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Biodegradability continuum and biodegradation kinetics of natural organic matter described by the beta distribution

Anssi V. Vähätalo · Hanna Aarnos · Samu Mäntyniemi

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Abstract We followed a long-term (up to 503 days) microbial mineralization of dissolved organic carbon (DOC) from lake water in a bioassay and described the kinetics of biodegradation with a new model based on a reactivity continuum approach. The biodegradability of DOC was expressed as the probability of biodegradation, which was assumed to follow a beta distribution. We compared the performance of our beta model to five earlier models: the simplest first order kinetic model, two G models, the power model and the gamma model. The simplest first order kinetic model described the decreasing microbial mineralization of DOC poorly ($r^2 = 0.73$), but the other models explained the observed kinetics of biodegradation well ($r^2 > 0.95$). When we assessed the extrapolation power of models beyond the length of the bioassay by reducing the amount of data, the predictive power of the G models was poor. Instead, the beta model predicted the biodegradation kinetics consistently and correctly based on even only three observations in time. The beta model provided also long-term predictions (up to 5,000 years) along the observed long-term mineralization trajectory of organic carbon in sediments. Additionally, the beta model formulated the biodegradability continuum of DOC, which was skewed towards low biodegradability. During the bioassay, the skew towards low biodegradability increased as the most biodegradable parts of DOC were consumed. The beta model describes the biodegradability continuum quantitatively and can predict biodegradation in a realistic manner, thus, improving our understanding about the biodegradability and the role of natural organic matter in the environment.

Keywords Beta distribution · Decomposition · Reactivity continuum · Dissolved organic matter · Kinetic model

A. V. Vähätalo · H. Aarnos
Lammi Biological Station, University of Helsinki, Helsinki, Finland

A. V. Vähätalo (✉) · H. Aarnos
Department of Environmental Sciences, University of Helsinki, P.O. Box 65, 00014 Helsinki, Finland
e-mail: anssi.vahatalo@helsinki.fi

S. Mäntyniemi
Fisheries and Environmental Management Group (FEM), Department of Environmental Sciences, University of Helsinki, Helsinki, Finland

Introduction

Natural organic matter (NOM) is the largest reactive reservoir of reduced carbon (C) on the Earth with the largest amounts in surface soil ($1{,}600 \times 10^{15}$ g C), sediment ($1{,}000 \times 10^{15}$ g C) and dissolved in the ocean (775×10^{15} g C; Hedges et al. 2000). Biodegradation mineralizes NOM to CO_2 and supports heterotrophic food webs, which contribute remarkably to the productivity of ecosystems (Mann 1988).

In order to understand the cycling of C and the functioning of many ecosystems, one needs to be able to describe the decomposition kinetics and the biodegradability of NOM.

The decomposition kinetics of NOM is often described by first order kinetics. The simplest first order kinetic model uses a single constant decay coefficient, k, which states that all components of NOM decompose at the same rate. NOM consists of numerous components with different biodegradability and therefore a single decay coefficient often fails to describe the biodegradation kinetics of NOM (Jørgensen 1978; del Giorgio and Davies 2003).

First order kinetic models can also include several pools of NOM each having different biodegradability. In these G (or multi-exponential) models, the total concentration of NOM at time t ($C_{tot,t}$) is expressed as a sum of discrete pools of NOM:

$$C_{tot,t} = \sum_{1}^{i} C_{i,0} \exp(-k_i t) \quad (1)$$

each (i) having their own initial ($t = 0$) concentration ($C_{i,0}$) and first order decay coefficient k_i (Ogura 1975; Jørgensen 1978; Westrich and Berner 1984; Harmon et al. 2009). The G models with two or three pools fit well to biodegradation data and describe the kinetics of biodegradation better than a model with a single constant k (e.g., Hopkinson et al. 2002). Theoretically, the G models can include any number of pools representing potentially all biodegradability-pools found in NOM. However, the practical applications of G models typically use two or three pools, because the number of parameters increases with the number of pools and the estimation of parameters becomes very difficult with more than three pools (Ogura 1975; Westrich and Berner 1984; Hopkinson et al. 2002).

Results from early studies showed that the mean first order decay coefficient of NOM ($\overline{k}$) decreases in time and this decrease can be described by a power model (Jørgensen 1978; Janssen 1984; Middelburg 1989). Here, $\overline{k}$ refers to a time-dependent decay coefficient, which describes the decomposition of total NOM including all pools of different reactivity. The power model describes the decrease of $\overline{k}$ in time as

$$\overline{k} = p(a + t)^{-q} \quad (2)$$

where p [unit t^{-1}] is the intercept of log $\overline{k}$ versus log t plot, q is the slope of plot [dimensionless] and a is the apparent age of NOM [unit t, Middelburg 1989]. In sediments, the decrease of $\overline{k}$ in time follows $\overline{k} = 0.16(a + t)^{-0.95}$ from short-term (days) biodegradation experiments with the large $\overline{k}$ of ca. 100 year^{-1} to a long-term decomposition of NOM with the small $\overline{k}$ of ca. 0.000001 year^{-1} over 100,000 year time scale (Middelburg 1989). By setting the apparent age of NOM (a) to 0, the fit of the power model to the data set of Middelburg (1989) shortens to $\overline{k} = 0.2\ t^{-1}$ (Boudreau et al. 2008). This shortened version of the power model indicates that the time of past decomposition is the primary regulator for the degradability of NOM in sediments. It should be noted that the power model is conceptually different from G models in that it does not divide NOM into pools of different reactivity nor does it describe the heterogeneity of NOM.

The decomposition kinetics of NOM have also been described successfully with first order kinetic models using a reactivity continuum (RC) approach. RC models divide NOM into pools of different reactivity like G models, but instead of a few discrete pools, the RC models use an infinite number of pools. The theoretical basis of RC models were described decades ago (e.g., Aris and Gavalas 1966 and references therein). Boudreau and Ruddick (1991) were the first to apply a RC model to NOM in sediments and formulated the RC of k using the gamma distribution. In the gamma distribution, the initial ($t = 0$) distribution of k,

$$f_0(k|a, \nu) = \Gamma(\nu)^{-1} a^{\nu} k^{\nu-1} \exp(-ak) \quad (3)$$

depends on two parameters (Boudreau and Ruddick 1991). The parameter a [unit t] describes the average life-time of more reactive components and ν [dimensionless] describes the shape of the distribution near $k = 0$. Notation $\Gamma()$ refers to the gamma function. The gamma model by Boudreau and Ruddick (1991) provides a complete quantitative description of the heterogeneity of NOM in the terms of biodegradation, which agrees with the known high degree of chemical heterogeneity of NOM and the theoretical qualitative descriptions of biodegradation kinetics for NOM (e.g., Amon and Benner 1996; Sleighter and Hatcher 2008).

