Riparian Zone Influence on Stream Water Dissolved Organic Carbon Concentrations at the Swedish Integrated Monitoring Sites

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Abstract Short-term variability in stream water dissolved organic carbon (DOC) concentrations is controlled by hydrology, climate and atmospheric deposition. Using the Riparian flow-concentration Integration Model (RIM), we evaluated factors controlling stream water DOC in the Swedish Integrated Monitoring (IM) catchments by separating out hydrological effects on stream DOC dynamics. Model residuals were correlated with climate and deposition-related drivers. DOC was most strongly correlated to water flow in the northern catchment (Gammtratten). The southern Aneboda and Kindla catchments had pronounced seasonal DOC signals, which correlated weakly to flow. DOC concentrations at Gårdsjön increased, potentially in response to declining acid deposition. Soil temperature correlated strongly with model residuals at all sites. Incorporating soil temperature in RIM improved model performance substantially (20–62% lower median absolute error). According to the simulations, the RIM conceptualization of riparian processes explains between 36% (Kindla) and 61% (Aneboda) of the DOC dynamics at the IM sites.

Keywords DOC · RIM · Modeling · Riparian zone ·
Organic carbon · Soil temperature

INTRODUCTION

Natural organic matter (NOM) is one of the main chemical constituents of many natural waters and plays an important role in the biogeochemistry and ecology of the streams, rivers, and lakes of the world. Most NOM is composed of carbon (Schulten and Schnitzer 1993) and is an integral part of the global carbon cycle as a vector for carbon transport from the terrestrial environment to aquatic and marine environments followed by sedimentation and remineralization (Cole et al. 2007). Consequently, NOM is often estimated by measuring the amount of dissolved organic carbon (DOC) or total organic carbon (TOC) in the water. During the last couple of decades, increasing concentrations of DOC in streams, rivers and lakes in North America and Europe have been observed (Driscoll et al. 2003; Evans et al. 2005; Monteith et al. 2007), indicating changing NOM dynamics. Hence, there is currently a great deal of interest in studying the origin, transport and fate of DOC.

Discharge has been shown to be a first-order control on short-term DOC dynamics in many watercourses around the world, signifying the influence of water flow paths on the delivery of DOC to surface waters (Hinton et al. 1998; Köhler et al. 2009). However, the flow–DOC relationship varies depending on landscape cover. Catchments with extensive wetland and peatland coverage often show a negative correlation between flow and DOC concentration, whereas the correlation in forested catchments and catchments associated with organo-mineral soils is often positive (Laudon et al. 2004; Eimers et al. 2008). Bishop et al. (2004) have proposed a conceptual explanation for the flow-concentration relationship in boreal forested catchments, which highlights the importance of water flow paths and the variability of soil solution concentration with depth in the riparian zone.

Other important variables for the temporal variability of DOC include soil temperature, soil moisture, ionic strength and acid deposition (Christ and David 1996; Kalbitz et al. 2000; Monteith et al. 2007; Evans et al. 2008; Hruska et al. 2009). Many of these factors correlate nonlinearly with DOC concentrations (Christ and David 1996) and the mechanisms behind the relationships are not yet well understood (Davidson et al. 2006).

Hence, there is still a great deal of uncertainty about the factors driving the temporal patterns of DOC in natural waters.

During the last 20 years, declining or stable DOC concentrations have been observed in soil water, primarily in recharge areas, at 70 forested sites in southern Sweden. It has been proposed that changes in aluminum chemistry and declining ionic strength in the soils due to recovery from acidification are responsible for the long-term DOC trends (Löfgren et al. 2010; Löfgren and Zetterberg 2011). Hence, the trend in soil water DOC concentrations is converse to that reported for surface waters (Evans et al. 2005; Monteith et al. 2007). Thus, it appears that processes in the riparian zones and peatlands, rather than freely drained uphill soils, govern the stream water DOC variations (Löfgren et al. 2010; Löfgren and Zetterberg 2011), thereby supporting the conceptual explanation proposed by Bishop et al. (2004).

Environmental models are often developed to aid environmental management or assessment. However, because of inherent uncertainties in measured data, model structures and parameters, caution should be exercised when using and analyzing model simulations (Beven 2006, 2009). Because of the limitations of environmental models it has been suggested that models should be used more as a learning process and as tools for testing hypotheses about the systems under study (Beven 2007, 2010).

The Riparian flow-concentration Integration Model (RIM) is a parameter parsimonious semi-empirical modeling framework that has been shown to account for the discharge effect on DOC dynamics in boreal headwater streams (Seibert et al. 2009). It has also been used to investigate other important variables affecting the concentration of DOC, e.g. soil temperature and soil moisture (Ågren et al. 2010; Winterdahl et al. 2011).

In response to interest in studying acid deposition effects on forest ecosystems, four intensively monitored catchments were included in the Swedish Integrated Monitoring of Ecosystems (IM) programme in the mid 1990s (Lundin et al. 2001). This programme has now been running for more than a decade and substantial amounts of data gathered. The principal objective of the work described in this article was to investigate the causes of the temporal variability in stream DOC concentrations at these IM sites and explain the differences between the catchments. We chose a model-based approach using RIM to extract discharge effects on DOC dynamics in order to investigate possible second-order drivers of the temporal patterns in DOC. The second objective of the study was to exemplify the use of RIM as a tool for testing hypotheses regarding factors affecting stream water dynamics.

