Biogeosciences Discuss., 12, 9005–9041, 2015
www.biogeosciences-discuss.net/12/9005/2015/
doi:10.5194/bgd-12-9005-2015

Biogeosciences
Discussions
Open Access

Map-based prediction of organic carbon in headwaters streams improved by downstream observations from the river outlet

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Received: 25 May 2015 – Accepted: 26 May 2015 – Published: 16 June 2015

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

Abstract

In spite of the great abundance and ecological importance of headwater streams, managers are usually limited by a lack of information about water chemistry in these headwaters. In this study we test whether river outlet chemistry can be used as an additional source of information to improve the prediction of the chemistry of upstream headwaters (size $< 2\,\mathrm{km}^2$), relative to models based on map information alone. Between 2000 and 2008, we conducted 17 synoptic surveys of streams within 9 mesoscale catchments (size 32–235 km^2). Over 900 water samples were collected from catchments ranging in size from 0.03 to $235\,\mathrm{km}^2$. First we used partial least square regression (PLS) to model headwater stream total organic carbon (TOC) median and interquartile values for a given catchment, based on a large number of candidate variables including catchment characteristics from GIS, and measured chemistry at the catchment outlet. The best candidate variables from the PLS models were then used in hierarchical linear mixed models (MM) to model TOC in individual headwater streams. Three predictor variables were consistently selected for the MM calibration sets: (1) proportion of forested wetlands in the sub-catchment (positively correlated with headwater stream TOC), (2) proportion of lake surface cover in the sub-catchment (negatively correlated with headwater stream TOC), and (3) whole-catchment river outlet TOC (positively correlated with headwater stream TOC). Including river outlet TOC as a predictor in the models gave 5–15 % lower prediction errors than using map information alone. Thus, data on water chemistry measured at river outlets offers information which can complement GIS-based modelling of headwater stream chemistry.

1 Introduction

Headwaters make up most of the watercourse length and hence provide a large proportion of the lotic habitat in a landscape (Meyer et al., 2007). The headwaters also combine to provide much of the water and solutes to downstream locations (Person et al., 1936; Leopold et al., 1964). It is widely known that variability in water chemistry changes with catchment size, typically with small watercourses showing the highest variability in space (Wolock et al., 1997; Temnerud and Bishop, 2005) and time (Nagorski et al., 2003; Buffam et al., 2007). Significant field sampling efforts (Hutchins et al., 1999; Smart et al., 2001; Likens and Buso, 2006; McGuire et al., 2014) have been made to quantify the variability of headwaters in individual catchments. Readily derived GIS data from maps and satellite images have been used to model some chemical constituents in larger rivers (Alexander et al., 2007), but are seldom effective at predicting the chemistry of individual headwater streams (Strayer et al., 2003b, a; Temnerud et al., 2010). This is presumably in large part due to the greater importance of small-scale heterogeneity in headwater catchment characteristics, as compared to riverine catchments where much of the variability averages out at larger spatial scales (Gomi et al., 2002; MacDonald and Coe, 2007).

Since aquatic monitoring activities are generally located at downstream sites (Evans et al., 2010), this might provide information about the headwaters upstream from the monitoring sites. In an attempt to use environmental monitoring data to predict seldom assessed headwater streams, the chemistry at the river outlet was used by Temnerud et al. (2010) to predict the median and interquartile range (IQR) of several environmentally relevant stream chemistry parameters, including total organic carbon (TOC), acid neutralizing capacity (ANC) and pH. This demonstrated that the river outlets were correlated to statistical features of the upstream population of headwaters. In that study significant relationships were found for ANC, pH and TOC between headwaters median and IQR vs. the river outlets, with the strongest relationships for ANC, and the weakest for TOC. Of seven different leave-one-out attempts one model was significant for headwater median TOC and none for headwater TOC IQR (Temnerud et al., 2010). No map information was employed in that study.

In this study the goal was to test whether map information can be combined with river outlet chemistry to predict TOC in individual headwaters. More specifically, did the combination of map and river outlet chemistry gave a better prediction than either one used separately. In this follow-up study we have chosen to focus solely on the prediction of TOC, for two main reasons. First, TOC is of great ecological importance for boreal and many north temperate watercourses because of its influence on pH, buffering capacity, bioavailability of nutrients, metals and pollutants, as well as light climate, energy available to micro-organisms and of course impacts on carbon cycling (Wetzel, 2001; Schwarzenbach et al., 2003). Secondly, the statistical distribution of headwater TOC was not well predicted in the previous study using only downstream chemistry as the predictor (Temnerud et al., 2010). If the approach succeeds with TOC, then there is reason to hope that it would be even more effective in predicting other aspects of water chemistry.

An important aspect of modelling headwaters is that the spatial variation is largely dependent on temporal factors, often flow-related (Buffam et al., 2007), but also season (temperature and precipitation) and even long-term trends (Hytteborn et al., 2015). This temporal variation within a single headwater can be greater than the variation of TOC between catchments in the same biome. We want to make the reader aware that it could be easier to model headwaters in different catchments (at the same time) than headwaters in the same catchments that are sampled at different times.

Thus we modelled headwaters TOC-concentration’s on several occasions in different stream networks by combining catchment map information (Andersson and Nyberg, 2009), to complement data on the river outlet TOC-concentration.

While this may seem straight-forward, there are in fact some theoretical challenges; the method must deal with both strong correlations between observations and between explanatory variables. We used a two-step modelling approach to handle these challenges. First we used partial least square regression (PLS), which can deal with strong correlations between explanatory variables, to model headwater stream TOC median and IQR-values from information derived from catchment land cover, geology, soil type maps and vegetation (kNN). Candidate explanatory variables from the PLS models were then used in hierarchical linear mixed models (MM). Such MM have the advantage of being able to deal with strong correlations between observations, so MM were used in the next step to model individual headwater streams. Thus, MM can account for the clustered data structure of catchment properties in a drainage network (Littell et al., 2006). Mixed models have been used rather successfully in related types of data evaluation (Jager et al., 2011; Sakamaki and Richardson, 2013). Two major distinguishing features of what we present here are that we (i) tested a combination of information from maps (GIS) with direct measurements of chemistry at the river outlet, to create models of individual headwaters and (ii) we tested our models on data that was not used in the calibrations.

2 Methods

2.1 Sampling approach

The synoptic surveys used in this study were designed to provide a snapshot of the water chemistry in stream networks (Table 1 and Fig. 1). In total there were data from 17 synoptic surveys conducted between 2000 and 2008 in nine catchments distributed across Sweden (Fig. 1). This data set amounted to 938 stream samples of which 420 were from headwaters. The catchments span a north–south gradient of 800 km through the north-temperate and boreal zones. All sampling during a given survey was carried out during a one to three day period, except for R. Krycklan in winter 2005 (two weeks due to cold weather and difficulties finding the streams in deep snow, but discharge was stable winter base flow).

Five of the nine catchments have at least one headwater stream site that has been monitored for runoff and chemistry regularly for a decade or more (Edström and Rystam, 1994; Temnerud et al., 2009; Köhler et al., 2008; Löfgren et al., 2011; Laudon et al., 2013). Of the other four catchments, R. Ottervattsbäcken was sampled twice and R. Vänjaurbäcken sampled once (the name R. Sörbäcken are used in the references, which is a tributary in R. Vänjaurbäcken, Temnerud and Bishop, 2005; Temnerud et al., 2007) while R. Viggan and R. Mangslidsälven were sampled once, for this study.

2.2 Study sites

Headwaters are defined as first order streams with catchments smaller than 2 km^2 in each of the nine drainage networks sampled (Table 1). All catchments consisted mainly of forest (> 80 %) with a dominance of Norway spruce (*Picea abies*) (Table S1 in the Supplement). Mires and small humic lakes made up most of the remaining parts of the catchments, while the proportion of agricultural and developed areas were minimal (< 1 %). The mean annual air temperature in the river catchments (1990–2010) ranged from 7.8 °C in the southernmost river, R. Anråse å, to 2.6 °C in the northernmost, Krycklan. Mean annual precipitation (1990–2010) ranged from 980 mm at R. Anråse å, to 649 mm at R. Vänjaurbäcken.

Daily mean air temperature, daily precipitation and daily runoff for 1961–2010 at each river outlet was modelled by the Swedish Meteorological and Hydrological Institute (SMHI) (Johansson, 2000; Johansson and Chen, 2003), data received 20 June 2013 from http://luftweb.smhi.se. Daily runoff for 1990–2010 at each river outlet was modelled based on Hydrological Predictions for the Environment program (HYPE) (Lindström et al., 2010), data received 20 June 2013 from http://vattenweb.smhi.se. Typical accuracy in the HYPE modelling for small catchments (< 200 km^2) is 10 % (Strömqvist et al., 2012; Arheimer and Lindström, 2013). Catchment-specific daily mean air temperature, total precipitation and mean specific discharge are illustrated in (Fig. S1 in the Supplement) for the period of 30 days up to and including each sampling.

