Biogeosciences Discuss., 10, 15913–15949, 2013
www.biogeosciences-discuss.net/10/15913/2013/
doi:10.5194/bgd-10-15913-2013

Biogeosciences
Discussions
Open Access

Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements?

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Received: 16 September 2013 – Accepted: 3 October 2013 – Published: 15 October 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The controls on stream dissolved organic carbon (DOC) concentrations were investigated in a 68 km^2 catchment by applying a landscape-mixing model to test if downstream concentrations could be predicted from contributing landscape elements. The landscape-mixing model reproduced the DOC concentration well throughout the stream network during times of high discharge, but was even more useful for providing a baseline for residual analysis, which highlighted areas for further conceptual model development. The landscape-mixing model approach is conceptually simple and easy to apply, requiring relatively few field measurements and minimal parameterization. The residual analysis highlighted areas of the stream network that were not well represented by simple mixing of headwaters, as well as flow conditions during which simple mixing based on headwater watershed characteristics did not apply. Specifically, we found that during periods of base flow the larger valley streams underlain by fine sorted sediments had much lower DOC concentrations than would be predicted by simple mixing; while peatland streams had higher DOC than predicted. During periods of intermediate and high flow the model made more accurate predictions of downstream DOC. Our interpretation is that the higher degree of hydrological connectivity during high flows, possibly combined with shorter stream residence times, increased the predictive power of this whole-watershed based mixing model. However, there was still a clear pattern during high discharge periods, with peatland streams having lower DOC than would be predicted by simple mixing while forested streams had higher DOC. These observations suggest several potential mechanisms to be further explored using more focused field and process-based modeling studies, especially on the role of changing hydrological pathways.

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Can dissolved organic carbon be explained by landscape elements?

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1 Introduction

Dissolved organic carbon (DOC) is a key constituent in surface waters as it has fundamental implications for the ecology and biogeochemistry of aquatic ecosystems. The important role of stream DOC has resulted in several recent investigations to better understand the mechanisms of DOC regulation across temporal and spatial scales (Tank et al., 2012; Temnerud and Bishop, 2005). A general finding has been that the variability of stream DOC concentrations within and between adjacent streams can be as large as the variability found on a regional or even global scale (Bishop et al., 2008). Although much of this variability can be explained by the occurrence of organic soils in the catchments (Creed et al., 2003; Walker et al., 2012), peatlands alone do not explain the large spatial heterogeneity of DOC in the landscape (Mattsson et al., 2009; Ågren et al., 2007).

The highest surface water DOC concentrations in mid- to high latitudes can be found in the boreal biome (Mulholland, 2002). Simplified, this regional pattern occurs because of climatic and hydrological conditions favoring high DOC production in the boreal landscape by stimulating plant growth (leading to relatively large litter production) and by limiting the mineralization of organic carbon due to low temperature and high water content (Laudon et al., 2012). Despite these generally high DOC concentrations in the boreal landscape, there is a large spatial heterogeneity in stream water DOC derived from different landscapes that varies because of catchment characteristics, topography and size (Temnerud et al., 2007; Tank et al., 2012). While the accumulation of organic matter in unforested mires make them the major source of DOC in the boreal landscape (Rantakari et al., 2010; Ågren et al., 2007), forested areas which generally have the greatest aerial extent in the boreal biome, also contribute large DOC concentrations because of the presence of organic rich riparian soils (Grabs et al., 2012; Knorr, 2012).

The relative proportion of mires and forest in the landscape can be used as a first order approximation to predict the stream DOC concentration in small streams (Aitkenhead et al., 1999; Laudon et al., 2012). However, as the catchment size increases from headwaters to meso-scale catchments, so does the complexity of the contributing factors controlling stream water chemistry (Bloschl and Sivapalan, 1995). This increased complexity can be related to new contributing landscape features becoming increasingly important downstream, but also because there may be scale dependent processes that can have considerable effects on the stream DOC concentrations as the rivers grow (Cey et al., 1998; Pacific et al., 2010).

Another characteristic feature of DOC is the large temporal variability related to hydrological events, seasonal differences and inter-annual conditions (Dawson et al., 2011). Hydrology has a first-order control on DOC concentrations in individual catchments (Hinton et al., 1997; Laudon et al., 2011; Raymond and Saiers, 2010). Drying and re-wetting of catchment soils (Köhler et al., 2008), soil temperature (D'Amore et al., 2010), winter climatic conditions (Haei et al., 2010) and antecedent conditions controlling the pool of sorbed, potentially soluble organic carbon (Ågren et al., 2010; Yurova et al., 2008) can affect DOC concentrations on an event, seasonal and annual time scale. This temporal variability adds to the spatial complexity of DOC concentration as different catchment characteristics can differ in response to hydrological and climatic forcing depending on catchment soils, vegetation and topography. Furthermore, depending on the spatial configuration of the landscape, the residence time of water in the surface water network can moderate or exaggerate the response in downstream locations in ways that are not easily predictable.

Because of the large complexity of factors controlling stream DOC concentrations we tested a simple conceptual landscape-mixing model as a predictive and diagnostic tool on a large nested boreal stream dataset, to better understand how DOC is regulated during different seasons and across scales. The main objectives of this study were to test: (1) if the spatial heterogeneity of stream DOC concentrations can be explained by the major contributing landscape elements; and (2) if their contribution varies during different seasons and hydrological conditions. To answer these questions we used a landscape-mixing model on the 68 km^2 well studied boreal Krycklan catchment. A landscape-mixing model (Cooper et al., 2000, 2004; Evans et al., 2001) offers a simple approach to modelling stream biogeochemistry by lumping processes into dominating landscape elements that can be used to examine if the DOC concentration is simply due to the conservative mixing of contributing sources. First, we investigate how the landscape-mixing could be used to predict DOC, using several model assessment criteria. Secondly, we analyse the model residuals to investigate model performance and thereby answer the question of where in the landscape simple mixing of stream water does not adequately characterise stream DOC behavior. By running and validating the model on data sampled on seven different occasions, we also addressed the question of whether the landscape-mixing model performed better at certain times of the year, or under certain flow conditions. Using this simple conceptual approach the ultimate goal was to provide new insights of the regulation mechanisms of stream DOC and how it varies across a landscape and during different times of the year.

