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Modeling the dissolved organic carbon output from a boreal mire using the convection-dispersion equation: Importance of representing sorption

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[1] In this paper we present a model of the dissolved organic carbon (DOC) concentrations and fluxes in mire water based on the convection-dispersion equation. The dynamics of sorbed, potentially soluble organic carbon (SPSOC) in the peat matrix are simulated in parallel with DOC. First, the model is applied solely to stagnant water conditions in order to interpret the results of laboratory peat incubations, with the focus on sorption processes. Some important model parameters are derived using literature data complemented by information from new incubation experiments. Second, the model is fully applied to simulate the DOC concentrations in the outlet of a steam draining a small headwater mire in northern Sweden during the period 1993–2001. A relatively good model fit (mean bias error (MBE) = -0.6–2.2 mg L^{-1}, Willmott index of agreement $d > 0.7$ for the daily concentrations) was found for all the categories of stream discharge, except periods with very low flow ($q < 0.3$ mm d^{-1}). When seeking explanations for the interannual variability in DOC concentrations, we, like previous authors, could find the influence of temperature, flow path, and intensity. However, the model has helped to demonstrate that the system also has a "memory": the store of sorbed, potentially soluble organic carbon in a year affects the DOC concentrations and fluxes in the following year.

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1. Introduction

[2] In the boreal systems, the flux of dissolved organic carbon (DOC) is much greater than the particulate organic carbon (POC) and dissolved inorganic carbon (DIC) fluxes [*Cole et al.*, 2007; *Jonsson et al.*, 2007]. Export of DOC is likely to occur mainly from areas where flowing water bypasses the adsorbing mineral soils, i.e., in surface and subsurface flows from riparian zones and wetlands [e.g., *McKnight and Aiken*, 1998; *Qualls*, 2000]. Field data collected from various locations within the boreal region have highlighted the importance of mire, a specific type of wetland with a naturally accumulated peat layer at the surface, as one of the major sources of terrestrially derived DOC reaching aquatic ecosystems [e.g., *Aitkenhead et al.*, 1999]. The amounts of DOC exported from mires are sufficiently large to be included in regional C balances [e.g., *Jonsson et al.*, 2007] and to contribute to the mire C balance [*Moore et al.*, 1998; *Fraser et al.*, 2001; *Billett et al.*, 2004; *Roulet et al.*, 2007]. Not only average DOC fluxes are significant, but also interannual variation is comparable to that of vertical net carbon exchange [*Roulet et al.*, 2007; *Sagerfors*, 2007]. The role of particular environmental factors, including temperature and precipitation, in determining the variability of the DOC concentration and fluxes is still open to debate [e.g., *Freeman et al.*, 2001a; *Monteith et al.*, 2007; *Worrall et al.*, 2004; *Erlandsson et al.*, 2008]. It is widely appreciated that both in situ microbial DOC transformation (production and mineralization) and hydrological transport are important influences on DOC concentrations [e.g., *Tranvik and Jansson*, 2002], but the relative contribution of each factor remains largely unknown. Experimental evidence supports the view that the sorption equilibrium, based only on physicochemical properties, is likely to be as important for the export of the DOC from the wetland as biotic and hydrological processes [*Qualls and Richardson*, 2003].

[3] The complexity of the problem has encouraged the development of several process-based models of DOC in soils and stream water [e.g., *Grieve*, 1991; *Neff and Asner*, 2001; *Michalzik et al.*, 2003; *Futter et al.*, 2007]. The interest in modeling terrestrial DOC export and DOC concentrations in aquatic bodies is spread over many scientific disciplines (hydrology, geochemistry, soil science, limnology, aquatic chemistry and microbiology, ecosystem science etc.), which naturally leads to the coexistence of

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different mathematical formulations of the problem. Thus, much analytical work is needed to transfer achievements and innovations from one model to another, particularly so if laboratory data are used for modeling the situation in the field. These difficulties can be, at least partially, avoided by having a common mathematical framework. Making an analogy with similar fields, such as pesticide or nutrient transport in soil, we believe that the classical convection-dispersion equation [e.g., *van Genuchten and Wagenet*, 1989] is a sensible choice for a common framework that, to our knowledge, has not previously been applied to the DOC problem.

[4] Here we test the ability of the convection-dispersion equation to reproduce the DOC concentrations observed in a boreal stream draining a mire. The presented model is built up in two separate stages, the ultimate goal being to simulate DOC export from boreal mires. First, the model version applicable to a situation with stagnant water and constant temperature is used to explore the implications of the model for laboratory incubation studies, including incubations with peat samples collected from the studied mire, to help derive the model parameters. Second, the predictive form of the model is used to simulate DOC buildup and transport from a small boreal mire in northern Sweden during the period 1993–2001.

[5] One of our main purposes was to explore the role of sorption as a major mechanism regulating DOC concentration and release rates. While laboratory studies have shown that DOC sorption is time-dependent [e.g., *Qualls*, 2000; D. P. Rasse et al. Sorption and diffusion kinetics of DOC in acid forest soils, manuscript in preparation, 2008], previous DOC models have treated it as an instantaneous process. In the model developed by *Grieve* [1991] (also applied by *Boyer et al.* [1996]), the ratio between the store of soluble C and DOC concentration in water is an empirically fitted constant, while the models of *Neff and Asner* [2001] and *Michalzik et al.* [2003] make use of an equilibrium distribution constant, based on laboratory soil incubations, to relate the amounts of dissolved and sorbed OC. Here we aim to demonstrate the advantage of the dynamic approach over a static one when modeling DOC sorption. This approach is particularly important when trying to use laboratory studies to parameterize models. We also advocate here that temporal variations of sorbed, potentially soluble organic carbon (SPSOC) are as important to model as those of DOC: unlike DOC in flowing water, SPSOC in peat matrix can accumulate over longer periods (“memory effect”), but being released because of desorption SPSOC affects strongly the DOC concentration.

2. Model

[6] The complete model formulation includes three key components: heat flux, hydrology, and DOC mass balance. We use the mixed mire water and heat (MMWH) model [*Granberg et al.*, 1999] to describe water fluxes, vertical distribution of water content in the acrotelm, snow dynamics and heat transfer in the peat profile. The system of two mass balance equations, one for the sorbed and one for the dissolved OC, is solved in a 1-D (vertical) peat profile to estimate DOC concentration in the pore water. The model is developed in C++ code (Microsoft Visual C++) and the numerical solution of the system of DOC and SPSOC mass balance equations is calculated using the CVODE program package [*Cohen and Hindmarsh*, 1996] (program codes and documentation available at http://www.llnl.gov/casc/sundials/). The vertical resolution of the model is 5 cm in the acrotelm and 10 cm in the catotelm. The time steps within the model are hourly, and the results were analyzed using daily averaging. Simplified DOC and SPSOC mass balance equations are relevant on their own to application of the model under laboratory conditions with constant temperature, constant water content and no water flow.

2.1. DOC Concentration

[7] The detailed model equations are given in Appendix A and here we will refer to the relevant equation numbers in Appendix A (e.g., equation (A1)).

[8] The model presented here is based on two main premises:

[9] 1. Soluble organic carbon is present in the mire system in two states: dissolved (DOC) and sorbed, potentially soluble, but currently solid (SPSOC). The balance between the two phases varies over time, and adsorption and desorption can be described using first-order kinetics.

[10] 2. A convection-dispersion equation can provide a suitable model of DOC transport. Including the terms accounting for the adsorption-desorption as well as microbial production and mineralization in this equation, accounts for the full mass balance for DOC which can be resolved only in parallel with the mass balance for the sorbed phase (equation system (A1) and (A2)).

[11] The underlying concept of the model is the schematic representation of processes that generate and consume DOC in a mire ecosystem, as presented by *Qualls and Richardson* [2003]. The processes that contribute to in situ changes in pore water DOC concentration (sorption, microbial transformation) are distinguished from the various transport processes, including dispersion and advection by both vertical and horizontal flow (Figure 1a). We model sorption and microbially mediated transformations of the DOC according to the scheme presented in Figure 1b. This part of the model (shaded in Figure 1a) was used alone to study situations with no water flow, e.g., systems with stagnant water in laboratory conditions (equations (A7a) and (A7b)). A 1-D hydrological scheme (vertical discretization) was used here to model water movement in the mire and no lateral import of DOC into the mire from surrounding areas was assumed, therefore a 1-D form of a 3-D equation system was actually solved under field conditions (equations (A6a) and (A6b)).

