho(q',t)dq' - \frac{u(q)}{e(q)} \rho(q,t) + I(q) \]

### Table 1. List of symbols with default values.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e(q))</td>
<td>Decomposer efficiency</td>
<td>Function</td>
<td>–</td>
</tr>
<tr>
<td>(e_0)</td>
<td>Constant decomposer efficiency</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>(q, q')</td>
<td>Carbon quality</td>
<td>Variable</td>
<td>–</td>
</tr>
<tr>
<td>(q_0)</td>
<td>Initial quality of spruce litter</td>
<td>0.747</td>
<td>–</td>
</tr>
<tr>
<td>(t)</td>
<td>Time</td>
<td>Variable</td>
<td>yr</td>
</tr>
<tr>
<td>(\omega(q))</td>
<td>Decomposer growth rate per unit carbon</td>
<td>Function</td>
<td>yr(^{-1})</td>
</tr>
<tr>
<td>(u_0)</td>
<td>Base parameter in decomposer growth rate per unit carbon</td>
<td>Variable (10(^7))</td>
<td>yr(^{-1})</td>
</tr>
<tr>
<td>(D(q,q'))</td>
<td>Dispersion function</td>
<td>Function</td>
<td>–</td>
</tr>
<tr>
<td>(l(q))</td>
<td>Litter input</td>
<td>Function</td>
<td>kg m(^{-2}) yr(^{-1})</td>
</tr>
<tr>
<td>(l_0)</td>
<td>Constant litter input</td>
<td>0.1</td>
<td>kg m(^{-2}) yr(^{-1})</td>
</tr>
<tr>
<td>(T)</td>
<td>Temperature</td>
<td>Variable</td>
<td>K</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Shape parameter of dispersion function</td>
<td>20</td>
<td>–</td>
</tr>
<tr>
<td>(\lambda_A)</td>
<td>Leaching rate of DOC with Model A</td>
<td>Variable (10(^{-7}))</td>
<td>yr(^{-1})</td>
</tr>
<tr>
<td>(\lambda_B)</td>
<td>Leaching rate of DOC with Model B</td>
<td>Variable (0.289)</td>
<td>–</td>
</tr>
<tr>
<td>(\lambda_C)</td>
<td>Leaching rate of DOC with Model C</td>
<td>Variable (0.0863)</td>
<td>–</td>
</tr>
<tr>
<td>(\lambda_{14})</td>
<td>Decay rate of (^{14})C</td>
<td>0.000121</td>
<td>yr(^{-1})</td>
</tr>
<tr>
<td>(\rho(q,t))</td>
<td>Carbon distribution</td>
<td>Function</td>
<td>kg m(^{-2})</td>
</tr>
<tr>
<td>(\tau_{14})</td>
<td>Half-life of (^{14})C</td>
<td>5730</td>
<td>yr</td>
</tr>
<tr>
<td>([\Delta Q]^0/R)</td>
<td>Activation energy divided by gas constant</td>
<td>14</td>
<td>K</td>
</tr>
</tbody>
</table>
We will use exact solutions to Eq. [1] and Eq. [4a–4c] by following Bosatta and Ågren (2003). This requires that we define the functions describing decomposer properties in a particular way.

For the decomposer efficiency (the ratio between biomass production and assimilation) we use the standard assumption that the efficiency is independent of C quality and which is the only one for which we have analytical solutions:

\[ e(q) = e_0 \]  

[5]

The choice of a constant decompose efficiency is a simplification but information for using a more complex function is limited (e.g., Manzoni et al., 2012).

For decomposer growth rate we use the thermodynamic formulation (Bosatta and Ågren 1999):

\[ u(q) = u_0 \exp \left( \frac{[-\Delta G^0]}{qRT} \right) \]  

[6]

Equation [6] can be derived from dynamics of enzyme reactions in SOC and relates \( q \) to thermodynamics. \( T \) is absolute temperature, \( R \) the gas constant, and \( \Delta G^0 \) the change in free energy in the enzymatic reactions that transform C in SOC to CO\(_2\), and \( u_0 \) a basic rate constant.