2 Materials and methods

2.1 Study catchment

The 68 km^2 Krycklan catchment (64°16′ N, 19°46′ E) was used as a study catchment for modeling the spatial variability of DOC in the stream network (Laudon et al., 2013). The Kryklan catchment is a glaciated forested catchment (forest cover 87 % and peatland cover 9 %). The forest is dominated by Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) with an understorey dominated by ericaceous shrubs, mostly bilberry (*Vaccinium myrtillus*) and cowberry (*Vaccinium vitis-idaea*) on moss-mats of *Hylocomium splendens* and *Pleurozium schreberi* (Forsum et al., 2008). Quarternary deposits of till, peat and fine sorted sediments are the dominant overburden (Fig. 1). The peat is dominated by *Sphagnum* species and consists of mostly minerogenic, acid and oligotrophic mires with varying proportions of micro-topographic units (e.g. strings/lawns). Rock outcrops and thin soils are common on hilltops. The region is af-

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fected by isostatic postglacial rebound. The highest postglacial coastline crosses the catchment at approximately 256 m a.s.l., and 45 % is situated above the former coastline. In the lower lying parts of the catchment, there is an old postglacial delta with deposits of mostly silty sediment. While there are a number of small lakes in the catchment, the overall lake coverage is small at 0.6 %. Human impact is low and agricultural land covers only 2 % of the catchment. The bedrock consists of 94 % sedimentary rocks (Precambrian metagreywacke) with smaller patches of basic volcanic rocks and acid volcanic rocks, covering 3 and 4 % respectively. The site conditions are characterised by long winters, with snow cover typically from November to the beginning of May. The 30 yr (1981–2010) mean air temperature was 1.8 °C and the annual precipitation is 640 mm, of which approximately half enters streams as runoff (Oni et al., 2013).

2.2 Stream water sampling

Stream water was sampled at 115 sites on 7 occasions from May 2003 to September 2008 (Table 1 and Fig. 2). The sampling campaigns were designed to take a "snapshot" of the spatial variability of the stream network, and all sites were sampled during a single day, except during winter baseflow where sampling extended over a week. The sampling was carried out during different seasons and hydrological conditions (Fig. 2, Table 1). While 115 site locations were sampled, the number of sites sampled on any particular survey varied between 73 to 89. A subset of 42 sites was sampled on all 7 occasions.

Discharge was measured in a 2nd order stream in the central area of the catchment (called Svartberget or C7 in previous studies, Laudon et al., 2007) at a 90° V-notch weir located inside heated housing. Pressure transducers connected to Campbell scientific data loggers, USA or duplicate WT-HR capacitive water stage loggers, Trutrack Inc., New Zealand were used to record the water level. Using established rating curves water stage was transformed into discharge. We assume that the specific discharge is the same throughout the catchment. The uncertainty this assumption introduces has been calculated to be on average at most 12 % (Ågren et al., 2007), but can be higher under

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particularly low flow conditions (Lyon et al., 2012). The water samples were collected in acid washed and sample-rinsed high density polyethylene (HDPE) bottles (Embalator Mellerudplast, Mellerud, Sweden) and were stored frozen until they were analysed for DOC using a Shimadzu TOC-VCPH/CPN analyser (Shimadzu, Kyoto, Japan).

2.3 Watershed characteristics

Lidar (light detection and ranging) measurements of the catchment have been made at a point density of 3.3–10.2 measurements per m^2. These data were used to generate a 0.5 m high resolution DEM. For hydrological modeling the DEM was aggregated to a 5 m resolution. In order to make the DEM flow compatible it was manually corrected where bridges and road culverts obstructed the flow algorithm, and all sinks were filled. The catchment delineation was then derived automatically from the DEM using ArcGIS 10.0. Care was taken to ensure that the catchment delineation was correct for all 115 catchments, and manual adjustments were made to the DEM in questionable sections based on a 3-D version of the 0.5 m DEM combined with field observations. For each subcatchment the catchment characteristics were derived using map data. DOC was modelled from the soil cover based on the soil map (1:100 000) (Geological Survey of Sweden, Uppsala, Sweden). Additional catchment characteristics were derived for all subcatchments for potential use as covariates in the residual analysis. These characteristics included stream order, catchment area, slope, topographic wetness index (TWI_{MD8}) (Grabs et al., 2009), proportion above the highest coastline, as well as the land cover from the road (1 : 100 000) and the property maps (1 : 12 500) (Lantmäteriet, Gävle, Sweden). With the aid of IR-orthophotos, combined with a detailed forest inventory, the whole catchment has been divided into 1751 stands (areas with a similar mix of known tree species and age). Based on the Lidar measurements and regression models with field observations, detailed maps were constructed providing, for each 10 × 10 m pixel, forest stand height, birch biomass, lodgepole pine biomass, Norway spruce biomass, Scots pine biomass, total biomass and mean forest stand age. For

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the residual analysis averages of all the forest variables were calculated for each sub-catchment.

2.4 End-members and landscape-mixing modelling

The landscape-mixing model, which was based on Cooper et al. (2004) predicts water chemistry throughout a stream network from landscape properties. The model is based on the assumption that the variability within a landscape type is smaller than between landscape types, and that different landscape elements generate different solute concentrations. These landscape concentrations are estimated from sampling data at stream locations draining subcatchments with known upstream proportions of each landscape. A detailed DEM (digital elevation model) with 5 m resolution and the presence of many sampling sites in our study allows us to work with the actual sub-catchments and at a high resolution. We used a statistical approach to calculate the end-member concentrations from the different landscapes. In order to more easily compare model performance between all 7 sampling occasions we selected headwater catchments that were sampled on all occasions as the dataset for model parameterization. Small catchments with more uniform landscape characteristics will tend to have concentrations which are closer to the different end-members and more representative of sources while larger catchments, through mixing of upstream sources, show a reduced variability (Temnerud and Bishop, 2005). We therefore selected only catchments with area less than or equal to 3 km^2 for model parameterization. Fifteen catchments fulfilled both criteria (sampled on all occasions, size $\leq 3\,km^2$); the remaining sampling sites were used to assess model performance, particularly to test the simple mixing hypothesis.

Previous research in the catchments has identified three source types which might account for the concentrations of DOC (Ågren et al., 2007; Buffam et al., 2008): peat, till, and fine sorted sediments. These three forms of overburden ("soil types") have been shown to be associated with different water chemistry. Based on this previous knowledge DOC was modelled using these three catchment soil types. From soil map information each of the 115 catchments was classified as peat, till (this also includes the class "thin soil" which in essence is a shallow layer of till on bedrock), sorted sediments (silt, sand and ice-river alluvium) or "other" (lakes and rock outcrops). The aggregated soil map variables were calculated for each sampling site. Based on the 15 selected headwater sites in the construction dataset, a regression model (Eq. 1) was constructed to calculate the end-member concentrations for each soil type and on each sample date. By setting the intercept to 0 in the model and using the areal coverage of the soil types in proportions (0–1) instead of percentages, the estimates (A-D) were expressed directly as the end-member concentration for DOC in $\mathrm{mg\,L^{-1}}$ for each soil type.

$$\mathrm{DOC}\ (\mathrm{mg\,L^{-1}}) = A \times \text{ Peat } + B \times \text{ Till } + C \times \text{ Sorted sediment } + D \times \text{ Other} \qquad (1)$$

Because of problems with normal distribution, a bootstrapping approach was used to iteratively solve the "landscape concentrations". The bootstrapping procedure was done by sampling with replacement to generate samples of the same size as the original data set. Under this procedure, a random number of streams were deleted from the dataset, from the remaining dataset some streams were then included twice, or more, until the dataset again comprised 15 streams. Slopes and constants were calculated for every new dataset, then the randomization process was repeated 1000 times. Finally, mean concentrations were computed for each landscape component and used in the model (Table 1). This method has the additional benefit that it provides an estimate of the uncertainty in the end-member concentrations. Based on the repeated runs the standard errors, confidence intervals, and correlations were calculated for each end-member concentration. The uncertainty in the calculated end-member concentrations was later used to analyse the total uncertainty of the models. All bootstrapping calculations were done in PASW Statistics 18 (SPSS Inc.). Initially, the bootstrapping procedure sometimes generated unrealistic estimates. To overcome this, constraints were set on the end-member concentrations. Soil water data from the catchment were used as constraints for concentrations of each soil type. For peat, lower and upper limits of