2.2. Sorption

[12] In our model we use a linear kinetic equation to simulate the adsorption of soluble organic matter to, and its desorption from solid organic matter. Sorption plays a key role in controlling the DOC concentration in pore water. As shown by *Qualls* [2000] and *Qualls and Richardson* [2003], peat always contains substantial quantities of potentially soluble OC sorbed to solid organic matter (SPSOC); there is always more of this than the amount dissolved during any single leaching event. In laboratory peat incubations, it is possible to observe the rapid release of DOC into newly added pore water. This occurs as previously sorbed DOC is desorbed, and during the period before DOC concentrations in the sorbed and dissolved phases reach equilibrium

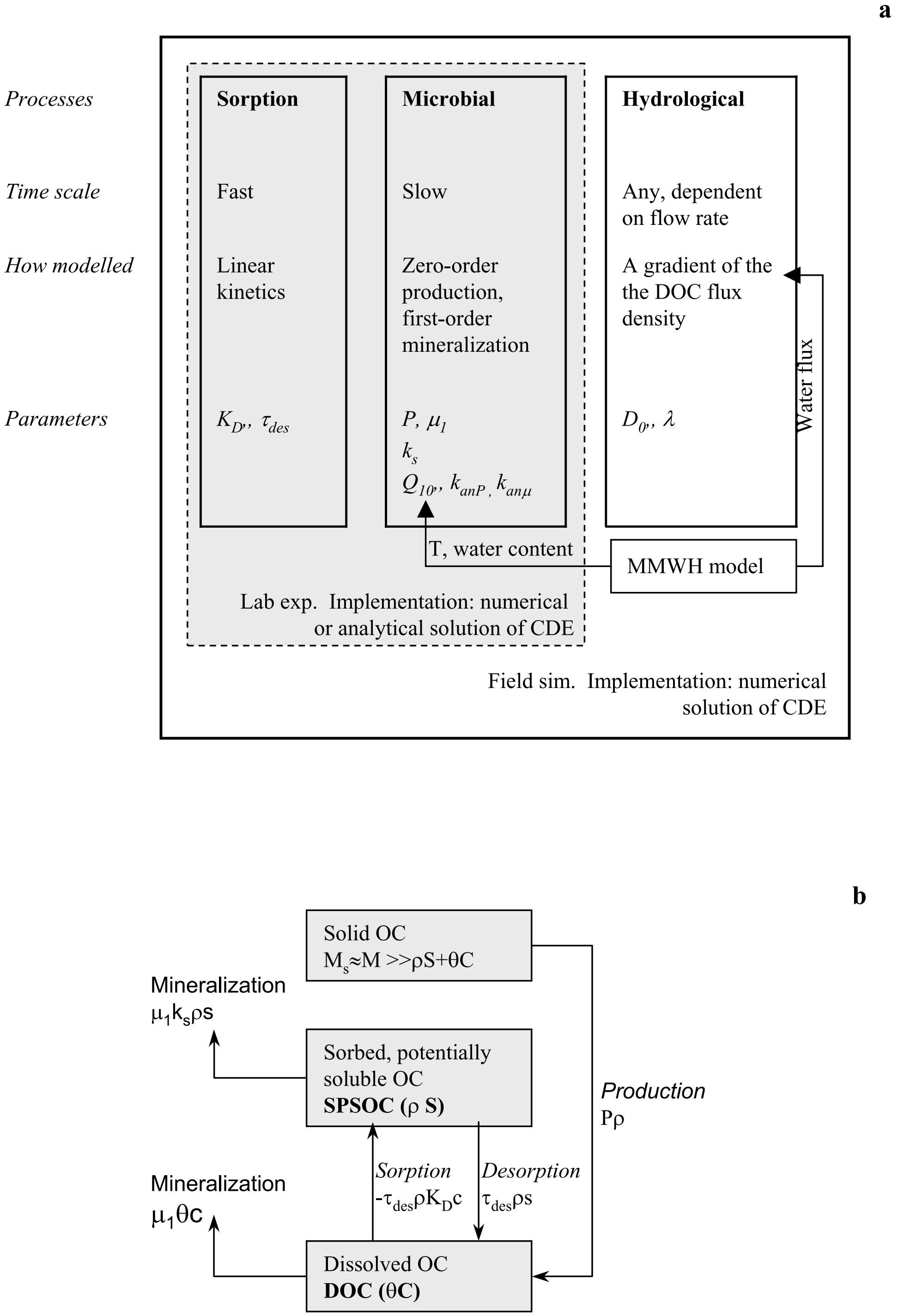

Figure 1. (a) Schematic diagram of the model formulation. (b) Schematic diagram of the modeled pools of soluble organic matter and processes that control microbially mediated transformation (production and mineralization) and abiotic exchanges (adsorption and desorption) between the solid and dissolved phases.

[*Qualls*, 2000]. Equilibration is not achieved immediately, and the rate of change in the DOC concentration due to sorption is highest at the beginning of an experiment, decreases during incubation, and is negligible only after 2–4 days (e.g., Rasse et al., manuscript in preparation, 2008). In this paper we use the term "first steady state" for the local equilibrium between the DOC solution and the initial SPSOC concentration in the peat matrix reached after the rapid release of DOC in the initial phase of the experiment; while the "second phase" stands here for the further DOC dynamics observed in a long-term laboratory peat incubation (Text S1 in the supplementary materials[1]).

[13] We argue that equilibrium sorption models may not describe the dynamics of the process adequately, since they are based on the assumption that exchange between the

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2007WR006523.

sorbed and dissolved phases is so rapid that there is always a fixed ratio between the two. Hence, we believe a linear kinetic model is a better when modeling DOC with a relatively high time resolution. On the other hand, we recognize that our assumption about the constant sorption equilibrium distribution coefficient (K_D) is an oversimplification. There are models that describe the dependency of K_D on the charge of the organic matter [e.g., *Tipping and Woof*, 1991; *Lofts et al.*, 2001]. These models incorporate the effects of pH and ionic strength, thus providing a fuller simulation of the sorption.

2.3. Microbially Mediated Transformations

[14] Metabolic transformations mediated by microorganisms also strongly affect the DOC balance. Acting at slower rates than adsorption-desorption processes, such transformations determine the total amount of soluble OC produced by exoenzymatic dissolution of insoluble organic matter. In addition, they control the rate of mineralization of DOC and SPSOC.

[15] In our simplified model, like many models of soil organic matter dynamics [e.g., reviewed by *Ågren et al.*, 1991], microbial biomass is not explicitly included. Instead, we simulate microbially mediated transformations of the DOC (production and mineralization) that are affected by temperature (equation (A3)) and the presence of O_2 (equation (A4)). We assume first-order kinetics for the mineralization of DOC and SPSOC. A zero-order production constant is hypothesized on the basis of the assumption that substrates for the formation of DOC are not limited in the peat organic matter. In our model we made use of separate mineralization rate coefficients for DOC and sorbed potentially soluble organic carbon (SPSOC) (equation (A5)), to account for the stabilizing effect of sorption on microbial decomposition [e.g., *Kalbitz et al.*, 2005].

[16] Bulk DOC concentration is simulated without specifying chemical fractions; we deliberately avoided separating organic matter into different fractions. As the model parameterization presented below is based solely on data from laboratory peat incubations in which the bulk DOC of the peat solution was measured, the dynamics of short-lived substances, such as root exudates and simple products of decomposition, cannot be adequately described by the current model formulation.

2.4. Hydrology

[17] Two layers can be distinguished within the peat profile: the upper, periodically aerated layer consisting largely of living and lightly decomposed plant material (active layer or acrotelm), which is not usually more than 60 cm deep, and the permanently saturated, lower zone, consisting largely of compacted, relatively highly decomposed plant material (inert layer or catotelm). The hydraulic conductivity is high in the upper acrotelm and usually declines strongly with depth [*Ivanov*, 1981]. Consequently, water in the acrotelm moves rapidly and usually accounts for most of the discharge from the mire. For many mires, especially those with a dominantly atmospheric water supply, the water in the catotelm is mostly stagnant [e.g., *Sirin et al.*, 1997]; if, however, the underlying mineral soil is highly permeable and/or groundwater upwelling is present, significant vertical movements can occur [e.g., *Reeve et al.*, 2000; *Tsvetkova and Sirin*, 2003]. It has also been suggested that the acrotelm is the major source of DOC within mires [e.g., *McKnight et al.*, 1985], since decomposition is much slower in the permanently anaerobic layers, where organic matter is aged and the enzymes regulating organic matter transformation are suppressed [*Freeman et al.*, 2001a, 2001b], and accumulation of CH_4 and CO_2 further inhibit decomposition [*Blodau et al.*, 2004].