The RC models describe the decrease of $\overline{k}$ in time like the power models. For example, the mean k of the gamma distribution represents $\overline{k}$:

$$\overline{k} = v(a+t)^{-1} \quad (4)$$

The mathematical formulation of mean k in the gamma distribution is similar to the $\overline{k}$ of power model (Eq. 2). When the parameter q in the power model is 1, the equations for $\overline{k}$ are identical in the power and the gamma model (Tarutis 1994). Therefore an adequately formulated RC model describes the kinetics of biodegradation at the same accuracy as the power model (Boudreau et al. 2008).

This study describes the biodegradation kinetics of NOM with a new RC model. Unlike the models presented in the introduction, our RC model expresses biodegradation through probability. The probability of biodegradation can be also converted into a first order decay coefficient. The mathematical formulation of our model follows the probability density function of the beta distribution. Consequently, we call this model the beta model. We apply the beta model to the biodegradation of dissolved organic C (DOC) and compare our model to the gamma, the power and the most commonly used G models. Our results indicate that the beta model has remarkable similarities to another earlier RC model, the gamma model. The beta model describes the biodegradability continuum of NOM, expresses the decrease of $\overline{k}$ in time and provides plausible predictions for the future beyond the time of experimental data.

Methods

Bioassay

In order to measure the biodegradation of DOC, we carried out a long-term (up to 503 days) bioassay with Lake Pääjärvi water. In this lake, 2/3 of secondary production is based on the microbial utilization of allochthonous DOC (Sarvala et al. 1981), and therefore the biodegradation of DOC is a key for understanding the functioning of the Lake Pääjärvi ecosystem. For the bioassay, surface water (0–1.2 m) was collected with a Limnos-sampler from the middle of Lake Pääjärvi, southern Finland (61°04′N, 25°08′E) on 4 June 2007. The water sample was filtered with a 0.22-μm tangential flow cassette (Pellicon, Millipore), and then amended with a microbial inoculum (10-μm filtrate of Lake Pääjärvi water, 1% vol/vol%) and KH_2PO_4 to a final concentration of 575 μg P l^{-1}. The water sample with microbes was aliquoted into 11 pre-combusted (+450°C, >2 h) borosilicate bottles (100 ml) with ground glass stoppers. In order to guarantee the supply of oxygen, each bottle had an air headspace (50% of bottle volume). The bottles were incubated in the dark at 21°C and a separate bottle was sacrificed each time for the determination of DOC on days 0, 12, 26, 40, 54, 78, 139, 293, 342, 405 and 503. The concentration of DOC was determined from 0.22-μm filtered (Minisart, Sartorius) water by a high catalytic oxidation technique with a TOC-5000A instrument (Shimadzu) calibrated with phthalate-standards. The decrease in the concentration of DOC was considered biodegradation (i.e., the microbial mineralization of DOC). The adsorption of DOC onto the walls of the bottles and the flocculation of DOC followed by sedimentation could also have potentially caused a decrease in DOC, but in our water samples those losses of DOC must have been negligible. Cohesive forces among molecules alone or assisted by light flocculate primarily "fresh" DOC in streams and headwater lakes (Kerner et al. 2003; von Wachenfeldt et al. 2008), and therefore such processes were unlikely for our water samples kept in the dark and collected from the middle of Lake Pääjärvi, a 13.4-km^2 lake with a 3–4 year water residence time. The adsorptive loss of DOC on glass was highly unlikely at the pH of Lake Pääjärvi (pH 7), where the functional groups of DOC are primarily negatively charged with negligible adsorption on similarly charged glass walls of bottles.

Beta model

Our beta model is a RC model and assumes that DOC is comprised of an infinite number of C pools which all are biodegradable. The model assumes that the biodegradability of DOC changes over time as microbes consume the pools of DOC according to the pool-specific biodegradability.

The beta model is derived from the probability of biodegradation. In the beta model, DOC consists of an infinite number of pools each having the probability of biodegradation, p, between 0 and 1. For a single infinitely small pool of DOC (i) having the initial concentration ($C_{i,0}$) and the biodegradation probability (p_i) during one unit of time, the concentration ($C_{i,1}$) after one unit of time ($t = 1$) is:

$$C_{i,1} = C_{i,0}(1 - p_i) \quad (5)$$

because the fraction p_i has decomposed and left the fraction $1 - p_i$ intact. Consequently, the concentration of the pool i ($C_{i,t}$) after t units of time is:

$$C_{i,t} = C_{i,0}(1 - p_i)^t \quad (6)$$

For the total DOC with infinite pools having the biodegradation probability p between 0 and 1, one needs to describe the initial distribution of p with a suitable function, $f_0(p)$. In this case, the total concentration of DOC at time t is an integral over the range of degradation probabilities, $f_0(p)$:

$$C_t = C_0 \int_0^1 f_0(p)(1 - p)^t dp \quad (7)$$

The analytical tractability of this integral depends on the choice of the density function $f_0(p)$. This can be achieved, for example, by choosing $f_0(p)$ that integrates to 1 and includes $1 - p$ as a multiplier. One of the well known probability distributions meeting these criteria is the beta distribution, which has the density function

$$f_0(p|\alpha, \beta) = \frac{\Gamma(\alpha + \beta)}{\Gamma(\alpha)\Gamma(\beta)} p^{\alpha-1}(1 - p)^{\beta-1} \quad (8)$$

where α and β are the shape parameters of the distribution and $\Gamma()$ denotes the gamma-function. The mean and variance of p are also the function of parameters α and β (see Appendix, Eqs. 21 and 22). A biodegradation probability, p, can be converted to a first order decay coefficient, k, by noting that the concentration of DOC having coefficient k decreases by $\exp(-k)$ during one unit of time. Thus, $k = -\ln(1 - p)$.

When the beta distribution is selected for the distribution of biodegradability, the concentration of DOC at time t can be expressed as (see Appendix for details):

$$C_t = C_0 \frac{\Gamma(\alpha + \beta)\Gamma(\beta + t)}{\Gamma(\beta)\Gamma(\alpha + \beta + t)} \quad (9)$$

Parameters α and β can be estimated by standard curve fitting tools found in most mathematical software packages. It should be noted, however, that usually the computational software provides the values of the Γ-function on ln-scale for numerical stability. For that purpose, Eq. 9 was reformulated to:

$$C_t = C_0 \exp\{\ln(\Gamma(\alpha + \beta)) + \ln(\Gamma(\beta + t)) - \ln(\Gamma(\beta)) - \ln(\Gamma(\alpha + \beta + t))\} \quad (10)$$

The G, gamma and power models

The concentration of DOC during the bioassay was also described by five other models: the simplest first order kinetic model, two G models, the gamma, and the power model.