To make exact solutions possible we have to choose the function \( D \) as:

\[ D(q,q') = \begin{cases} \alpha q^{-\frac{1}{\frac{1}{\alpha}+1}} & \text{if } q \leq q' \\ 0 & \text{if } q > q' \end{cases} \]  

[7]

where \( \alpha \geq 0 \). A consequence of Eq. [7] is that the quality of a C atom will always be decreasing with time and hence the initial litter quality \( (q_0) \) is also the upper limit of qualities.

We will focus on long-term processes and steady state conditions. The choice of steady state is made because this provides a well-defined state of the system for comparisons between the different model versions and is also characteristic for the long-term behavior of the system and avoids short-term, more or less random fluctuations. Then, the procedure for solving Eq. [4a–4c] is given in the Appendix. An important aspect of the solutions is that they will consist of two terms. One term describes the decomposition rate (0.35 yr\(^{-1}\)) and the other term is \( C \) that has been cycled through the decomposers and will be described by a distribution of qualities, \( q < q_0 \).

For Model A, we can calculate a cut-off quality, \( q_{c} \), where losses from leaching and respiration are equal \( [u(q_c)/e(q_c)] = \lambda_A \) giving:

\[ q_c = -\frac{[\Delta G^0]}{RT\ln(\lambda_A e_0/u_0)} \]  

[8]

We will also calculate \( 14C \) ages for the steady state C store. The \( 14C \) age (\( \tau_{14C} \)) is defined by:

\[ \tau_{14C} = \tau_{14} \ln \left( \frac{12C_{ss}}{14C_{ss}} \right) \]  

[9]

where \( \tau_{14} \) is the mean life of \( 14C \) (8033 yr), and \( 12C_{ss} \) and \( 14C_{ss} \) are the steady state stores of \( 12C \) and \( 14C \), respectively (Stuiver and Polach 1977). It should be noted that for non-homogeneous materials, such as the SOC we are investigating, the \( 14C \) age will be much larger than the turnover time (Trumbore & Druffel 1995); the turnover time is dominated by the high-quality C whereas the \( 14C \) depleted low-quality C weighs heavily in the \( 14C \) age. When calculating \( 14C \) stores we will assume that with the exception of radioactive losses of \( 14C \), the dynamics of the two isotopes behave identically (see however, Ågren et al.1996 for an analysis of isotope effect).

We can also calculate what happens in underlying soil layers. All we have to do is to replace the input term \( I(q) \) in Eq. [4a–4c] with the term defining the leaching losses for each of the models and solve the system with this new input term. The resulting expressions are more complicated by still manageable. However, the leaching rates \( (\lambda) \) should in general be different between layers and other parameters might also differ and we will not pursue this analysis further.

**PARAMETERIZATION**

As a first step in the parameterization of the model we have fitted parameters to decomposition of Scots pine (\textit{Pinus sylvestris} L.) needles (data from Berg et al., 1991) at a location in Central Sweden, close to Knottäsen to be used as a test site (Jädraås, 60°49’ N, 16°30’ E; mean annual temperature 3.8°C); this is one of the most extensive data sets available. Leaching of DOC from the needles in these experiments is likely to be small and all the mass loss can be considered as a result of decomposition (Franklin et al., 2003). Five parameters \( (\alpha, [\Delta G^0]/R, e_0, q_0 \) and \( u_0 \) have to be estimated. We use the same \( e_0 = 0.25 \) as in previous estimates (Ågren and Bosatta 1998). Second, the temperature sensitivity of decomposition depends only on \( [\Delta G^0]/(RT^2q_0) \) and we have chosen this parameter combination (to equal 18.2) such that an increase in temperature from 5 to 15°C increases the initial decomposition rate of a litter cohort with a factor of 1.9. The parameter \( u_0 \) was the set to 10\(^7\) to give the right initial decomposition rate (0.35 yr\(^{-1}\)). We also wanted parameter combinations that lead to steady state C stores under constant litter input rates (see Appendix Eq. [A13b] and [A13c]), which requires \( \alpha \) to be sufficiently large relative to \( [\Delta G^0]/RT \). To achieve that, we have chosen \( [\Delta G^0]/RT = 14 \), and finally \( q_0 = 0.770 \). The parameter \( \alpha \) was finally adjusted to give the best fit to data. With \( \alpha = 20 \), the model for decomposition of a single litter cohort explains 94% of the variability in the data (n = 133). We also need to parameterize the model for Norway spruce litter instead of Scots pine. Berg (2000) compared the initial rate of decomposition of Scots pine and Norway spruce needles at different sites. We have assumed that the only factor causing a difference in decomposition rate in his study is the initial litter quality. This gives \( q_0 = 0.747 \) for Norway spruce needles; a value we will use.
henceforth. Although root litter probably differs from needle litter we have not enough data to estimate separate parameters for root litter but will use the same values as for needles.