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4 and 84 $mg\,L^{-1}$ were set, based on measurements from groundwater wells in a wetland in the catchment (Yurova et al., 2008). For till the acceptable range was set to 1–97 $mg\,L^{-1}$ given the variability in lysimeter measurements from 10 soil profiles in till soils in the catchment (Grabs et al., 2012). In fine sorted sediments the constraint was set to 1–46 $mg\,L^{-1}$ given the variability in lysimeter measurements from 3 soil profiles in the fine sorted sedimentary soils in the catchment (Grabs et al., 2012). In the first attempt, the end-member concentration for the landscape type "other", consisting of lakes and bare rock (D in Eq. 1) was calculated. The evaluation showed that the end-member concentration for D was extremely variable and uncertain and including these values did not improve the fit for the overall model. Because of this uncertainty and since the class "other" had such a minor areal coverage (on average about 2 % and at maximum below 10 % coverage, Fig. 3), the parameter D in Eq. (1) was set to 0.

2.5 Landscape-mixing modelling in GIS

The high resolution DEM facilitated modelling of DOC concentrations every 5 m throughout the entire stream network using the landscape-mixing model and ArcMap 10 hydrological modelling tools. Using a weighting raster containing the end-member concentrations for the aggregated soil map (aggregated into the 4 classes) when performing the flow accumulation calculation the DOC export from each cell was calculated. The DOC export was then divided by estimated discharge to calculate the DOC concentrations for all 5×5 m cells in the landscape. The modelled DOC concentration for the sampling sites could then be extracted. The modelled DOC values were compared to the measured values for the respective site on each sampling occasion. A layer showing the modelled DOC concentrations for every 5 m section of the stream network could also be displayed (Fig. 1).

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2.6 Model validation

Model performance was assessed using data from the sites that were not used for model construction. We calculated several measures (Table 2 and Fig. 4). Root mean square error (RMSE) has the benefit that it gives the error in units of $mg\,L^{-1}$. To standardise RMSE we calculated the RMSE-observation standard variation ratio (RSR). A low RSR indicate a better model and values below 0.7 are considered a satisfactory model (Moriasi et al., 2007). As a measure of the average tendency of the modelled values to be larger or smaller than observed values the percent bias (PBIAS) was calculated. For PBIAS the optimum value is 0, negative values indicate a model overestimation bias and positive values an underestimation of modelled values. We also plotted the measured and modelled values (Fig. 4) and used standard regression measures of R^2 and slope. A slope near 1 indicates that the model is close to the 1 : 1 line, a large diversion from 1 indicates a systematic error in the model. As an example, a slope below 1 means that high DOC concentrations are underestimated and low values are overestimated. The R^2 value indicates how good the relationship is between the measured and predicted values, but does not take into account a systematic error (slope). Nash Sutcliffe Efficiency (NSE) indicates how well the scatter fits the 1 : 1 line, the value of NSE is similar to R^2 in that a value close to 1 indicates a good fit and a value close to zero indicates a poor fit.

2.7 Uncertainty

One source of uncertainty in the model is the representativeness of the 15 selected catchments. To test how this affected the modelled DOC, the bootstrapping routine was rerun using all available sites to calculate the end-member concentrations for the entire dataset. The landscape-mixing model was then rerun on new estimates and an evaluation on how that affected RMSE, RSR, PBIAS and NSE was calculated (Table 3).

A second source of uncertainty was related to the end-member concentrations. However, by using the bootstrapping method this uncertainty is calculated (Fig. 5). A Monte

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Carlo analysis was performed to propagate the uncertainties of the end-member concentrations to calculate an overall uncertainty for the modelled values. The overall uncertainty was calculated using 10 000 realizations with random parameters assuming that the uncertainty in A, B and C was normally distributed. The uncertainty was expressed as coefficient of variation (standard deviation of the modelled values/average of the modelled values) (Table 1).

2.8 Residual analysis

The residuals (modelled–measured) were analysed using a multivariate statistical approach, partial least squares projections to latent structures (PLS), to identify where and when the model failed. PLS is a method for relating two data matrices, **X** and **Y**, to each other by a linear multivariate model (Eriksson et al., 2006b). PLS is similar to principal component analysis (PCA), but instead of extracting the principal components so that they maximize the variance in the **X**-matrix (as in PCA) the PLS method extracts the principal components so that they maximize the correlation between the **X**-matrix and **Y**-matrix. The strength of the PLS method is the ability to analyse data with "many, noisy, collinear, and even incomplete variable's in both X and Y" (Eriksson et al., 2006b, a). The PLS analysis was conducted using the multivariate statistical program SIMCA-P+ 12.0.1, Umetrics, Umeå. In short, PLS was used to show where in the landscape the landscape-mixing model failed. The first step was to get an overview of the relationship between the response and explanatory variables and the residuals. To achieve this, the residuals (modelled DOC – measured DOC) for all occasions (**Y**-matrix) were related to the catchment characteristics (**X**-matrix) using a PLS model (Fig. 7). When it was found that the behaviour of the residuals varied according to hydrological conditions, two new models were constructed, one for high and intermediate flow (Fig. 8a) and one for base flow (Fig. 8b). In order to facilitate the interpretation of the graphs in Fig. 8, the PLS models were refined to include only significant variables with high weight in the model, these being the important variables in accounting for the residual variance.

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3 Results

The bootstrapping estimates of the end-members show that peat has the highest DOC concentrations followed by till and lastly, fine sorted sediments (Table 1 and Fig. 5). Plotting the end-member concentration as a function of discharge for the sampling occasions revealed that the DOC concentrations increased with discharge (Fig. 5). For silt and till this increase could be approximated by a linear relationship. For peat, the curve estimation procedure in PASW suggested a sigmoid curve ($p < 0.1$) The standard error for the end-member concentration was low for till (on average $2\,\mathrm{mg\,L^{-1}}$) but higher for peat and fine sorted sediments (on average $9\,\mathrm{mg\,L^{-1}}$) where sediment has the relatively highest standard error (Fig. 5).

Figure 1 shows an example, from Sept 2008, of the modelled DOC concentrations using the landscape-mixing model combined with GIS and a high resolution DEM. This shows the strength of this approach, where DOC concentrations can be modelled throughout an entire stream network based on a few headwater observations. It is clear that many of the streams originate in peatlands and have high concentrations initially (red). As the streams run into the area dominated by till and thin soils the concentrations begin to decrease (streams turn orange/yellow) due to the intermediate concentrations from that composite landscape type. The streams draining the sedimentary area in the valley have the lowest DOC concentrations and as these small streams mix into the larger main stream the concentrations continue to decrease (light green) towards the outlet.