Our simplest first order kinetic model predicts the concentration of DOC at time t (C_t) as:

$$C_t = C_1 \exp(-k_1 t) \quad (11)$$

where C_1 is the initial concentration of a single fully degradable pool of DOC at time zero and k_1 is the first order decay coefficient of C_1 [unit t^{-1}].

In the two-pool G model, the concentration of DOC at time t is the sum of two fully degradable pools (C_1 and C_2) and their corresponding decay coefficients (k_1 and k_2):

$$C_t = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (12)$$

The three-pool G model is like the previous model, but includes also one non-degradable pool (C_3):

$$C_t = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) + C_3 \quad (13)$$

We assessed the biodegradation of DOC also with an earlier RC model, the gamma model (Boudreau and Ruddick 1991). In the gamma model, the concentration of DOC at time t (C_t) depends on:

$$C_t = C_0 \left(a(a + t)^{-1}\right)^v \quad (14)$$

the initial concentration of DOC (C_0), the average life-time of more reactive components of DOC (a) and the shape of the gamma distribution near $k = 0$ characterized by v.

The power model was applied to the biodegradation of DOC in its integrated form (Janssen 1984). In the power model, the concentration of DOC at time t is:

$$C_t = C_0 \exp\left\{p'\left((a + t)^{q'} - a^{q'}\right)\right\} \quad (15)$$

where a is the initial apparent age of DOC at time zero, and where p' and q' describe the time-dependence of biodegradability.

Mean first order decay coefficient

At time t, the mean first order decay coefficient of DOC ($\overline{k}$) was calculated for each model from two predicted concentrations of DOC on subsequent days as:

$$\overline{k} = 1/\Delta t \ln(C_t/C_{t+\Delta t}) \quad (16)$$

where Δt is 1 day, C_t is the predicted concentration of DOC at time t, and $C_{t+\Delta t}$ is the predicted concentration of DOC on the following day (e.g., Janssen 1984; Middelburg 1989).

For the gamma model, $\overline{k}$ can also be calculated directly by replacing the estimated parameters to Eq. 4. For the power model, $\overline{k}$ can be also calculated directly according to the parameters p′ and q′ of Eq. 15, when they are replaced to Eq. 2 as $p = -p'q'$ and $q = 1 - q'$.

Estimation of parameters

The model parameters were estimated from the measured concentrations of DOC using the curve fitting tool of Matlab 7.9.0 (The MathWorks Inc.). We applied the default options of fitting, which include a non-linear least squares method and a trust-region algorithm allowing the lower and the upper limits of parameters to be specified. The C pools (C_0, C_1, C_2, C_3) were set between 0 and 20 mg C l^{-1}, ks between 0 and 0.7 day^{-1}; the parameters α, β, a, p, q and v between −5 and 1,000.

Results

Bioassay

In the beginning of the bioassay with Lake Pääjärvi DOC, the measured concentration of DOC was 11 mg C l^{-1} (Fig. 1). Microbes mineralized DOC most rapidly in the early phase of the bioassay. Later the biodegradation of DOC slowed down with time. Because the residence time of water in Lake Pääjärvi is 3–4 years, our 503-days (1.4-year) long bioassay describes only partially the potential biodegradation of DOC during its residence in the lake. Therefore, we fitted the G, the beta, the gamma, and the power models to the data set and extrapolated the biodegradation of DOC up to the residence time of water in the lake.

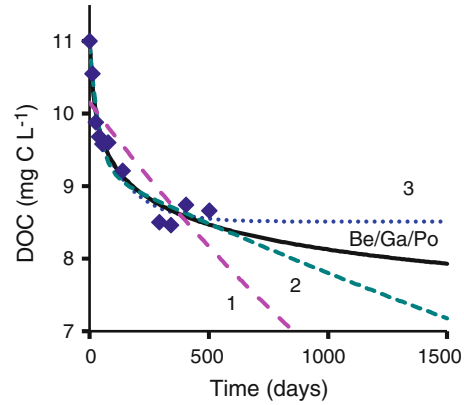

Fig. 1 The measured concentration of DOC during a 503-days bioassay (*diamonds*) and the predicted concentrations according to six models (*curves*). The numbers refer to the pools of G models and "Be/Ga/Po" indicates the overlapping curves of the beta, the gamma and the power models (see Table 1)

The concentration of DOC described by models

When the simplest first order kinetic model with one DOC pool was fitted to the data set, the model underestimated the biodegradation of DOC in the beginning of bioassay and overestimated the biodegradation of DOC at the end of bioassay (model 1 in Table 1 and Fig. 1).

The G model with two pools had better fit than the one-pool model (model 2, Fig. 1, Table 1). The two-pool G model divided DOC into a fast (k_1 = 0.0258 day^{-1}) decomposing pool (C_1 = 1.73 mg C l^{-1}) and a slow (k_2 = 0.00017 day^{-1}) decomposing pool (C_2 = 9.23 mg C l^{-1}). Beyond 503 days, the two-pool G model extrapolated the second highest biodegradation among the tested models (model 2, Fig. 1, Table 1).

According to the three-pool model with one non-degradable pool, microbes decomposed the most reactive pool of DOC (C_1 = 0.91 mg C l^{-1}) with the decay coefficient (k_1) of 0.068 day^{-1} (model 3, Table 1). The decay coefficient k_2 for the second most reactive pool (C_2 = 1.62 mg C l^{-1}) was 0.0073 day^{-1}. The magnitude of non-degradable pool (C_3) was 8.51 mg C l^{-1} indicating that 77% of DOC resisted biodegradation. The extrapolation by the three-pool model predicted a nearly complete stop of biodegradation soon after 503 days (model 3, Fig. 1).

The beta model fitted to the data similarly to the three-pool model (model beta, Table 1, Fig. 1). Beyond 503 days, the beta model predicted

Table 1 The models, their parameters and coefficient of determination (r^2) for the measured concentrations of DOC during the bioassay (Fig. 1)

1. $C_t = C_1 \exp(-k_1\, t)$		2. $C_t = C_1 \exp(-k_1\, t) + C_2 \exp(-k_2\, t)$		3. $C_t = C_1 \exp(-k_1\, t) + C_2 \exp(-k_2\, t) + C_3$	
C_1	10.15	C_1	1.73	C_1	0.906
k_1	0.00043	C_2	9.23	C_2	1.62
r^2	0.728	k_1	0.0258	C_3	8.51
		k_2	0.00017	k_1	0.0682
		r^2	0.952	k_2	0.00732
				r^2	0.971
Beta $C_t = C_0 \exp\{\ln(\Gamma(\alpha+\beta)) + \ln(\Gamma(\beta+t)) - \ln(\Gamma(\beta)) - \ln(\Gamma(\alpha+\beta+t))\}$		Gamma $C_t = C_0\,(a\,(a+t)^{-1})^{v}$		Power $C_t = C_0 \exp\{p'((a+t)^{q'} - a^{q'})\}$	
C_0	11.0	C_0	11.0	C_0	11.03
α	0.0605	a	6.43	a	6.58
β	6.90	v	0.0605	p'	14.01
r^2	0.962	r^2	0.962	q'	−0.004413
				r^2	0.962

continuous biodegradation with a rate decreasing in time. The gamma and the power model described the concentration of DOC nearly identically with the beta model as seen by the overlapping curves in Fig. 1 (models gamma and power, Table 1).