[18] The MMWH hydrological model used here was designed to simulate the flow and moisture dynamics in acrotelm [*Granberg et al.*, 1999]. A zero flux (impermeable) lower boundary is placed at the level of constant saturation, and it is assumed that no flow occurs below this (see *Sirin et al.* [1997] and *Reeve et al.* [2000] for an examination of the validity of this assumption). The model is based on steady state vertical moisture distribution curves [*Romanov*, 1961], which was found to be applicable to the parameter values and time step used in this study. The model considers variable lateral flow at different levels, to account for reduction in hydraulic conductivity with depth [e.g., *Ivanov*, 1981]. The MMWH model was first developed for the hydrology of an area with prescribed geometry and a single vegetation type [*Granberg et al.*, 1999]. Here it was applied to the whole mire and model parameters characterizing the geometry and hydraulic conductivity of the mire were combined into the calibrated parameters α, β and l_E [*Yurova et al.*, 2007]. In addition, a generalized form of the Manning equation [e.g., *Beven*, 2001] was applied here to describe overland flow, and, consequently, one additional lumped multiplier $\alpha_{s,}$ accounting for mire surface roughness, was added to the model formulation.

[19] The heat balance equation was solved in a slightly different way than in the original MMWH, mainly for practical reasons. We used a solution presented by R. Wania et al. (Integrating peatlands and permafrost in a dynamic global vegetation model: 1. Land surface processes, submitted to *Global Biogechemical Cycles*, 2008) and implemented it using a C++ program. One important difference from the formulation of *Granberg et al.* [1999] is that the snow layer and meltwater pooled on the mire surface are included as additional layers in the vertical profile when simulating the heat balance.

3. Model Parameterization

[20] The model parameters and initial conditions needed to solve equations (A6a) and (A6b) in a predictive way are summarized in Table 1. Four parameters, the sorption equilibrium distribution coefficient (K_D), the initial SPSOC concentration (s_0), and the rates of microbial DOC production (P), and DOC mineralization (μ_1), were estimated using data obtained from our long-term peat and water incubations (experimental design in supplementary materials, Text S1, and methodology for obtaining the coefficients in supplementary materials, Text S2). In addition, we reviewed the available literature relating to the rates of DOC release into water during long-term experiments to obtain ranges of estimates for two parameters: the DOC production rate (P) and the DOC mineralization rate (μ_1) (supplementary materials, Text S2).

[21] The parameters α, β, α_s and l_E, used in the hydrology submodel, were optimized by minimizing the mean squared difference between the modeled and observed specific

Table 1. Model Parameters and Constants

Symbol	Value	Units	Description	Source
			Hydrology	
α	0.045	cm^{-1}	lumped parameter, equation (1)	calibrated
β	0.20	cm^{-1}	lumped transmittivity parameter	calibrated from the data range of *Ivanov* [1981]
α_s	0.11	$cm^{-0.67}\ h^{-1}$	lumped parameter, equation (2)	calibrated
l_E	0.03	-	lumped evapotranspiration parameter	calibrated from the data range of *Virta* [1966], *Romanov* [1961]
ϕ	0.92, 0.98	-	porosity: acrotelm, catotelm	by analogy [e.g., *Granberg et al.*, 1999]
z_{cat}	−30	cm	acrotelm depth	by analogy, as average
sph	90	%	proportion of *Sphagnum* remains in the peat	measured
ca	5	%	proportion of *Carex* remains in the peat	measured
ρ	0.02, 0.06	$g\ cm^{-3}$	peat density: acrotelm; catotelm	by analogy [e.g., *Nungesser*, 2003]
			DOC Dynamics	
K_D	0.033	$L\ g^{-1}$	sorption distribution constant	estimated from equation (A7b)
τ_{des}	0.078	h^{-1}	desorption kinetic constant	Rasse et al. (manuscript in preparation, 2008): surface peat from a mire in Norway
P_{basal}	1.4×10^{-3}	$mg\ g^{-1}\ h^{-1}$	microbial DOC production rate in the acrotelm at 20°C	average Table 2 (second row, fourth column)
f_{Ps}	1.8	-	correction for the DOC production by vegetation	*Moore and Dalva* [2001], comp. *Sphagnum* and fibric peat
μ_{1basal}	0.4×10^{-4}	h^{-1}	DOC mineralization rate in the acrotelm at 20°C	water incubation Table 2
k_s	1/6	-	the constant reducing the microbial mineralization rate when the soluble OC is sorbed	*Kalbitz et al.* [2005]: podzol organic horizon
Q_{10}	1.7	-	modifier to account for the effect of temperature on P and μ_1	*Moore and Dalva* [2001]: fibric and sapric peat
k_{anP}	0.07	-	ratio of anaerobic to aerobic DOC production	calibrated from the data range of *Moore and Dalva* [1997]
$k_{an\mu}$	1	-	ratio of anaerobic to aerobic DOC mineralization	Calibrated from the data range of *Moore and Dalva* [1997]
D_0	4.3×10^{-2}	$cm^2\ h^{-1}$	molecular diffusion coefficient	*Karlström* [1995]
λ	10	cm	dispersivity	*Reeve et al.* [2001]
D_s	0.19	$cm^2\ h^{-1}$	surface dispersion coefficient	calibrated

discharge. The only three parameters that were adjusted in the DOC concentration submodel were the dispersion coefficient for overland flow, D_s, the ratio of anoxic to oxic DOC production rate, k_{anP}, and the ratio of anoxic to oxic DOC mineralization rate, $k_{an\mu}$.

4. Model Analysis on Laboratory Material

[22] In addition to model parameterization, our main purpose with the "stagnant water" model version was to explore the role of sorption as a major mechanism regulating DOC concentration and to find out if sorption alone can account for some differences in DOC release rates observed in laboratory conditions. This was achieved by:

[23] 1. The partitioning of day-to-day DOC concentration tendency during the incubations between net sorption (adsorption minus desorption) and net microbial production (production minus mineralization) done by numerically estimating each term in (A7a).

[24] 2. Applying differential sensitivity analysis [e.g., *Saltelli*, 2000] to the key model parameters K_D, τ_{des}, P and μ_1 (details in supplementary materials, Text S4, section 1).

[25] 3. Evaluating two important characteristics: the DOC concentration during the first steady state (c_1), and the rate of DOC release into the water during the second stage of the incubation $\frac{\Delta c \cdot V}{\Delta t \cdot M}$, as well as their dependency on the initial SPSOC concentration (s_0) and the peat-to-water ratio (M/V) (equations (A8) and (A9)).

5. Modeling Protocol for the Field Model Application

[26] The model was run for the Kallkällsmyren mire site (Figure 2; detailed description of the site and the measurements can be found in supplementary materials, Text S3) using a series of climate data for temperature, precipitation and potential evapotranspiration recorded at the nearby Svartberget research station [*Löfvenius et al.*, 2003]. The following model simulations were conducted.

[27] 1. Model initialization with climate data from 1986 to 1993, the start of the actual simulation period.

[28] 2. A model run (full, kinetic version) for the whole simulation period (1993–2001).

[29] 3. A run with the model equations formulated for the steady state partitioning between the solid and dissolved phases (no kinetics, sorption is assumed to be instantaneous).

[30] 4. A run with the amount of sorbed organic carbon held constant and calibrated together with the DOC production rate (range in Table 2) at the values, which best fit the data set as a whole. In this the long-term (interannual) memory effect of SPSOC is effectively "turned off."

[31] 5. A series of Monte Carlo runs (1000) to determine the model sensitivity to specific parameters and constants

