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# Spatial variation in discharge and concentrations of organic carbon in a catchment network of boreal streams in northern Sweden

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Landscape variation;  
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Boreal streams;  
Specific discharge;  
REA (representative  
elementary area);  
Monte Carlo simulation

**Summary** Total organic carbon (TOC) is an important feature of water quality in Fennoscandia's till catchments. In this study we estimated the contribution of headwater streams to downstream TOC, tested the hypothesis that TOC-concentration decreases downstream and explored mechanisms for the observed patterns. The drainage network of a boreal catchment (66 sites) in northern Sweden, with subcatchment sizes 0.11–78 km<sup>2</sup>, was sampled in August 2002. In the headwaters there was a large variation in TOC-concentration (4–66 mg l<sup>-1</sup>) as well as other chemical parameters and specific discharge (0.13–8.2 l s<sup>-1</sup> km<sup>-2</sup>). Further downstream there was less variation in both chemistry and specific discharge. Both flow and chemistry stabilized at catchment areas larger than 5 km<sup>2</sup>. No clear indication of in-stream processing effects on downstream TOC was observed, though there was TOC loss at lakes and some stream junctions. To test whether the observed downstream decrease is different than that expected from conservative mixing along the stream network, we used a Monte Carlo approach to simulate downstream conservative mixing. The observed spatial variability was higher than the simulated, indicating that landscape-scale patterns are more than conservative mixing of random inputs. While the importance of in-stream processes that alter TOC-concentrations cannot be ruled out, and loci of TOC loss do exist, we propose that headwater/downstream patterns in TOC, and related parameters depend largely on the mosaic of landscape elements (mires, lakes and forest) together with specific discharge.

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## Introduction

In boreal areas of Fenno-Scandia where watercourses are noticeably colored by organic carbon (OC), the observation has commonly been made that the color of the watercourse decreases as the watercourse increases in size. One early example of this comes from 1929 when Eriksson noted this in his summary of decades of experience with Swedish water chemistry (Eriksson, 1929). Different headwater/downstream patterns in OC are reported for other landscapes. For instance Scottish headwaters are reported to have low OC-concentrations, an increase in the middle of the catchment and then a decrease towards the outlet (Hope et al., 1997). Temperate forests and grasslands also often have an increase in OC downstream, though the absolute values are much lower than found in boreal regions (Findlay and Sinsabaugh, 1999; Mulholland and Kuenzler, 1979).

In Fenno-Scandia and Canada the general understanding of boreal forested catchments is that OC-concentrations are lower downstream (Löfgren et al., 2003; Naiman et al., 1987). These differences in the concentration of OC between boreal headwaters and downstream continue to be identified as an important aspect of understanding large-scale spatial and temporal patterns of OC and related water chemistry parameters in more recent studies as well (Dawson et al., 2004; Humborg et al., 2004; Laudon et al., 2004; Moore, 2003). Given OC's importance for water chemistry (Schwarzenbach et al., 2003; Stumm and Morgan, 1996) and the biota (Dangles et al., 2004), the existence of a general downstream pattern of OC decline would be of great significance for the ecology and assessment of boreal landscapes. More generally, the importance of headwater contributions relative to in-stream processes on OC further downstream is relevant for catchment management decisions focused on water quality objectives at downstream sites.

There are, however, few studies that quantify the downstream patterns of OC in Fenno-Scandia (Eriksson, 1929; Meili, 1992). Lack of a process-level understanding of the reasons for an eventual downstream pattern in OC complicates efforts to monitor and assess the boreal landscape, as well as to predict how climate change and other human influences will alter the aquatic ecosystems spread across the landscape in the network of watercourses and lakes.

Consistent downstream OC declines could result from either differences in downstream runoff inputs or in-stream transformation of OC (Bengtsson and Törneman, 2004; Kortelainen and Saukkonen, 1998; Köhler et al., 2002; Laudon et al., 2004; Mattsson et al., 2003; Sedell and Dahm, 1990). In theory many abiotic and biotic in-stream processes can influence the concentration and character of OC in aquatic systems, even if one only considers processes which could decrease OC in boreal streams during summer base flow (i.e. the period for this study). One example of an abiotic process is precipitation of OC influenced by redox conditions that in turn depend on iron and manganese as catalytic surfaces together with sunlight as an external energy source (McKnight and Bencala, 1990). Other abiotic factors are changes in pH, alkalinity, ionic strength, chemical species differences in the solution matrix (particularly iron and calcium), or mixing with groundwater through the

hyporheic zone (Stumm and Morgan, 1996). At stream junctions with quick mixing of water, abiotic factors could have a large impact. Increasing retention time (e.g. in lakes) increases the impact of rate-limited biotic factors (Pers et al., 2001). Examples of biotic factors are respiration and other metabolic processes (in animals, plants and microorganisms), both passive exudation as well as active uptake and release of OC (Fisher et al., 2002).

In order to quantify the landscape-scale patterns of total organic carbon (TOC) and lay a foundation for understanding their origins, streams from almost the entire drainage network of two catchments, Ottervattsbäcken and Sörbäcken, in northern Sweden were sampled in June 2000 (Temnerud and Bishop, 2005). That survey revealed large inter-stream variability in the TOC of headwaters, and different patterns of TOC when moving downstream along different branches of the drainage networks. Discharge, however, was only measured at a few locations besides the outlet in that study. These observations are the starting point for an analysis in this paper of how contributions from different subcatchments, modified by in-stream processes, create the TOC-concentration patterns in the landscape. The in-stream processes are not measured in this study, but their impact on TOC are estimated through the literature.

A description of landscape-scale patterns in chemical outputs requires that the spatial variation of the discharge has the same resolution of sampling as sites for water chemistry (Grayson et al., 1997; Salvia et al., 1999). Thus in order to make a more adequate analysis of the factors creating downstream TOC patterns, one of the catchments (Ottervattsbäcken) from the 2000 study was resampled in August 2002. This time discharge was measured at many of the sampling sites. This study tests the hypothesis that headwater/downstream differences can be reasonably explained solely by conservative mixing of headwaters with downstream catchment inputs (i.e. without reference to in-stream transformations). Although the focus in this article is on TOC; iron, aluminum, and calcium could be involved in the in-stream processing (precipitation) of TOC. These in-stream processes can also be influenced by alkalinity, pH and ionic strength (here estimated by electrical conductivity). Thus these parameters are also reported, as well as potassium and sodium which are included as semi-conservative tracers.