Assessing the extrapolation of biodegradation kinetics

In order to evaluate the accuracy of extrapolations shown in Fig. 1, we assessed the predictive power of the beta and the G models by sequentially dropping out the observations from the end of the bioassay and then estimated the model parameters again with increasingly shorter bioassays (Fig. 2). When the length of bioassay was sequentially reduced down to the first six observations, the parameter estimates of the beta model and consequently the predicted kinetics were similar to those obtained when using the full data set (Fig. 2a–c). For example, the beta model fitted to a reduced 78-day-long bioassay with six observations predicted that on day 503 the concentration of DOC was 8.5 mg C l^{-1} and within the standard deviation of the measured value (8.7 ± 0.4 mg C l^{-1}, mean ± standard deviation of five replicated determinations, Fig. 2a). When examining ≤ the first five observations, the estimates of α and β deviated from those of the full bioassay (Fig. 2c). The primary reason for this deviation is that the rate of biodegradation did not reduce as strongly in the early phase compared to the later phase of the bioassay. We also tested the estimation of parameters with the minimum amount of three observations describing a temporal reduction in the biodegradation of DOC. For example, when the parameters were estimated on the basis of measured DOC on days 0, 54 and 405, their estimates ($C_0 = 11$, $\alpha = 0.0466$, $\beta = 3.39$) and the predictive power were similar to those obtained from the full set of data (curve '0,54,405' in Fig. 2a). This exercise indicates that in the beta model, the estimates of parameters were insensitive to the length of the bioassay, and even the minimum number of observations ($n = 3$) predicted the kinetics adequately.

For comparison, we also evaluated the predictive power of G models in a similar manner as for the beta model. For the simplest first order kinetic model, k_1 and C_1 increased consistently when they were estimated from increasingly shorter bioassays (data not shown). The behavior of two- and three-pool models was more complex and inconsistent with the length of bioassay. For example, when the last (11th) observation was dropped out, the estimated parameters and the prediction of the three-pool model were similar to that of full bioassay (Fig. 2d–g). An additional drop of data caused a drastic decrease in C_3 (Fig. 2g), which was compensated for by changes in the C_2-pool (Fig. 2f), but overestimated biodegradation (curve '9' in

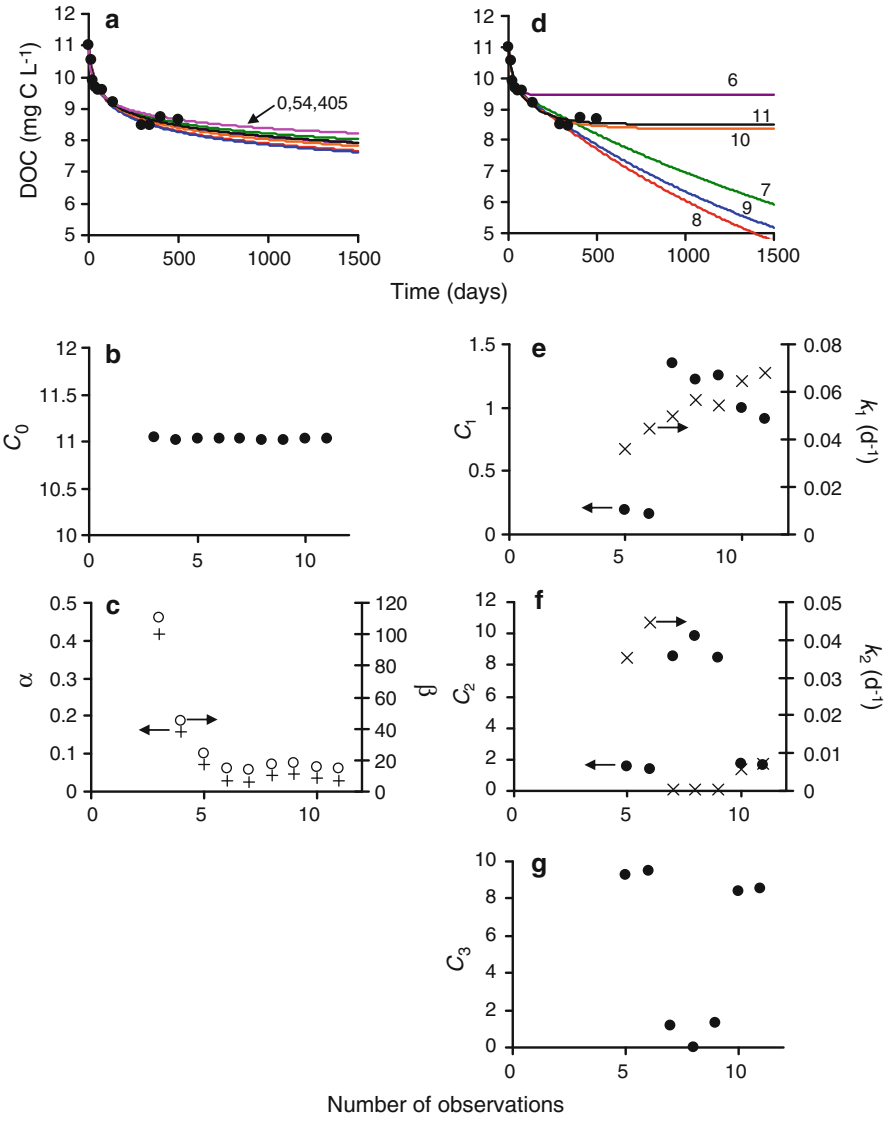

Fig. 2 The predicted DOC and the estimated parameters of two models applied to bioassay data with a reduced number of observations. Panels **a–c** show the predicted concentration of DOC and the estimated parameters according to the beta model applied to the bioassays with the first 6–11 observations. The corresponding estimates of the three-pool G model are shown in the panels **d–g**. Panel **a** includes additionally a "0,54,405"-curve showing the DOC predicted by the beta model applied to the bioassay with DOC measured on days 0, 54 and 405

Fig. 2d). A similar overestimation was observed when the model parameters were estimated with the first seven and eight observations (Fig. 2d). A model estimated according to the first six observations, instead, underestimated biodegradation. These exercises indicate that parameter estimates for the G models were time dependent either consistently (one pool) or inconsistently (two and three pools). Although the two- and three-pool models described the kinetics of DOC well within the bioassay (Fig. 1), their predictive power was weak and the fractionation of DOC into pools inconsistent.