2.3 Map information

To relate headwater TOC to catchment characteristics, we began with 34 catchment parameters (Table S1 in the Supplement) taken from the Swedish land cover data map (SMD), year 2000, version 2.1, which is based on the CORINE database (Bossard et al., 2000) as well as Geology and Quaternary deposits from the Geological Survey of Sweden (SGU) map, scale 1.1 million. The kNN-database of vegetation that has forestry variables estimated from LANDSAT 5 and LANDSAT 7 satellite photos (version

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year 2000, Reese et al., 2003, 2002), provided data about the average age and height of the forest as well as volume of the biomass for different tree species. All catchment map information uses the same version, year and scale of the maps so that the map data are commensurate between catchments (Table S1 in the Supplement).

2.4 Chemical analyses

After collection, all water samples were kept dark and cool until they were analysed. Total organic carbon (TOC) was measured by combustion and analysis as CO_2 using a Shimadzu TOC-VPCH analyser after acidification and sparging to remove inorganic carbon. Dissolved organic carbon (DOC) is the concentration of organic carbon in a filtered (common cut-off is 0.45 µm filter) water sample. It has previously been shown that DOC and TOC differ on average by less than 5 % (Ivarsson and Jansson, 1994; Köhler, 1999), so TOC is essentially identical to DOC in the large majority of the Swedish surface waters (see also Gadmar et al., 2002; Laudon et al., 2011).

2.5 Statistical analysis

The main objective of this article is to model the TOC of individual headwaters based on map information and river outlet TOC. To be able to reproduce correct TOC levels in the headwaters we need to be able to (i) predict the average level for each catchment and (ii) describe variation within the catchments. We use the following two-step approach:

i. first we describe the distribution of the response variable, headwater's TOC, on a catchment level using map information and river outlet TOC. For this we model the median of headwater TOC using PLS on median values of available explanatory variables. We also predict the variation within each catchment, expressed as interquartile range (IQR), using the same explanatory variables. PLS is in both cases used since we have many potentially correlated candidate variables.

ii. In the next step we model the TOC of individual headwaters by hierarchical linear mixed models (MM), which can account for the clustered data structure of our dataset, i.e. can account for correlations between headwaters within the same catchment. For this model the explanatory variables that were identified as important in step (i) are used. To further be able to describe within-catchment variation additional explanatory variables were also tested.

We are particularly interested in determining whether models based on geographical data, like lake surface coverage, forest coverage or altitude can be improved by adding concentrations measured at the river outlet.

2.5.1 Modelling headwater median and interquartile range

To model the median and interquartile range of TOC in headwaters in different catchments we use partial least squares regression (PLS). Variables included in this model are TOC at the river outlet (OutletTOC) and a number of variables describing information derived from land cover, geology, soil type maps and vegetation (kNN) (Table S1 in the Supplement).

All data, both explanatory and response variables, were centred by mean normalisation and weighted by dividing the variables with the standard deviation prior to PLS analysis in SIMCA for Windows v13.0 (Umetrics). PLS identifies the relationship between explanatory variables and response variables through a linear model, and is less sensitive to correlated explanatory variables (so-called multicollinearity) when compared to multiple linear regression approaches (Geladi and Kowalski, 1986), since the explanatory variables are combined to factors. For the same reason PLS also allows the inclusion of more explanatory variables than there are observations.

In the PLS analyses, the goodness-of-fit parameter Q^2 was used to quantify the model performance, which is the average ($n = 7$, default value in SIMCA) explained variance of a randomly selected fraction (1/7 of the data) of the validation data not used to fit the model. In robust models, R^2 and Q^2 are often similar, but the latter will decline as models become increasingly over-fit. Even though PLS models work by defining factors, i.e. combinations of explanatory variables, it is also possible to compute coefficients and weights that describe the direction and relative strength of the individual explanatory variables on the response variable; weights with larger absolute values indicate greater importance to a given latent component. All PLS-models were refined by iteratively removing variables that had non-significant coefficients. This procedure served to minimize the difference between R^2 and Q^2 values while retaining high explanatory power, i.e. to find a model that can be generalized to new data, while retaining good explanatory power. The relative importance of each explanatory variable is ranked using “variable importance on the projection” (VIP) scores, derived as the sum of square of the PLS weights across all components. VIP values greater than one are considered to indicate variables that are most important to the overall model (Eriksson et al., 2006).

PLS allows for more explanatory variables than observations and gives us therefore the possibility to include many candidate variables. Still, some of the variables available needed to be excluded for the following reasons:

- some variables, e.g. volume of oak, had zero value for all observations or only few observations different from zero. These variables could not be included due to the lack of variation in them.
- Geographical variables for the river outlet were not included, since they correlate highly with the median of the corresponding variable at the headwater scale. The latter is considered to bear more information and was therefore included.

The analysis was run on three calibration data sets: one with data from year 2000 where headwaters within four mesoscale catchments (these catchments are called A) were sampled $\mathrm{Cal_{PLS}00_A}$ ($n = 4$; M0, O0, Vä0, Vi0). In $\mathrm{Cal_{PLS}07_B}$ the headwaters of five mesoscale catchments (catchments B) were sampled in 2007 ($n = 5$; A7, D7, G7, K7, L7) and in $\mathrm{Cal_{PLS}08_B}$, the same five mesoscale catchments as in $\mathrm{Cal_{PLS}07}$, were sampled in 2008 ($n = 5$; A8, D8, G8, K8, L8). The test data sets consist of the same groupings, but were not used in the calibrations ($\text{Test}_{\text{PLS}}00_{\text{A}}$, $\text{Test}_{\text{PLS}}07_{\text{B}}$, $\text{Test}_{\text{PLS}}08_{\text{B}}$).

After running the three different models we determined whether the same variables appeared to be important (VIP > 1) in the model fittings. These variables were taken as good candidates to reproduce the general TOC level of the headwaters and therefore included in the modelling of the individual headwaters. An additional test set was created, $\text{Test}_{\text{PLS}}02\&05_{\text{C}}$, which was comprised of data from the two catchments sampled once in 2002 and twice in 2005 (catchments C, $n = 3$; O2, K5s, K5w, where s stands for summer and w for winter). No calibration was done on this data set.

2.5.2 Modelling individual headwaters

When modelling individual headwaters we want to reproduce individual values for the different headwaters in all catchments, which leads to a new data structure, where we need to assume that headwaters within the same catchment are more similar to each other than to headwaters from other catchments. To model this data structure we use hierarchical linear mixed models (MM; Littell et al., 2006), which allow the estimation of the correlation between headwaters within the same catchment and adjusts the analysis accordingly. A MM does not allow highly correlated explanatory variables, so the number of explanatory variables must be substantially smaller than the number of observations. To fit these models we use candidate explanatory variables from the PLS approach described in Sect. 2.5.1. In the PLS analysis some explanatory variables were excluded due to a large number of zero values. Some of these variables can still be interesting in modelling individual headwaters, for example lake surface coverage. If lakes have a moderately large volume (appreciable residence time) they are known to influence the organic content (Eriksson, 1929; Birge and Juday, 1926). Therefore lake cover surface is expected to have an influence on the prediction of individual headwater TOC, even though this variable could not be used in the PLS (median value was zero) to explain the median TOC of several headwaters.

MMs were performed using package lme4 (version 1.1-7) in the software R (version 3.1.2) (R Development Core Team, 2014). Headwater data from year 2000 (numbers of headwaters = 69; M0, O0, Vä0, Vi0), 2007 ($n_{\mathrm{HW}} = 138$; A7, D7, G7, K7, L7) or 2008 ($n_{\mathrm{HW}} = 148$; A8, D8, G8, K8, L8) were used as calibration data sets (denoted $\mathrm{Cal_{MM}00_A}$, $\mathrm{Cal_{MM}07_B}$ and $\mathrm{Cal_{MM}08_B}$, respectively), one set at a time. We have two objectives in this approach:

i. to make predictions on the same headwaters but at different time points. For this observations for 2008 ($\mathrm{Test_{MM}08_B}$) are predicted by the calibration $\mathrm{Cal_{MM}07_B}$, and observations for 2007 ($\mathrm{Test_{MM}07_B}$) are predicted by $\mathrm{Cal_{MM}08_B}$.

ii. To make predictions on a new set of headwaters at a different time point. For this:

  - observations from 2002 and 2005 ($\mathrm{Test_{MM}02\&05_C}$), 2007 ($\mathrm{Test_{MM}07_B}$) and 2008 ($\mathrm{Test_{MM}08_B}$) respectively were predicted by $\mathrm{Cal_{MM}00_A}$ and
  - observations from 2000 ($\mathrm{Test_{MM}00_A}$), 2002 and 2005 ($\mathrm{Test_{MM}02\&05_C}$) were predicted by $\mathrm{Cal_{MM}07_B}$ and $\mathrm{Cal_{MM}08_B}$, respectively.