We have applied this parameterization to three Norway spruce [Picea abies (L.) Karst.] stands located from northern to southern Sweden (Flakaliden 64°07′ N, 19°27′ E, mean annual temperature 1.2°C; Knottåsen 61°00′ N, 16°13′ E, mean annual temperature 3.4°C; Asa 57°08′ N, 14°45′ E, mean annual temperature 5.5°C); for details see Table 2 and Kleja et al. (2008). We have considered two horizons in these stands, the O horizon and the top 45 cm of the mineral soil. Measured aboveground tree and ground vegetation litter and root litter production have served as inputs. From lack of information, we have assumed that all litters have the same initial quality as that of Norway spruce needles. For each site we have used the actual mean annual temperature and then adjusted the leaching parameters ($\lambda_A$, $\lambda_B$, $\lambda_C$) first for the O horizon and then for the mineral soil horizon until observed and simulated C stocks agree, Table 2. A problem has been that, in spite of the warmer climate, the turnover time of C at the Asa site is approximately twice that of the other two sites. We attribute this slower turnover to effects of the higher nitrogen deposition in the south. Ågren et al. (2001) and Franklin et al. (2003) showed that nitrogen deposition could slow decomposition by increasing decomposer efficiency. To account for this effect, we have increased $\epsilon_0$ from 0.25 to 0.28 at the Asa site; although a small parameter change, this is enough to correspond to an increase in a steady state C stock (without leaching) with a factor of 2.5.

RESULTS

General Results

We will first present a series of general results for different leaching intensities ($\lambda_A$, $\lambda_B$, $\lambda_C$) using parameters for the Knottåsen site and then for the three Norway spruce stands. Since the parameters controlling the leaching rates are not easily comparable between the three models of leaching, we have instead chosen to compare the models when leaching results in the same decrease in total soil steady state C store (70% of the no leaching case will be used as a representative case). This should make the numerically very different leaching rates comparable in terms of impact on SOC. In Fig. 2 it is shown how soil steady state C store varies with leaching intensity. Steady state soil C decreases smoothly with increasing leaching intensity in Models B and C but is extremely sensitive to the leaching intensity in Model A (note the logarithmic scale for $\lambda_A$). The stores are calculated based on a constant litter influx of 0.1 kg (C) m$^{-2}$ yr$^{-1}$, which is approximately a rate to be used later. The C store with no leaching is 2.16 kg m$^{-2}$.

![Fig. 2. Relationship between leaching intensity ($\lambda$) and steady state C stores for Models A, B, and C, respectively. Note the logarithmic scale for $\lambda_A$. The stores are calculated based on a constant litter influx of 0.1 kg (C) m$^{-2}$ yr$^{-1}$, which is approximately a rate to be used later. The C store with no leaching is 2.16 kg m$^{-2}$.](image)

Table 2. Site properties† and estimated leaching parameters for fitting of observed data to simulations.

<table>
<thead>
<tr>
<th>Lat./Long.</th>
<th>Asa</th>
<th>Knottåsen</th>
<th>Flakaliden</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean annual temperature, °C</td>
<td>5.5</td>
<td>3.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Mean annual precipitation, mm</td>
<td>190</td>
<td>160</td>
<td>120</td>
</tr>
<tr>
<td>Stand age, yr</td>
<td>38</td>
<td>37</td>
<td>42</td>
</tr>
<tr>
<td>Basal area, m$^2$ ha$^{-1}$</td>
<td>26</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Leaching parameter</td>
<td>O horizon</td>
<td>Mineral soil</td>
<td>O horizon</td>
</tr>
<tr>
<td>$\lambda_A$</td>
<td>$2.65 \times 10^{-6}$</td>
<td>0.00283</td>
<td>0.00815</td>
</tr>
<tr>
<td>$\lambda_B$</td>
<td>$3.80 \times 10^{-14}$</td>
<td>0</td>
<td>$5.0 \times 10^{-17}$</td>
</tr>
<tr>
<td>$\lambda_C$</td>
<td>0.477</td>
<td>1.13</td>
<td>1.53</td>
</tr>
</tbody>
</table>