The many measures used for evaluating model performance showed somewhat different results (Table 2). The root mean square error (RMSE) ranged from 2 to $5\,\mathrm{mg\,L^{-1}}$. Following the guidelines from Moriasi et al. (2007) the RMSE-observation standard variation ratio (RSR) indicated that only two occasions are considered to be modelled satisfactorily (RSR < 0.70). The mostly negative PBIAS values found (Table 2) indicate a general model overestimation bias. However using this measure all models except February 2005 performed reasonably well, except for the February 2005 data. The plotted measured and modelled values (Fig. 4) and the slope indicate a systematic bias on all occasions demonstrating that high DOC concentrations were underestimated and low concentrations were overestimated in the model. The severity of this phenomenon varied and on three occasions the slope was judged good while the other four occasions was judged unsatisfactory (baseflow + April 2004) (Table 2 and Fig. 4). According to the model evaluation guidelines by Moriasi et al. (2007), based on the Nash Sutcliffe Efficiency (NSE) measure only two models would be classified as satisfactory (NSE > 0.5). To summarize, the many measures of model efficiency gave different results and contained different information. The most suitable model fit measure depends on the question we are trying to answer. We believe that the RSR (standardized RMSE) and NSE (Nash Sutcliffe efficiency) give the best overall description of the model performance. Taking into account all model performance measures, the interpretation is that 2 models performed well (May 2003 and Sept 2008), one model performed unsatisfactorily (February 2005) and the rest performed satisfactorily.

3.1 Uncertainty

Overall, the representativeness of the 15 selected sites was good, but a few outliers are found in the validation dataset (Figs. 3 and 4). There were for example a few sites with a higher peat coverage compared with the sites that were used for constructing the model (highlighted as unfilled circles in Fig. 4). To evaluate how this affected the end-member concentrations, all sites were used to calculate the end-members (n = 73–89) in Eq. (1). The performance of this new model was then compared to the initial model (n = 15). For most occasions, the model performance did not change substantially; including all sites to calculate the end-member concentrations only improved (judged from improvement in NSE) between 5 % and 10 % (Table 3). However in the worst case (February 2005) the improvement was 73 %, indicating that the original construction dataset sites were not representative for this occasion. This shows that there is room for model improvement by increasing the number of observations in the construction

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datset. However, for this study we wanted to leave as many sites as possible for the validation dataset and the residual analysis.

The second source of uncertainty was related to the uncertainty of the estimates of the end-member concentrations. Using the uncertainty from the bootstrapping estimates a Monte Carlo analysis was performed to propagate the uncertainties into an overall uncertainty for the modelled values. As expected, when there were difficulties in constructing a good bootstrapping model, indicated by low R^2 for the model (Table 1, Fig. 6), the uncertainties of the modelled values were high. The model uncertainty also affected its performance (Tables 1 and 2 and Fig. 6). February 2002 had the highest uncertainty and had the worst model fit, while the models that performed best (May 2003 and September 2008) had a lower model uncertainty.

3.2 Residual analysis

The first PLS model that gave an overview of the data had 2 significant components, R2Y = 0.35, R2X = 0.57, Q2 = 0.21 (R2Y and R2X are goodness of fit and Q2 is the goodness of prediction) (Fig. 7). In a PLS loading plot, variables that lie close together co-vary, so, the PLS analysis of the residuals (Fig. 7) showed that the residuals clustered based on the discharge of the sampling occasion. The residuals from the high and intermediate flow situations clustered along the first component (black squares in Fig. 7), while the residuals from baseflow measurements clustered higher along the second axis (black triangles in Fig. 7). In order to interpret which variables correlate to high residuals two different models had to be constructed, one for high and intermediate flow, and one for base flow conditions.

Both the model for the high and intermediate flow and the one for base flow gave PLS models with one significant component. After refining the model to only include significant variables with a high weight, the PLS analysis during high and intermediate discharge created a model with R2Y = 0.34, R2X = 0.66, Q2 = 0.29 (Fig. 8a). That means that the variability in the 23 X-variables could be reduced to one component explaining 34 % of the variability in Y. The 9 significant X-variables with a high weight

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explained 66 % of the variability in the extracted component. The PLS loading plot show the Y-weights (c) and the X-weights (w*). The PLS easily handles many covariate variables (Fig. 8a), all X-weights that correlate positively to Y-weights are different measures of mires and all X-weights that correlate negatively to Y-weights are different measures of the forest. If both X and Y-weights are positive that means that they are positively correlated. So, the interpretation of Fig. 8a is that during high and intermediate discharge the landscape-mixing model overestimated the concentrations that were found in subcatchments with a high coverage of mires and that the underestimated values were found in those with a high proportion of forest. Subsequently, the PLS loading plot for the residuals during baseflow (1 significant component, $R2Y = 0.33$, $R2X = 0.50$, $Q2 = 0.26$) (Fig. 8b) showed that the overestimated concentrations were found in large downstream subcatchments while the underestimated values were those in subcatchments dominated by peatlands.

4 Discussion

4.1 Selection of end-members for the mixing model

We found that the peatlands were associated with the highest DOC concentrations, followed by till soils and fine sorted sediments (Table 1, Fig. 5). Dissolved organic carbon in north temperate and boreal streams is mostly of terrestrial origin, and peat-containing wetlands are often the major source of DOC (Creed et al., 2008; Dillon and Molot, 1997; Evans et al., 2007; Gergel et al., 1999; Walker et al., 2012). Streams draining the silty sediment area had the lowest concentration, which can be explained by a combination of factors. In Krycklan, catchments underlain by silty sediments are located in the valley bottom of the downstream larger catchments (Fig. 1). A combination of longer flow paths and a high subsurface water transit time can increase the decomposition of DOC (Wolock et al., 1997). In addition a high specific surface area of

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the fine sorted sediments can lead to increased adsorption to mineral surfaces (Kalbitz et al., 2003).

As previously described, the mixing model is based on the assumption that the variability within a landscape type is smaller than between landscape types, and that different landscape elements generate different solute concentrations. This assumption was true during the high flow situations, indicated by the separation of the error bars in Fig. 5, but during baseflow there was some overlap of the variability in the end-members. Previous research has found that hydrology has a first order control (Hornberger et al., 1994; Seibert et al., 2009) on the temporal variability of the DOC concentrations in streams. Plotting the end-member concentrations as a function of discharge gave a slight positive relationship between DOC and discharge at all soil types (Fig. 5). We expected, but did not find, a negative relationship between DOC concentration and discharge in mire dominated catchments as suggested by other studies in the study area (Ågren et al., 2012) and in UK and Canada (Clark et al., 2007; Hinton et al., 1997). A likely reason for this is that the DOC dilution primarily occurs during the snow melt period when large amounts of snow melt water runoff as overland flow over frozen soil (Laudon et al., 2011). As we are mixing autumn rain events and snowmelt events in this analysis this seasonality difference will not be picked up by the model but will instead provide a poorer model fit.