$\mathrm{Test_{MM}02\&05}$ is sampled in one catchment 2002 and two times in another catchment in 2005 ($n_{\mathrm{HW}} = 65$; O2, K5s, K5w, where s stands for summer and w for winter), no calibration was done on this data set. We used the testing to see if the calibrations worked on other data sets which were not included in the calibration.

To test the impact of including TOC at river outlet (OutletTOC) on the MM performance, three versions of each calibration data set were run:

- version Out includes OutletTOC but no map information,
- version Map includes map information but not OutletTOC while
- version OutMap includes both OutletTOC and map information.

In total nine different MM were calibrated.

For model fitting of the MM, Akaike information criterion (AIC) (Akaike, 1974) and p values were used. AIC is a goodness-of fit measure, which is corrected for the complexity of the model, similar to the adjusted R^2. The p values in regression models determine if parameter estimates are significantly different from zero, i.e. if there is a significant relationship between an explanatory variable and the response. The p values were calculated according to Kenward and Roger (1997) using “krmodcomp” in R package “pbkrtest” (version 0.4-1). During the model fitting, added variables were checked to see if they increased the predictive ability of the model by computing the prediction error sum of squares (PRESS). The smaller the PRESS value the closer is the prediction to the observed values. Kenward and Roger (1997) version of R^2 for predictions is called P^2 (similar to Q^2 for PLS). The P^2 were calculated according to Méndez Mediavilla et al. (2008), with the modification that instead of leave-one-out validation we compute P^2 on the evaluation test sets: $P^2 = 1 - \text{PRESS}/\text{TSS}$ where TSS is the total sum of squared differences between modelled values and the mean of observations in the evaluation set. Median absolute (MedAE) and relative errors (MedRE%) were also calculated.

As an additional step in the evaluation of the models the most successful MM from the nine MM calibrations was tested on the sites between the headwaters and the river outlets, the intermediate sites ($n = 501$).

3 Results

For all synoptic surveys the headwater median TOCs were higher than the values at the respective outlets (Table 2), with large differences (> 20 %) for 14 of 17 synoptic surveys. The headwater median TOC for all surveys together (12 mg L^{-1}) was higher than the median outlet TOC of 10 mg L^{-1} (Fig. 2 and Table 2). For all synoptic surveys, except A8, there was a funnel-shape in the TOC concentration with larger variation in smaller catchments that attenuates with increasing catchment size (Fig. 2). Reproducing this variation in the headwaters, and assigning individual headwaters to the proper value within that large variation, is one of the challenges of modelling water chemistry in a landscape perspective.

3.1 Modelling headwater median

For both PLS calibration sets year 2007 and 2008 the first principal component (PC) was significant in the PLS-models for median headwater TOC, but not the second PC. No significant PLS-model was established using calibration set year 2000 ($\mathrm{Cal_{PLS}00_A}$). Calibration using data set 2007 ($\mathrm{Cal_{PLS}07_B}$) gave higher R^2 and Q^2 than using data set for 2008 calibration ($\mathrm{Cal_{PLS}08_B}$) (Table 3). Verification based on the evaluation data of $\mathrm{Cal_{PLS}08_B}$, that is all other data than 2008, had lower PRESS for median TOC than similar data for $\mathrm{Cal_{PLS}07_B}$ (Table 3). Based on PLS-modelling of median headwater TOC, suitable candidates for the mixed models (MM) of individual headwaters were: altitude of sampling sites, OutletTOC, proportion of clear-felled, coniferous forest, mixed forest, wet mires, coniferous forest on mires as well as the volume of birch-, spruce- and total forest volume.

3.2 Modelling headwater interquartile range (IQR)

For both PLS calibration sets year 2007 and 2008 the first principal component (PC) was significant in the PLS-models for IQR headwater TOC, but not the second PC. No significant PLS-model was established using calibration set year 2000 ($\mathrm{Cal_{PLS}00_A}$). Verification based on the evaluation data of $\mathrm{Cal_{PLS}07_B}$, that is all other data than 2007, had lower PRESS for TOC IQR than similar data for $\mathrm{Cal_{PLS}08_B}$ (Table 3). Headwaters IQR of TOC modelled by PLS indicates three variables as suitable candidates for the MM: OutletTOC, proportion of clear-felled area and birch volume.

3.3 Modelling individual headwaters

The PLS approach from Sect. 3.1 identified the variables that can determine the median level of TOC on a range of different catchments. In the following analysis we seek variables to reproduce both the median levels as well as describe the within-catchment variability. We did this with two separate approaches:

i. We determine which variables best can capture the within-catchment variation in headwater TOC. To do this we fit a model to $\mathrm{Cal_{MM}07_B}$ and $\mathrm{Cal_{MM}08_B}$ respectively and predict the observations from 2007 ($\mathrm{Test_{MM}07_B}$) and 2008 ($\mathrm{Test_{MM}08_B}$).

ii. We examined which variables can determine the correct overall level of TOC as well as capture the within-catchment variation. To do this we fit a model to $\mathrm{Cal_{MM}00_A}$, one model for all these catchments, and predict observations from 2002 and 2005 ($\mathrm{Test_{MM}02\&05_C}$), 2007 ($\mathrm{Test_{MM}07_B}$) and 2008 ($\mathrm{Test_{MM}08_B}$). A model for $\mathrm{Cal_{MM}07_B}$ and $\mathrm{Cal_{MM}08_B}$ was used to predict values from 2000 ($\mathrm{Test_{MM}00_A}$), 2002 and 2005 ($\mathrm{Test_{MM}02\&05_C}$).

3.3.1 Modelling individual headwaters and predicting those same headwaters at other points in time

When we fit the models to a calibration set, e.g. headwaters measured in 2007, we start with a base model consisting of the variables identified by the PLS model for the interquartile range, i.e. OutletTOC on the catchment scale and proportion wet mires as well as volume birch, with different values for different headwaters. The base model was fitted with a MM using catchment as the random factor describing the hierarchical structure. Other variables were included in a forward selection procedure always adding the most significant variable of the remaining set of variables. Candidate variables used in this were all land use variables (including lake surface coverage) and all variables giving the volume of different tree species with exception of the volume of oak and beech, since these volumes are generally very low and zero for many headwaters. After fitting the model the ability to predict new data was tested and non-significant variables in the model were individually removed to check if their removal also worsened the predictive ability of the model.

The models gained from this procedure are listed in Table 4. The models produced by $Cal_{MM}07_B$ and $Cal_{MM}08_B$ were very similar and can predict the data at the same sites quite well, i.e. the $Cal_{MM}07_B$ model can predict the $Test_{MM}08_B$ data set well and the other way round (Figs. 4 and 5 and Table 5).

3.3.2 Modelling individual headwaters and predicting new headwaters at other time points

When we use the calibration set $Cal_{MM}00_A$ to fit a model, the variables selected (same procedure as in Sect. 3.3.1) were OutletTOC, lake surface coverage and coniferous forest on mires. We evaluate this model by predicting values in the test sets $Test_{MM}07_B$ and $Test_{MM}08_B$ (Fig. 3). The best prediction model parameters are given in Table 4, with model performance in Fig. 3 and error results in Table 5. Predictions for new sites in the test set $Test_{MM}00_A$ and $Test_{MM}02\&05_C$ are less satisfactory and indicate that the models might be over fitting the data.

3.3.3 Evaluation on intermediate sites

The headwater models were also tested on the sites of intermediate size (i.e. $> 2\,km^2$) but excluding the river outlet (lower parts of Table 5). In general the intermediate sites were modelled as successfully as the headwaters (Table 5). $Cal_{MM}07_B$ gave predictions for the intermediate sites which were not as good as for the other data sets, i.e. higher MedRE%, than $Cal_{MM}08_B$ and $Cal_{MM}00_A$.

3.3.4 Evaluation of river outlets

In an attempt to test the effect of including the river outlet TOC on the performance of MM predictions for individual headwaters, three versions of each calibration were used with same map variables for each calibration data set but different calibrated coefficients (Table 4). Out of 27 different combinations of MM (three different calibration data sets, three versions of each calibration (Out, Map, OutMap) and three different test data sets), the OutMap version (OutletTOC and map information combined) gave the best performance with the lowest PRESS, while two Map versions (map information only, no OutletTOC included) gave the lowest PRESS (Table 5 and Figs. 3–5). Similar results were observed for the intermediate sites (Table 5 and Figs. 3–5). The OutMap version gave 5–15 % better predictions than Map only.