† From Kleja et al. (2008).
qualities because leaching is coupled to the decomposer growth rate and the distribution over qualities decays smoothly, but more rapidly than without leaching, with decreasing quality.

As a result of the shift toward higher C qualities in Model A, the overall losses are almost exclusively through respiration (Fig. 4). It may then seem paradoxical that as the leaching rate increases, the higher qualities associated with higher leaching rates (Fig. 3) are accompanied by a larger fraction of C lost as leaching. However, the litter input is constant and if leaching losses increase, respiration losses have to go down to maintain steady state. In Models B and C leaching can go up to 20% of the total losses (leaching plus decomposer respiration). At similar leaching intensities, leaching losses with Model B are approximately three-fold as large as with Model C, because in Model B leaching is coupled to the SOC stock whereas in Model C it is coupled to the smaller decomposer C stock.

With all three models, the losses of C are mostly reducing the content of C of the lowest qualities. As a consequence, the average C quality increases as leaching intensity is increasing, Fig. 5. The effect is most pronounced for Model A and least pronounced for Model B, with Model C approximately halfway between the other two. The quality of DOC leached out of the horizon is by definition equal to the quality of C in the horizon with Model A. With Models B and C the quality is much higher and almost insensitive to the leaching rate. Another consequence of the shift in quality toward more high-quality C with increased leaching intensity is a decreasing $^{14}$C age of the C, Fig. 6. With no leaching the $^{14}$C age of steady state C store is 5550 yr, but this declines to about half that age in Models B and C but down to only 500 yr in Model A when leaching is strong enough to reduce steady state C store to half the value with no leaching. Again, the $^{14}$C age of DOC in Model A equals the $^{14}$C age of the store. In contrast, the $^{14}$C age of leached DOC in Models B and C is only around 10 yr with a slight decline with leaching rate. The much stronger effect of leaching rate on $^{14}$C age in Model A compared to Models B and C results from the concentration to DOC losses of C of low quality and hence $^{14}$C depleted C in Model A compared to Models B and C where the losses are spread over all qualities.

The large difference in $^{14}$C ages and qualities of DOC between Model A on one hand and Models B and C on the other hand is a result of the different modes of DOC production. In Model A, where C of different qualities are leached in proportion to their abundance, more C of low quality, and thus old, is included in DOC compared to Models B and C, where DOC production is weighed by the decomposer growth rate (Eq. [6]; Fig. 7). The shift toward high-quality C in DOC in Models B and C is so strong that the average quality of the leachate is almost completely insensitive to the leaching intensity, whereas in...
Model A there is a considerable increase in C quality in the leachate with increasing leaching intensity.

**Comparison between Model and Observation**

Unfortunately, there is no simple way of estimating $\lambda$ other than by fitting C pools in the respective horizon of the leaching from the horizon. Our $\lambda$ includes various processes such as the water flux through the horizon and adsorption/desorption that are explicitly described by several parameters in other DOC models. The leaching parameters used to fit the C stores for the three Norway spruce soils are given in Table 2 and all results are summarized in Fig. 8. For all three models the Asa site has the smallest leaching parameters for both the organic and mineral horizons and Flakaliden the largest for the organic horizon whereas Knottåsen and Flakaliden have similar leaching parameters for the mineral soil. The estimated DOC flux for Model A is almost 0 in the Asa site but agrees with observations for Model C and, in particular, Model B. In spite of the very low DOC leaching at the Asa site in Model A, the accompanying lower DOC quality leads to a higher C store in the mineral soil with Model A than with Models B and C. All three models, and Model B in particular, overestimate DOC fluxes from the O horizon at the Knottåsen and Flakaliden sites. Because of the very small observed fluxes at Knottåsen and Flakaliden from the mineral soil it is difficult to say if the simulated zero fluxes with Models A and B agree or not with observations, whereas Model C predicts a larger flux than observed.