In this application of the model, we used a bootstrapping approach to calculate the end-member concentration for the different landscape elements based on headwater stream DOC concentrations. Other approaches for assigning end-members could be tested. For example, targeting specific catchments believed to be closer to being true end-members can give a better spread of end-member concentrations. Using DOC measurements from soil water from the different landscape elements might also provide a more accurate end-member concentration in some circumstances. Grabs et al. (2012) showed that the soil water concentrations from the fine sorted sediments riparian soils are low in Krycklan, around 6 $mg\,L^{-1}$. Furthermore, soil water DOC concentrations in till in dry locations have also been found to be relatively low, on average

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$10\,mg\,L^{-1}$, whereas they were $27\,mg\,L^{-1}$ and $33\,mg\,L^{-1}$ in humid and wet sites, respectively. By classifying the till soils into three classes (dry, humid, wet) from topographic wetness index we could potentially improve the predictability of the landscape-mixing model for DOC in the landscape. However, this modeling study does not aim to maximize the predictability of DOC in the landscape, instead the residual analysis is to be seen as a diagnostic tool to examine when and where simple land characteristics can explain the variability in DOC concentration on the landscape scale. Hence, this study should not be seen foremost as a predictive model but rather a learning framework for further development of our conceptual understanding.

4.2 Landscape-mixing model performance

The landscape-mixing model (Cooper et al., 2004) combined with the high resolution DEM offers a simple way of estimating stream DOC concentrations throughout the stream network (Fig. 1) based on a few headwater observations. How well the model performed is related to how well the end-member concentrations can be determined (e.g., Fig. 6), if the modelled solutes are conservative, and also to how well the soil and stream are hydrologically connected (Inamdar et al., 2004). Creed and Band (1998) suggest that stream nutrient export dynamics can be regulated by variable source area dynamics. Our study lends support to that idea as the model worked better when the hydrological connectivity to the soils was good, i.e. during high flow situations (Fig. 4). During baseflow large areas are hydrologically disconnected and hence the landscape-mixing model performed less well (Fig. 4) since it calculates the stream concentrations based on soil characteristics of the entire catchment.

4.3 Residual analysis

Using the landscape-mixing model for periods when the approach worked less well, the residual analysis can be used to identify other processes that control stream DOC. The residual analysis showed that the model failures were related to hydrological con-

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dition (Fig. 7), indicating that different mechanisms for controls of DOC are important during different low vs. high flow periods. During high and intermediate discharge the landscape-mixing model overestimated DOC in subcatchments with a high peat coverage (Fig. 8a) while the model underestimated the DOC in the same subcatchments during baseflow (Fig. 8b). Higher concentrations from the wetland during baseflow and lower during high flow would have improved the model according to the residual analysis (Fig. 8a and b). A possible reason for the inability to predict the peatland-DOC relationship with high accuracy is that the model was constructed on a dataset with peat coverage of 0–30 % while it was applied to subcatchments in the validation dataset with a peat coverage of up to 55 % (highlighted as unfilled circles in Fig. 4). Another cause for the model underestimating high values and overestimating low values could be a dampening effect in the bootstrapping approach similar to other regression approaches (Gupta et al., 2009).

The PLS analysis of the residuals showed that during high and intermediate discharge (Fig. 8a) the model underestimates DOC in subcatchments with much forest and overestimates DOC in subcatchments with a high peat-cover. Given that forests and peatlands are the most common landscape types in the study catchment this makes it difficult to interpret the results, because that means that forest and peatlands are highly correlated (Pearson correlation −0.94; $p < 0.001$). This can create model artifacts as the overestimated DOC in forest rich subcatchments could be because of our inability to capture the true variability in peatland DOC, as discussed above. On the other hand, it could also be a causal relationship. Berggren et al. (2009) showed in a forest-mire gradient in the study area that mixed catchments change their dominant DOC source depending on discharge and that during high discharge the forests become more important as a DOC source.

It should be noted that the landscape-mixing model will only work, in the simple form applied here, if the concentrations downstream are the result of simple mixing of upstream water sources, i.e. that solute transport is conservative. The residual analysis during low flow situations shows that the mixing model overestimated the DOC

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concentrations in the lower lying large downstream catchments, with high stream order (Fig. 8b). This highlights the importance of including in-stream processes such as bacterial degradation and/or photooxidation of DOC, as well as changing flow paths. These processes need to be included in the conceptual framework when modeling DOC during baseflow. Moody et al. (2013) recorded high photo-oxidation rates (exceeding 10 $\mathrm{mg\,C\,L^{-1}\,day^{-1}}$) during the first 1–2 days of exposure of fresh peat-derived DOC in UK headwater streams. However, a photo-oxidation experiment, also on water from the study catchment estimated the DOC loss to be 4.8 $\mathrm{mg\,C\,L^{-1}\,day^{-1}}$ during the first 2.7 days (Köhler et al., 2002). Bioassays on water from the study catchment, (Berggren et al., 2010) showed that bacterial respiration rates increase with temperature which should generate seasonal variability in the bacterial degradation of DOC. The bacterial degradation and/or photooxidation of DOC could potentially explain the over prediction of DOC at downstream sites during summer when these processes are active, but not during winter when the stream temperatures are low and streams are ice and snow covered. However, both summer and winter baseflow showed the same pattern in this residual analysis (Fig. 8b) and the fact that summer and winter baseflow did not separate in the model is an indication that the bacterial degradation and/or photooxidation are not a major control of DOC during baseflow in this catchment.

During baseflow it was the large downstream catchments that had the highest over predictions of DOC (Fig. 8b). The fact that this landscape type was significant only during baseflow indicates that it is related to changing flow paths in large catchments during baseflow. Lyon et al. (2012) have shown that there is considerable variability in specific discharge in the study catchment and that this affects the DOC exports to the different sites within the catchment. The water in the downstream main stem has a signal more similar to deep groundwater with low DOC concentrations and high base cation concentrations (Klaminder et al., 2011). The over predicted DOC concentration in the main stem of Krycklan could therefore be related to a large contribution of deeper low DOC groundwater at this scale, diluting the DOC concentrations during baseflow situations. In the factor analysis by Lyon et al. (2012), high specific discharge during

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baseflow correlates with areas rich in sediment, which are the same sites where the DOC concentration are underestimated using the landscape-mixing approach (Fig. 7). This lends support to the idea that low DOC groundwater from the sedimentary downstream part of the catchment could be an important source of water during baseflow, and help to explain the low model performance during those conditions. However, more work is needed to quantify and fully understand the change in hydrological pathways during baseflow.

To conclude, the landscape-mixing model was a useful tool for predicting stream DOC, especially during high flows. Using the landscape-mixing model as a base-line in combination with a residual analysis, showed when and where simple mixing did not apply and how the conceptual framework for DOC models must be adapted in space and time. During baseflow it may be necessary to consider dilution by low DOC groundwater as another end-member in larger downstream catchments.

Acknowledgements. The study is a part of the Krycklan Catchment Study (KCS) which is funded by The Swedish Research Council, Formas, ForWater, Future Forests, SKB, Kempe foundation and involves many skilled, helpful scientists and students. Particular thanks go to the Krycklan crew for excellent field and lab support.