The TOC data were also used to investigate the contention that downstream mixing of tributaries is associated with a representative elemental area (REA) at which a clear "landscape signal" emerges. Wood et al. (1988) and Beven et al. (1988) proposed the REA as a fundamental building block of catchment modeling. The REA is supposed to be a scale where variability between catchments is at a minimum. The idea is that when the catchment area is large enough, the landscape is sampled sufficiently to represent a mixture of the important characteristics such as hillslopes, wetlands, soils, etc. In the first studies the REA was determined based on modeling (TOPMODEL), where topography and rainfall were considered to vary in space. Later the REA concept was also tested on runoff measurements (Woods et al., 1995). Fan and Bras (1995) raised doubts about the existence and potential utility of the REA concept. One problem with the REA concept is that the different stream sites in the landscape do not represent

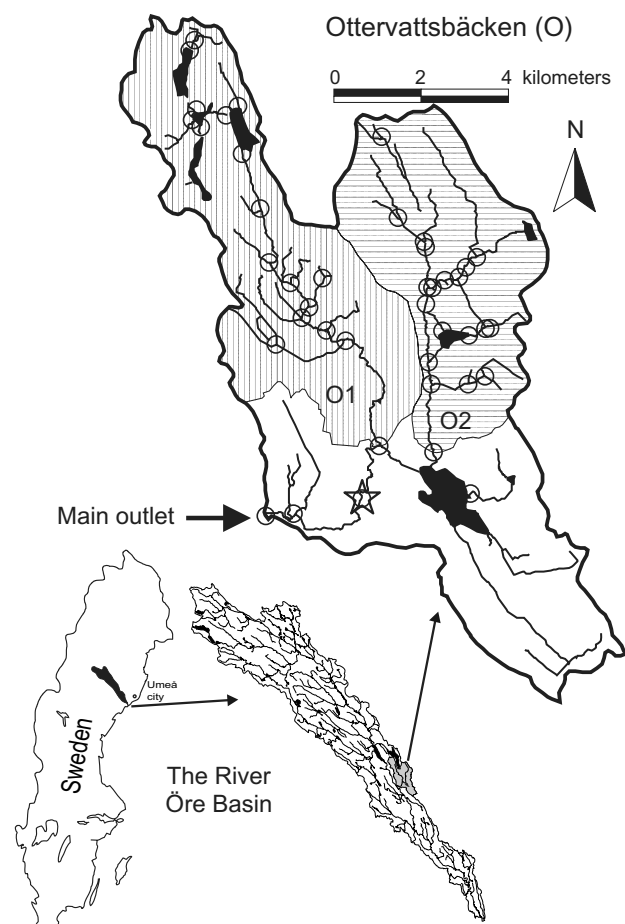
independent measurements but are spatially correlated along the stream network, i.e. the water at a downstream location consists partly of water which already has been measured at an upstream location. The fact that water at downstream locations within a stream network is largely a mixture of water at upstream locations is a simple explanation for the decrease of variability with increasing area. The question is whether the observed decrease is different than the decrease that could be expected from conservative mixing along the stream network. To test this we used a Monte Carlo approach to simulate downstream conservative mixing.

## Study area

The catchment Ottervattsbäcken (78 km<sup>2</sup>) is located in the River Öre basin, northern Sweden (Fig. 1). The catchment elevation ranges from 196 to 370 m a.s.l. with the outlet at N64°02' and E19°06'. The sampled headwater catchments varied in size from 0.11 to 3.5 km<sup>2</sup> with a median area of 0.92 km<sup>2</sup>. The bedrock consists mainly of biotite-rich gneisses of sedimentary origin; the tills are mostly silty-sandy to sandy-silty (Ivarsson and Karlsson, 1992). Till is the dominant soil material (>60%) in the subcatchments, followed by peat 17–26%. The most common soil type is podzol, with an average humus layer thickness of 7 cm (Ivarsson and Karlsson, 1992), followed by wetlands. The riparian zone is often comprised of peat of varying thickness. The mean annual temperature in the study area is 1.0 °C and the precipitation is 650 mm year<sup>-1</sup> (30–45% as snow) with an annual average discharge of 350 mm year<sup>-1</sup> and a calculated evapotranspiration of 300 mm year<sup>-1</sup> (Alexandersson et al., 1991). Forests (approximately 70%) and mires (approximately 18%) dominate the landscape of this catchment, and there is almost no agriculture. The dominant forest types are mixed stands of Norway spruce (*Picea abies*) and Scots pine (*Pinus silvestris*) with a minor contribution of hardwoods, mainly birch (*Betula* spp.). Approximately 55% of Sweden's area is covered by forest, and most of this forested area (82%) is coniferous (NBF, 2004). There is little overt human influence beyond low-intensity forestry. In general the study area represents a common landscape in Sweden and the boreal zone.

The Ottervattsbäcken stream (O) has two main branches, the western Hammonsbäcken (O1, area 28 km<sup>2</sup>) and the eastern Marrabäcken (O2, area 22 km<sup>2</sup>) (Fig. 1). Parts of the catchment (30%) are situated above the highest post-glacial coastline located at approximately 232 m a.s.l. Most of the fine grained materials, clay–silt, in the O catchment are found downstream of the highest post-glacial shoreline. Thus, the small amount of arable land is found downstream of O1 and O2. The relative abundance of lakes, soils and topography in the two branches differs slightly. O1 has a greater percentage of lake surface area (4%) and sand (8%) than O2, which had 2% lake surface and 0% sand. The O2 branch has a greater percentage of wetland (25%) and peat (26%) than O1, which has 18% wetland and 19% peat. See Temnerud and Bishop (2005) for more information about the study area.