The estimated contribution of DOC to the mineral soil C stock is least at the Asa site (average 41% for the three models) compared with 61 and 59%, respectively for the Knottåsen and Flakaliden sites. Model B leads to the least and Model C to the greatest contribution from DOC to mineral soil C stock. Depending on the model and site, the contribution of DOC to mineral soil C stock ranges from 31% (Model B at Asa) to 75% (Model C at Flakaliden); the rest of the C stock was produced from root litter.

The quality of DOC leached from the O horizon is lowest at the Asa site and highest at the Flakaliden site independently of model. Similarly, the qualities of DOC leached from the O horizon rank B > C > A independently of site. The quality of DOC is in all cases much lower than the quality of the fresh litter; note that already as small differences as between 0.747 (Norway spruce) and 0.770 (Scots pine) implies a doubling of a steady state C stock.

Fröberg et al. (2006) measured $^{14}$C in soil horizons and DOC at the Asa and Knottåsen sites and observed small differences between soil and soil solutions indicating that Model A might best described these observations.

**DISCUSSION**

The different mechanisms for producing DOC in the three models result in DOC with widely different properties. Models B and C share many properties, whereas Model A always differs from the other two; we would like to particularly emphasize the strong sensitivity of DOC quality to leaching rate in Model A compared to no sensitivity in Models B and C (Fig. 5). The major differences between Models B and C appear when we consider the DOC leached from one horizon to an underlying one. A larger fraction (Fig. 4) with a higher quality (Fig. 5) of litter input is leached with Model B than with Model C. The importance of quality is larger than that of quantity such that with Model B the DOC input to underlying horizons results in a smaller C stock than with Model C.

Model A is special with its high sensitivity to the leaching rate. This is a consequence of the decoupling between leaching and a strongly quality-dependent decomposer C utilization rate, which separates C losses into two quality categories; one with low-quality C and where leaching dominates losses and one with high-quality C where respiration dominates. Since the production rate of low-quality C is low, already low rates of leaching are...
Similarly, Hagedorn et al. (2004) estimated the contribution from DOC collected under the horizon derived from this source. Horst in the stand at the Asa site and found that only 4% of the contribution from fresh litter added on top of the organic undecomposed plant material. Fröberg et al. (2007) measured and thus retain plant signatures. Increasing the leaching rate in part of the DOC derived from the undecomposed plant material has passed through the decomposers (Fig. 7). At least for Models B and C, although with Model C all the DOC produced has passed through the decomposers (Fig. 7). At least part of the DOC derived from the undecomposed plant material with Model C should consist of unmetabolized substances and thus retain plant signatures. Increasing the leaching rate in Model A, however, increases the fraction of DOC coming from undecomposed plant material. Fröberg et al. (2007) measured the contribution from fresh litter added on top of the organic horizon in the stand at the Asa site and found that only 4% of the DOC collected under the horizon derived from this source. Similarly, Hagedorn et al. (2004) estimated the contribution from recent litter C in DOC to be 5 to 10%. The values from the model calculations and these two studies are, however, not directly comparable. The experiments mentioned will underestimate the contribution from undecomposed plant material, as defined in the model, because in the experiments only contributions from recent litter are measured whereas the models account for undecomposed plant material of all ages. Park and Matzner (2003) and Fröberg et al. (2005) also concluded that DOC should be produced from all SOC and not only recent litter. This comparison indicates, however, that Models B and C are likely to overestimate the contribution of undecomposed plant material in DOC.

With Model A the 14C age of DOC becomes equal to the 14C age of the substrate, because DOC is a direct reflection of the substrate, and, except for high leaching rates, the age of DOC is of the order of thousands of years. In contrast, Models B and C yield DOC with low 14C ages because the utilization function, \( u(q) \), strongly favors production of young DOC. Observations of 14C concentrations in DOC (e.g., Karlton et al., 2005, Fröberg et al., 2007) show a high content of C from recently produced litter, consistent with Models B and C. The differences between Models B and C with respect to 14C ages are small and would probably be hard to separate experimentally.