4 Discussion

With the approach in this study we were able to achieve P^2 values around 50 %, indicating that about 50 % of the variation in the individual headwater test sets can be explained with a model including the explanatory variables OutletTOC, lake surface coverage and proportion of coniferous forests on mires. In two of the three calibrations, the proportion of broad-leaved forest and elevation were also significant.

In 25 of 27 tests, including OutletTOC resulted in lower errors in predictions of the TOC for individual headwaters and intermediate sites, compared to using map information alone. The measurements at the river outlet were necessary to reproduce more correct average headwater TOC levels. Excluding the OutletTOC measurements leads to the assumption that average TOC levels in the headwaters were similar in different catchment stream networks if the map information is similar, which is not always true (cf sampling 2007 and 2008).

To predict the correct mean values for headwater TOC is still a challenge in our application of mixed models, since the calibration sets consist of 4–5 catchment systems, and these were sampled only a few times for each calibration. This clearly makes generalisations to new catchments or flow-situations difficult and uncertain. Calibration sets Cal07 and Cal08 share most of the catchments, but are measured during different years and perhaps more importantly, during different flow situations and seasons. Even if most headwaters are the same in $\text{Cal}_{\text{MM}}07_{\text{B}}$ and $\text{Cal}_{\text{MM}}08_{\text{B}}$, and the models produced were similar, it was still not possible to account for more than about 50 % of the variation in the other set of data, indicating that there is large variability in time.

Weather is a factor that varies with time and influences stream water chemistry. In our approach we did not include the weather related data (temperature, precipitation, flow) in the models (PLS and MM) since it was not available for headwaters, but only for the river outlet. Presumably discharge for each headwater could benefit the models, but measuring discharge at all individual headwaters would have been very time consuming (and were not performed). To model discharge with appropriate accuracy at all these headwaters (size $< 2\,\text{km}^2$) is so far too difficult to perform due to large heterogeneity at these small scales (Lyon et al., 2012), and lack of precipitation data for all these headwaters.

Most lakes in these catchments are dimictic (mixing of the lake from the surface to bottom twice each year). Some of the data used in this study (year 2007 and 2008) has been used to evaluate the impact of lakes on stream water chemistry and there were indications that lake influence differs as a function of season, catchment and constituent (Lyon et al., 2011). The presence of lakes had a stronger influence on stream water TOC levels in October 2007 than in April 2008. Thus the presence of lakes could influence the impact of river outlet TOC on headwater TOC in MM. Lakes are known to often decrease TOC concentration (Müller et al., 2013; Weyhenmeyer et al., 2012), although this effect is not always visible at a landscape scale (Lottig et al., 2013) and lakes can also delay pulses of TOC within river networks, which is a complicating factor (Hytteborn et al., 2015).

The proportion of coniferous forest on mires had a positive sign and proportion of lake surface coverage had a negative sign for all calibration sets, which is plausible based on earlier studies (Andersson and Nyberg, 2009; Pers et al., 2001; Oni et al., 2013; Lottig et al., 2013; Clark et al., 2010). Ågren et al. (2014), Hope et al. (1997), Löfgren et al. (2014), Mattsson et al. (2003) and Walker et al. (2012) have also found that the amount of organic matter in the catchment soils (mire, wet- or peat land proportion) is often positively correlated with stream TOC concentration (e.g. Mulholland et al., 2001), even if the extent of organic soils can be hard to estimate from maps (Creed et al., 2003; Johnston et al., 2008).

That broad-leaved forest had a negative coefficient for $\mathrm{Cal07_B}$ and $\mathrm{Cal08_B}$ (Tables 4 and 5) could be related to several factors. In these systems most of the broad-leaved forest is made up of birch (*Betula pendula*). The negative coefficient of broad-leaved/birch could be a direct effect of birch on water chemistry; more birch in a coniferous landscape could give runoff with lower organic carbon (Brandtberg et al., 2000; Fröberg et al., 2011). However, in a set of explanatory variables like this, with a large amount of geographical information, many of the variables are correlated. This results in the fact that similarly good models could be found with other sets of explanatory variables. For instance, in our data set we found high correlations among volume of various tree species, furthermore volume of Pine also had high correlation with these variables: proportion of coniferous forest, site altitude, volume of birch, broad-leaved forest and volume of spruce.

In this work we use calibration sets and test sets rather than the popular leave-one-out cross-validation method, since we have dependent, clustered data. Shao (1993) showed that leave-one-out cross-validation tends to select unnecessarily large models if observations are correlated. Libiseller and Grimvall (2003) showed that this is true for data that are serially correlated, since a single removed observation can be reproduced easily by observations in the temporal vicinity of the left-out observation. The same should hold for clustered data, where a single left-out headwater would be reasonably predicted by other headwaters in the same catchment.

In Temnerud et al. (2010) data from A7, D7, G7, K5, L7, O0 and S0 (S is a tributary in Vä0 and most data are the same) were used in leave-one-out cross-validation linear models on median and IQR TOC. In that study, one model of seven gave a significant median TOC model. In the current data set with nine catchments we observed that the differences between catchments were quite large and could partly (P^2 around 50 %; Table 5) be described by the included variables for individual headwaters.

5 Conclusion

The mixed models approach, using river outlets TOC and map information, could explain up to 52 % of the variance in TOC among individual headwater streams. This is far better performance than the attempt by Temnerud et al. (2010) in which only one of seven different leave-one-out attempts gave a significant model for headwater median TOC and none gave significant models for headwater TOC IQR. Since the used method increased the predictability for TOC, it would be interesting to evaluate if the method could improve prediction of headwaters pH and ANC, which worked better than TOC in Temnerud et al. (2010).

In order to have the same map resolution for all catchments, due to lack of universal availability of fine-scale data, a rather coarse resolution was used (e.g. 50 m grid data for altitude and soil map of scale 1.1 million). The Swedish authorities are LiDAR scanning all of Sweden to build a 2 m grid digital elevation model and are generating maps connecting all watercourses up to the headwaters (through lakes and wetlands), which by 2017 will provide new data that could help in modelling the headwaters. This improved map information might further improve the mixed model approach demonstrated here that which includes river outlet chemistry. This will hopefully get us closer to the ability to predict individual headwaters that are such vital building blocks of aquatic ecosystems, but remain so very difficult to model.

The Supplement related to this article is available online at doi:10.5194/bgd-12-9005-2015-supplement.

Acknowledgements. Financial support for this research was provided by the Swedish University of Agricultural Sciences, the Swedish Environmental Protection Agency project Climate Change and Environmental Objectives (CLEO), MISTRA Future Forests and, for Johan Temnerud, the Knowledge Foundation. We would like to thank all samplers and laboratories for

excellent work. Mats Fröberg is acknowledged for help on birch impact on organic carbon in soils and streams.

References

Ågren, A. M., Buffam, I., Cooper, D. M., Tiwari, T., Evans, C. D., and Laudon, H.: Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements?, Biogeosciences, 11, 1199–1213, doi:10.5194/bg-11-1199-2014, 2014.

Akaike, H.: A new look at the statistical model identification, IEEE T. Autom. Contr., 19, 716–723, doi:10.1109/TAC.1974.1100705, 1974.

Alexander, R. B., Boyer, E. W., Smith, R. A., Schwarz, G. E., and Moore, R. B.: The role of headwater streams in downstream water quality, J. Am. Water Resour. As., 43, 41–59, doi:10.1111/j.1752-1688.2007.00005.x, 2007.

Andersson, J.-O. and Nyberg, L.: Using official map data on topography, wetlands and vegetation cover for prediction of stream water chemistry in boreal headwater catchments, Hydrol. Earth Syst. Sci., 13, 537–549, doi:10.5194/hess-13-537-2009, 2009.

Arheimer, B. and Lindström, G.: Implementing the EU Water Framework Directive in Sweden, in: Runoff Predictions in Ungauged Basins – Synthesis across Processes, Places and Scales, edited by: Blöschl, G., Sivapalan, M., Wagener, T., Viglione, A., and Savenije, H., Cambridge University Press, Cambridge, 353–359, 2013.

Birge, E. A. and Juday, C.: The organic content of lake water, P. Natl. Acad. Sci. USA, 12, 515–519, 1926.

Bossard, M., Feranec, J., and Otahel, J.: CORINE land cover technical guide – Addendum 2000, European Environment Agency, Copenhagen, 105 pp., available at: http://www.eea.europa.eu/publications/COR0-landcover (last access: 12 June 2015), 2000.