An earlier synoptic survey of the drainage network on Ottervattsbäcken and another nearby catchment, showed



**Figure 1** Map of the River Öre basin, with the catchment Ottervattsbäcken (O), the western branch Hammonsbäcken (O1) and the eastern branch Marrabäcken (O2). Sites not in either O1 or O2 are O3. Open circles are samplings sites, with only one circle for each sampled stream junction. The open star is the stage measurement site and broad solid lines are surface water. Note the presence of 4 lakes in the headwaters of O1, and only one lake in the headwaters of O2.

inter-stream TOC-concentration from catchments <15 km<sup>2</sup> was larger (15 times difference between max and min) than downstream in larger catchments where the difference between max and min was a factor of 2.6. The TOC-concentrations were also higher in headwaters (median of 19 mg l<sup>-1</sup>) than downstream (11 mg l<sup>-1</sup>) on one of the tributary branches, but there was little difference on the other branch (median of 21 and 23 mg l<sup>-1</sup> respectively) (Temnerud and Bishop, 2005).

## Methods

A grab sample was taken approximately 10 m upstream and downstream from almost every stream junction in the study area (90% of those seen on the national 1:50 000 topographic maps and having any running water). In this article, the term headwater is used as a synonym for stream order one catchments (Strahler, 1957). Higher order streams are denoted "downstream". Catchment sizes larger than 15 km<sup>2</sup> were mostly stream order 3 or larger based on 1:50 000 maps

(Temnerud and Bishop, 2005). The stream network of the catchment was sampled during 19–22 August, 2002. This period of low discharge was chosen to ensure stable flow conditions. There was no rainfall during the sampling period. This improved the ability to identify in-stream transformations and point-sources or sinks of TOC (e.g. mires or lakes). A total of 66 sites (O) were sampled of which 21 were headwaters. Of these 66 sites, 31 were from O1 (10 of which were headwaters) and 27 were from O2 (of which nine were headwaters). Sites located neither in O1 nor in O2 were labeled O3; there were eight such sites of which two were headwater streams.

## Chemical analysis

Two bottles of stream water were collected at each location. One was a 500 ml dark glass bottle used for analysis of pH and electrical conductivity. The other was a 1 l polyethylene bottle from which aliquots were taken for measurement of other chemical parameters that were analyzed up to 1 month later. The samples were run in a random order during all analysis to prevent instrumental drift from being interpreted as a spatial trend. The stream temperature was measured in situ. The pH was measured with an electrode (Orion model 9272) designed for low ionic strength (these streams had a mean electrical conductivity of  $39 \mu\text{S m cm}^{-1}$ ). Both pH and electrical conductivity (SDM 2010) were measured at 20 °C on the sampling day (using a water bath). Alkalinity was measured according to the Swedish standard to the pH endpoint of 5.6. Metals, unfiltered, were analyzed using ICP-MS (Agilent 450 equipped with an ultrasonic nebuliser, U-6000AT+) on samples acidified with concentrated nitric acid (re-distilled from reagent grade acid) to a final concentration of 1% v/v on the sampling day.

Samples for organic carbon analysis were stored at 4 °C and analyzed on a Shimadzu TOC-V within a week. The TOC-V combusts carbon at 680 °C and TOC was calculated using the difference between total carbon and inorganic carbon (volatile inorganic carbon was driven off by phosphoric acid). All TOC-measurements were analyzed with three replicates per sample and the mean standard deviation of these replicates was  $0.38 \text{ mg l}^{-1}$ . For Fenno-Scandia's boreal forest areas it has earlier been shown that TOC and dissolved organic carbon (DOC, defined as that organic carbon which can pass a  $0.45 \mu\text{m}$  filter) differ by less than 5% (Gadmar et al., 2002; Ivarsson and Jansson, 1994; Köhler et al., 1999; Mattsson et al., 2003). A specialized study on filtration of boreal water has shown that in these waters the particulate OC are so consistently low that errors introduced by filtering mean that it is better to avoid filtration (Gadmar et al., 2002). Therefore our study works with TOC, though it should be borne in mind that the results are as applicable for DOC in this environment.

## Discharge measurements

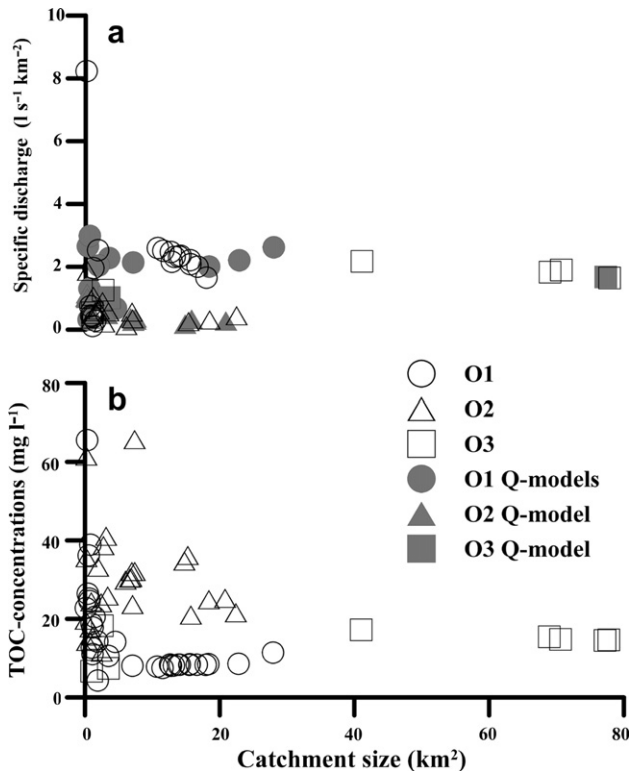
A key factor in the analysis of landscape patterns of chemistry is the discharge in the stream at the time of sampling. The small-scale spatial variation of specific discharge ( $q$ ) in the Swedish boreal landscape, however, is poorly character-

ized. In analyzing the June 2000 synoptic survey of Ottervattsbäcken, a uniform specific discharge was assumed due to a lack of more detailed flow information (Temnerud and Bishop, 2005). In the synoptic survey reported here, we measured discharge using salt dilution with an instantaneous slug injection wherever feasible (41 of the 66 sample sites) immediately after the water sample was taken. The uncertainty of these measurements was assumed to be 5% (at 95% level) (ISO, 1997). In the morning and evening of all four sampling days, runoff was also measured at one downstream location draining 91% of the catchment where a stage-discharge relationship had been established previously (Hans Ivarsson and others, unpublished data, 2000; the site marked with an open star in Fig. 1).