A key parameter in the model is the leaching rate, \( \lambda \). In \( \lambda \) we have included various processes such as the water flux through the horizon and adsorption and/or desorption. Our use of the leaching rate is a simplification bypassing numerous processes and parameters in other models. Changing the thickness of a horizon, for example, in litter addition experiments, will therefore not only change the amount of C exposed to leaching but also the effective rate of leaching because a C atom leaching from the extra thickness will pass through a thicker horizon and therefore have a higher probability of being respired than atoms released in the original horizon. A possible way to improve the understanding of the leaching parameter could be to take a given horizon and divide it into two. The leaching of the divided horizon calculated from the equations for two horizons should then equal that for a single horizon.

The estimates of the leaching rates (\( \lambda \)) given in Table 2 are based on the assumption that the soil horizons are at steady state. This is not likely to be the case as the time required for reaching steady state is of the order of several thousand years (Ågren et
al., 2007). The leaching rates are therefore overestimations. The consequences of this are particularly serious for the estimates of 14C ages where even a small tail of old C weighs heavily in the estimated age.

Temperature effects on DOC production under field conditions are not conclusive (Kalbitz et al., 2000) but can appear clearly and with temperature responses typical of litter decomposition rates (Christ and David, 1996). The production of DOC has also been found to be strongly correlated to respiration in laboratory experiments (Michel et al., 2006), indicating a coupling to microbial activity. The lack of temperature response under field conditions speaks in favor of Model A, which has no direct temperature effects, but the lack of temperature effects on DOC production could also be a result of confounding effects of temperature and water availability. The clear temperature response under controlled laboratory conditions points, on the other hand, toward Models B and C.

Lehmann and Kleber (2015) argue in a critical review for a continuum approach to soil organic matter that focuses on the ability of decomposer organisms to access soil organic matter. Kaiser and Kalbitz (2012) similarly argue that microbial processing is critical to forming SOC. We believe that our model corresponds well to these requests although we have not included the sorption/desorption processes that they emphasize. Interactions with soil minerals has been analyzed in another version of the model (Bosatta and Ågren, 1997) but this aspect has not been pursued as the understanding of how the interaction between SOC and minerals depends on C quality is missing. Cotrufo et al. (2013) propose the MEMS framework to explain the formation of SOC. Our work fits well into this framework by having a focus on microbial transformations of substrates although some features should be expanded, such as a variable carbon use efficiency rather than a constant, Eq. [5], and a simplified description of microbial conversions of substrates, \( D(q,q') \) is summarized in a single parameter; simplifications made for mathematical convenience but also for lack of empirical data on which to define more realistic functions. For the same reasons we have left out explicit interactions between organic material and a mineral matrix, too. The latter is also a consequence of our application to coniferous forests with a large fraction of DOC produced in the upper mineral-free organic horizon (Kleja et al., 2008).

Our three models for DOC production represent different compositions of DOC. With Model A, DOC will consist of a mixture of plant and microbial. With Model B, DOC is mainly by-products from microbial decomposition of plant material and microbes. With Model C, DOC will mostly consist of microbial C.

There has also been a considerable development of DOC models (e.g., Wu et al., 2014; Camino-Serrano et al., 2018; Braakhekke et al., 2011) intended to provide inputs to global C models. These models differ from our model by being focused on providing numbers for other models rather than understanding (see Rastetter, 2017).

We can, as Fig. 8 shows, parameterize the model to fit experimental data. Agreements and disagreements must, however, be considered with some caution because assumptions in the model application do not always correspond to field conditions. A necessary simplifying assumption in the model is that of steady state. As shown by Ågren et al. (2007) the approach to steady state is very slow and observed pools should therefore be smaller than what is predicted. On the other hand, the fine root litter input is probably underestimated (Kleja et al., 2008). These two factors could therefore compensate each other. We have also treated all litters as being identical, but tests indicate that litter quality is probably not such a strongly controlling variable. Model A fails to estimate the leaching from the O horizon for all sites whereas Model B is in agreement for the Asa site but largely overestimates leaching at the other two sites. Model C on the other hand, underestimates leaching at Asa but fits better at the other sites. All three models predict very low leaching from the mineral soil, even to the extent that Model B does not allow any losses at all. The leaching rates rank along a gradient from north to south: \( \lambda_{Flakliden} > \lambda_{Knörråsen} > \lambda_{Asa} \) (except \( \lambda_A \) for the mineral soil at Flakaliden). This may reflect differences in water transport through the soils, annual precipitations are similar at the three sites but the temperature gradient from south to north should decrease evapotranspiration and leave more water for transporting DOC in the north.