Mean decay coefficient described by models

In order to further assess the performance of models, we calculated the mean decay coefficient ($\overline{k}$) from the predicted concentrations of DOC during the bioassay (0–503 days) but also up to the times of 2×10^6 days (=5,479 years = ca. residence time of water in the ocean). Additionally we compared our calculated $\overline{k}$ for the biological mineralization of DOC to an earlier observed long-term decrease in $\overline{k}$ for organic C mineralization in sediments (Fig. 3, Middelburg 1989). For the simplest first order kinetic

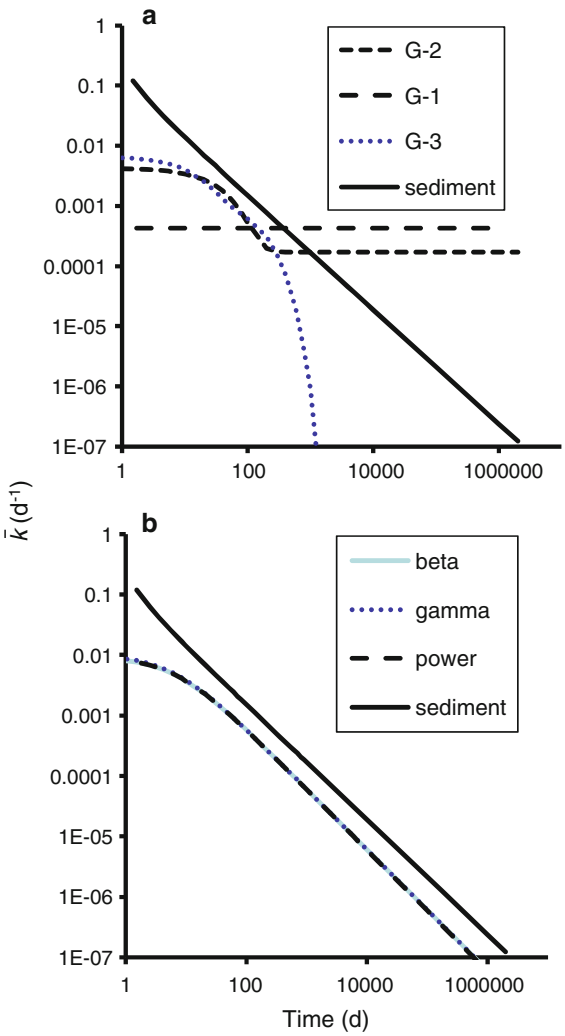

Fig. 3 The mean first order decay coefficient ($\bar{k}$) for the mineralization of DOC according to **a** the simplest first order kinetic model (G-1), the two (G-2) and three (G-3) pool G models and **b** the beta, the gamma and the power models. The modeled $\bar{k}$ values are compared to the typical trend characterizing the mineralization of organic carbon in sediments (Middelburg 1989)

model, $\bar{k}$ was constant in time (Fig. 3a). In the two-pool G model, $\bar{k}$ was close to k_1 when the C_1-pool dominated decomposition in the beginning of bioassay, but later $\bar{k}$ equalled k_2 following the decomposition of C_2-pool. In the three-pool G model, $\bar{k}$ decreased in time, until it reached zero beyond 1,000 days after the complete loss of the two degradable (C_1 and C_2) pools.

The $\bar{k}$s of beta, gamma and power models were nearly identical and plotted as a single curve in Fig. 3b. During the first 10 days of the bioassay, the modeled $\bar{k}$s were smaller and decreased more gradually in time than the $\bar{k}$ in sediments (Fig. 3b). Later in the bioassay (10–503 days), the trend of $\bar{k}$ was similar for DOC and for NOM in sediments (Fig. 3b). Beyond 503 days, the beta, the gamma and the power models predicted that the trend of $\bar{k}$ continued like that observed for sediments. In agreement with a good fit of models to the data (Fig. 1) and large r^2-values (Table 1), the results concerning $\bar{k}$ show that the G, the beta, the gamma and the power models described the biodegradation of DOC equally well during the bioassay (<503 days). The prediction capabilities (>503 days) differed among the models, but the similarity in the trend of $\bar{k}$ for DOC and organic C in sediments indicates that the beta, the gamma and the power models predicted the long-term decomposition of DOC in a manner matching the observed long-term decomposition kinetics of organic C in sediments.

Biodegradability continuum of DOC

The beta model not only describes the decomposition kinetics of total DOC, but it also defines the biodegradability of DOC as a reactivity continuum, which changes in time. Figure 4 examines the biodegradability continuum of Lake Pääjärvi DOC at the different bioassay times as (a) probabilities, (b–c) first order decay coefficients and (d) turnover times.

Figure 4a illustrates how microbes preferred the most biodegradable parts of DOC and shifted the probability distribution towards low biodegradability on days 10, 50 and 500. In the beginning of the bioassay (time = 0), the initial biodegradability distribution of DOC, $f_0(p|\alpha,\ \beta_0)$, was characterized by $\alpha = 0.0605$ and $\beta_0 = 6.9$ (Table 1, Eq. 8, Fig. 4a). At $t = 0$, a negligible fraction of DOC had a probability of biodegradation close to one and for >90% of DOC the probability of biodegradation was <0.02 with the mean, μ_0, 0.0087 (Fig. 4a, Eq. 21). Later, the biodegradability distribution of DOC followed the beta(α, $\beta + t$)-distribution ($f_t(p|\alpha,\ \beta_t)$; Eq. 19). For example, on day 10 of the bioassay, α remained 0.0605 but β_{10} was ($\beta_0 + 10 = 6.9 + 10 =$) 16.9 and the mean ($\mu_{10}$) was 0.00357.