Partial least square (PLS) regression models were constructed to predict specific discharge ( $q$ ) at the 25 sites where discharge had not been measured. Logarithmic values of  $q$  were used in this analysis. The following data derived from topographic maps (1:20000, year 2000) were used in the models: percentages of forest, wetland, arable, open land and lake surface area for every subcatchment. Four different PLS-models were used. The specific discharge values from O1 were grouped by whether or not the site was located downstream from any lake. This created the basis for two PLS-models for O1, O1–N for sites with no lakes and O1–L for sites influenced by lakes. Sites influenced by lakes were mostly stream order  $>1$ , while sites not influenced by lakes were mostly headwaters. The third model was for O2, which was more influenced by mires. Downstream of O1 and O2, there was arable land and a fourth model was used for those sites (O3). For O1–N the median measured specific discharge was  $0.75 \text{ l s}^{-1} \text{ km}^{-2}$  ( $n=7$ ,  $q$  minimum 0.12 and max 8.2) and for O1–L the median was  $2.2 \text{ l s}^{-1} \text{ km}^{-2}$  ( $n=13$ ,  $q=1.7$ – $2.6$ , Fig. 2). In O2 the median measured  $q$  was  $0.56 \text{ l s}^{-1} \text{ km}^{-2}$  ( $n=15$ ,  $q=0.13$ – $1.9$ ). For O3 the median measured  $q$  was  $1.7 \text{ l s}^{-1} \text{ km}^{-2}$  ( $n=6$ ,  $q=0.54$ – $2.2$ ). All PLS-regressions were performed using The Unscrambler 9.0 (CAMO PROCESS AS, Norway).

A 20 year record of daily flow from the nearby Vindeln Experimental Forests' Svartberget  $0.5 \text{ km}^2$  catchment (characteristics similar to O2) was used to relate specific discharge at the time of sampling to the situation at other times of the year. At the outlet of the studied catchment the specific discharge was  $5.5 \text{ l s}^{-1} \text{ km}^{-2}$  for the sampling period in 2000 and  $1.9 \text{ l s}^{-1} \text{ km}^{-2}$  for the period in 2002. Although the specific discharge varies between streams in the same landscape, this allowed an assessment of the flow conditions during the sample period. At Svartberget the specific discharge was under  $5.5 \text{ l s}^{-1} \text{ km}^{-2}$  on some 60% of the days in that 20 year period (data from Lindström et al., 2002), and the flow was under  $1.9 \text{ l s}^{-1} \text{ km}^{-2}$  on 30% of the days.

To estimate water residence times in the channel network, the channel geometry and velocity were characterized from observations at each sampling site: First order streams had a mean width ( $w$ ) of 0.3 m, a mean depth ( $d$ ) of 0.2 m, and the water surface was ca. 0.3 m lower than the surrounding terrestrial surface (termed "lower"). For stream order 2: mean  $w=0.6$ , mean  $d=0.4$  and lower = 0.5 m. For stream order 3: mean  $w=1.3$ , mean  $d=0.5$  and lower = 0.6 m. For stream order 4: mean  $w=7.8$ , mean  $d=1.0$  and lower = 0.8 m. The water current



**Figure 2** TOC-concentrations ( $\text{mg l}^{-1}$ ) and specific discharge  $q$  ( $\text{l s}^{-1} \text{km}^{-2}$ ) variation with subcatchment size ( $\text{km}^2$ ). Catchment O, with the branches O1 ( $\circ$ ) and O2 ( $\triangle$ ), sites not in either (O3) are marked as ( $\square$ ) Symbols filled with grey are based on modeled values of discharge. The mean standard deviation of all TOC measurements is  $0.38 \text{ mg l}^{-1}$  and there is a 5% uncertainty for discharge measurements.

estimated from wetted channel cross-sections and discharge was  $0.1 \text{ m s}^{-1}$  for stream order 1,  $0.2$  for stream order 2,  $0.3$  for stream order 3 and  $0.4$  for stream order 4.

The theoretical stream water retention time with these velocities was estimated using the longest stream distance from a headwater down to the outlet (excluding lakes). The maximum calculated in-stream residence time was 1.0 days for O, 0.8 days for O1 and 0.7 days for O2.

### Volume-weighted calculations and statistical treatments

To compare headwaters to downstream waters, and assess the significance of headwaters for downstream conditions, volume-weighted mean concentrations ( $C_{\text{vw}}$ ) in headwaters and downstream were calculated (Eq. (1)). Assuming that in-stream processes have a negligible impact on the concentration, the concentration of the waters flowing into the channel (both lateral and vertical) below the headwaters ( $C_{\text{in}}$ ) can be calculated from the observed headwater and outlet concentrations, knowing the discharge of inflowing water (Eq. (2)). The water chemistry of inflowing water should not be confused with the chemistry of groundwater, since the inflowing water may be altered as it passes the riparian zone. The concentration of organic carbon in riparian zone soil water that was available for lateral transport

to the stream has been measured in a nearby catchment. The observed values there were between  $5$  and  $25 \text{ mg l}^{-1}$  during growing season, low flow situations (Bishop et al., 2004). These values were used to justify the calculated values from Eq. (2).