MATERIALS AND METHODS

Study Area

The catchments investigated in this work are the four Swedish IM sites (Lundin et al. 2001): Gårdsjön, Aneboda, Kindla, and Gammtratten. The catchments are all small forested headwater catchments without lakes or large wetlands (Table 1). They are relatively undisturbed areas with no significant forestry activity over the last 100 years. Gammtratten, Kindla, and Aneboda are situated on a north–south gradient through central Sweden, while Gårdsjön is located near the southwestern coast (see Figs. 1 and 2 in Löfgren et al. 2011). All catchments are covered by till underlain by a granitic bedrock, but both Kindla and Gårdsjön have extensive areas with very thin soil cover or bare rock. Soils are mainly podzols with organic-rich soils (gleysols and histosols) in wet areas. Vegetation is dominated by Norway spruce (*Picea abies*) in lower areas and Scots pine (*Pinus sylvestris*) in upper parts of the catchments.

In this work, data were used on discharge (Q), groundwater levels, precipitation, air and soil temperature, as well as streamwater pH, and concentrations of major cations and anions, ammonium, silica, and DOC. Samples from Gårdsjön were filtered, whereas samples from Aneboda, Kindla, and Gammtratten were unfiltered. Thus, the organic carbon data corresponded to DOC for Gårdsjön but TOC for the other catchments. However, studies have shown that more than 95% of TOC is dissolved in areas similar to the IM sites (Gadmar et al. 2002). Therefore, we henceforth refer to the organic carbon content as DOC for all sites. The study periods were limited by the available discharge data and corresponded to 1997–2008 in Aneboda and Kindla, 1999–2008 in Gammtratten, and 1989–2008 in Gårdsjön. Some data (e.g., soil temperature in some catchments) were not available for the entire period.

Model Description

The structure of RIM is a conceptualization of how the riparian soil solution concentration profile of DOC is exported to streams by lateral water flow across the riparian soil, according to the following equation (Bishop et al. 2004; Seibert et al. 2009):

$$E = C_{stream} \cdot Q = \int_z q_{rip}(z) C_{rip}(z) dz \qquad (1)$$

where E (mg s^{-1}) is the export of DOC in the stream, C_{stream} (mg l^{-1}) is stream DOC concentration, Q (l s^{-1}) is discharge, $q_{rip}(z)$ is a function describing the flow as a function of depth in the riparian soil, $C_{rip}(z)$ is the DOC soil

Table 1 Catchment characteristics

Catchment	Area (ha)	Altitude (m.a.s.l.)	Peat cover (%)	Till cover (%)	Bedrock outcrops or thin till cover (%)	Open mire (%)	Air temp (°C)	Precipitation (mm)	Discharge (mm)	Snow cover (days)	S dep. (kg S ha^{-1} year^{-1})	N dep. (kg N ha^{-1} year^{-1})
Gårdsjön	3.7	114–140	3	63	34	0	7.5	1076	570	55	5.2	8.7
Aneboda	18.9	210–240	12	87	<1	0	6.6	697	280	110	3.7	6.7
Kindla	20.4	312–415	3	56	41	1.3	5.3	744	423	130	3.0	4.8
Gammtratten	39.6	410–545	10	75	15	4.3	2.5	501	346	175	1.7	2.3

Annual means for air temperature, precipitation and discharge are calculated for the years 1997–2008 in Aneboda and Kindla, 1999–2008 in Gammtratten, and 1989–2008 in Gårdsjön. Deposition data is average values for 1996–2009

solution concentration profile, and z (m) is the depth in the soil. The flow function, $q_{\mathrm{rip}}(z)$, can be derived by differentiating the relationship between stream discharge and groundwater table (GWT) depth (Moldan and Wright 1998; Fölster 2001; Nyberg et al. 2001; Seibert et al. 2003):

$$q_{\mathrm{rip}}(z) = \frac{\mathrm{d}}{\mathrm{d}z} Q(z) = \frac{\mathrm{d}}{\mathrm{d}z} \alpha z^\beta = \alpha \beta^{\beta-1} \tag{2}$$

where α and β are parameters. In this article, we have adopted a power-law relationship for the Q–GWT relationship. The soil solution concentration profile can also be expressed as a power-law function:

$$C_{\mathrm{rip}}(z) = \gamma z^\delta \tag{3}$$

where γ and δ are parameters. The total export can then be formulated as follows:

$$E = \int_{z_0}^{z_1} \alpha \beta z^{\beta-1} \gamma z^\delta \mathrm{d}z \tag{4}$$

where z_1 is the upper limit (the position of the GWT) and z_0 is the lower limit. This implementation allows an analytical solution:

$$E = \alpha \beta \gamma \int_{z_0}^{z_1} z^{\beta-1+\delta} \mathrm{d}z = \left[\begin{array}{c} Q = \alpha z^\beta \Leftrightarrow \frac{Q}{\alpha} = z^\beta \Rightarrow z = \left(\frac{Q}{\alpha}\right)^{\frac{1}{\beta}} \\ \mathrm{d}z = \frac{1}{\alpha\beta}\left(\frac{Q}{\alpha}\right)^{\frac{1}{\beta}-1}\mathrm{d}Q \end{array} \right]$$

$$= \alpha\beta\gamma \int_0^{Q_1} \left[\left(\frac{Q}{\alpha}\right)^{\frac{1}{\beta}}\right]^{\beta+\delta-1} \frac{1}{\alpha\beta}\left(\frac{Q}{\alpha}\right)^{\frac{1}{\beta}-1} \mathrm{d}Q$$

$$= \gamma \int_0^{Q_1} \left(\frac{Q}{\alpha}\right)^{\frac{\beta+\delta-1}{\beta}} \left(\frac{Q}{\alpha}\right)^{\frac{1-\beta}{\beta}} \mathrm{d}Q = \gamma \int_0^{Q_1} \left(\frac{Q}{\alpha}\right)^{\frac{\delta}{\beta}} \mathrm{d}Q$$

$$= \frac{\gamma}{\alpha^{\frac{\delta}{\beta}}} \int_0^{Q_1} Q^{\frac{\delta}{\beta}} \mathrm{d}Q = \frac{\gamma}{\alpha^{\frac{\delta}{\beta}}} \left[\frac{Q^{\frac{\delta}{\beta}+1}}{\frac{\delta}{\beta}+1}\right]_0^{Q_1} = \frac{\gamma}{\alpha^{\frac{\delta}{\beta}}\left(\frac{\delta}{\beta}+1\right)} Q_1^{\delta/\beta+1}$$