Brandtberg, P. O., Lundkvist, H., and Bengtsson, J.: Changes in forest-floor chemistry caused by a birch admixture in Norway spruce stands, Forest Ecol. Manag., 130, 253–264, doi:10.1016/S0378-1127(99)00183-8, 2000.

Buffam, I., Laudon, H., Temnerud, J., Mörth, C.-M., and Bishop, K.: Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network, J. Geophys. Res.-Biogeo., 112, G01022, doi:10.1029/2006JG000218, 2007.

Clark, J. M., Bottrell, S. H., Evans, C. D., Monteith, D. T., Bartlett, R., Rose, R., Newton, R. J., and Chapman, P. J.: The importance of the relationship between scale and process in understanding long-term DOC dynamics, Sci. Total Environ., 408, 2768–2775, doi:10.1016/j.scitotenv.2010.02.046, 2010.

Creed, I. F., Sanford, S. E., Beall, F. D., Molot, L. A., and Dillon, P. J.: Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes, Hydrol. Process., 17, 3629–3648, doi:10.1002/hyp.1357, 2003.

Edström, M. and Rystam, P.: Network of stations for field research area (in Swedish: FFO – Stationsnät för fältforskningsområden), SMHI hydrology report 53, Swedish Meteorological and Hydrological Institute, Norrköping, 53 pp., 1994.

Eriksson, J. V.: Den kemiska denudationen i Sverige (The chemical denudation of Sweden, in Swedish with a French summary), Report Band 5, Swedish Meteorological and Hydrological Institute, Stockholm, nr. 3, 95 pp., 1929.

Eriksson, L., Johansson, E., Kettaneh-Wold, N., Trygg, J., Wikström, C., and Wold, S.: Multi- and Megavariate Data Analysis – Part 1: Basic Principles and Applications, Umetrics AB, Umeå, 2006.

Evans, C., Cooper, D., Monteith, D., Helliwell, R., Moldan, F., Hall, J., Rowe, E., and Cosby, B.: Linking monitoring and modelling: can long-term datasets be used more effectively as a basis for large-scale prediction?, Biogeochemistry, 101, 211–227, doi:10.1007/s10533-010-9413-x, 2010.

Fröberg, M., Hansson, K., Kleja Berggren, D., and Alavi, G.: Dissolved organic carbon and nitrogen leaching from Scots pine, Norway spruce and silver birch stands in southern Sweden, Forest Ecol. Manag., 262, 1742–1747, doi:10.1016/j.foreco.2011.07.033, 2011.

Gadmar, T. C., Vogt, R. D., and Østerhus, B.: The merits of the high temperature combustion method for determining the amount of natural organic carbon in surface freshwater samples, Int. J. Environ. An. Ch., 82, 451–461, doi:10.1080/0306731021000018099, 2002.

Geladi, P. and Kowalski, B. R.: Partial least-squares regression – a tutorial, Anal. Chim. Acta, 185, 1–17, doi:10.1016/0003-2670(86)80028-9, 1986.

Gomi, T., Sidle, R. C., and Richardson, J. S.: Understanding processes and downstream linkages of headwater systems, Bioscience, 52, 905–916, doi:10.1641/0006-3568(2002)052[0905:UPADLO]2.0.CO;2, 2002.

Hope, D., Billett, M. F., and Cresser, M. S.: Exports of organic carbon in two river systems in NE Scotland, J. Hydrol., 193, 61–82, doi:10.1016/S0022-1694(96)03150-2, 1997.

Hutchins, M. G., Smith, B., Rawlins, B. G., and Lister, T. R.: Temporal and spatial variability of stream waters in Wales, the Welsh borders and part of the West Midlands, UK. 1. Major ion concentrations, Water Res., 33, 3479–3491, doi:10.1016/S0043-1354(99)00057-3, 1999.

Hytteborn, J. K., Temnerud, J., Alexander, R. B., Boyer, E. W., Futter, M. N., Fröberg, M., Dahné, J., and Bishop, K. H.: Patterns and predictability in the intra-annual organic carbon variability across the boreal and hemiboreal landscape, Sci. Total Environ., 520, 260–269, doi:10.1016/j.scitotenv.2015.03.041, 2015.

Ivarsson, H. and Jansson, M.: Temporal variations in the concentration and character of dissolved organic matter in a highly colored stream in the coastal zone of northern Sweden, Arch. Hydrobiol., 132, 45–55, 1994.

Jager, H. I., Bevelhimer, M. S., King, R. L., and Smith, K. A.: Landscape influences on headwater streams on Fort Stewart, Georgia, USA, Environ. Manage., 48, 795–807, doi:10.1007/s00267-011-9722-4, 2011.

Johansson, B.: Areal precipitation and temperature in the Swedish Mountains – an evaluation from a hydrological perspective, Nord. Hydrol., 31, 207–228, 2000.

Johansson, B. and Chen, D. L.: The influence of wind and topography on precipitation distribution in Sweden: statistical analysis and modelling, Int. J. Climatol., 23, 1523–1535, doi:10.1002/joc.951, 2003.

Johnston, C. A., Shmagin, B. A., Frost, P. C., Cherrier, C., Larson, J. H., Lamberti, G. A., and Bridgham, S. D.: Wetland types and wetland maps differ in ability to predict dissolved organic carbon concentrations in streams, Sci. Total Environ., 404, 326–334, doi:10.1016/j.scitotenv.2007.11.005, 2008.

Kenward, M. G. and Roger, J. H.: Small sample inference for fixed effects from restricted maximum likelihood, Biometrics, 53, 983–997, doi:10.2307/2533558, 1997.

Köhler, S.: Quantifying the role of natural organic acids on pH and buffering in Swedish surface waters, Doctoral Thesis, Forest Ecology, Swedish University of Agricultural Sciences, Umeå, 163 pp., 1999.

Köhler, S. J., Buffam, I., Laudon, H., and Bishop, K. H.: Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements, J. Geophys. Res.-Biogeo., 113, G03012, doi:10.1029/2007JG000629, 2008.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., and Köhler, S.: Patterns and dynamics of dissolved organic carbon (DOC) in boreal streams: the role of processes, connectivity, and scaling, Ecosystems, 14, 880–893, doi:10.1007/s10021-011-9452-8, 2011.

Laudon, H., Taberman, I., Ågren, A., Futter, M., Ottosson-Löfvenius, M., and Bishop, K.: The Krycklan Catchment study – a flagship infrastructure for hydrology, biogeochemistry and climate research in the boreal landscape, Water Resour. Res., 49, 7154–7158, doi:10.1002/wrcr.20520, 2013.

Leopold, L. B., Wolman, M. G., and Miller, J. P.: Fluvial Processes in Geomorphology, A Series of Books in Geology, edited by: Gilluly, J. and Woodford, A. O., W. H. Freeman and Company, San Francisco, 522 pp., 1964.

Libiseller, C. and Grimvall, A.: Model selection for local and regional meteorological normalisation of background concentrations of tropospheric ozone, Atmos. Environ., 37, 3923–3931, doi:10.1016/S1352-2310(03)00502-8, 2003.

Likens, G. E. and Buso, D. C.: Variation in streamwater chemistry throughout the Hubbard Brook Valley, Biogeochemistry, 78, 1–30, doi:10.1007/s10533-005-2024-2, 2006.

Lindström, G., Pers, C., Rosberg, J., Strömqvist, J., and Arheimer, B.: Development and testing of the HYPE (Hydrological Predictions for the Environment) water quality model for different spatial scales, Hydrol. Res., 41, 295–319, doi:10.2166/nh.2010.007, 2010.

Littell, R., Milliken, G., Stroup, W., Wolfinger, R., and Schabenberger, O.: SAS for Mixed Models, 2nd Edn., SAS Institute, Cary, 828 pp., 2006.

Löfgren, S., Aastrup, M., Bringmark, L., Hultberg, H., Lewin-Pihlblad, L., Lundin, L., Karlsson, G. P., and Thunholm, B.: Recovery of soil water, groundwater, and streamwater from acidification at the Swedish Integrated Monitoring catchments, AMBIO, 40, 836–856, doi:10.1007/s13280-011-0207-8, 2011.

Löfgren, S., Fröberg, M., Yu, J., Nisell, J., and Ranneby, B.: Water chemistry in 179 randomly selected Swedish headwater streams related to forest production, clear-felling and climate, Environ. Monit. Assess., 186, 8907–8928, doi:10.1007/s10661-014-4054-5, 2014.

Lottig, N. R., Buffam, I., and Stanley, E. H.: Comparisons of wetland and drainage lake influences on stream dissolved carbon concentrations and yields in a north temperate lake-rich region, Aquat. Sci., 75, 1–12, doi:10.1007/s00027-013-0305-8, 2013.