The significance of differences in water chemistry between headwaters and downstream was tested using the  $t$ -test for differences in mean values. At stream junctions, and along stream reaches, differences between upstream and downstream water chemistry were tested using the paired Student's  $t$ -test. Principal component analysis (PCA) correlation matrix using NIPALS algorithms were performed using The Unscrambler 9.0 (CAMO PROCESS AS, Norway). Five lakes were checked for differences between inflows and outflows, but due to the small sample size no test of statistical significance was performed here.

$$C_{\text{vw}} = \frac{\sum_{i=1}^n C_{\text{Sub}_i} \cdot Q_{\text{Sub}_i}}{\sum_{i=1}^n Q_{\text{Sub}_i}} \quad (1)$$

$$C_{\text{in}} = \frac{C_{\text{Outlet}} \cdot Q_{\text{Outlet}} - \sum_{i=1}^n C_{\text{Head}_i} \cdot Q_{\text{Head}_i}}{Q_{\text{Outlet}} - \sum_{i=1}^n Q_{\text{Head}_i}} \quad (2)$$

where  $C$ : measured concentrations ( $\text{mg l}^{-1}$ );  $C_{\text{vw}}$  = volume-weighted concentration ( $\text{mg l}^{-1}$ );  $C_{\text{in}}$  = inflowing concentration ( $\text{mg l}^{-1}$ ), downstream of headwaters;  $C_{\text{Outlet}}$  = the outlet of catchment O, branches O1 and O2 ( $\text{mg l}^{-1}$ );  $Q$ : discharge ( $\text{l s}^{-1}$ );  $\text{Sub}_1, \dots, \text{Sub}_n$  = subcatchments (headwaters or downstream subcatchments) and  $\text{Head}_1, \dots, \text{Head}_n$  = headwater subcatchments.

### Error analysis

Estimation of the error in fluxes ( $\Delta F$ ) is calculated according to

$$\Delta F : (Q^2 \Delta C^2 + C^2 \Delta Q^2)^{0.5}, \quad (3)$$

where  $\Delta$ : error for discharge (5%) and concentration (standard deviation of three replicates, mean TOC of all samples are  $0.38 \text{ mg l}^{-1}$ ) and  $F$ : flux, computed as  $C$  times  $Q$  ( $\text{mg s}^{-1}$ ).

The sum of the flux errors can be computed as

$$\sum \Delta F = ((\Delta F_1)^2 + (\Delta F_2)^2 + \dots + (\Delta F_n)^2)^{0.5} \quad (4)$$

The error in volume-weighted concentrations ( $C_{\text{vw}}$ ; Eq. (1)) then becomes

$$\Delta C_{\text{vw}} = \left( \left( \frac{\sum \Delta F}{\sum Q} \right)^2 + \left( \frac{\sum \Delta Q \cdot \sum F}{(\sum Q)^2} \right)^2 \right)^{0.5} \quad (5)$$

The error for inflowing water concentrations ( $C_{\text{in}}$ ; Eq. (2)), was calculated using an equation similar to Eq. (5).

### Stream junctions

At 14 stream junctions in O, including seven from branch O1 and six from O2, the sum of TOC-fluxes of both upstream sites were divided by downstream site discharge and compared with the measured TOC-concentration downstream from that stream junction. Since the downstream sampling site was at least 10 m downstream of the junction, it was assumed that mixing of both tributaries had occurred in those

streams (Heard et al., 2001). The percentage difference between measured TOC and volume-weighted TOC-concentration predicted from conservation of mass was calculated. Negative percentage values indicate a loss of TOC coming out of the junction relative to what entered the junction. The relative differences in subcatchment size were calculated, with the smallest subcatchment size value divided by the combined size of the two subcatchments. The same approach was used for discharge. The arithmetic mean TOC-concentration for the upstream sites was also compared to the downstream site to represent the subjective impression one would get from looking at the streams in the field without the information needed for volume-weighting.

### Stream reaches

Along stream reaches where maps (scale 1:50 000) did not show any additional in-coming streams, a comparison of TOC measured above and below the reach was made to determine whether in-stream processes led to a consistent change in TOC-concentration and TOC-fluxes along such reaches. In O there were 20 stream reaches, of which nine were from O1 and 7 from O2. The length of the stream between the sampling sites at the start and end of each reach, as well as the percentage difference in catchment size were also calculated.

### Lakes

The inputs from all measured streams draining to each lake were compared to the lake outlet. For TOC-concentrations, the arithmetic mean TOC-concentration of inflowing streams was compared to the outlet to calculate the percentage difference. As for stream junctions, this comparison reflects the subjective impression an observer would get in the field of the differences between what enters and leaves a lake. For TOC-fluxes the sum of fluxes for all inflowing streams was compared to the flux at the outlet, and the percentage difference was calculated. Five lakes were investigated in O, of which three were in O1, one in O2 and one in O3.

### REA – Monte Carlo simulation of spatial variation in mixing of TOC along the streams

In streams a decline in the inter-stream variation among streams of the same stream order and/or approximate size was observed as one went downstream. Mixing of waters with different concentrations, as stream tributaries join together, is one factor that contributes to this. This is one premise in the contention that an REA exists for stream water chemistry in a landscape. To test whether the observed downstream decline in inter-stream variability is the result of such mixing, a model was constructed in which the landscape was treated as a collection of independent stream segments. The TOC-concentrations of these stream segments were assumed to follow the distribution of headwater concentrations for the O-catchment.

We derived a frequency distribution of the observed TOC-concentrations in headwater streams. A lognormal dis-

tribution function fitted this data well and we used random values from this fitted distribution function to generate different stochastic realizations of TOC-concentrations. A random value was assigned to each headwater catchment. Similarly random values were also assigned to all the areas entering the stream network between the observation points. If such an area was larger than 3 km<sup>2</sup> (the maximum size of headwaters), they were subdivided into a number of smaller areas of equal size ( $\leq 3$  km<sup>2</sup>). The resulting concentration for each sample site was computed by downstream mixing. For simplicity we assumed a spatially uniform specific discharge. This procedure was repeated 10 000 times with different realizations of the random field and the associated downstream variation of concentrations. The change of variability with subcatchment area was evaluated as the coefficient of variation calculated on a 10-value window moving along the sample points sorted by area. Both the observed concentrations and the concentrations computed from the Monte Carlo mixing model were evaluated in this way.