For Fig. 4b and c, the probabilities of biodegradation (p) were converted into first order decay coefficients according to $k = -\ln(1 - p)$. These

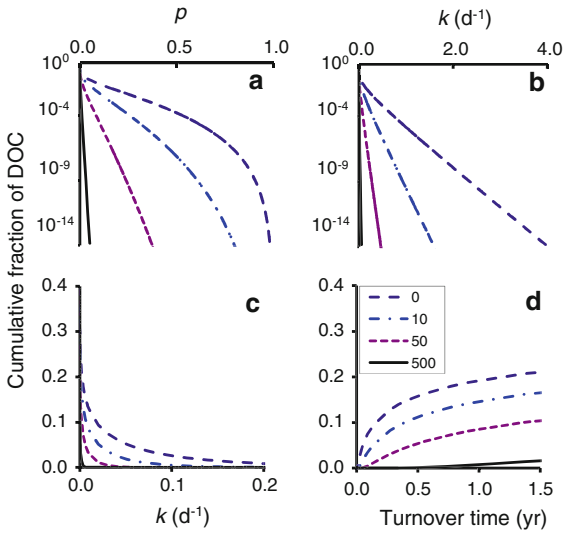

Fig. 4 The reactivity continuum for the biodegradability of DOC described by the beta model on the days 0, 10, 50 and 500 of bioassay. The biodegradability continuum is described as **a** probabilities, p; **b–c** first order decay coefficients, k; and **d** turnover times, k^{-1}. **a** Describes the probability for biodegradation, p, as a continuum characterized by the beta distribution (Eq. 8) with $\alpha = 0.0605$ and $\beta = 6.9$ at time 0 and later with the beta(α,$\beta + t$)-distribution (Eq. 19). For the **b–c** p was transformed to k according to $k = -\ln(1 - p)$

figures describe the changes in the continuum of first order decay coefficients, k, also illustrating how microbes preferably consumed DOC with the largest k. The logarithmically scaled Fig. 4b highlights the changes in DOC with highest k. A linearly scaled Fig. 4c illustrates the same shift towards lower k for the majority of DOC at $k < 0.2$ day^{-1}.

The inverse of the first order decay coefficient, k^{-1}, illustrates the turnover times of DOC (Fig. 4d). From the curves (Fig. 4d), one can estimate the turnover time for any fraction of DOC. For example, the turnover time for the most reactive 10% of DOC is found by matching the value 0.1 on the curve to the position on the X-axis. In the beginning of the bioassay ($t = 0$), the most reactive 10% of DOC had the turnover time of 0.14 years (50 days). On day 10 of the bioassay, the turnover time for the most reactive 10% of DOC was 0.5 years. After 50 and 500 days of bioassay, the turnover times for the most reactive 10% of DOC were 1.5 and 10 years, respectively. Altogether Fig. 4 illustrates quantitatively how the time of previous biodegradation ("aging") reduced the biodegradability of DOC and shifted the biodegradability continuum towards low biodegradability.

Discussion

Modeling the concentration of NOM within experimental data

In our study as in numerous previous studies, the mean decay coefficient for biodegradation ($\overline{k}$) slows down in time and is inadequately described by the simplest first order kinetic model (e.g., Hopkinson et al. 2002). When the decrease in $\overline{k}$ is accounted for by using more complex models, biodegradation of NOM is well described within a bioassay (e.g., this study, Hopkinson et al. 2002). These findings indicate that for the times less than the length of experimental data, the interpolations of the models tested describe the concentration of NOM equally well.

As pointed out previously by Boudreau and Ruddick (1991), the beta and gamma models contain fewer parameters than most of the other models tested in this study. The beta and gamma models contain only two parameters, while for example, the three-pool G model requires five parameters. Therefore, the beta and gamma model can be applied to bioassays with three observations in time, while the three-pool G model needs a minimum of six observations over time. Our study agrees with that of Boudreau and Ruddick (1991) and indicates that the RC models, the beta and gamma, interpolate the biodegradation of NOM within the experimental data like the other models, but with the smallest number of parameters.

To our knowledge, this study applies the beta distribution to the biodegradation of NOM for the first time. In our study, an earlier two-parameter RC model, the gamma model, describes the biodegradation of DOC like the beta model. The gamma model is derived from the continuum of first order decay coefficients, while the beta model is derived from the continuum of biodegradation probabilities. The mean of the beta distribution (Eq. 21) describes the mean probability of biodegradation, while the mean of the gamma distribution is $\overline{k}$ (Eq. 4). Despite these differences, the beta and gamma models express the concentration of DOC and $\overline{k}$ in a nearly identical way in this study. In addition to these two models,

complex chemical kinetics can be formulated according to Gaussian and Weibull distributions, which may also be applicable to processes describing NOM (Burnham and Braun 1999). This study applies the beta model to the biodegradation of DOC, but the beta model should be applicable also to the biodegradation of NOM in soils and sediments. Therefore, in addition to the previously used gamma model, the beta model presented here provides a powerful alternative for describing the biodegradation kinetics of NOM.

Extrapolations: the predictive power of models

Although nearly all the models used in this study can interpolate the concentration of DOC equally well, their predictive performance (i.e., extrapolation into the future) differs considerably. Our study indicates that for the G models, the predicted concentration of DOC changes remarkably depending on the number of observations used to estimate model parameters. Our study further emphasizes that in the G models, the estimated pool sizes and their decomposition coefficients are sensitive to the dates of data collection and the number of data points. These findings have implications for the application of G models. The application of G models should be limited to interpolation only and the comparison of pools (C_1, C_2, C_3) should be limited to studies where data points are collected at the same time intervals.

Our modeling exercise with the shortened bioassay shows that the beta model can predict the concentration of DOC consistently, correctly matching the observed concentration of DOC used to validate the predictions. For example, our validation exercise with a reduced 78-day-long bioassay shows that the beta model can predict the concentration of DOC correctly at least up to 503 days, 6.5-times longer than the bioassay length (78 days).

The mineralization of organic C in sediments provides an interesting reference to the biodegradation of DOC described in our study. In undisturbed layered sediments, the sedimentation provides new organic C on top of the sediment, which becomes altered and mineralized as it is buried deeper in the sediment. From the dated sediments, one can calculate realistic estimates for the mineralization of organic C over long periods of time (10^6 years) exceeding the time scales of experiments. The biological mineralization of DOC can also take place at long time scales. The residence time and the biodegradation of DOC last for years in medium-sized lakes such as Lake Pääjärvi. Biodegradation may last from decades to hundreds of years in large lakes or even thousands of years in the ocean. Unlike for organic C in the sediments, the long-term rates of biological mineralization cannot be directly calculated for DOC for various reasons (e.g., mixing with newly produced DOC, flocculation, photolysis). Therefore, it is interesting to compare the biodegradation kinetics of DOC predicted by our study to the known biodegradation kinetics of organic C in sediments (e.g., Middelburg 1989).