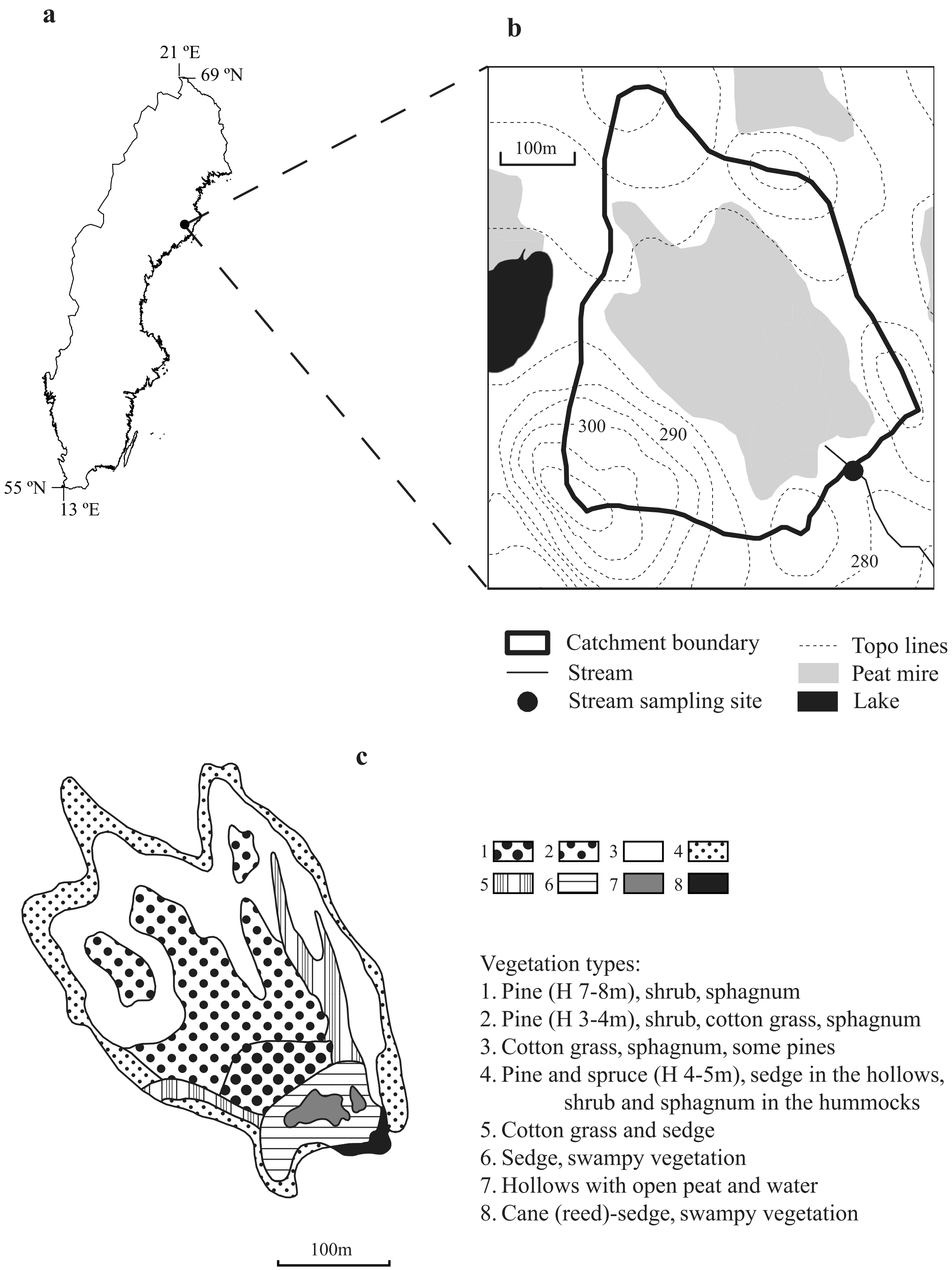

Figure 2. (a) Map of Sweden with study site location. (b) Upper portion of the Nyänget drainage basin at Svartberget near Vindeln, Västerbotten, in northern Sweden, showing the location of the Kallkällsmyren mire and the measurement site at the stream origin. (c) Vegetation map of the Kallkällsmyren mire.

(Table 3, methodology in supplementary materials, Text S4, section 2).

[32] The model results were analyzed on the basis of daily averages. Observed annual DOC fluxes were estimated on the basis of interpolated DOC concentrations measured at the stream outlet. To evaluate the annual DOC balance predicted by the model, the total production and mineralization in the acrotelm were simulated separately and the net production was estimated as the difference between the two summed over a year. Annual net production in

Table 2. Fates of DOC Production, P_{basal}, and Mineralization, μ_{1basal}, Derived From the Long-Term Laboratory Peat and Water Incubations at Approximately 20°C

Sample and Location	Peat-to-Water Ratio (g L^{-1})	Net DOC Release Measured (mg g^{-1} h^{-1})	P_{basal} (mg g^{-1} h^{-1})	μ_{1basal}[a] (h^{-1})	Source and Comments
Peat water	-	-		0.4×10^{-4}	This study
Surface *Sphagnum* peat, small headwater mire	10–14	5.0×10^{-4} to 9.6×10^{-4}	4.0×10^{-4} to 2.4×10^{-3}	$\ldots -1.0 \times 10^{-4}$	This study (c_0 = 0.3 mg L^{-1})
Surface *Sphagnum* peat, small headwater mire	14	2.9×10^{-4}	4.2×10^{-4} to 7.1×10^{-4}	-	This study (c_0 = 44 mg L^{-1})
Fibric *Sphagnum* peat, bog	10–100[b,c]	2.0×10^{-3}	3.1×10^{-3} to 1.8×10^{-2}	-	*Moore and Dalva* [2001]
Sapric *Sphagnum* peat, bog	10–100[b]	1.3×10^{-3}	2.1×10^{-3} to 1.1×10^{-2}	-	*Moore and Dalva* [2001]
Surface peaty soil with 19% OC, river delta	140	2.2×10^{-3}	7.6×10^{-3} to 2.3×10^{-2}	-	*Aguilar and Thibodeaux* [2005]
Subsurface fibrous peat, river delta	3.3×10^{3}	-2.8×10^{-7}[c]	5.8×10^{-7} to 3.6×10^{-6}	1.9×10^{-4} to 6.7×10^{-4}	*Chow et al.* [2006][d]
Subsurface fibrous peat, river delta	1.4×10^{3}	-2.9×10^{-6}[c]	3.3×10^{-6} to 1.9×10^{-5}	1.1×10^{-3} to 3.7×10^{-3}	*Chow et al.* [2006][d]
Subsurface fibrous peat, river delta	500	-1.3×10^{-5}[c]	1.4×10^{-6} to 6.7×10^{-5}	4.6×10^{-4} to 1.4×10^{-3}	*Chow et al.* [2006][d]

[a] If no value is given, not detectable by the parameter optimization.
[b] Presented as a range in the source publication [*Moore and Dalva*, 2001].
[c] From day 7 to day 60.
[d] This study uses different techniques to determine the DOC release rate, so the data on total soluble OC (SPSOC plus DOC) were used for the calculations here.

the acrotelm was then compared with the stream export (flux) of DOC and the total amounts of SPSOC and DOC stored in the acrotelm as predicted by the model. In addition, the annual volume-weighted DOC concentrations were calculated on the basis of the observed data and model simulations, to distinguish the role of concentration changes from flow on the DOC fluxes. This reveals how the mean concentrations vary between years. Volume-weighted concentration (both observed and modeled) was then correlated to the modeled sum of SPSOC and DOC stored in the acrotelm before the spring flood event, to determine whether the latter is related to the former. Simulated volume-weighted

Table 3. Range of Parameters and Constants Used in the Sensitivity Analysis[a]

Parameter	RPCC	Parameter Range[a] Minimum	Parameter Range[a] Maximum	Source and Comments
P_{basal}	0.84	0.4×10^{-3}	2.4×10^{-3}	Table 2
Q_{10}	−0.78	1.6	4	*Chow et al.* [2006]; *Moore and Dalva* [1997]
k_{anP}	0.64	0.07	1	*Bergman* [1998]; *Moore and Dalva* [1997]
μ_{1basal}	−0.54	0.4×10^{-4}	1.0×10^{-4}	Table 2
τ_{des}	0.53	−50%	50%	-
K_D	−0.51	0.019	0.091	*Qualls* [2000]; Rasse et al. (manuscript in preparation, 2008)
$k_{an\mu}$	−0.33	0.07	1	*Moore and Dalva* [1997]
β	0.21	12	34	from optimization
k_s	−0.19	1/6	1/3	*Kalbitz et al.* [2005]
l_E	0.13	0.01	0.03	from optimization
α_σ	0.09	0.09	0.6	from optimization
α	−0.07	0.0113	0.0693	from optimization
D_0	−0.06	1.2×10^{-2}	7.2×10^{-2}	*Karlström* [1995]
D_s	0.05	0.01	1	-
λ	−0.04	0.2	100	*Reeve et al.* [2001]; *Ours et al.* [1997]
f_{Ps}	0.01	1	3	-

[a] Units as in Table 1.

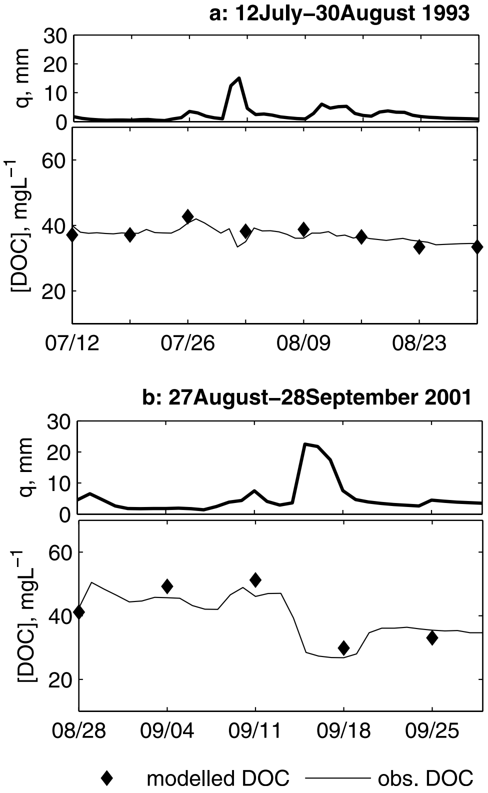

Figure 3. Simulated and measured DOC concentrations for two episodes: (a) 12 July to 30 August 1993 and (b) 27 August to 28 September 2001. The top plots illustrate the measured total stream discharges plotted with y axis inverted (i.e., with peak flows pointing downward).

concentrations for each season were correlated to the simulated stored amounts of SPSOC and DOC in the preceding seasons. The seasons were defined arbitrarily as: "winter," the period when the surface temperature of the peat was at or below 0°C; "spring," the period from the start of snowmelt till the leveling off of the spring flood flow rate; and "summer" as the rest of the year.