Data from 10 catchments (20–3000 km<sup>2</sup>, median 250 km<sup>2</sup>) in the River Öre basin (Ivarsson and Jansson, 1994) were included in the simulations, hereafter denoted ‘‘River Öre data’’. These catchments were sampled during 1990–1991 (Ivarsson and Jansson, unpublished data, 2000) and 1995–1996 (Catharina Pettersson, unpublished data, 2002). Only data from August were used to provide an estimate of spatial variability at this larger scale.

## Results

### Headwaters compared to downstream

#### Concentrations

There was an order of magnitude variation in the concentrations of TOC in the headwaters (range 4.3–66 mg l<sup>-1</sup>) (Fig. 2). Downstream, though, the TOC-concentrations were less variable when looking at each branch individually. The two branches, O1 and O2, also show two different patterns of TOC-concentration variation with subcatchment size (Fig. 2). Downstream sites in O1 had stable median TOC-concentrations of about 8.4 mg l<sup>-1</sup> (25th and 75th percentiles were 8.3 and 11 mg l<sup>-1</sup> TOC, respectively), while O2 downstream sites varied more and were on average 25 mg l<sup>-1</sup> (25th and 75th percentiles were 21 and 32 mg l<sup>-1</sup> TOC). TOC decreased downstream for branch O1 from a median of 21–8.4 mg l<sup>-1</sup> but remained stable downstream on O2 (26–25 mg l<sup>-1</sup>). The range of TOC concentrations did not decrease for the downstream sites in O2.

There were high positive correlations between TOC-concentration and iron ( $r_{\text{spearman}} 0.91$ ), aluminum (0.78), calcium (0.63) and low pH (–0.69). Weaker correlations with TOC were found for sodium (0.50), potassium (0.40) and alkalinity (0.20). All these Spearman rank correlation coefficients ( $r_{\text{spearman}}$ ) were significant ( $p = 0.01$ ) except for alkalinity. The mean pH was lower in headwaters than at downstream sites (6.0 vs 6.4) and had a larger variation in headwaters ( $\sigma = 0.50$ ) than for downstream sites ( $\sigma = 0.39$ ). The pH difference between headwaters and downstream sites was larger in O1 than in O2 (Table 1). Electrical conductivity was low, approximately 39  $\mu\text{Sm cm}^{-1}$ , in

**Table 1** Mean chemistry, volume-weighted and inflowing concentration in the catchment O, with branches O1 and O2, grouped into headwaters (stream order 1) and downstream (stream order 2–4)

	Eq.	O	O1	O2
Headwater sites		Number	21	10
Downstream sites		Number	45	21
Headwater sites		Area <sup>a</sup>	1.2	0.84
Downstream sites		Area <sup>a</sup>	16	12
Headwater mean		pH <sup>a</sup>	6.0	6.0
Downstream mean		pH <sup>a</sup>	6.4	6.6
Headwater mean		El.cond <sup>a</sup>	36	36
Downstream mean		El.cond <sup>a</sup>	38	39
Headwater mean		Temp <sup>a</sup>	16	17
Downstream mean		Temp <sup>a</sup>	17	17
Headwater volume weight	$C_{VW}$	TOC <sup>b</sup>	19	19
Downstream volume weight	$C_{VW}$	TOC <sup>b</sup>	13**	8.9**
Inflowing concentration	$C_{In}$	TOC <sup>c</sup>	14	10
Outlet measured		TOC	15	11
Headwater volume weight	$C_{VW}$	Alk <sup>b</sup>	0.12	0.12
Downstream volume weight	$C_{VW}$	Alk <sup>b</sup>	0.097**	0.095**
Inflowing concentration	$C_{In}$	Alk <sup>c</sup>	0.10	0.18
Outlet measured		Alk	0.11	0.18
Headwater volume weight	$C_{VW}$	Fe <sup>b</sup>	2.0	2.1
Downstream volume weight	$C_{VW}$	Fe <sup>b</sup>	1.0**	0.48**
Inflowing concentration	$C_{In}$	Fe <sup>c</sup>	1.1	1.3
Outlet measured		Fe	1.2	1.4
Headwater volume weight	$C_{VW}$	Al <sup>b</sup>	0.13	0.13
Downstream volume weight	$C_{VW}$	Al <sup>b</sup>	0.078**	0.046**
Inflowing concentration	$C_{In}$	Al <sup>c</sup>	0.065	0.038
Outlet measured		Al	0.077	0.051
Headwater volume weight	$C_{VW}$	Ca <sup>b</sup>	4.0	3.3
Downstream volume weight	$C_{VW}$	Ca <sup>b</sup>	2.7**	2.2**
Inflowing concentration	$C_{In}$	Ca <sup>c</sup>	2.8	2.8
Outlet measured		Ca	3.0	2.8
Headwater volume weight	$C_{VW}$	K <sup>b</sup>	0.69	0.44
Downstream volume weight	$C_{VW}$	K <sup>b</sup>	0.43**	0.34**
Inflowing concentration	$C_{In}$	K <sup>c</sup>	0.46	0.35
Outlet measured		K	0.43	0.34
Headwater volume weight	$C_{VW}$	Na <sup>b</sup>	1.6	1.3
Downstream volume weight	$C_{VW}$	Na <sup>b</sup>	1.1**	1.0**
Inflowing concentration	$C_{In}$	Na <sup>c</sup>	0.93	0.93
Outlet measured		Na	1.0	0.91

\*,\*\*Significant differences between headwater and downstream are marked with a \* at  $p = 0.05$  and \*\* at  $p = 0.01$ .

<sup>a</sup> Mean area (km<sup>2</sup>), pH, electrical conductivity ( $\mu\text{Sm cm}^{-1}$ ), and stream temperature (°C) with standard deviation is in hard brackets.