By introducing the parameter Γ:

$$\Gamma = \frac{\delta}{\beta} \tag{5}$$

and dividing by the flow, the stream DOC concentration is derived:

$$C_{\mathrm{stream}} = \frac{\gamma}{\alpha^\Gamma (\Gamma+1)} Q^\Gamma \tag{6}$$

This solution is similar to that reported by Seibert et al. (2009), which employs exponential functions for the Q–GWT relationship and the soil solution concentration profile. Consequently, the static version of RIM (hereafter referred to as RIM$_{\mathrm{static}}$) can be simplified to a rating curve expression. Without any information about soil solution data and groundwater levels it is identical to a rating curve.

Winterdahl et al. (2011) extended the RIM to include a time-dependent soil solution concentration profile. One advantage of the dynamic version of RIM is that seasonality in DOC concentrations can be simulated, but a drawback is that extra input data and parameters are required. The soil solution concentration profile may vary with time in two different ways. It may vary because of a simple translation, i.e., a change in the depth-averaged concentration, which is represented in RIM as a change in the base parameter γ. Alternatively, the shape of the profile may vary with time, as reflected by a time-dependent δ parameter in RIM. Therefore, the dynamic RIM can be expressed as follows:

$$C_{\mathrm{stream}} = \frac{\gamma(t)}{\alpha^{\Gamma(t)}(\Gamma(t)+1)} Q^{\Gamma(t)} \tag{7}$$

Winterdahl et al. (2011) implemented the γ and δ parameters as linear functions of soil temperature or antecedent flow. This approach is questionable, particularly with regard to temperature effects. In chemical kinetics theory, temperature dependence is often modeled as non-linear functions, such as the van't Hoff, Arrhenius or Q_{10} equations (Davidson and Janssens 2006; Davidson et al. 2006). In our model, we

assumed the temperature dependence of the δ and γ parameters in RIM could be described by the van't Hoff equation.

$$\gamma(T_{soil}) = \gamma_0 e^{\kappa T_{soil}} \tag{8}$$

$$\delta(T_{soil}) = \delta_0 e^{\eta T_{soil}} \tag{9}$$

Without any information about groundwater levels or soil solution concentrations it is not possible to empirically estimate any of the parameters. The β and δ_0 parameters can be combined into a single parameter (Γ_0) resulting in a 5-parameter model with stream discharge and soil temperature as input data.

$$C_{stream} = \frac{\gamma_0 e^{\kappa T_{soil}}}{\alpha^{\Gamma_0 e^{\eta T_{soil}}} (\Gamma_0 e^{\eta T_{soil}} + 1)} Q^{\Gamma_0 e^{\eta T_{soil}}} \tag{10}$$

Parameter Estimation and Uncertainty Analysis

As mentioned above, RIM$_{static}$ reduces to a rating curve expression in the absence of information about soil solution data or groundwater data. RIM$_{static}$ parameters were therefore estimated using least squares regression. Model conditioning and uncertainty analysis of the dynamic RIM were performed using Generalized Likelihood Uncertainty Estimation (GLUE, Beven and Binley 1992; Beven 2009). Five hundred thousand parameter sets were drawn from continuous uniform distributions with predefined parameter limits (Table 2) based on physical interpretation (if possible) and preliminary tests. The conditioning of the flow parameters α and β was constrained with a soft calibration (Seibert and McDonnell 2002) so that model performance was weighted based on the simulated median and maximum depth to the GWT (Eq. 2). Reasonable depths to the GWT were estimated from observed GWT depths in the riparian soil. The estimations were based on data from two groundwater tubes in Gårdsjön (F1GV5: median groundwater depth = 7 cm, $n = 38$; F1GV8: median groundwater depth = 12 cm, $n = 35$), two groundwater tubes in Aneboda (tube 31: median groundwater depth = 12 cm, $n = 27$; tube 32: median groundwater depth = 13 cm, $n = 28$), three tubes in Kindla (tube 101: median groundwater depth = 13 cm, $n = 9$; tube 301: median

groundwater depth = 8 cm, $n = 9$; tube 601: median groundwater depth = 5 cm, $n = 9$), and two tubes in Gammtratten (tube 31: median groundwater depth = 40 cm, $n = 13$; tube 32: median groundwater depth = 59 cm, $n = 12$).

Behavioral models were selected based on limits of acceptability (LOA, Beven 2006, 2009), which were chosen as observed concentrations $\pm 20\%$. This was probably an underestimation of total uncertainty because the reported uncertainty in measured TOC alone is 13–15% (Swedish University of Agricultural Sciences 2011) and LOA are supposed to account for uncertainty in observed data, model structure errors and parameter uncertainty. If more than 50% of simulated concentrations were within the LOA, the model was classified as behavioral. Model performance was evaluated based on the Nash–Sutcliffe efficiency index (NS; Nash and Sutcliffe 1970), mean absolute errors (MAE) and median absolute errors (MedAE).

Statistical Analysis

Since the concentrations of many of the chemical substances studied depend on discharge, RIM$_{static}$ was used to remove the effects of discharge. The influence of different physical and chemical parameters on DOC dynamics were investigated with a Partial Least Squares (PLS) analysis of the RIM$_{static}$ residuals to find important variables correlating with the temporal evolution of DOC. This was complemented by a correlation analysis (both Pearson's and Spearman's correlation) of model residuals and DOC. Residuals were calculated as the difference between observed stream concentrations and RIM$_{static}$ simulated concentrations. Variables tested included discharge, change in flow (dQ/dt), antecedent flow, precipitation, air and soil temperature, pH, and the concentrations of major cations and anions, ammonium, and silica. Antecedent flow was estimated as the cumulative stream discharge over n days, where n was between 1 and 365. The change in flow at day i was calculated as the difference in flow between day i and day $i - 1$.