[33] To investigate the dynamics of the stream DOC concentration during hydrological episodes when DOC concentration was high, two "rain-driven" flow events were chosen to characterize the system behavior. The episodes differed in the intensity of the rain event. There was more rainfall during the second event than the first. In both cases the stream DOC concentration increased with the first peak in the discharge. After the second (larger) runoff peak, the concentration stabilized at approximately the same level as prior to the first event (12 July to 30 August 1993, Figure 3a) and dropped about 10 mg L^{-1} during the second event (27 August to 28 September 2001, Figure 3b).

6. Results

6.1. Parameterization Results From Laboratory Incubations

[34] Our estimate of the sorption distribution coefficient K_D was 0.033 L g^{-1}; lower than that estimated by Rasse et al. (manuscript in preparation, 2008) on the basis of a surface peat sample from a mire in Norway (K_D = 0.091 L g^{-1}). Our K_D was also slightly higher than 0.019 L g^{-1}, which is the value we calculated using the data by *Qualls* [2000], who analyzed a surface peat sample from a marsh in the Everglades (Florida, USA). Our estimate of the initial SPSOC concentration s_0 = 2.0 mg g^{-1} is close to that in a *Lamnela* peat sample from a drained black spruce forest soils in Alaska (s_0 = 2.7 mg g^{-1} [*Qualls and Richardson*, 2003]).

[35] As summarized in Table 2, the rate of microbial production was substantially higher than the rate of release of DOC from peat into water. As interpreted by our model, the rate of release is less than the rate of production because soluble OC produced by microbial transformations of the peat is distributed by sorption between the solid and dissolved phases. In experiments, measurements of DOC in solution will only record the increases in the dissolved phase.

[36] The estimated rate of microbial production we found in our incubation of surface *Sphagnum* peat is of the same order as that from the sapric *Sphagnum* peat sample incubations of *Moore and Dalva* [2001] (Table 2). A fibric peat sample [*Moore and Dalva*, 2001] and a peat sample from a river delta [*Aguilar and Thibodeaux*, 2005] had higher rates of microbial production, while a different river delta sample [*Chow et al.*, 2006] showed much lower production, resulting in net mineralization. The upper limit for the mineralization rate in our sample, defined by the optimization, was $1.0\text{–}10^{-4}$ h^{-1}. This is of the same order as the upper range of the decay constant of the slowly decaying DOC fraction in soil and stream water (0.4×10^{-4} h^{-1}) [*Qualls*, 2000].

6.2. Abiotic Factors Affecting the First (Local) Steady State DOC Concentration and the Rate of DOC Release During the Second Phase of the Long-Term Peat Incubation

[37] As expected on the basis of the formulation of the model, the amount of DOC that was rapidly released during the first phase of incubation (c_1) exhibited a linear relationship with the amounts of soluble OC originally sorbed on the peat matrix (Figure 4a). Increases in the ratio of peat mass to water volume resulted in nonlinear increases in the amount of DOC released (Figure 4b). There was also a notable difference in the DOC release rate during the second phase of incubation depending on the experimental setup.

[38] 1. The DOC release rate has a negative linear relationship to the initial SPSOC concentration, s_0 (Figure 4c). The initial SPSOC concentration presumably varies naturally among peat samples of different origins and is also affected by the rinsing or washing of the sample before the start of the experiment. Within the expected natural range of SPSOC concentrations the effect on DOC release rate is presumably not high (up to 10%), but it is significant.

[39] 2. The DOC release rate is nonlinearly negatively related to the peat mass-to-water ratio in the experiment, M/V (Figure 4d). For example, DOC release per mass unit is much smaller for an unsaturated sample than for a saturated or flooded sample. This is noteworthy, since here we only deal with the adsorption-desorption processes affected by the relative proportion of the solid phase and the effect of moisture on microbial activities is not considered.

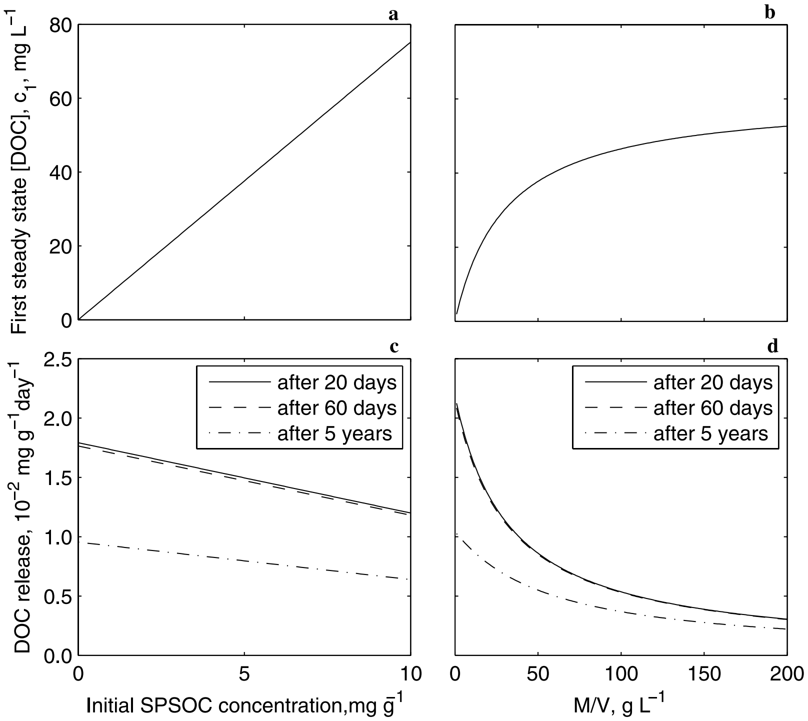

Figure 4. Simulated effect of the initial soluble solid organic carbon (SPSOC) concentration, and peat-to-water ratio (*M*/*V*) (a, b) on the first steady state DOC concentration and (c, d) on the DOC release rate during the second phase of a long-term peat incubation (K_D = 0.033 L g^{-1}, c_0 = 0.0 mg L^{-1}, *P* = 1.0 10^{-3} mg g^{-1} h^{-1}, μ_1 = 4 10^{-5} h^{-1}, k_s = 0.3; *M*/*V* = 10.0 g L^{-1} (Figures 3a and 3c) and s_0 = 2.0 mg g^{-1} (Figures 3b and 3d)). A *Sphagnum* peat sample with density of 0.02 g cm^{-3} and porosity 0.98 is saturated at *M*/*V* = 20 g L^{-1} and oversaturated when *M*/*V* is below 20 g L^{-1}. Lines for "after 20 days" and "after 60 days" in Figure 3d coincide.

6.3. General Agreement Between Simulated and Measured Discharge, Stream DOC Concentrations, and Fluxes: Error Assessment

[40] The simulated discharge corresponded well with the measurements at the mire outlet (MBE = −0.11 mm, RMSE = 1.5 mm *d* = 0.85 mean = 1.1 mm) and no systematic bias was found for particular periods or discharge categories. The largest discrepancies (both negative and positive) between the modeled and measured discharge occurred during the spring flood.

[41] Seven years after the start of the simulation (1986) the model performance was no longer influenced by the initial conditions. The simulated values for DOC concentration from the runs with different initial SPSOC concentrations converged after about 5 years.

[42] We found relatively good agreement between the simulated and measured DOC concentrations both overall (Figure 5) and for particular events (Figure 3). However, the model performance varied greatly between the categories for total discharge (Table 4). The model performed very poorly when the discharge was below 0.3 mm d^{-1} (Table 4 and diamond symbols on Figure 5). Above this threshold, the model performance increased sharply and the best fit between the modeled and measured DOC concentrations was found for the highest discharge category (Table 4).

6.4. Sensitivity Analysis

[43] Sensitivity analysis (Table 3) revealed that the most influential model parameters are the DOC production rate (P_{basal}), its dependence on temperature (Q_{10}, definition in Appendix A), and the parameter accounting for the decrease in the DOC production rate under anaerobic conditions (k_{anP}). Also important, but less so, are the DOC mineralization rate (μ_{1basal}) and the sorption constants (τ_{des} and K_D). The other parameters exerted less influence over the model performance.