In summary, there are no evidences clearly identifying one of the three models as explaining all observations, although Model C might be the better one. A major reason is that the three models represent three idealized situations. In reality all three processes should be operating. There are clear evidences for microbial activities being important (temperature sensitivity, microbial of origin of DOC). On the other hand, direct physical leaching must also play a role as in Model A. The evidence most strongly pointing against Model A is the high 14C age of DOC resulting from this model. Distinguishing between Models B and C cannot be done with current information but studies of the behavior of the C properties in horizons produced from DOC might provide an answer. Effects of sorption/desorption have not been included in our analyses although some studies (e.g., Fan et al., 2010) indicate that those processes are important for the transport of DOC through soil profiles. However, we have restricted the analyses to steady state conditions and sorption/desorption processes should be more important for balancing short-term fluctuations than long-term stocks.

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APPENDIX
Exact Solution to the Continuous-Quality Equation with DOC Losses at Steady State
Add a term \( \lambda(q)\rho(q,t) \) to the basic Eq. [1], with input
\[
\frac{\partial q}{\partial t} = \left[ \frac{u(q)}{e(q)} + \lambda(q) \right] q(t) + \int_q^\infty D(q', q)u(q')q(t)q' + I(q, q') \frac{\partial D}{\partial q} \left( q \right) dq' + I \delta(q - q_0)
\]

Let \( g(q) = \frac{u(q)}{e(q)} + \lambda(q) \)

At steady state

\[0 = -g + \int_q^\infty D(q, q)u(q) + I \delta(q - q_0)\]

Differentiate with respect to \( q \)

\[0 = -\rho \frac{dg}{dq} - \frac{d\rho}{dq} D(q, q)u_0 + \int_0^\infty \frac{\partial D}{\partial q} u_0 dq' + dI \]

Let \( \frac{\partial D}{\partial q} = f(q)D \) and combine Eq. [A2] and Eq. [A3]

\[\frac{d\rho}{dq} = \left\{ -\frac{dg}{dq} - D(q, q)u_0 + f(q) \right\} \rho + dI \frac{dq}{dq} \]

\[\frac{d\rho}{dq} = \left\{ -\frac{dg}{dq} - \ln g + \frac{uD(q, q)}{g} + f(q) \right\} \rho + \frac{dI}{dq} - fI \]

Let \( uD(q, q) = Bu' / e_0 \)

Define

\[H(q) = -\frac{1}{\lambda} \ln \left[ \frac{u(q)}{e_0} + \lambda \right] + F(q)\]

Consider now three special cases

Case A. If \( \lambda(q) = \text{constant} = \lambda_A \), then

\[H_A(q) = -(1 + B) \ln \left[ \frac{u(q)}{e_0} + \lambda_A \right] + F(q)\]

Case B. If \( \lambda(q) = \lambda_B u(q) \), then

\[H_B(q) = \ln \left[ 1 + \frac{1}{e_0 + \lambda_B} \right] + B \ln u + F\]

Case C. If \( D(q, q') \rightarrow (1 - \lambda_C) D(q, q') \) and \( \lambda(q) = 0 \), then

\[H_C(q) = [1 + (1 - \lambda_C) B] \ln \left[ \frac{u(q)}{e_0} \right] + F(q)\]

The solution to Eq. [A5] is

\[\frac{d}{dq} \left[ e^{H(q)} \rho(q) \right] = e^{-H(q)} \left[ I' - fI \right] \frac{u(q)}{e_0 + \lambda(q)}\]