<sup>b</sup> Volume-weighted concentrations ( $C_{VW}$ ) of TOC, Fe, Al, Ca, K and Na in mg l<sup>-1</sup>, alkalinity in mequiv l<sup>-1</sup> according to Eq. (1). Estimate of error according to Eq. (5) in rounded brackets.

<sup>c</sup> Measured outlet concentration with the calculated downstream inflowing concentration ( $C_{In}$ ; Eq. (2)), assuming there are no in-stream processes that alter concentrations (same units as in <sup>b</sup>). Estimation of error according to Eq. (5) in rounded brackets.

both headwaters and downstream sites in O1 and O2 (Table 1). Note that this low conductivity is typical of headwater streams in blanket mires, where there has been minimal contact of water with underlying mineral soils or rocks. Stream temperature was 16 °C in headwaters and 17 °C at downstream sites, with no difference downstream at O1

while there was a temperature difference along O2 of one degree between headwaters and downstream sites.

#### Discharge

The weather was dry and sunny, without rain, during the sampling period. The groundwater table was low for this period of

the year (SGU, 2002). The specific discharge measured at the outlet of Ottervattsbäcken was  $1.9 \text{ l s}^{-1} \text{ km}^{-2}$ . The average specific discharge measured on O1, with most sites downstream from lakes was higher ( $2.2 \text{ l s}^{-1} \text{ km}^{-2}$ ) and less varied (range 1.7–2.6) than the mean specific discharge measured on O2  $0.56 \text{ l s}^{-1} \text{ km}^{-2}$ , with a range from 0.13 to 1.9 (Fig. 2).

The relative contribution of headwaters discharge at the outlet of O1 was 14% and 60% for O2. The catchment area of headwaters was 30% of O1 and 48% of O2 (Fig. 3a). The relative contribution of the headwaters to the total water discharge at the outlet of O was 18%, although headwater catchments account for 33% of the catchment area at the outlet (Fig. 3a). Specific discharges were negatively correlated to TOC-concentration with Spearman rank correlation coefficients of  $-0.45$  for O1 (significant at  $p = 0.05$ ) and  $-0.69$  for O2 (significant at  $p = 0.01$ ).

### Volume-weighted concentrations

For the catchment as a whole, volume-weighted (Eq. (1),  $C_{vw}$ ) headwater concentrations of TOC were higher than the outlet TOC-concentration (19 vs.  $15 \text{ mg l}^{-1}$ ). The patterns along the two tributaries were quite different. O1 headwaters had volume-weighted TOC-concentrations that were over twice as high as those downstream ( $19$  compared to  $8.9 \text{ mg l}^{-1}$ ), while in O2 there was no difference between headwaters and downstream (both had  $28 \text{ mg l}^{-1}$ ; Table 1). O2 had volume-weighted values of TOC, iron, aluminum, calcium, potassium and sodium that were 31–400% higher than in O1 (in both headwaters and downstream waters; Table 1). O1 headwaters had significantly higher volume-weighted concentrations of alkalinity, iron, aluminum, calcium, potassium and sodium than were found downstream (Table 1). For O2 there was almost no difference in the volume-weighted concentrations for aluminum between headwaters and downstream, while there were significant differences for alkalinity, iron, calcium, potassium and sodium (Table 1).

### Fluxes

The 24% headwater contribution of TOC-flux for the entire catchment, O, was slightly higher than the headwater contribution to discharge. The median specific TOC-flux from headwaters in O1 was  $0.011$  and  $0.018 \text{ kg ha}^{-1} \text{ day}^{-1}$  from O2. The specific TOC-flux increased downstream on O1 to  $0.016 \text{ kg ha}^{-1} \text{ day}^{-1}$ , while on O2 specific flux decreased downstream to  $0.0087 \text{ kg ha}^{-1} \text{ day}^{-1}$ . The variation in specific TOC-flux between streams declines downstream markedly for O1, and slightly for O2. Using a uniform specific discharge for all sites when calculating fluxes resulted in lar-

ger headwater contributions for O (43%, Fig. 3b) and for O1 (50%), but a smaller contribution for O2 (67%).

Alkalinity, iron, calcium, potassium and sodium had lower contributions from the headwaters than from downstream discharge on O1, while the contribution was higher for aluminum (Fig. 3a). Headwater contributions on O2 were higher than downstream discharge for all chemical parameters, and especially for iron and calcium (Fig. 3a).

### Stream junctions

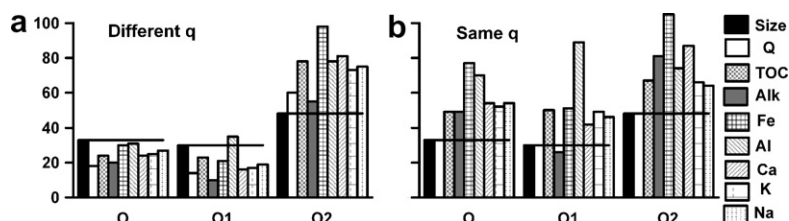
The mean TOC changes when passing a stream junction were  $-9.0\%$  for O,  $-16\%$  for O1 and  $-3.9\%$  for O2. There were four junctions with a loss of over 20%, and one with a gain of over 20%. The mean loss excluding those five junctions was  $-1.8\%$ . The difference between the observed TOC below the junctions and that predicted from conservative mixing was not significantly different (paired Student's  $t$ -test,  $p = 0.05$ ). Principal component analysis (PCA) indicated that aluminum, and to lesser degree iron, declined below the four junctions where there was a calculated loss of TOC and this decrease of aluminum and iron were correlated to losses of TOC (data not shown). A large difference in catchment size of the tributaries that mixed was also characteristic of the junctions where there was a loss in TOC. Mean TOC-concentrations of both tributaries at each stream junction were always higher than measured downstream TOC-concentrations. For O the mean TOC-concentration difference was  $-22\%$ ,  $-43\%$  for O1 and  $-2.8\%$  for O2 (Table 2). For O and O1 the differences were significant ( $p = 0.05$ ).