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Table 1. Discharge (mm day^{-1}) for each sampling occasion and the estimated end-member concentrations (mg L^{-1}) from bootstrapping ($n = 15$). R^2 is the R^2 from the bootstrapping procedure (Eq. 1). To the right is the uncertainty in modelled concentrations expressed as coefficient of variation (CV) from the Monte Carlo analysis.

	Discharge	Discharge	Peat (A)	Till (B)	Sorted sediments (C)	R^2	Uncertainty (CV)
	mm day^{-1}		mg L^{-1}	mg L^{-1}	mg L^{-1}		
May 2003	1.01	High	40.1	12.1	4.7	0.69	0.39
Apr 2004	2.70	High	38.9	16.2	10.5	0.53	0.38
Feb 2005	0.17	Low	33.8	10.4	6.6	0.07	1.20
Jun 2005	0.23	Low	24.6	12.9	4.3	0.38	0.61
Jul 2007	0.06	Low	18.0	9.6	1.0	0.18	1.02
May 2008	0.98	High	30.8	12.0	4.7	0.53	0.48
Sep 2008	0.56	Intermediate	68.0	14.4	1.2	0.64	0.55

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Table 2. Model performance measures for the landscape-mixing model ($n = 15$). Root mean square error (RMSE), percent bias (PBIAS), standard regression measures of R^2 and slope from solid line in Fig. 4, RMSE-observation standard variation ratio (RSR) and Nash Sutcliffe Efficiency (NSE).

	Flow	RMSE	RSR	PBIAS (%)	R^2 from Fig. 4	Slope from Fig. 4	NSE
May 2003	High	2.84	0.68	−1	0.56	0.68	0.54
Apr 2004	High	3.91	0.87	−5	0.28	0.35	0.22
Feb 2005	Low	4.81	1.07	−40	0.61	0.42	−0.15
Jun 2005	Low	4.01	0.80	−6	0.46	0.27	0.36
Jul 2007	Low	3.67	0.80	3	0.46	0.24	0.35
May 2008	High	2.24	0.80	−9	0.54	0.63	0.34
Sep 2008	Intermediate	4.46	0.70	−6	0.57	0.72	0.50

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Table 3. The left-hand columns denote the RMSE, RSR, NSE and PBIAS for the model if the bootstrapping calculations of the end-member concentrations were done using the whole dataset ($n = 73$–89). The improvement in the model performance when using the whole dataset for calculating the end-member concentrations compared to $n = 15$ is shown in the last four columns.

	RMSE	RSR	NSE	PBIAS (%)	Improvement in RMSE between $n = 15$ and $n = 73$–89	Improvement in RSR between $n = 15$ and $n = 73$–89	Improvement in NSE between $n = 15$ and $n = 73$–89	Improvement in PBIAS between $n = 15$ and $n = 73$–89
May 2003	2.73	0.65	0.57	0	0.11	0.03	0.03	1
Apr 2004	3.70	0.83	0.30	−1	0.21	0.04	0.05	4
Feb 2005	2.86	0.63	0.59	−7	1.95	0.44	0.73	33
Jun 2005	3.58	0.71	0.49	−1	0.43	0.09	0.12	5
Jul 2007	3.39	0.74	0.45	0	0.28	0.06	0.09	3
May 2008	1.86	0.67	0.55	−2	0.38	0.13	0.18	7
Sep 2008	4.07	0.64	0.59	−1	0.39	0.06	0.08	5

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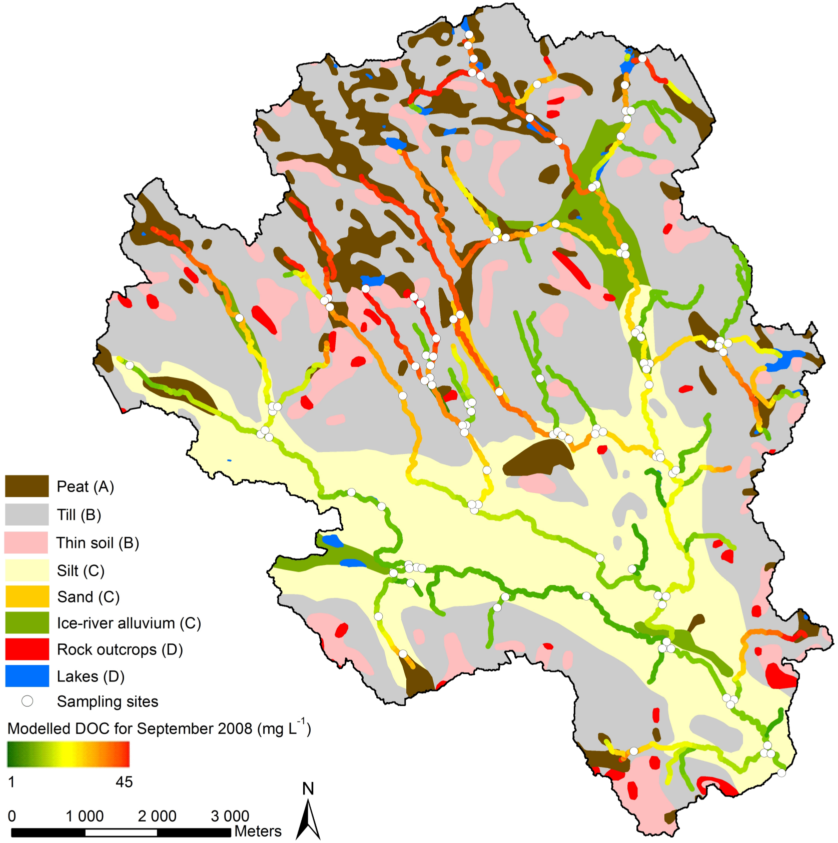

Fig. 1. Map showing the quaternary deposits for the catchment, the aggregation of the soil cover into groups is indicated in the legend (letters A–D) according to the regression model used to estimate DOC concentrations. Superimposed on the map is a layer showing the modelled DOC concentrations (September 2008) for every 5 m section of the stream network. The white dots indicate the 115 sampling sites.

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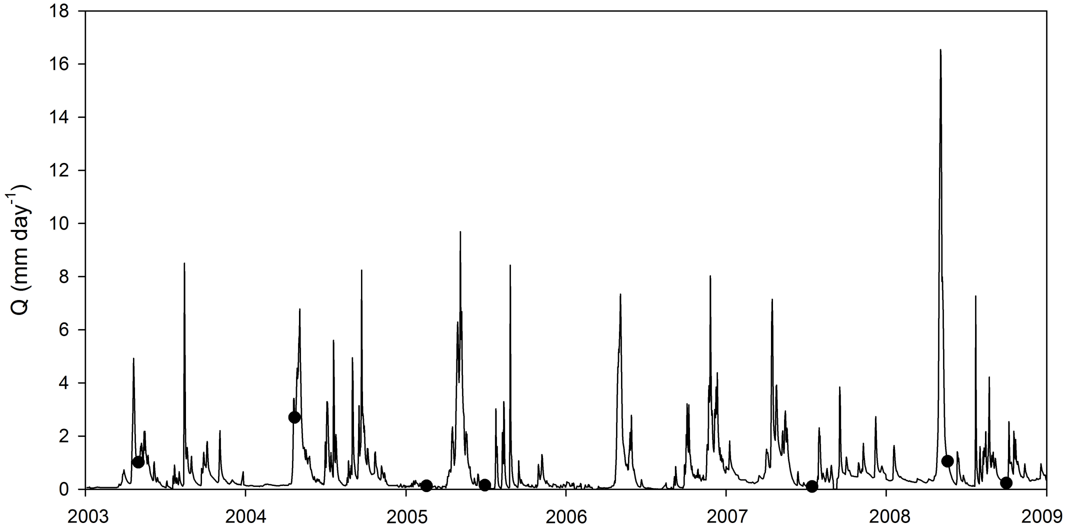

Fig. 2. The variability in discharge 2003–2008, the black dots indicate the dates for the 7 sampling occasions.