6.5. Role of Sorption as a Regulator of DOC Concentrations

6.5.1. Peat Incubations

[44] Both methods that we used to distinguish sorption from microbial processes (Figures 6a and 6b) indicated that there is a clear division between the two phases of DOC release into water during long-term peat incubations. The first phase was short (39 h for the model fitted to our laboratory study) and governed solely by sorption, while further, much slower, increases in DOC concentration during the second phase were due to microbial activity. The kinetic constant of sorption, τ_{des}, was the most important parameter for the first 14 h of incubation, after that the sorption distribution coefficient K_D was most important (Figure 6b). After 39 h the sensitivity coefficient for the production rate *P* became higher than that for the kinetic desorption τ_{des} coefficient (Figure 6b). The two coefficients related to sorption have distinctly different meanings. While τ_{des} is indicative of the time-dependent kinetics of the process, K_D characterizes the partitioning between the solid and dissolved phase when the system is in a steady state

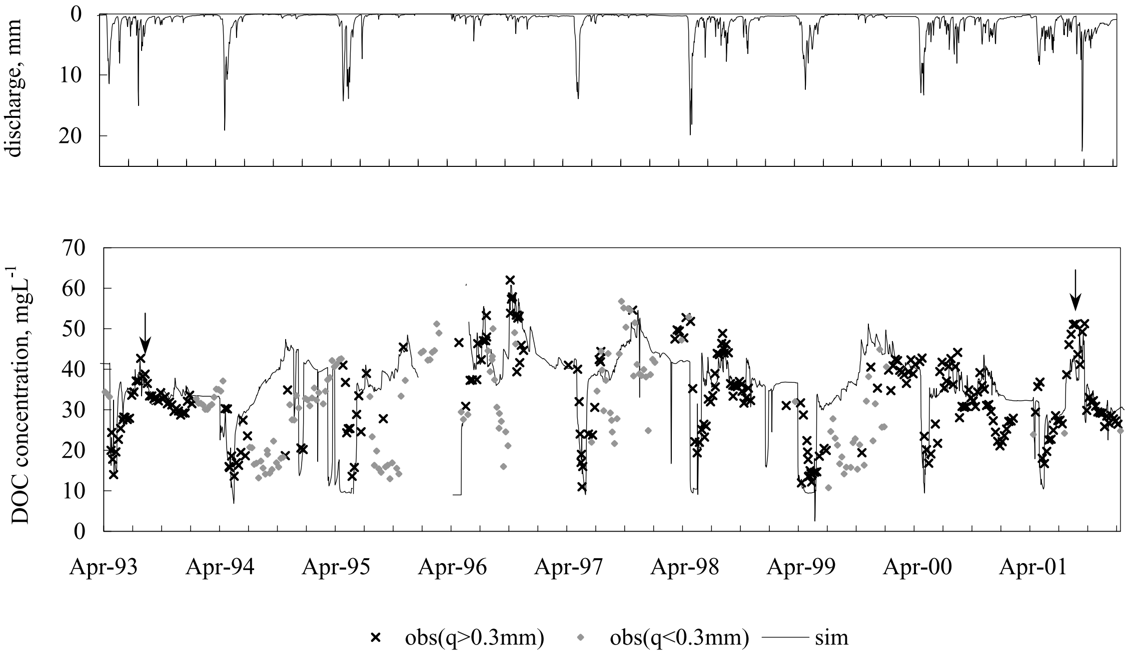

Figure 5. Simulated (line) versus measured (symbols) DOC concentrations at the outlet of Kallkällsmyren mire. Diamonds, DOC measurements corresponding to stream discharge values less than 0.3 mm; crosses, DOC measurements corresponding to stream discharge value greater than 0.3 mm. Arrows point to episodes illustrated in Figure 5. The top plot shows measured stream discharge plotted with *y* axis inverted (i.e., with peak flows pointing downward).

with respect to sorption. It is therefore possible to distinguish between the first phase when sorption kinetics dominated and the second phase when the observed DOC concentration was in equilibrium, with adsorptive partitioning of microbially produced DOC.

6.5.2. Mire DOC Concentrations

[45] On a daily time step the model performed generally weaker with an assumption of the sorption steady state as compared to the standard model version (Table 4). "Sorption steady state" model performance was especially poor for the highest discharge category (Table 4) and, notably, during some major high and low DOC concentration events (e.g., Figure S2 in supplementary materials). Comparing the results produced by the full kinetic and the steady state model versions and averaged over different time intervals, we found that not only day to day but also seasonal and interannual variations in the DOC concentration are better predicted with the full kinetic model (Figure S1 in the supplementary materials). The model performance was strongly degraded under an assumption that the amount of sorbed potentially soluble OC is constant over the simulation period (Table 4 and Figures S1 and S2 in the supplementary materials).

Table 4. Quantitative Measures of Model Performance With Respect to DOC Concentrations[a]

Daily Discharge Interval[b] (mm)	MBE	RMSE	*d*
0–0.15	**11.8**, 13.4, 16.7	**16.1**, 17.0, 20.7	**0.00**, 0.00, 0.00
0.16–0.3	**4.0**, 5.6, 3.6	**11.7**, 11.8, 12.0	**0.60**, 0.63, 0.43
0.3–0.49	**2.2**, 3.2, 3.6	**7.7**, 8.0, 9.9	**0.81**, 0.80, 0.64
0.5–1.4	**1.3**, 3.3, 5.5	**8.8**, 9.9, 12.6	**0.77**, 0.72, 0.41
1.5–23	**−0.6**, 3.0, 5.7	**7.2**, 9.9, 12.3	**0.90**, 0.76, 0.63
All	**3.4**, 5.4, 7.1	**10.6**, 11.5, 14.0	**0.68**, 0.58, 0.29

[a] The first number (in bold) is from the "full, kinetic" model, the second number is from the "sorption steady state" model, and the third number is from the "constant SPSOC" model version. MBE, mean bias error; RMSE, root mean square error; *d*, Willmott index of agreement *Willmott* [1982] (d = 0, no agreement; d = 1, perfect match) calculated for the whole simulation period and for particular discharge categories.

[b] N = 657.

6.6. Components of the Annual DOC-SPSOC Balance

[46] Two main simulated components of the annual DOC-SPSOC balance, net microbial production within the acrotelm and stream export, are of a similar order of magnitude but are not equal for the years under consideration; in fact, the difference between the two can be large (Figure 7). Interannual variation in the volume-weighted DOC concentration reflects the variation in the amounts of DOC and SPSOC stored within the acrotelm in the previous year (Figure 8a; the DOC and SPSOC are the model estimates at the start of the current "hydrological" year, and are also equal to those at the end of the preceding year). The correlation between the volume-weighted stream DOC concentration in any given season and the store of DOC and SPSOC in the preceding season is high for the winter (r = 0.75, $P = 5.8 \times 10^{-5}$) and summer ($r = 0.87$, $P = 1.9 \times 10^{-5}$), but lower for the spring (r = 0.40, P = 0.023) (Figure 8b).

7. Discussion

[47] The convection-dispersion equation used in this paper was developed to describe the transport and transformations of DOC in a mire system. To our knowledge this

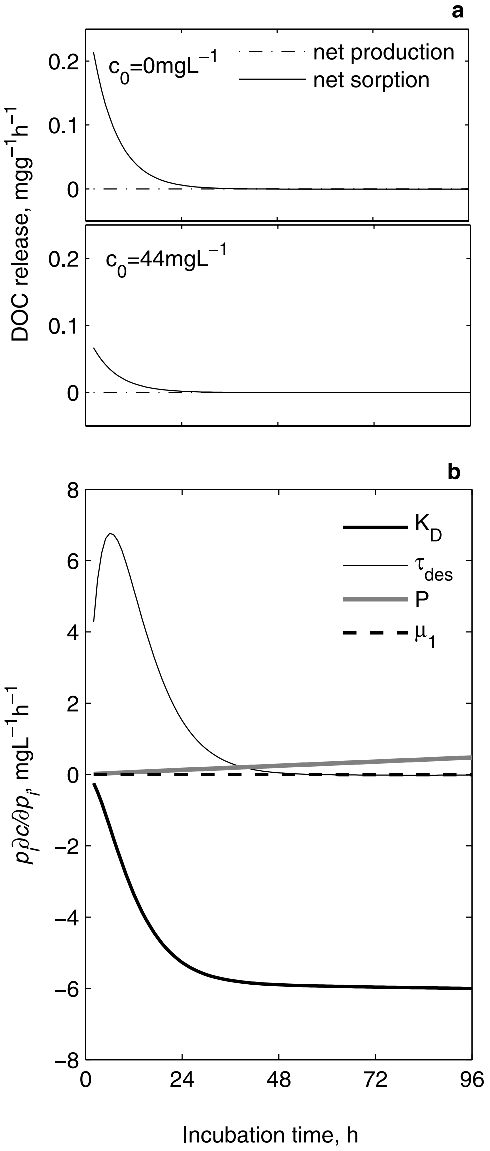

Figure 6. (a) Modeled estimates of partitioning of the DOC release rate observed in laboratory peat incubations into net sorption (desorption minus adsorption) and net production (microbial production minus mineralization) components in incubations with two starting DOC concentrations (c_0) in water. (b) Normalized first-order local sensitivity coefficients computed by the forward direct method for the main parameters in the model applied to laboratory incubations (calculated for an experiment with c_0 = 0.0 mg L^{-1}).

mathematical approach to the problem of DOC dynamics is new, although in analogous fields of hydrology, such as pesticide transport in soil, solving the convection-dispersion equation has become almost standard practice [e.g., *Lapidus and Amundson*, 1952; *van Genuchten and Wagenet*, 1989; *Baskaran et al.*, 1996].