The insensitivity of PLS to interdependencies in explanatory variables and deviations from normality makes it a suitable method for finding possible drivers of DOC variability (Geladi and Kowalski 1986). R^2 is the percent variation of the training set explained by the PLS model, while Q^2 is the percent variation predicted by the model according to cross validation. VIP-values (Variable Influence on Projection) indicate the relevance of the explanatory variables for explaining the response variable (Eriksson et al. 1995). A VIP-value larger than 1 indicates an important explanatory variable in the model, while VIP-values below 0.5 usually indicate unimportant explanatory variables. The importance of variables with VIP between

Table 2 Parameter values and limits for the dynamic RIM in the four IM catchments

Parameter	Gårdsjön	Aneboda	Kindla	Gammtratten
α	0–0.012	0–0.25	0–0.15	0–2
β	−3 to −0.7	−4 to −0.5	−4 to 0	−12 to −1
γ_0	2–15	5–20	2–7	2–9
κ	−0.05 to 0.15	0–0.2	0–0.12	−0.08 to 0.15
δ_0	−0.3 to 0.2	−0.3 to 0.1	−0.5 to 0.1	−2.5 to 0
η	−0.3 to 0.2	−1 to 0.2	−0.9 to 0.2	−0.6 to 0.5

0.5 and 1 is uncertain and dependent on the size of the data set. The PLS analyses were performed on original data in the multivariate statistical software program SIMCA-P+ (version 12.0.1, Umetrics AB).

Trends in concentrations were analyzed using the Seasonal Mann–Kendall method (Hirsch and Slack 1984). Information from this method was only used to detect significant trends and not used for quantitative estimates of the magnitude of possible trends.

RESULTS

Both DOC concentrations and dynamics differed between the IM streams (Table 3). Aneboda displayed the highest concentrations, whereas Kindla and Gammtratten had the lowest concentrations on average. Both Gårdsjön and Kindla had increasing concentrations of DOC accompanied by decreasing concentrations of sulfate, calcium, and magnesium ($p < 0.05$) during the study period. Sulfate concentration decreased significantly in all four catchments and there were significant decreases in chloride concentrations in Gårdsjön and Aneboda. In Gårdsjön and Gammtratten, the logarithm of the DOC concentration correlated strongly with the logarithm of discharge ($r = 0.47$, $p < 0.001$ and $r = 0.65$, $p < 0.001$, respectively). DOC dynamics in Aneboda and Kindla were clearly seasonal with weak correlations to discharge ($r = -0.31$, $p < 0.001$ and $r = -0.20$, $p < 0.001$, respectively) and sharp peaks in the fall of 2002. The peak in DOC concentration occurred alongside peaks in pH, ammonium and Ca concentrations.

The trend in DOC concentrations in Gårdsjön caused problems when applying the RIM, since the model cannot handle trends that are not driven by discharge or, in the case of the dynamic version, soil temperature. Therefore, we compared the models' performance with DOC data that had the trend removed. Although model performance was higher with the detrended data, RIM$_{static}$ still did not simulate DOC dynamics well (Table 4). The NS value when using detrended data was 0.16 compared to 0.13 before trend removal.

As expected from the weak correlation between discharge and DOC, RIM$_{static}$ did not simulate stream DOC concentrations well in Aneboda or Kindla (Table 4). Model performance did not improve when detrended DOC data was used for Kindla. The static RIM performed substantially better in Gammtratten compared to the other catchments.

The PLS models for RIM$_{static}$ residuals in Gårdsjön and Gammtratten had very low explanatory power (Table 4), but simple Pearson's and Spearman's correlations revealed the same important variables. PLS models for Aneboda and

Table 3 Average values and variability of explanatory variables

Catchment	Precipitation	Discharge	Air temp	Soil temp	DOC	pH	Ca	Mg	Na	K	SO$_4$	Cl	NO$_3$	NH$_4$	Si
Gårdsjön	3.0 (6.0)	**0.2 (0.7)**	7.5 (7.2)	7.3 (2.9)	**10.2 (3.4)**	**4.2 (0.1)**	0.9 (0.3)	1.4 (0.5)	9.6 (1.6)	0.5 (0.2)	3.1 (1.3)	16.4 (4.4)	11 (40)	<u>10 (21)</u>	3.3 (0.7)
Aneboda	2.2 (5.2)	1.5 (1.4)	6.6 (7.4)	4.3 (3.9)	18.7 (9.9)	**4.5 (0.1)**	<u>1.8 (0.2)</u>	1.0 (0.2)	5.0 (0.3)	**0.5 (0.2)**	7.2 (2.6)	6.6 (0.7)	**17 (35)**	**17 (20)**	4.2 (0.8)
Kindla	**2.4 (4.8)**	1.4 (2.8)	**5.3 (8.0)**	**4.6 (2.8)**	**7.2 (2.3)**	**4.6 (0.1)**	0.5 (0.1)	0.3 (< 0.1)	**2.1 (0.2)**	0.1 (<0.1)	5.3 (1.4)	2.1 (0.3)	5 (8)	8 (7)	3.0 (0.6)
Gammtratten	1.6 (3.8)	2.9 (6.5)	2.5 (9.3)	1.9 (3.6)	7.2 (3.0)	5.7 (0.2)	1.2 (0.2)	0.3 (0.1)	**1.4 (0.2)**	0.2 (0.1)	<u>2.0 (0.4)</u>	0.7 (0.1)	6 (13)	6 (3)	3.4 (0.9)