Our biodegradation kinetics of DOC shows both differences and similarities to the mineralization of organic C in sediments when assessed as the changes of $\overline{k}$ over time. During the first 10 days of our bioassay, $\overline{k}$ is lower for DOC than for a few-day-old organic C selected to represent freshly deposited organic matter on the top of sediment (Middelburg 1989). This can be explained by the larger homogeneity and biodegradability of organic matter in freshly deposited sediments than for the DOC of Lake Pääjärvi, which is a heterogenous mixture including old (perhaps ca. 3–4 year-old as the residence time of the lake) recalcitrant and freshly produced (few days old) highly biodegradable organic matter. For the later phases of our bioassay (the days ca. 10–503), $\overline{k}$ decreases with a similar trend for the DOC of Lake Pääjärvi and for organic C in sediments. This similarity continues also beyond the length of the bioassay (>503 days) for the biodegradation of DOC predicted by the beta, the gamma and the power models. It seems that after the biodegradation of labile DOC during the first 10 days of bioassay, the pool of DOC became more homogenous and the biodegradation of DOC followed the typical mineralization of organic C in sediments. Because the biodegradation of DOC predicted up to thousands of years by the beta, the gamma and the power model follows a typical long-term mineralization of organic C in logical way, this similarity further suggests that these models can predict also the long-term biodegradation of NOM in realistic way. This observation suggests that the long-term predictions of beta model for the future may be correct for much longer time period than 6.5-times of the length of the bioassay as found in our validation exercise.

Biodegradability continuum

Although the concept of a biodegradability continuum has been considered previously in the context of DOC (Amon and Benner 1996), our study formulates the biodegradability continuum of DOC quantitatively for the first time. The continuum concept also agrees with the recent analytical characterization of NOM, which reveals that even a single water sample consists of numerous ($>10^3$) chemically distinct DOC molecules (Sleighter and Hatcher 2008). It would be surprising for such a large diversity of molecules to form only two or three discrete biodegradability pools as embodied in G models. Rather, the biodegradability of such a diverse mixture of molecules is most realistically described as a continuum. The parameters α and β of the beta model can potentially define the shape of this continuum in numerous ways, but in this study the biodegradability continuum of DOC is strongly shifted towards low reactivity. The probability density of a beta distribution is strictly decreasing with $\alpha < 1$ and $\beta \geq 1$ as was the case with the parameters estimated for the biodegradability of DOC in our study. A similar shape also characterizes the biodegradability of organic matter in sediments (Boudreau and Ruddick 1991). The concept of a biodegradability continuum states that the biodegradability of DOC decreases along diagenetic states from fresh to old (Amon and Benner 1996). This concept is mathematically formulated in our beta model, which demonstrates shift towards lower reactivity during our bioassay. Thus, the beta model accounts for the primary concepts of the biodegradability continuum and captures it in a quantitative manner.

In some cases, it is convenient to divide the biodegradability of NOM into conceptual classes such as labile, semilabile and refractory (Carlson 1998). According to this and an earlier study (Hopkinson et al. 2002), the G models fractionate NOM inconsistently in time without good representation of the conceptual classes. Instead, the beta model, along with other models based on reactivity continuums, can fractionate NOM quantitatively into any conceptual class. For example, Ogura (1975) classified DOC based on first order decay coefficients. In his classification, k is ≥ 0.01 day^{-1} for labile DOC, ≤ 0.001 day^{-1} for refractory DOC and between 0.01 and 0.001 day^{-1} for semilabile DOC. The amount of DOC within these classes can be calculated from the cumulative distribution function of the beta distribution found in mathematical and statistical software (e.g., the 'betadist'-function of MS Excel). According to the beta distribution, Lake Pääjärvi DOC is mostly refractory (76%; $k \leq 0.001$ day^{-1}), the rest 13% being labile ($k \geq 0.01$ day^{-1}) and 11% semilabile (0.01 day$^{-1} > k > 0.001$ day^{-1}). When we applied parameters a and v of the gamma model (Table 1) to Eq. 3 and examined the fractionation of DOC into the biodegradability classes with the 'gammadist'-function in MS Excel, the fractionation of DOC into classes was the same as with the beta model. Thus, the beta or the gamma models can fractionate DOC quantitatively into conceptual classes of biodegradability and allow direct comparison among different samples and studies.

Bioassays and the fate of DOC in aquatic ecosystems

In receiving waters, the major fates of DOC are biodegradation, but also photo-oxidation and flocculation with subsequent sedimentation. Depending on the routing of DOC through the possible fates described above, its impact on the aquatic ecosystems is different. The biodegradation of DOC will benefit plankton communities directly. Flocculation directs DOC to the benthic community and may lead to long-term preservation in sediments. Photo-oxidation can stimulate plankton indirectly as it re-mineralizes the nutrients of DOM and produces labile DOC, but the photochemical production of CO_2 bypasses the utilization of DOC by plankton. All the potential processes transforming DOC are non-linear in time and have typically the fastest rates with fresh DOC entering aquatic ecosystems. Examples of non-linear decrease in the transformation of DOC are the biodegradation, photodegradation and flocculation of DOC, which all transform fresh DOC entering aquatic ecosystems with the fastest rates (this study, del Giorgio and Davies 2003; Vähätalo and Wetzel 2004; von Wachenfeldt et al. 2008). Therefore, the total loss of DOC in lakes is fastest in small lakes with short water retention time but it becomes increasingly slower in larger lakes with longer water residence times (Fig. 5, Algesten et al. 2003). In order to understand the direct coupling of DOC to plankton communities it is necessary to separate biodegradation from other processes and to formulate the biodegradation of DOC adequately.

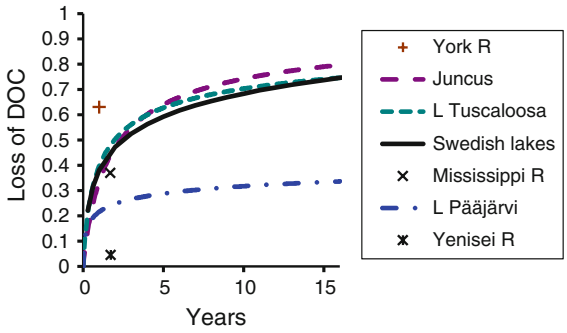

Fig. 5 The loss of DOC in long-term bioassays and in Swedish lakes. The bioassays describe the biodegradation of DOC alone, but the loss of DOC in 79,536 Swedish lakes includes also photo-oxidation and flocculation versus water residence time (Algesten et al. 2003). The points show the extent of biodegradation in the end of bioassays for York River (Raymond and Bauer 2001), Mississippi River plume (Hernes and Benner 2003), and Yenisei River (Köhler et al. 2003). The curves describe the predictions according to the beta model applied to the bioassay of *Juncus*-leachate ($\alpha = 0.544$, $\beta = 323$; Vähätalo and Wetzel 2008), Lake Tuscaloosa ($\alpha = 0.343$, $\beta = 110$; Vähätalo and Wetzel 2004) and Lake Pääjärvi (this study)