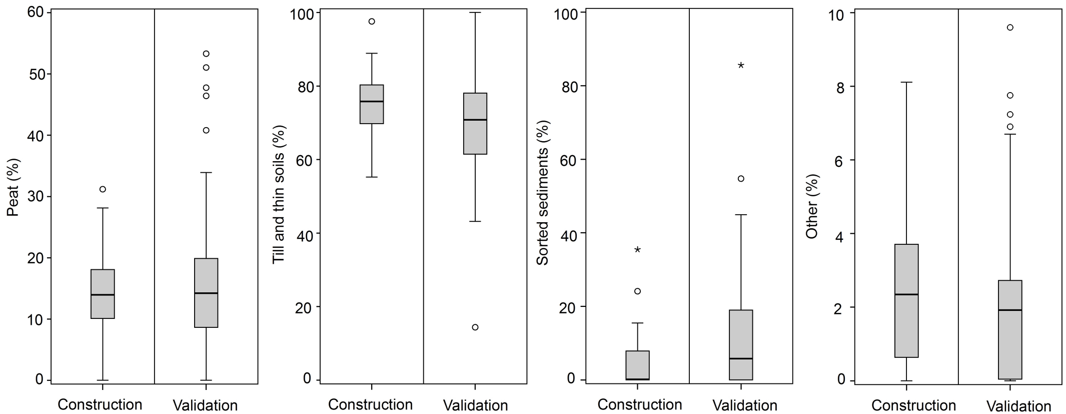

Fig. 3. Boxplots showing the variability of the different soil coverage for the subcatchments of the construction dataset ($n = 15$) and the validation dataset ($n = 100$).

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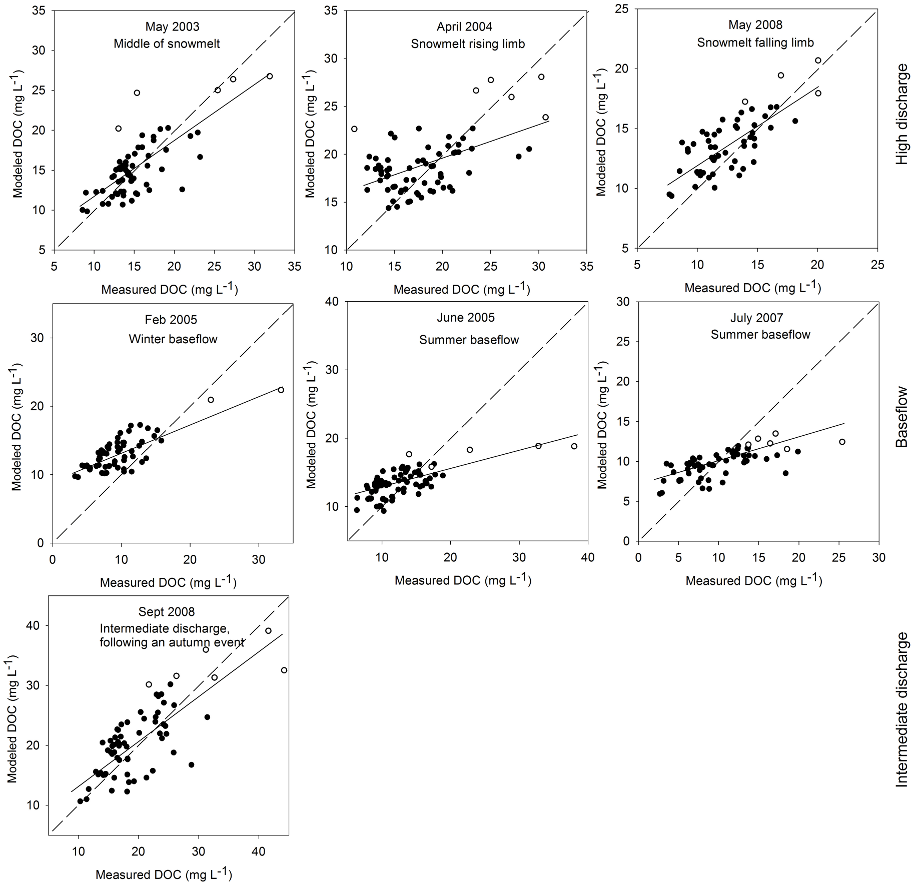

Fig. 4. Modelled vs. measured DOC concentrations for the 7 occasions. Catchments with peat coverage above 30 % are highlighted with unfilled circles. The dashed line is the 1 : 1 line and black line show the regression line for all sites (black dots and unfilled circles).

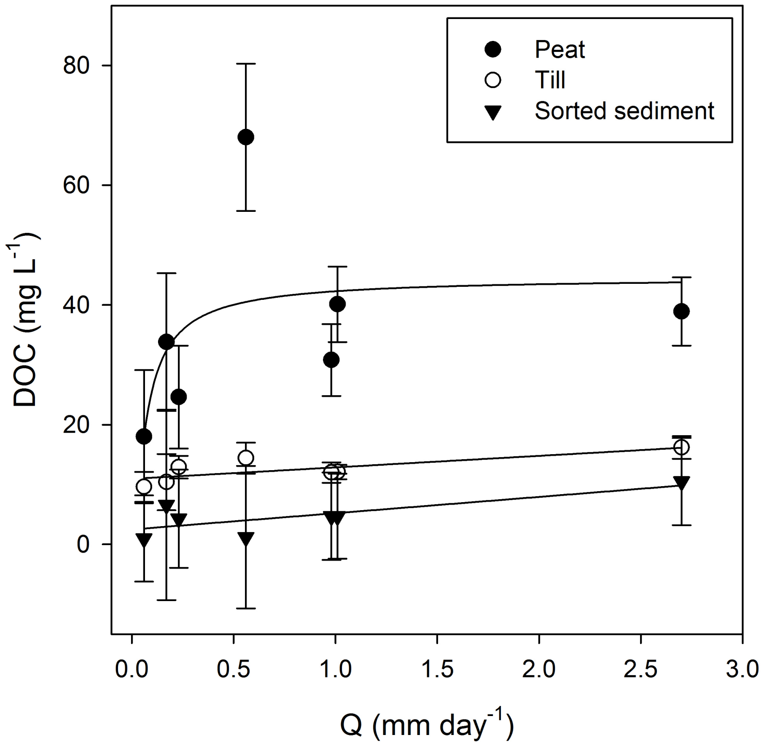

Fig. 5. The end-member concentrations as a function of discharge. Error bars give standard error for the bootstrapped end-member concentrations. Sorted sediment (R^2 = 0.59, p = 0.04) and till (R^2 = 0.60, p = 0.04) are described with linear relationships, and peat (R^2 = 0.52, p = 0.06) with an S-curve.