Values are mean values, with standard deviation in parentheses, for precipitation, air and soil temperature, and median, with median absolute deviation (MAD) in parentheses, for all other variables

Units are °C for air and soil temp., mm for precipitation, l s^{-1} for discharge, mg l^{-1} for all chemical parameters except pH, NO$_3^-$ (µg l^{-1}) and NH$_4^+$ (µg l^{-1})

Numbers in bold indicate a significantly increasing trend as indicated by Seasonal–Kendall analyses ($p < 0.05$), while underlined numbers indicate a significantly decreasing trend

Table 4 Model performance of the PLS models and the static and dynamic RIM in the four IM catchments

Catchment	PLS		RIM$_{static}$			Dynamic RIM			
	R^2	Q^2	NS	MAE	MedAE	NS	MAE	MedAE	n
Gårdsjön	0.17	0.16	0.16	2.7	2.0	0.39	2.5	1.6	2786
Aneboda	0.71	0.67	0.08	9.1	6.6	0.61	4.9	2.5	4778
Kindla	0.60	0.50	−0.02	2.2	1.4	0.36	1.5	0.7	12 375
Gammtratten	0.28	0.21	0.36	2.2	1.5	0.51	1.9	1.1	458

NS Nash–Sutcliffe efficiency index; *MAE* Mean Absolute Error; *MedAE* Median Absolute Error. *n* is the number of behavioral parameter sets. Units for MAE and MedAE are mg l^{-1}

Kindla had much better explanatory power. The analyses revealed some common patterns among the IM sites. In all four catchments, sulfate concentration, soil, and air temperature were important explanatory variables of DOC variability not explained by RIM$_{static}$ (Fig. 1). Sulfate concentration correlated negatively with DOC concentration and model residuals, whereas soil and air temperature correlated positively. Variables related to deposition of sea salt (chloride, sodium, calcium, sulfate, and magnesium concentrations) were important in Gårdsjön and negatively related to both DOC concentrations and model residuals. Streamwater Ca concentration was also an important variable in Gammtratten. The concentration of ammonium was indicated as an important variable in both Aneboda and Kindla. However, this result was probably influenced by outliers since Spearman's correlation coefficients were low in both catchments ($\rho = 0.20$, $p < 0.001$ and

$\rho = 0.11$, $p = 0.053$, respectively) and not significant in Kindla. The purpose of using RIM$_{static}$ was to remove discharge effects on DOC variability. Consequently, discharge was not important in the PLS models for any of the catchments, although there still seemed to be a small effect in Aneboda and Kindla (VIP between 1 and 0.5).

The dynamic RIM, involving the soil solution profile (γ and δ parameters) as a function of soil temperature, was able to reproduce stream DOC concentrations more closely than RIM$_{static}$ in all catchments (Fig. 2; Table 4). In Aneboda and Kindla, there was a considerable improvement in the results of the dynamic model compared to RIM$_{static}$. The simulated soil solution DOC concentration profiles differed between RIM$_{static}$ and the dynamic RIM. Seasonal variability was evident for all sites in the changing soil solution profiles simulated by the dynamic RIM (Fig. 3).