Lyon, S. W., Braun, H., and Temnerud, J.: Accounting for instream lakes when interpolating stream water chemistry observations, Journal of Spatial Hydrology, 11, 1–20, available at: http://www.spatialhydrology.net/index.php/JOSH/article/view/102 (last access: 12 June 2015), 2011.

Lyon, S. W., Nathanson, M., Spans, A., Grabs, T., Laudon, H., Temnerud, J., Bishop, K. H., and Seibert, J.: Specific discharge variability in a boreal landscape, Water Resour. Res., 48, W08506, doi:10.1029/2011WR011073, 2012.

MacDonald, L. H. and Coe, D.: Influence of headwater streams on downstream reaches in forested areas, Forest Sci., 53, 148–168, 2007.

Mattsson, T., Finér, L., Kortelainen, P., and Sallantaus, T.: Brook water quality and background leaching from unmanaged forested catchments in Finland, Water Air Soil Poll., 147, 275–297, doi:10.1023/A:1024525328220, 2003.

McGuire, K. J., Torgersen, C. E., Likens, G. E., Buso, D. C., Lowe, W. H., and Bailey, S. W.: Network analysis reveals multiscale controls on streamwater chemistry, P. Natl. Acad. Sci. USA, 111, 7030–7035, doi:10.1073/pnas.1404820111, 2014.

Méndez Mediavilla, F. A., Landrum, F., and Shah, V.: A comparison of the coefficient of predictive power, the coefficient of determination and AIC for linear regression, in: Proceedings of the 39th Annual Meeting of the Decision Sciences Institute, Atlanta, 2008.

Meyer, J. L., Strayer, D. L., Wallace, J. B., Eggert, S. L., Helfman, G. S., and Leonard, N. E.: The contribution of headwater streams to biodiversity in river networks, J. Am. Water Resour. As., 43, 86–103, doi:10.1111/j.1752-1688.2007.00008.x, 2007.

Mulholland, P. J., Fellows, C. S., Tank, J. L., Grimm, N. B., Webster, J. R., Hamilton, S. K., Martí, E., Ashkenas, L., Bowden, W. B., Dodds, W. K., McDowell, W. H., Paul, M. J., and Peterson, B. J.: Inter-biome comparison of factors controlling stream metabolism, Freshwater Biol., 46, 1503–1517, doi:10.1046/j.1365-2427.2001.00773.x, 2001.

Müller, R. A., Futter, M. N., Sobek, S., Nisell, J., Bishop, K., and Weyhenmeyer, G. A.: Water renewal along the aquatic continuum offsets cumulative retention by lakes: implications for the character of organic carbon in boreal lakes, Aquat. Sci., 75, 535–545, doi:10.1007/s00027-013-0298-3, 2013.

Nagorski, S. A., Moore, J. N., McKinnon, T. E., and Smith, D. B.: Scale-dependent temporal variations in stream water geochemistry, Environ. Sci. Technol., 37, 859–864, doi:10.1021/es025983+, 2003.

Oni, S. K., Futter, M. N., Bishop, K., Köhler, S. J., Ottosson-Löfvenius, M., and Laudon, H.: Long-term patterns in dissolved organic carbon, major elements and trace metals in boreal headwater catchments: trends, mechanisms and heterogeneity, Biogeosciences, 10, 2315–2330, doi:10.5194/bg-10-2315-2013, 2013.

Pers, C., Rahm, L., Jonsson, A., Bergström, A.-K., and Jansson, M.: Modelling dissolved organic carbon turnover in humic Lake Örträsket, Sweden, Environ. Model. Assess., 6, 159–172, doi:10.1023/A:1011953730983, 2001.

Person, H. S., Johnston, C. E., and Beall, R. T.: Little waters; a study of headwater streams & other little waters, their use and relations to the land, the Upstream Engineering Conference, Washington DC, 1–82, available at: http://www.archive.org/details/littlewatersstud00persrich (last access: 12 June 2015), 1936.

Reese, H., Nilsson, M., Sandström, P., and Olsson, H.: Applications using estimates of forest parameters derived from satellite and forest inventory data, Comput. Electron. Agr., 37, 37–55, doi:10.1016/S0168-1699(02)00118-7, 2002.

Reese, H., Nilsson, M., Granqvist Pahlén, T., Hagner, O., Joyce, S., Tingelöf, U., Egberth, M., and Olsson, H.: Countrywide estimates of forest variables using satellite data and field data from the national forest inventory, AMBIO, 33, 542–548, doi:10.1579/0044-7447-32.8.542, 2003.

Sakamaki, T. and Richardson, J. S.: Nonlinear variation of stream–forest linkage along a stream-size gradient: an assessment using biogeochemical proxies of in-stream fine particulate organic matter, J. Appl. Ecol., 50, 1019–1027, doi:10.1111/1365-2664.12099, 2013.

Schwarzenbach, R. P., Gschwend, P. M., and Imboden, D. M.: Environmental Organic Chemistry, 2nd Edn., John Wiley, Hoboken, 1313 pp., 2003.

Shao, J.: Linear model selection by cross-validation, J. Am. Stat. Assoc., 88, 486–494, doi:10.1080/01621459.1993.10476299, 1993.

Smart, R. P., Soulsby, C., Cresser, M. S., Wade, A. J., Townend, J., Billett, M. F., and Langan, S.: Riparian zone influence on stream water chemistry at different spatial scales: a GIS-based modelling approach, an example for the Dee, NE Scotland, Sci. Total Environ., 280, 173–193, doi:10.1016/S0048-9697(01)00824-5, 2001.

Strayer, D. L., Beighley, R. E., Thompson, L. C., Brooks, S., Nilsson, C., Pinay, G., and Naiman, R. J.: Effects of land cover on stream ecosystems: roles of empirical models and scaling issues, Ecosystems, 6, 407–423, doi:10.1007/PL00021506, 2003a.

Strayer, D. L., Ewing, H. A., and Bigelow, S.: What kind of spatial and temporal details are required in models of heterogeneous systems?, Oikos, 102, 654–662, doi:10.1034/j.1600-0706.2003.12184.x, 2003b.

Strömqvist, J., Arheimer, B., Dahné, J., Donnelly, C., and Lindström, G.: Water and nutrient predictions in ungauged basins: set-up and evaluation of a model at the national scale, Hydrolog. Sci. J., 57, 229–247, doi:10.1080/02626667.2011.637497, 2012.

Temnerud, J. and Bishop, K.: Spatial variation of streamwater chemistry in two Swedish boreal catchments: implications for environmental assessment, Environ. Sci. Technol., 39, 1463–1469, doi:10.1021/es040045q, 2005.

Temnerud, J., Seibert, J., Jansson, M., and Bishop, K.: Spatial variation in discharge and concentrations of organic carbon in a catchment network of boreal streams in Northern Sweden, J. Hydrol., 342, 72–87, doi:10.1016/j.jhydrol.2007.05.015, 2007.

Temnerud, J., Fölster, J., Pilström, F., and Bishop, K.: Synoptisk provtagning av små vattendrag i södra Sverige oktober 2007 (Synoptical sampling of small watercourses in southern Sweden in October 2007, in Swedish), Swedish University of Agricultural Sciences, Uppsala, Report 2009:6, 56 pp., available at: http://publikationer.slu.se/Filer/Rapport2009-6.pdf (last access: 12 June 2015), 2009.

Temnerud, J., Fölster, J., Buffam, I., Laudon, H., Erlandsson, M., and Bishop, K.: Can the distribution of headwater stream chemistry be predicted from downstream observations?, Hydrol. Process., 24, 2269–2276, doi:10.1002/hyp.7615, 2010.

Walker, C. M., King, R. S., Whigham, D. F., and Baird, S. J.: Landscape and wetland influences on headwater stream chemistry in the Kenai Lowlands, Alaska, Wetlands, 32, 301–310, doi:10.1007/s13157-011-0260-x, 2012.

Wetzel, R. G.: Limnology. Lake and River Ecosystems, 3rd Edn., Academic Press, London, 1006 pp., 2001.

Weyhenmeyer, G. A., Fröberg, M., Karltun, E., Khalili, M., Kothawala, D., Temnerud, J., and Tranvik, L. J.: Selective decay of terrestrial organic carbon during transport from land to sea, Glob. Change Biol., 18, 349–355, doi:10.1111/j.1365-2486.2011.02544.x, 2012.

Wolock, D. M., Fan, J., and Lawrence, G. B.: Effects on basin size on low-flow stream chemistry and subsurface contact time in the Neversink river watershed, New York, Hydrol. Process., 11, 1273–1286, doi:10.1002/(SICI)1099-1085(199707)11:9<1273::AID-HYP557>3.0.CO;2-S, 1997.