[48] The dynamic, rather than static, representation of sorption kinetics is one of the strengths of the proposed model. In this paper we evaluated mathematically the mechanism of DOC regulation by sorption kinetics studied in laboratory experiments [e.g., *Qualls*, 2000; Rasse et al., manuscript in preparation, 2008]. It is known and often cited in relation to laboratory DOC studies that (1) the initially rapid release of DOC from the peat matrix into newly added water is mainly due to abiotic processes [e.g., *Qualls*, 2000; *Moore and Dalva*, 2001; *Aguilar and Thibodeaux*, 2005; *Chow et al.*, 2006] and (2) depending on the initial concentration, DOC can be either added to or removed from the solution as a result of sorption [*Qualls*, 2000]. In the current study we provide equations (A8) and (A9) to explicitly describe these mechanisms. Application of kinetic equations have helped to improve the model performance under field conditions as compared to the sorption steady state approximation (e.g., Figure S1 in the supplementary materials). Improvements were especially notable for the peak DOC concentrations and during high-flow conditions.

[49] One important by-product of our study was to show how the release of DOC into water during long-term incubations can vary substantially according to the experimental setup. The DOC release rate into solution was affected by the peat-to-water ratio (Figure 4d) and the initial amounts of soluble DOC sorbed on the peat matrix (Figure 4c). Both effects persisted for the whole time period we considered in our simulations (5 years). Different peat-to-water ratios resulted in different rates of DOC release because the same net production was partitioned differently between the sorbed and solid phases. This consideration is of great importance when conclusions about microbial processes are drawn by comparing the results of different laboratory incubations. Usually only changes in DOC concentration are measured and directly converted to production rates, without taking into account the peat-to-water ratio. The effect of sorption, rather than other factors such as, for example, the effect of moisture on microbial activity, could account for the different DOC release rates if data from two experiments with mixtures of peat and water in different ratios are compared.

[50] The relatively good overall results of the simulations indicate that the model may reproduce the main mechanisms responsible for the variability in measured DOC concentration at the outlet of the mire stream. Very generally, concentrations rise to their highest levels (e.g., the

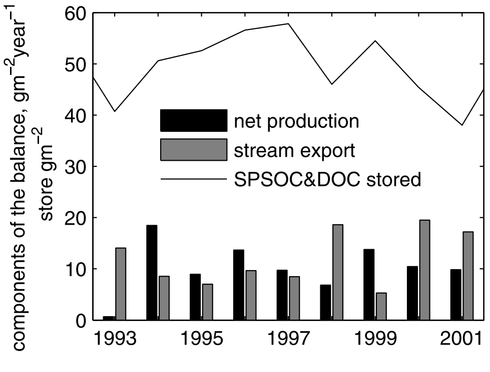

Figure 7. Simulated components of the annual DOC-SPSOC balance: microbially mediated net production and DOC stream export. Changes from year to year in the amounts of SPSOC and DOC (SPSOC $\gg$ DOC) stored in the acrotelm are also shown (estimated for the dates before the first autumn frost).

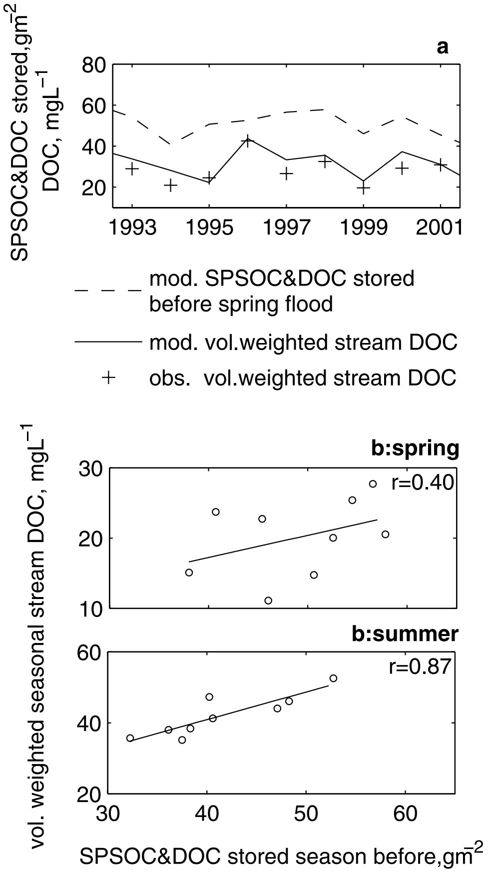

Figure 8. (a) Interannual variations in the amounts of SPSOC and DOC (SPSOC $\gg$ DOC) stored before the start of the hydrological year (spring flood) simulated by the model. Interannual variation in the volume-weighted annual stream DOC concentration, simulated by the model and calculated from the interpolated observations. (b) Correlation between the amounts of SPSOC and DOC stored in the preceding season (winter and spring, respectively) and the volume-weighted seasonal stream DOC concentrations in spring and summer simulated by the model.

episode in September 1996 in Figure 5) when conditions favorable for DOC production (good aeration and suitable temperatures) are combined with a shift of the flow depth to layers that were not previously exposed to water flow within the mire. Some precipitation is always needed to mobilize the DOC present in the unsaturated layer and to shift the sorption equilibrium to release SPSOC by adding low-DOC water. According to the model, this explains the correspondence in timing of the initial increase in stream DOC concentration and the increase in stream discharge following precipitation events (e.g., Figures 3a and 3b). Strong and prolonged events may, however, reduce the DOC concentrations (e.g., the 27 August to 28 September event shown in Figure 3b) through the removal of significant amounts of SPSOC from a particular layer. After the flow ceases, there is a build up of new DOC in the pore water; simultaneously, SPSOC may accumulate on the peat matrix as a result of both in situ production and dispersive and advective exchange with the adjacent layers. The lowest DOC concentrations were observed in the stream during the spring flood (Figure 5). The flow is so intensive during this period that significant amounts of SPSOC are removed from the acrotelm while the concentrations remain low. This could also explain the relatively slow recovery of concentrations after the spring flood (up to one month).

[51] Results of the sensitivity study show that only a few parameters strongly influence the model output. They are the DOC production rate and its modifiers that account for the effects of temperature and anoxic conditions (Table 3). In addition, the model predictions are also largely dependent on the chosen values of DOC mineralization rate and the two sorption constants. These parameters require further investigation to improve model generalization. In particular, although a considerable base of knowledge exists on sorption kinetics and equilibria for DOC in mineral soils, little is known about these dynamics in peat. This would be a fruitful area for further exploration.

[52] The balance between the net production of DOC and SPSOC and the DOC hydrological export, as predicted by the model (Figure 7), may go some way to explaining the interannual variability in the total amounts of SPSOC and DOC stored in the acrotelm. Although the amount of stored SPSOC and DOC in the acrotelm is several times larger than the annual export, the variation in the amount stored as a result of the dominance of either production or export in a given year is significant and may persist in subsequent years. The system therefore has a "memory," as demonstrated by the good correspondence between the simulated storage and the observed annual volume-weighted stream DOC concentration (Figure 8a). An example of system "memory" has been described by *Worrall et al.* [2006] discussing the role of drought in a mire in the UK. Unlike the example by *Worrall et al.* [2006], the mire we studied exhibits a link between the summer concentrations and the intensity and duration of the spring flood event, as shown by the very high correlation between the storage of DOC and SPSOC after the spring flood and the volume-weighted summer stream DOC concentration (Figure 8b, summer). The converse is also true: winter concentrations may be determined by the changes in SPSOC amounts during the previous summer. The situation during the spring flood is more complicated and the amount of DOC and SPSOC stored in the acrotelm before the event is not such a large determinant of the stream DOC concentration during spring (Figure 8b, spring). Both to simulate adequately the DOC concentration with a time step from daily to annual (Figures S1 and S2 in the supplementary materials) and to diagnose seasonal and interannual variability in DOC concentrations (Figure 8), explicit modeling of the time-variable SPSOC is needed.

[53] The model presented here is only one particular realization from the scope of possible formulations of the convection-dispersion equation, and we would like to stress that a well-developed theory built on hydrology by the long practice of solving the convection-dispersion equation [e.g., *van Genuchten and Wagenet*, 1989; *Selim and Ma*, 1998] can be easily used by DOC model developers aiming to have either more or less detailed models. In particular, it is very convenient to use this framework for testing the results of model simplifications, as we did here by comparing model outcomes produced by the sorption steady state approximation and a kinetic equation. In many cases the

numerical solution of the convection dispersion equation is available together with hydrological model packages (e.g., MODFLOW [*McDonald and Harbaugh*, 1988], TOPOG-Dynamic [*Silberstein et al.*, 1999]), and it is therefore possible to find a hydrological scheme of appropriate dimensionality and complexity to describe water flow.