Fig. 1 Partial Least Squares coefficients (first component) for the explanatory variables in predicting RIM$_{static}$ residuals in **a** Gårdsjön, **b** Aneboda, **c** Kindla, and **d** Gammtratten. The different *colors* of the bars indicate Variable Influence on Prediction (VIP) where *black* is VIP > 1, *gray* is $0.5 \leq$ VIP ≤ 1, and *white* is VIP < 0.5
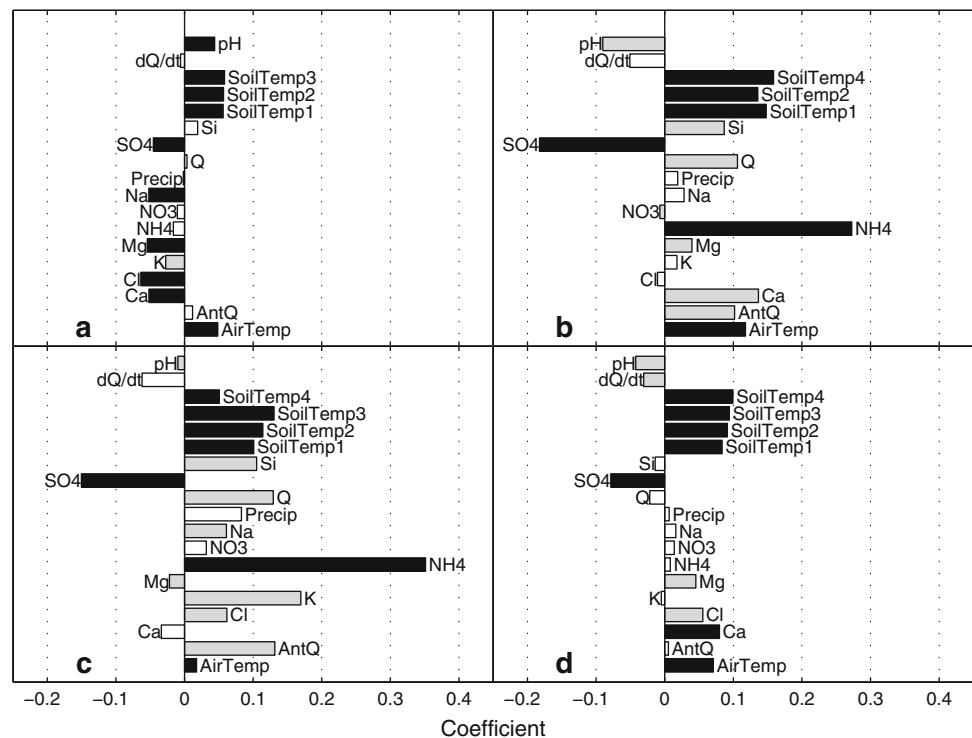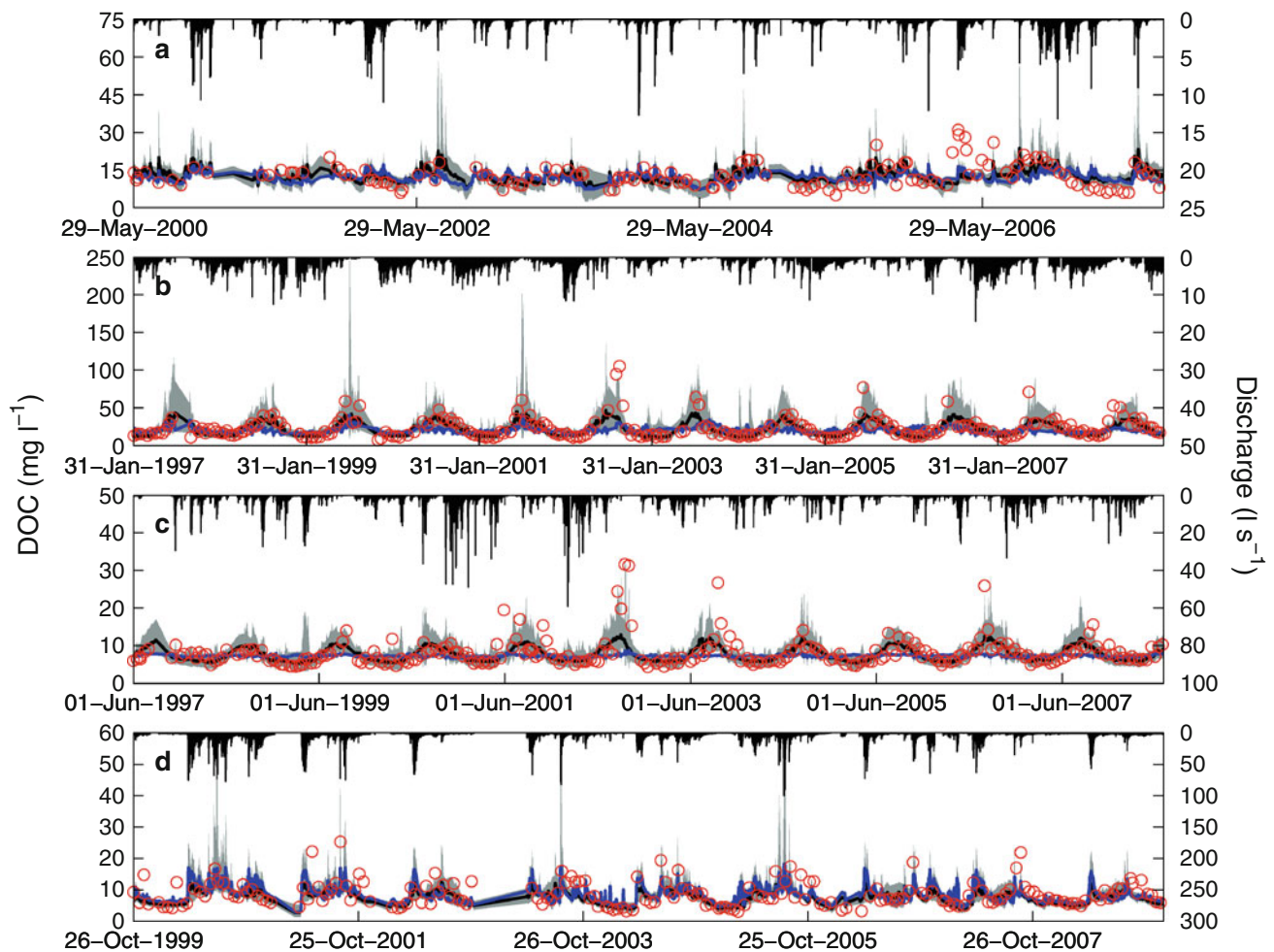
Fig. 2 Time series of discharge (*black bars*), observed (*red circles*) and simulated DOC concentrations in **a** Gårdsjön, **b** Aneboda, **c** Kindla, and **d** Gammtratten. *Blue solid line* is RIM$_{static}$ simulated concentrations, *gray areas* indicate uncertainty limits for dynamic RIM based on behavioral models and the *lower black solid line* is the median concentration from all behavioral models

DISCUSSION

Although appearing similar at the regional scale, the four IM catchments span gradients of temperature, precipitation, and atmospheric deposition (Table 1), all of which can influence DOC variability. The four catchments did indeed behave differently in terms of DOC dynamics; Aneboda and Kindla had a clear seasonal variability, whereas DOC in Gammtratten and Gårdsjön responded more directly to flow. However, statistical analyses of the temporal variability of stream DOC indicated that soil temperature and sulfate concentration were important in all catchments, according to the residuals of RIM$_{static}$.

Dissolved organic carbon in Gårdsjön was clearly influenced by the deposition of sea salt as DOC was negatively correlated to chloride and sodium concentrations as well as declining concentrations of sulfate. Deposition of both chloride and sulfate has been hypothesized to affect organic matter dynamics by both changing pH and ionic strength (Evans et al. 2006; Monteith et al. 2007; Löfgren et al. 2010). At Gårdsjön, marine derived Cl$^-$, Na$^+$ and Mg^{2+} contributed to $61 \pm 9\%$ of the ionic strength of stream water, on average, leaving $\sim 40\%$ to be accounted for sulfate and other ions (Löfgren et al. 2011). In addition, the results from this study showing the importance of chloride concentration to DOC variability in Gårdsjön agree with recent experimental results from a nearby catchment (Moldan et al. 2011).