Table 1. Characteristics of the rivers. Cluster is the different calibration and test sets used in the modelling. Air temperature (T °C) and specific discharge (q mm day^{-1}) are median of daily values for 1990–2010, precipitation (P mm) is median of yearly sum. P, T and q are modelled by SMHI, see Methods for more details.

Cluster	River	Lat. N and Long E	Size (km^2)	T	P	q
B	Anråse å[a] (A)	58°01′; 11°51′	74	7.8	983	0.95
B	Danshytteån[a] (D)	59°42′; 15°05′	72	6.1	774	0.70
B	Getryggsån[a] (G)	59°48′; 15°17′	32	5.9	800	0.84
B and C	Krycklan[b] (K)	64°14′; 19°46′	61	2.6	659	0.51
B	Lugnån[a] (L)	57°06′; 14°48′	122	6.1	831	0.60
A	Mangslidsälven (M)	60°23′; 12°54′	235	4.9	823	0.75
A and C	Ottervattsbäcken[c] (O)	64°02′; 19°06′	71	2.6	659	0.50
A	Vänjaurbäcken[c] (Vä)	64°19′; 18°43′	200	2.2	649	0.47
A	Viggan (Vi)	60°21′; 12°46′	116	3.9	870	0.85

[a] Temnerud et al. (2009), [b] Laudon et al. (2013), [c] Temnerud and Bishop (2005).

Table 2. Median values of total organic carbon (TOC, $\mathrm{mg\,L^{-1}}$), with 25 and 75-percentiles in brackets, see Table 1 for river names. Cluster is the different groups of calibration and test sets used in the modelling, set is the different data sets used. HW is headwaters. Month of sampling (M) and number of sampled HW (n_{HW}). Median of 30 Julian days before sampling, for the outlet, of modelled air temperature (T °C), precipitation (P mm) and specific discharge (q $\mathrm{mm\,day^{-1}}$).

Cluster	Set	Year	M	n_{HW}	$\mathrm{TOC_{HW}}$	OutletTOC	T	P	q
B	A7	2007	10	45	8.6 (5.8–12)	6.7	11	4.3	1.3
B	A8	2008	4	45	7.7 (6.6–9.9)	6.9	3.9	2.8	4.4
B	D7	2007	10	34	16 (13–29)	11	9.9	2.0	0.41
B	D8	2008	4	33	12 (9.6–17)	10	1.7	1.2	1.2
B	G7	2007	10	21	27 (18–36)	12	9.1	3.2	0.63
B	G8	2008	4	22	18 (13–20)	8.9	1.3	0.95	1.2
C	K5s	2005	6	24	15 (12–18)	10	13	1.8	0.69
C	K5w	2005	2	17	12 (6.9–17)	5.0	−5.1	0.75	0.16
B	K7	2007	7	12	12 (9.7–15)	4.3	14	2.1	0.26
B	K8	2008	9	22	20 (16–25)	15	11	4.7	1.6
B	L7	2007	10	26	20 (16–32)	15	7.9	1.9	0.91
B	L8	2008	4	26	15 (10–20)	12	0.7	1.2	1.3
A	M0	2000	8	7	19 (13–22)	14	15	1.8	1.3
A	O0	2000	6	31	20 (16–27)	15	9.7	1.4	1.3
C	O2	2002	8	24	20 (14–32)	15	17	3.0	0.21
A	Vä0	2000	6	18	12 (10–15)	9.5	9.9	2.2	1.8
A	Vi0	2000	8	13	16 (9.0–19)	15	14	2.2	1.5

Table 3. Partial least square regression (PLS) results predicting the median (Med) and the interquartile range (IQR) of headwater total organic carbon (TOC) concentration (mg L^{-1}). Cal is calibrated and 00, 07 and 08 refer to sampling year (2000, 2007 and 2008) of catchment (number = *n*). PRESS is the prediction error sum of squares.

Cal	Var	n	R^2	Q^2	PRESS
00_A	Med	4	ns	ns	ns
	IQR	4	ns	ns	ns
07_B	Med	5	96	94	581
	IQR	5	96	92	346
08_B	Med	5	90	83	192
	IQR	5	54	17	530

Table 4. Hierarchical linear mixed models (MM) different coefficients, where headwaters Log_{10} TOC is the response variable. See the Method section for more details.

MM model	Version	Intercept	OutletTOC (mg L^{-1})	Lake surface coverage*	Coniferous forest on mires*	Broad-leaved forest*	Sites altitude (m a.s.l.)
Cal00_A	Out	0.861	0.0245				
	Map	1.156		−1.509	0.592		
	OutMap	0.885	0.0201	−1.479	0.568		
Cal07_B	Out	0.822	0.0380				
	Map	1.074		−1.867	1.022	−0.900	0.000619
	OutMap	0.736	0.0363	−1.863	0.956	−0.970	0.000554
Cal08_B	Out	0.671	0.0439				
	Map	0.913		−0.675	1.303	−0.697	0.000903
	OutMap	0.700	0.0199	−0.684	1.243	−0.740	0.000940

* Is the proportion of respective land class.

Table 5. Hierarchical linear mixed models (MM) results predicting headwater (HW) organic carbon (TOC) concentration in Log10. Cal is calibrated and 00, 07 and 08 refer to sampling year (2000, 2007 and 2008). The different coefficients are found in Table 4. Each calibration has three versions (intercept is always included): Out, Map and OutMap. The Out version includes OutletTOC, the Map version includes the map information, while OutMap includes both OutletTOC and map information. The prediction error sum of squares (PRESS) is the squared differences between observed and predicted values for the *Y* data kept out of the model fitting of the Test sets (00 stands for year 2000, 02 and 05 for 2002 and 2005, 07 for 2007 and 08 for 2008). The bold values show the lowest PRESS of the three versions for that Test data. Intermediate sites (is) stands for sites between headwaters and the river outlet. R^2 for predictions is called P^2 (similar to Q^2 for PLS): $P^2 = 1 - \text{PRESS}/\text{TSS}$ where TSS is the total sum of squared differences between modelled and the mean of observations. AE is absolute error and RE is relative error, calculated on TOC in mg L^{-1}.

Cal	Version	00_A	00_A	00_A	07_B	07_B	07_B	08_B	08_B	08_B
Cal n_{HW}			69			138			148	
Test_{HW}		02 and 05_C	07_B	08_B	00_A	02 and 05_C	08_B	00_A	02 and 05_C	07_B
$n\ \text{Test}_{HW}$		65	138	148	69	65	148	69	65	138
PRESS_{HW}	Out	3.42	8.71	4.78	2.28	3.68	5.98	3.10	4.58	7.92
	Map	2.79	8.51	5.35	**2.24**	**2.70**	3.97	3.17	3.57	7.63
	OutMap	**2.47**	**7.82**	**4.00**	2.26	2.88	**3.92**	**3.01**	**3.45**	**6.26**
P^2_{HW}	Out	13.5	19.8	42.9	9.2	8.5	20.6	5.0	3.3	31.5
	Map	29.4	21.7	36.1	10.8	32.9	47.3	2.7	24.5	34.0
	OutMap	37.6	28.0	52.0	10.1	28.3	48.0	7.5	27.1	45.9
MedAE_{HW}	Out	6.85	8.00	4.99	3.30	4.61	4.89	6.30	6.85	7.52
	Map	4.54	7.24	5.56	7.67	5.79	4.91	7.84	5.43	7.34
	OutMap	6.32	6.59	5.03	8.29	7.51	4.57	7.14	6.84	5.80
$\text{MedRE\%}_{HW}$	Out	45.9	53.4	45.9	47.1	26.8	60.8	33.1	46.6	55.5
	Map	42.1	56.3	52.2	52.2	66.8	39.3	50.6	65.3	53.1
	OutMap	42.1	56.3	52.2	98.1	44.2	35.7	58.6	54.3	48.0
n_{is}		129	155	135	82	129	135	82	129	155
PRESS_{is}	Out	5.59	5.35	3.19	3.24	4.92	6.24	3.30	5.18	5.28
	Map	5.95	7.92	2.98	**2.42**	4.44	**1.71**	2.50	4.17	7.26
	OutMap	**4.45**	**3.93**	**1.41**	2.52	**3.15**	1.92	**2.46**	**3.31**	**4.59**
P^2_{is}	Out	20.3	47.9	52.4	−11.2	19.8	−46.8	−17.8	14.7	26.8
	Map	15.3	22.9	55.5	17.0	27.6	59.6	10.7	31.3	−0.46
	OutMap	36.6	61.8	78.9	13.6	48.6	54.9	12.1	45.4	36.4
MedAE_{is}	Out	3.97	4.22	2.08	5.89	5.10	2.27	5.65	5.22	3.81
	Map	3.74	4.69	3.57	2.90	3.99	2.22	3.29	3.64	4.78
	OutMap	3.63	3.00	2.42	4.18	4.48	2.62	2.66	3.60	3.78
$\text{MedRE\%}_{is}$	Out	40.9	43.0	43.2	69.9	53.6	84.0	41.4	38.9	34.9
	Map	68.2	59.0	36.8	40.6	94.6	23.1	37.3	72.2	50.3
	OutMap	38.2	33.5	23.5	88.4	73.6	25.0	41.6	52.0	40.3