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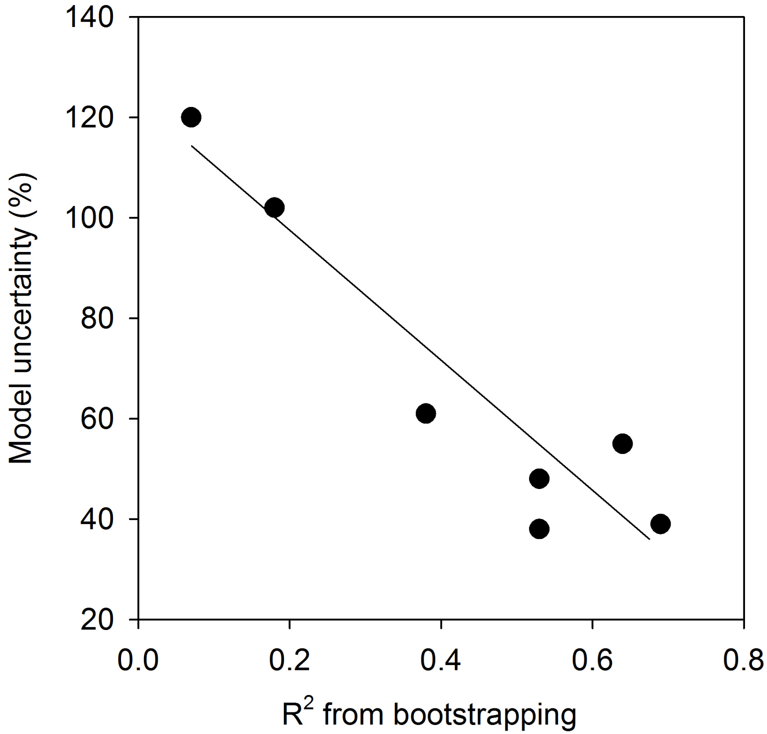

Fig. 6. The model uncertainty from the Monte Carlo analysis (%) for the different occasions plotted against the coefficient of determination (R^2) for the bootstrapping models where the estimates were constructed.

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Can dissolved organic carbon be explained by landscape elements?

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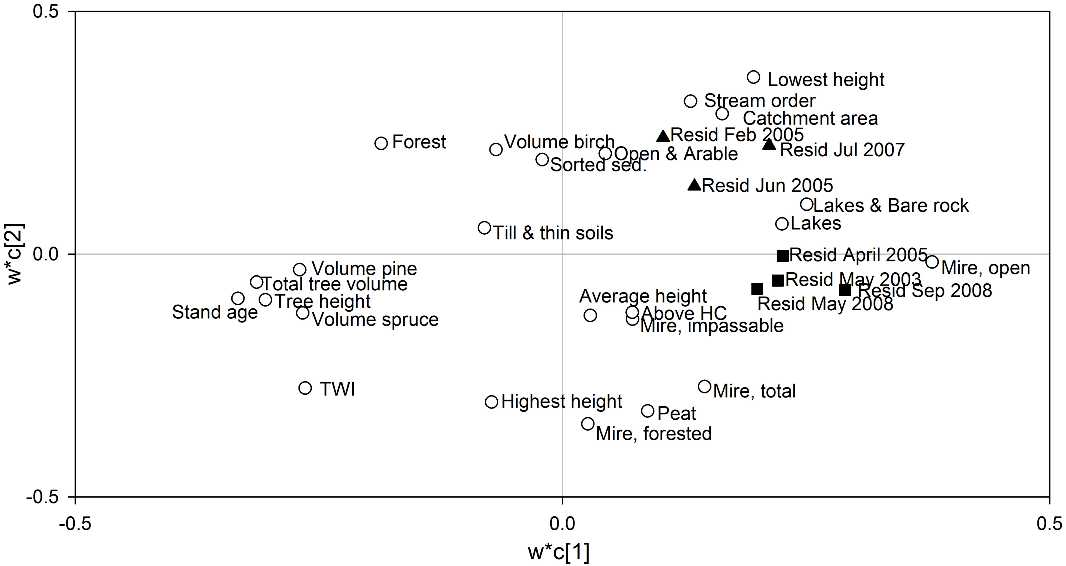

Fig. 7. PLS loading plot for all residuals and landscape properties. Open circles denotes *X* variables, black squares indicate the residuals during high and intermediate discharge and black triangles indicate the residuals from base flow occasions.

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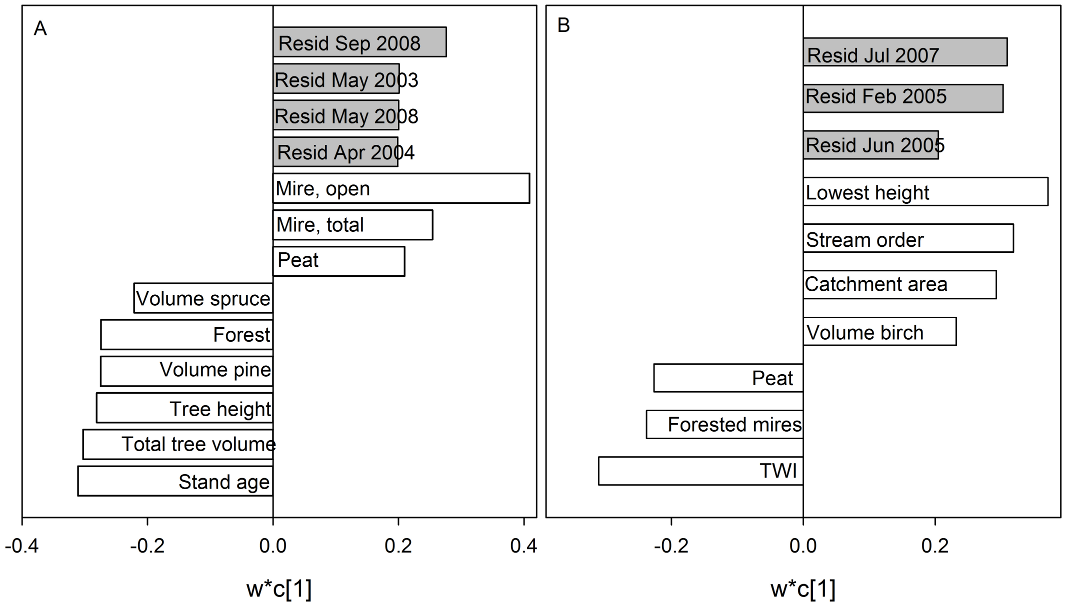

Fig. 8. PLS Loading plot showing the significant variables with high weight that explain the residuals during **(A)** high – intermediate discharge and **(B)** baseflow.

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Can dissolved organic carbon be explained by landscape elements?

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