Integrate from \( q \) to \( \infty \) with boundary condition \( \rho(\infty) = 0 \)

\[-e^{-H(q)} \rho(q) = \frac{-f(q_0)e^{-H(q_0)}}{u(q_0)/e_0 + \lambda(q_0)} I_0 + \int_q^\infty e^{-H(q')} I' \frac{d}{dq' \left[ g(q') \right]} \]

or

\[\rho(q) = \frac{e_0}{u(q_0) + e_0 \lambda(q_0)} I_0 \delta(q - q_0) + B \frac{u'(q_0)}{e_0} \frac{e^{H(q') - H(q_0)}}{g(q_0)} I_0\]

If we use Model C, then (Bosatta and Ågren, 2003)

\[
\begin{cases}
   u(q) = u_0 e^{\frac{A}{q^2}} & \gamma(q) = \frac{A}{q^2} \\
   D(q, q') = \frac{\alpha}{q^2} e^{-\frac{1}{2(q^2)}} & D(q, q) = \alpha / q^2 \\
   f(q) = -2/q^2 & F(q) = -2nq - \alpha / q \\
   B = e_0 \frac{\alpha T}{A} & A = \frac{\Delta G}{R}
\end{cases}
\]

Finally

\[\rho_A(q, q_0) = \frac{e_0}{u(q_0) + e_0 \lambda_A} I_0 \delta(q - q_0) + \frac{\alpha e_0^2}{q^2} \frac{u(q_0) + e_0 \lambda_A}{[u(q_0) + e_0 \lambda_A]^2 + e^{-\frac{1}{2(q^2)}} I_0}\]

or

\[\rho_B(q, q_0) = \frac{e_0}{u(q_0) + e_0 \lambda_B} I_0 \delta(q - q_0) + \frac{\alpha e_0^2}{q^2} \frac{u(q_0) + e_0 \lambda_B}{[u(q_0) + e_0 \lambda_B]^2 + e^{-\frac{1}{2(q^2)}} I_0}\]

In the limit of \( \lambda_A = \lambda_B = \lambda_C = 0 \), Eq. [A12a–12c] equal Eq. [22] in Bosatta and Ågren (2003).
The amounts of steady state C can be calculated analytically for Cases B and C, while only numerical solutions are possible for Case A:

\[
C_{\text{ss},A} = \int_0^\infty \rho_A(q, q_0) dq
\]

\[
C_{\text{ss},B} = \int_0^\infty \rho_B(q, q_0) dq
\]

\[
C_{\text{ss},C} = \int_0^\infty \rho_C(q, q_0) dq = \frac{\epsilon_0 I_0}{u(q_0)} + \frac{I_0}{u(q_0)} \alpha \left(1-\frac{\epsilon_0}{1+\epsilon_0}\right) \frac{1}{\lambda_T}
\]

\[
\frac{\partial C}{\partial t} = \frac{u(q)}{\epsilon(q)} + \lambda_\Lambda C \frac{\lambda_\Lambda}{\lambda_\Lambda + \lambda_{14}}
\]

For Case A, the solution is identical to the solution without radioactive decay if

\[
\lambda_\Lambda \rightarrow \lambda_\Lambda + \lambda_{14}
\]

For Case B, we can rewrite the first term of the left-hand side as

\[
\frac{\epsilon(q)}{\epsilon(q)} + \lambda_B \epsilon(q) + \lambda_{14} = \frac{\epsilon(q)}{\epsilon(q)} + \lambda_B \epsilon(q) + \lambda_{14}
\]

The solution for Case B is then the same as solution in Case A if the following substitutions are made

\[
\epsilon(q) \rightarrow \frac{\epsilon(q)}{1+\lambda_B \epsilon(q)}
\]

\[
\lambda_\Lambda \rightarrow \lambda_{14}
\]

In Case C, Eq. [A17] takes the form

\[
\frac{\partial C}{\partial t} = \frac{\epsilon(q)}{\epsilon(q)} + \lambda_{14} \frac{\epsilon(q)}{\epsilon(q)} + \lambda_{14}
\]

The solution for Case C is then the same as solution in Case A if the following substitutions are made

\[
\epsilon(q) \rightarrow (1-\lambda_C) \epsilon(q), \quad \lambda_\Lambda \rightarrow \lambda_{14}
\]

REFERENCES