Many studies have shown that soil temperature affects the variability in organic matter concentrations (Christ and David 1996; Clark et al. 2005) and our results support these findings. The dynamic RIM, incorporating soil temperature as a driver, was able to reproduce DOC concentrations more closely than RIM$_{static}$. However, it is hard to draw conclusions about causality based on these results. Soil temperature may simply correlate to processes responsible for DOC dynamics. It has been suggested that DOC production is due to microbial degradation of organic matter or
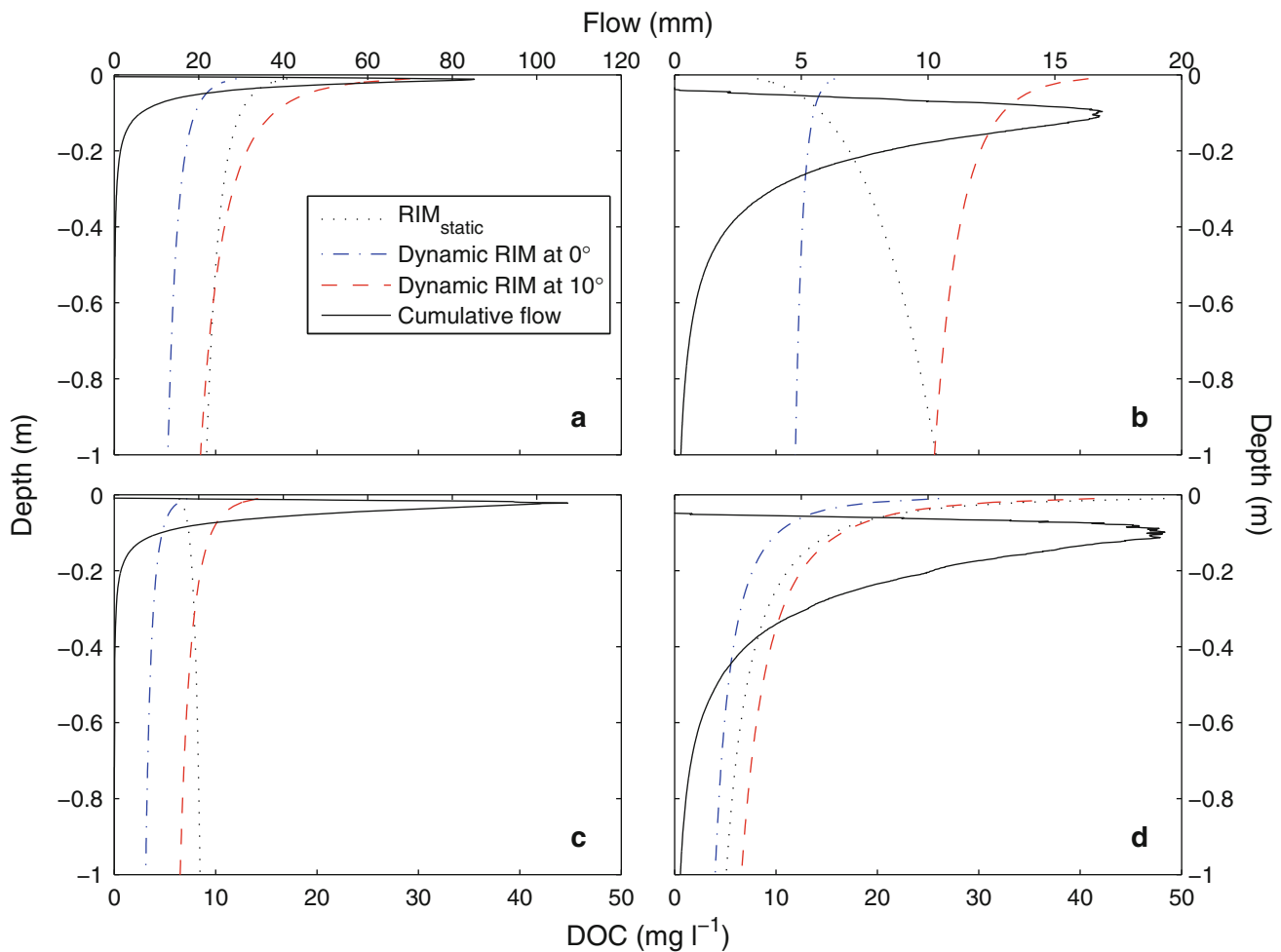
Fig. 3 Total simulated cumulative groundwater flow for the study period (*solid line*) and soil solution DOC concentration profiles for the static (*dotted line*) and the dynamic (*dash-dotted* and *dashed lines*) version of RIM in **a** Gårdsjön, **b** Aneboda, **c** Kindla, and **d** Gammtratten. The *dash-dotted line* indicates profiles at 0°C and the *dashed line* indicates profiles at 10°C. For comparison, the average soil temperatures in March and August were, respectively, 3 and 12°C in Gårdsjön (15 cm depth), 0 and 13°C in Aneboda (32 cm depth), 2 and 10°C in Kindla (20 cm depth), and 0 and 11°C in Gammtratten (29 cm depth)

generation of byproducts from photosynthesis (Kalbitz et al. 2000; Giesler et al. 2007). Both of these processes, as well as degradation of DOC, would be affected by changes in temperature (Davidson and Janssens 2006; Davidson et al. 2006). Hence, the temperature effect on DOC dynamics observed in this study is probably the net effect of temperature variability on DOC producing and degrading processes.