Bioassays such as the one presented here can describe the biodegradation of DOC quantitatively and allow the estimation of the biodegradation kinetics of DOC in the environment. The accuracy of these estimates depends on the similarity of the biodegradation kinetics between the bioassays and the ecosystems. The chemical composition (i.e., the biodegradability) of DOC regulates the performance and composition of microbial communities (Judd et al. 2006). For example, in our bioassay, the biodegradation of DOC formed a consistent decay pattern through time, although each observation represented biodegradation by an individual microbial community enclosed in a separate bottle. Our earlier work also suggests that the changes in the microbial communities along a transect from fresh to marine waters result in minor changes in the kinetics of biodegradation (Vähätalo and Wetzel 2004). Although drastic changes in environmental conditions (high salinity) and microbial communities can potentially change biodegradation kinetics (Kisand et al. 2008), the biodegradability of DOC seems to be the major controlling mechanism of biodegradation kinetics in both bioassays and in the water column of aquatic ecosystems. This conclusion for DOC is supported by the decomposition of organic C in sediments, where the mineralization of organic C is primarily regulated by the reactivity of organic C determined by the time of past decomposition (Middelburg 1989; Boudreau et al. 2008). Therefore bioassays are perhaps the best available method for predicting the biological utilization of DOC in ecosystems when combined with a proper formulation of biodegradation kinetics.

Even though bioassays are potentially powerful tools for assessing biodegradation of DOC in ecosystems, they have been seldom used for such purposes. The major obstacles have been the short duration of most bioassays and the lack of proper formulation of biodegradation kinetics. Only a few bioassays have lasted longer than a year and can estimate biodegradation at the times relevant to the residence of DOC in lakes and marine waters (Fig. 5, Raymond and Bauer 2001; Hernes and Benner 2003; Köhler et al. 2003; Vähätalo and Wetzel 2004, 2008). These long-term bioassays illustrate large differences in the biodegradability of DOC. For example, during a 1 year bioassay with York River water, microbes mineralized 63% of DOC (Fig. 5, Raymond and Bauer 2001). In comparison to York River the biodegradability of DOC was low in Yenisei River, where microbes mineralized 4.5% of DOC over 1.7 years (Fig. 5, Köhler et al. 2003). It is difficult to extend the results of these bioassays to times beyond the end of the bioassay without a proper description of biodegradation kinetics. The application of the beta model allows for an extension of results from bioassays to any time as long as the primary data includes three observations in time and describes adequately the temporal reduction in the rate of biodegradation. In addition to the DOC of Lake Pääjärvi, we applied the beta model to our earlier bioassays of DOC concerning Lake Tuscaloosa and the leachate of *Juncus effusus* (Fig. 5, Vähätalo and Wetzel 2004, 2008). In these cases, the biodegradation of DOC is similar initially, but later *Juncus* and Lake Tuscaloosa DOC show higher biodegradation than the Lake Pääjärvi DOC (Fig. 5). The biodegradation kinetics of DOC predicted by the beta model has a shape similar to the loss of DOC in Swedish (Fig. 5, Algesten et al. 2003) or Canadian (Curtis and Schindler 1997) lakes. This similarity and the high biodegradability of DOM in some cases suggest that biodegradation can be the primary decomposing mechanism of DOC in many lakes with the residence

time < several years and thus supports plankton communities directly. When the residence time is more than several years, the loss of DOC in lakes can be more rapid than biodegradation, as observed for example by the crossing of curves for the loss of DOC in Swedish lakes and the biodegradation of Lake Tuscaloosa DOC (Fig. 5). The photochemical decomposition of biologically recalcitrant DOC may explain the faster loss of DOC in lakes than that predicted by bioassays. The data in Fig. 5 suggests that the biodegradability of DOC can vary considerably, and that biodegradation can be the major decomposing mechanism for DOC in aquatic environments. The validation of these interpretations definitely requires further study regarding the biodegradability of DOC, the fate of DOC in aquatic environments, and the appropriate formulation of the reactivity continuum with models such as the beta model.

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Appendix

When the beta distribution beta(α, β) is selected to describe the kinetics of biodegradation, the initial distribution of the biodegradation probabilities among molecules of DOC is

$$f_0(p|\alpha,\beta) = \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} p^{\alpha-1}(1-p)^{\beta-1} \tag{8}$$

Consequently, based on Eq. 7, the concentration at time t (C_t) can be expressed as

$$C_t = C_0 \int_0^1 \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} p^{\alpha-1}(1-p)^{\beta-1}(1-p)^t dp \tag{17}$$

which simplifies to

$$C_t = C_0 \int_0^1 \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} p^{\alpha-1}(1-p)^{\beta+t-1} dp \tag{18}$$

There are multiple alternatives for solving the integral of Eq. 18. The one demonstrated here is based on the strategy of manipulating the integral in such a way that the integration can be performed over a probability density function, for which the integral is always equal to 1. This can be achieved by factorizing the constant $\Gamma(\alpha+\beta)\Gamma(\alpha)^{-1}\Gamma(\beta)^{-1}$ in a suitable manner. In Eq. 18, the factor depending on p has already the shape of the beta(α, $\beta+t$) distribution:

$$f_t(p|\alpha,\beta+t) = \frac{\Gamma(\alpha+\beta+t)}{\Gamma(\alpha)\Gamma(\beta+t)} p^{\alpha-1}(1-p)^{\beta+t-1} \tag{19}$$

Thus, if the constant of the integral (Eq. 18) can be manipulated to be $\Gamma(\alpha+\beta+t)\Gamma(\alpha)^{-1}\Gamma(\beta+t)^{-1}$ then the integral becomes the density function of the beta(α,β + t) distribution. The following factorization satisfies this condition:

$$C_t = C_0 \frac{\Gamma(\beta+t)\Gamma(\alpha+\beta)}{\Gamma(\alpha+\beta+t)\Gamma(\beta)} \int_0^1 \frac{\Gamma(\alpha+\beta+t)}{\Gamma(\alpha)\Gamma(\beta+t)} p^{\alpha-1} \times (1-p)^{\beta+t-1} dp \tag{20}$$

Now the integral of Eq. 20 is analytically tractable. Since the integration over a probability density function yields 1 by definition, the equation reduces to Eq. 9.

Furthermore, the distribution of p after time t is the beta(α,$\beta+t$) (Eq. 19), which means that the distribution of biodegradability of the remaining DOC can be examined at any point of time. The mean and variance of the probability of biodegradation, p, at time t are given by

$$\mu_t = \frac{\alpha}{\alpha+\beta+t} \tag{21}$$

$$\sigma_t^2 = \frac{\alpha(\beta+t)}{(\alpha+\beta+t)^2(\alpha+\beta+1+t)} \tag{22}$$

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