[54] Other challenges for further model development are to introduce the DOC "quality" [e.g., as interpreted by the Q theory, *Ågren and Bosatta*, 1998] as well as to describe the dependency of sorption on the charge on the organic matter [e.g., *Lofts et al.*, 2001] and, especially as influenced by the presence of metal or S ions [e.g., *Skyllberg and Magnusson*, 1995; *Clark et al.*, 2006].

[55] For the mire studied here we hypothesize that the poor model performance during periods of very low flow (Table 4 and diamonds in Figure 5) has resulted from excluding deep flow mechanism from the hydrological formulation. The water discharged during such periods appears to be groundwater from the podzols surrounding the mire, which has bypassed the peat soils of the mire. In terms of the total DOC budget, the groundwater contribution is rather low, since the flow itself is low; this input is, however, persistent. During periods of low flow, when flow out of the mire virtually ceases, the groundwater bypass can strongly influence the DOC concentrations at the outlet. This bypass may be related to the hydrochemical anomaly observed by *Sirin et al.* [1998] at a depth of 2 m in the catotelm. We also would like to point that at the current stage, a choice of the model parameters describing how anaerobic conditions influence the rates of microbial DOC production and mineralization is not fully justified, and it certainly deserves further attention.

8. Conclusions

[56] In this paper we highlighted the importance of modeling sorptive exchange as a dynamic process, rather than a simple steady state, when considering data from laboratory peat incubations. In addition, we demonstrated how some abiotic factors may, through the action of sorption, strongly affect the rate of DOC release into water, as observed during long-term laboratory incubations.

[57] DOC concentrations recorded during 1993–2001 at the outlet of a steam draining a small headwater mire in northern Sweden were simulated here by a newly formulated model based on the convection-dispersion equation. Relatively good agreement between the measured and simulated DOC concentrations was found both for the whole simulation period and for particular events. The results of this study indicate the following.

[58] 1. Sorption is an important process in determining DOC concentration and fluxes. It may cause a release of DOC into the peat pore water in some layers and removal in others, similar in magnitude to the amount of microbially produced DOC. During each event, part of the DOC in the stream export originates from that which was stored in peat pore waters prior to the event, part is released into the solution from the peat matrix because of desorption and the remainder is newly produced.

[59] 2. Interannual variability in the SPSOC and DOC stores within the acrotelm depends on the conditions for microbially mediated DOC production and mineralization during the current year (temperature, aeration) and flow intensity. Some "memory" is, however, characteristic of the system, meaning that the store in a year affects the concentrations and fluxes in the following year.

Appendix A: Model Equations

A1. Main State-Variable Equations

[60] The mass balance equation for the concentration of DOC in pore water, c, can be written in the 3-D form of the convection-dispersion equation

$$\frac{\partial(\theta \cdot c)}{\partial t} = \nabla \bullet (\theta \cdot \boldsymbol{D} \cdot \nabla \bullet c) - \nabla \bullet (\boldsymbol{q} \cdot c) + \tau_{des}\rho(s - K_D \cdot c) + P \cdot \rho - \mu_1 \cdot \theta \cdot c, \tag{A1}$$

where θ is volumetric water content, ρ is peat bulk density, vector $\boldsymbol{q}\{q_x, q_y, q_z\}$ is composed of water flux in horizontal and vertical directions, $\boldsymbol{D}\{D_x, D_y, D_z\}$ is a vector of dispersion coefficients, τ_{des} is the kinetic rate of desorption (or adsorption if the third term in equation (A1) becomes negative), K_D is the distribution constant, characterizing an equilibrium between the sorbed and dissolved phases, P is the microbial production rate of DOC, and μ_1 is the first-order microbial DOC mineralization constant.

[61] The dispersion coefficient is defined as

$$D = D_0 + \lambda \left| \frac{q}{\theta} \right|,$$

where D_0 is the molecular diffusion coefficient, and λ is dispersivity.

[62] A mass balance for the concentration of the sorbed potentially soluble organic carbon (SPSOC), s, leads to

$$\rho \frac{\partial s}{\partial t} = -\tau_{des}\rho(s - K_D \cdot c) - \mu_2 \cdot \rho \cdot s, \tag{A2}$$

where μ_2 is the first-order microbial mineralization constant for the SPSOC.

[63] A modified van't Hoff equation is used to account for the temperature dependency of DOC production and mineralization:

$$\begin{aligned} P &= P_{basal} \times Q_{10}^{((T - T_{basal})/10)} \\ \mu_1 &= \mu_{1basal} \times Q_{10}^{((T - Tbasal)/10)}, \end{aligned} \tag{A3}$$

where Q_{10} is the relative rate of increase in metabolic rates per 10°C increase in temperature, and T_{basal} is a reference temperature (20°C was used here) at which basal rates of microbial DOC production (P_{basal}) and mineralization (μ_{1basal}) are estimated.

[64] The constant fractions k_{anP} and $k_{an\mu}$ are used to relate the anoxic rates of DOC production and mineralization to the corresponding DOC production and mineralization rates under aerobic conditions:

$$\begin{aligned} &\text{for anaerobic conditions} \\ &P = P \times k_{anP} \\ &\mu_1 = \mu_1 \times k_{an\mu}, \end{aligned} \tag{A4}$$

[65] The parameter k_s is defined as

$$k_s = \frac{\mu_2}{\mu_1}; \tag{A5}$$

that is, the mineralization rate of SPSOC (μ_2) is k_s times less then the mineralization rate of DOC (μ_1).

A2. Convection-Dispersion Equation for 1-D Hydrological Scheme

[66] If a 1-D hydrological scheme (vertical discretization) is used and there is no lateral import of DOC into the mire from surrounding areas, the finite difference form of system (A1)–(A2) can be written as

$$\begin{aligned}\frac{\Delta(\theta\cdot c)}{\Delta t} = D_z \frac{\Delta\left(\theta\frac{\Delta c}{\Delta z}\right)}{\Delta z} - \frac{q_s c}{\Delta z} - \frac{\Delta(q_z c)}{\Delta z} + \tau_{des}\rho(s - K_D\cdot c)\\ + P\cdot\rho - \mu_1\theta\cdot c\end{aligned} \tag{A6a}$$

$$\rho\frac{\Delta s}{\Delta t} = -\tau_{des}\rho(s - K_D\cdot c) - \mu_2\cdot\rho\cdot s, \tag{A6b}$$

where Δz is the depth of a specific layer, q_z is the vertical water flux and q_s is the specific (area) lateral discharge from the layer z.

A3. Equations for Interpreting the Results of Laboratory Peat Incubations With Stagnant Water

[67] Under laboratory conditions there is no advective water flow and diffusive mixing within the peat sample can be considered instantaneous. Therefore, equations (A1) and (A2) can be simplified as

$$\frac{\partial a_c}{\partial t} = -\tau_{des}K_D\frac{a_c\cdot M}{V} + \tau_{des}\cdot a_s + P\cdot M - \mu_1\cdot a_c \tag{A7a}$$

$$\frac{\partial a_s}{\partial t} = \tau_{des}K_D\frac{a_c\cdot M}{V} - \tau_{des}\cdot a_s - \mu_2\cdot a_s, \tag{A7b}$$

where M is the mass of the peat sample, V the volume of water added, while a_c and a_s are the amounts of DOC and SPSOC, respectively, defined as $a_c = cV$ and $a_s = sM$.

[68] The analytical solution of equations (A7a) and (A7b) can then be obtained, assuming that the sorption reaction system is in quasi-equilibrium, that is $s(t) = K_D c(t)$:

$$\begin{aligned}c(t)\cdot V = &\left(c_1\cdot V - \frac{P\cdot M}{\mu_1\left(1 + k_s K_D\frac{M}{V}\right)}\right)\\ &\cdot\exp\left(-\mu_1\left(\frac{1 + k_s K_D\frac{M}{V}}{1 + K_D\frac{M}{V}}\right)(t - t_1)\right)\\ &+ \frac{P\cdot M}{\mu_1\left(1 + k_s K_D\frac{M}{V}\right)},\end{aligned} \tag{A8}$$

where c_1 is the DOC concentration at time t_1, the end of the initial phase of incubation when the first steady state is established between the sorbed and dissolved phases. Assuming that the steady state has been reached, c_1 can be calculated from the mass conservation as follows:

$$c_1 = \frac{s_0\frac{M}{V} + c_0}{K_D\frac{M}{V} + 1}, \tag{A9}$$

where c_0 and s_0 are the initial DOC and SPSOC concentrations, respectively.

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