When using the RIM, we assumed that flow was a key driver of DOC variability, even when stream discharge correlated weakly with stream DOC concentrations. Discharge often varies by several orders of magnitude, whereas concentrations rarely vary by more than a factor of ten (Godsey et al. 2009). Therefore, the dominant driver of DOC export is discharge and high flow events can have a disproportionately large role in the total export of organic carbon (Raymond and Saiers 2010). Water is the dominant transport medium of organic matter and even a lack of correlation between discharge and DOC concentrations

could be meaningful since this implies chemostatic behavior, i.e., the concentration does not change with flow (Godsey et al. 2009). In terms of the RIM, this means that the soil water concentrations would be more or less constant with depth in the soil. The only IM catchment to display near chemostatic behavior was Kindla (Fig. 3). In Aneboda, there was a negative correlation between DOC and discharge, and the soil solution profiles simulated using RIM$_{static}$ showed DOC concentration increased as a function of depth (Fig. 3). In contrast, simulated soil solution concentration profiles in Gammtratten and Gårdsjön, where DOC and discharge correlated positively, displayed decreasing concentrations with depth. The same patterns at Gammtratten and Gårdsjön were retained in the dynamic RIM, but with varying profile shapes. The simulated dynamic RIM soil solution profiles in Aneboda and Kindla were nearly vertical, corresponding to almost constant DOC concentrations with increasing depth (in contrast to

the RIM$_{static}$ profile for Aneboda, which showed increasing DOC concentrations with depth). Seasonal change was simulated by moving these vertical profiles (varying the γ parameter) to higher or lower DOC concentrations in response to changing soil temperature without substantially altering the profile shape (dependent on δ). The simulated soil solution concentration profiles agreed closely with observations from earlier studies in Aneboda, Kindla, and Gammtratten (Fölster 2001; Löfgren and Cory 2010).

The characteristic soil solution profiles suggest possible explanations for the different DOC variability in the IM catchments. Since the simulated soil solution DOC concentrations were nearly independent of depth in the soil for Aneboda and Kindla, streamwater DOC concentrations would be invariant to changing flow paths (changing discharge). In contrast, similar changes in flow paths may result in large changes in stream DOC concentrations in Gammtratten and Gårdsjön depending on how the cumulative distribution of lateral flows (right hand y-axis of the plot in Fig. 3) traverses the soil solution profile. Lowering the GWT from 0.1 to 1 m in the simulation resulted in a decrease in the predicted streamwater DOC concentration in Gammtratten to less than half, whereas a similar change in Kindla had only marginal effects on stream DOC concentration. In contrast, the dynamics in Kindla and Aneboda seem to be driven by the net effect of DOC producing and degrading processes, which are affected by seasonal climate variability.

The conspicuous episode in the fall of 2002 at Aneboda and Kindla was dominated by dry conditions with only small amounts of precipitation and rather high temperatures (10–15°C). Concentration through evaporation may be a possible cause of the event, but if this were the case the concentrations of all solutes would be expected to increase, which does not occur. One hypothesis for increasing DOC concentrations is drought-induced acidification caused by oxidation of reduced sulfur compounds to sulfate (Clark et al. 2005). However, sulfate concentration did not increase substantially during the event. Another possibility is shifts in the dominant flow paths, with deeper flow paths occurring during dry conditions (Tipping et al. 2010). Davidson et al. (2006) have highlighted the importance of diffusion of organic matter degrading enzymes on the variability in soil respiration. Drought would increase the diffusion of enzymes in wet organic soils, whereas diffusion would be limited in mineral soil. It is likely that these factors may also be important for the production and degradation of DOC. Discharge areas are dominated by organic soils in both Aneboda and Kindla, so drought may induce increased DOC concentrations because of increased diffusion of soil organic matter degrading enzymes.

Laboratory experiments have shown that up to 10% of DOC can be degraded by in-stream processes within 24 h (Köhler et al. 2002), mostly caused by photo-degradation. In another laboratory experiment, an average of 4.7% of the DOC in water from 38 different Swedish lakes was found to be photo-degraded within 8 h (Bertilsson and Tranvik 2000). The extent of degradation was proportional to the total absorbed radiation energy. However, in this work we assumed that in-stream processing of DOC was negligible, as the IM streams are small and the average residence times in the streams are short (in the order of 24 h or less). In addition, all the IM streams are within forested catchments and well shaded by the forest.

The results from the simulations with both the static and dynamic versions of RIM indicate that the soils hydrologically connected to the stream share similarities with organic-rich soils (Fig. 3). The soil solution concentration profiles for Aneboda and Kindla reveal the concentrations are essentially independent of soil depth, suggesting either homogenous DOC delivery throughout the vertical soil horizon, or DOC delivery primarily through lateral groundwater flow in organic horizons irrespective of runoff levels. The first of these hypotheses is unrealistic according to measurements of soil water and groundwater DOC concentrations in both glacial till and peat at Aneboda and Kindla (Löfgren and Cory 2010). The latter hypothesis is possible if topography, bedrock, and soil morphology forces a substantial share of uphill groundwater through peatlands and/or organic-rich riparian zones. In both Aneboda and Kindla, such wet soils (histosols) are common in all depressions. For these sites, the negative correlation between DOC and discharge suggests partial overland flow in the organic-rich valley bottoms at high groundwater levels, supporting the hypothesis of superficial groundwater routing along main flow paths generating stream water runoff. This hypothesis could be tested with the semi-distributed TRIM model (Grabs 2010).

CONCLUSIONS

While the IM catchments may appear similar at first glance, they behave quite differently regarding DOC dynamics. Aneboda and Kindla have a strong seasonal signature correlating with soil temperature. The variability in DOC concentrations in Gammtratten is mainly driven by flow, although soil temperature also correlates with DOC. The strongest driver in Gårdsjön also appears to be flow, but deposition of sea salt and anthropogenic sulfate affect the variability in DOC. While RIM$_{static}$ satisfactorily simulated DOC concentrations in the flow-dominated catchments, the performance for the temperature-driven catchments was low. By incorporating functions of soil temperature in a dynamic RIM, we succeeded in improving model performance in all catchments. In addition, RIM

proved to be a valuable tool for investigating possible reasons for short-term DOC variability.

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