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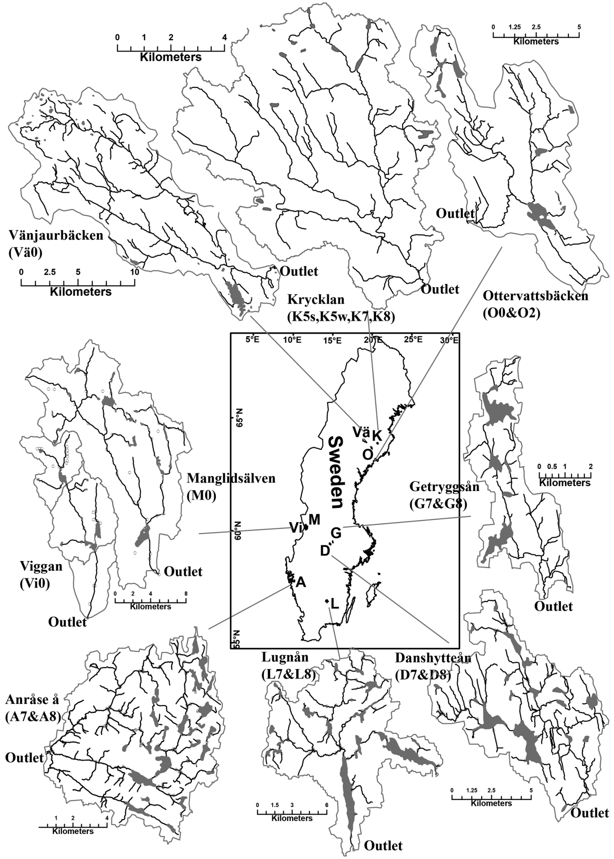

Figure 1. Map of Sweden with the nine investigated catchments, see Table 1 for coordinates. Labels in brackets are the abbreviated names of the catchments and year of sampling.

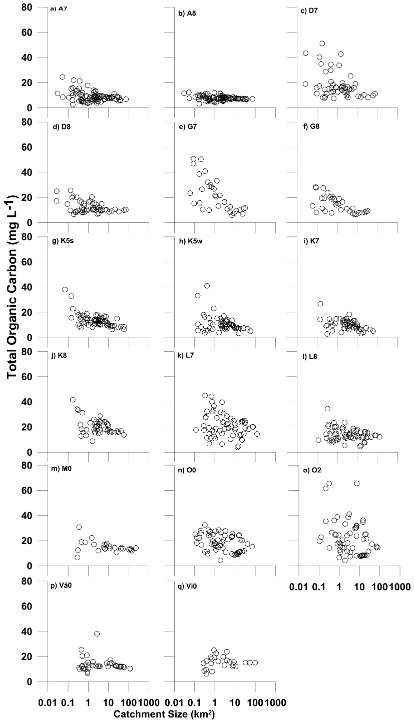

Figure 2. Total organic carbon (TOC in mg L^{-1}) as a function of catchment size (km^2 in Log_{10}) for the nine mesoscale catchments, in total 17 synoptical studies; **(a)** is A7, **(b)** is A8, **(c)** is D7, **(d)** is D8, **(e)** is G7, **(f)** is G8, **(g)** is K5s, **(h)** is K5w, **(i)** is K7, **(j)** is K8, **(k)** is L7, **(l)** is L8, **(m)** is M0, **(n)** is O0, **(o)** is O2, **(p)** is Vä0 and **(q)** is Vi0. See Table 1 for the full catchment names.

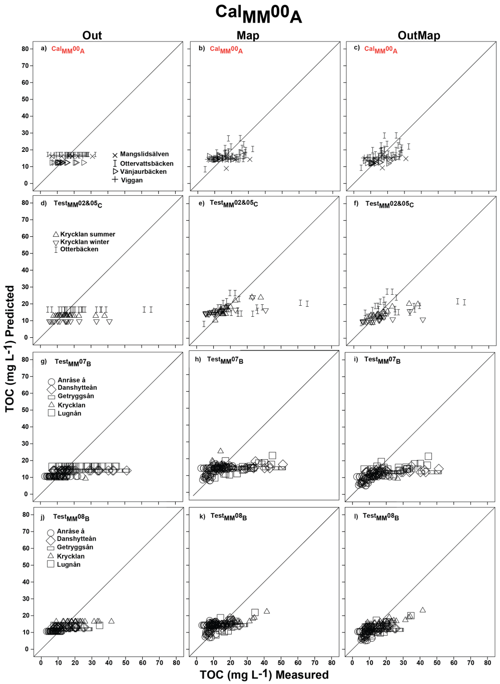

Figure 3. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x axis, and the three different versions of the mixed models $Cal_{MM}00_A$ on the y axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2000 ($Cal_{MM}00_A$) on the top row, followed by Test data; second row 2002 and 2005 data, third row is 2007 data and the last row is 2008 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1 : 1-line.

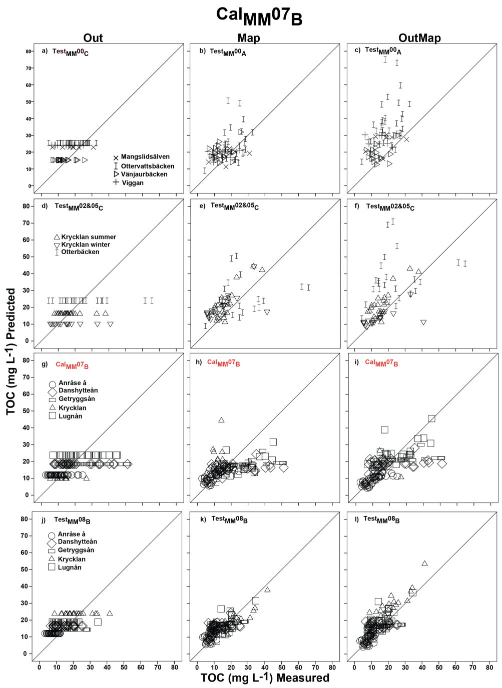

Figure 4. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x axis, and the three different versions of the mixed models $Cal_{MM}07_B$ on the y axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2007 (Cal07) on the third row, followed by Test data; first row 2000 data, second row 2002 and 2005 data and the last row is 2008 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1 : 1-line.

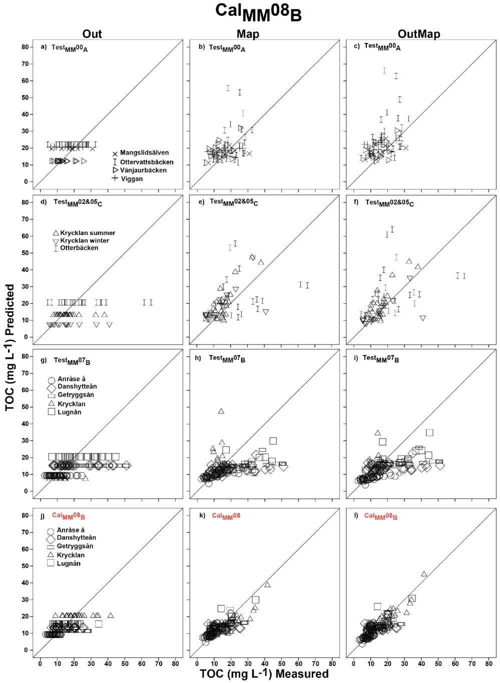

Figure 5. Scatterplots of measured headwaters with total organic carbon (TOC in mg L^{-1}) on the x axis, and the three different versions of the mixed models Cal08 on the y axis: Out version on the left panel, OutMap version on the right panel and Map in-between. Data for year 2008 ($Cal_{MM}08_B$) on the last row, followed by Test data; first row 2000 data, second row 2002 and 2005 data and the third row is 2007 data. R. Anråse å indicated by circles, R. Danshytteån by diamonds, R. Getryggsån by rectangles, R. Krycklan by triangles (winter 2005 by upside-down triangles), R. Lugnån by squares, R. Mangslidsälven by multiplication sign, R. Ottervattsbäcken by up-side-down triangles, R. Vänjaurbäcken by right tilted triangles and R. Viggan by plus sign. The black line is the 1 : 1-line.