### Stream reaches

The mean length of the stream reaches was 981 m for O (Table 3) with a mean difference in catchment size along the same reach of 19% for O. The mean discharge increase along the reaches was 15%. Mean TOC-concentrations increased slightly along stream reaches in O (4.5%) (Table 3). The mean stream reach increase in TOC-flux along the reaches was 23%. The differences along stream reaches were not significant, except for TOC-fluxes on O2, using a paired Student's  $t$ -test and  $p = 0.05$ .

### Lake effects

The mean difference in catchment size between the incoming streams and the outlets of the lake was 131% (Table 4),



**Figure 3** Headwater percentage contribution of total catchment area (size), discharge ( $Q$ ) and fluxes of TOC, alkalinity, iron, aluminum, calcium, potassium and sodium for the catchment O, with branches O1 and O2. Horizontal line identifies the headwater contribution to total discharge of water. (a) Using the measured or modeled specific discharge for each site. (b) Using a uniform specific discharge for all sites.



**Table 2** Stream junction TOC-concentrations in O, with branches O1 and O2

Catchment	Diff. area <sup>a</sup> (%)	Up <sub>Ave</sub> TOC <sup>b</sup> (mg l <sup>-1</sup> )	Down <sup>c</sup>	Down <sup>d</sup>	Diff. TOC down-Up <sub>Ave</sub> <sup>e</sup> (%)	Diff. TOC down-calc <sup>f</sup> (%)
			TOC (mg l <sup>-1</sup> )	TOC <sub>calc</sub> (mg l <sup>-1</sup> )		
O1	29	44	25	42	-43	-40
O1	8.9	13	8.4	8.3	-34	1.2
O1	3.2	17	8.1	8.2	-53	-0.18
O1	9.1	14	8.3	8.5	-42	-1.9
O1	3.5	22	8.4	9.1	-63	-8.0
O1	44	26	14	32	-45	-56
O1	20	11	8.6	8.9	-24	-3.8
O1 <sub>Ave</sub> <sup>g</sup>	17	21	12	17	-43 <sup>h</sup>	-16
O2	3.0	46	31	33	-34	-7.8
O2	1.5	26	24	32	-8.5	-25
O2	50	49	35	47	-29	-26
O2	14	16	25	18	53	37
O2	29	16	16	16	-2.2	-3.5
O2	12	25	25	25	3.0	2.3
O2 <sub>Ave</sub> <sup>g</sup>	18	30	26	29	-2.8	-3.9
O1 + O3	40	14	15	15	7.9	5.8
O <sub>Ave</sub> <sup>g</sup>	19	24	18	22	-22 <sup>h</sup>	-9.0

Sites not in O1 or O2 are O3.

<sup>a</sup> Diff. area = percentage difference between smallest catchment size divided with size for both tributaries.

<sup>b</sup> Up<sub>Ave</sub> is the mean TOC of both tributaries to the stream junction.

<sup>c</sup> The TOC downstream from the stream junction.

<sup>d</sup> Down<sub>calc</sub> is the TOC-flux calculated on the assumption of conservative mixing, see Methods for more details.

<sup>e</sup> Diff. TOC Down-Up<sub>Ave</sub> is the difference between TOC at the downstream site and the mean of upstream sites, and does not take into account any differences in discharge between the two tributaries.

<sup>f</sup> Diff. TOC down-calc is the difference between measured TOC and calculated TOC.

<sup>g</sup> The mean values for respective parameters.

<sup>h</sup> The concentration difference is significantly different at  $p = 0.01$ .

whereas the mean increase in discharge from the lake inlets to the lake outlets was 237%. The mean TOC-concentration decrease was -28%, while the mean TOC-flux increase was 148% (Table 4).

### REA – Monte Carlo simulations of TOC-concentrations

The Monte Carlo runs of the mixing model for predicting TOC-concentrations along the stream network from a random field of concentrations showed the expected decrease of the variation with increasing area. The median of the predicted coefficient of variation (cv) of the concentrations at the observation points along the stream network decreased from 0.42 for the 10 smallest catchments to 0.08 for the 10 largest catchments (Fig. 4). The pattern in cv for the observed data was more complex. (N.B. The observed pattern is just one realization whereas the Monte Carlo results are based on 10000 realizations.) The observed coefficient of variation started at 0.50 for the smallest subcatchments and remained fairly constant until it increased to an inter-stream cv around 1 for subcatchments of about 10 km<sup>2</sup>, before dropping back to a cv of 0.36 for the largest subcatchments on O.

The variability for larger catchments, “River Öre data” (see Methods, the REA section), was evaluated for comparison. The coefficient of variation for these 10 catchments

(median area of 250 km<sup>2</sup>) was on average 0.29 (0.18–0.49 for the 10% and 90% percentiles).

## Discussion

### Headwaters compared to downstream

The TOC-concentration at the outlet of the entire catchment (O) was lower than both the median value of the sampled headwaters and the volume weighted headwater mean. Within O, however, there were distinctly different patterns in TOC-concentration along each of the two main branches. The median TOC-concentration for headwaters decreased downstream along O1, but increased slightly along O2 (Table 1). A factor in the rapid decline of TOC-concentration along O1 is the presence of lakes in the upper reaches of the O1 catchment, while in O2 there are fewer lakes in the headwaters. Similar patterns had been observed when the catchment was sampled in 2000, also during a period of low flow (Temnerud and Bishop, 2005).

The differences between the branches affects the “boundary” for where the landscape-scale TOC signal stabilizes. If each branch is evaluated separately, the landscape signal stabilized at approximately 5 km<sup>2</sup> for both flow and chemistry. If both branches are considered together, the signal stabilizes at 15 km<sup>2</sup> (Temnerud and Bishop, 2005).

**Table 3** Stream reach difference in TOC on O, with branches O1 and O2

Catchment	Str <sup>a</sup>	Area <sup>b</sup> (%)	Length <sup>c</sup> (m)	TOC <sup>d</sup>	TOC <sup>e</sup>	Diff. Conc <sup>f</sup> (%)	Diff. flux <sup>g</sup> (%)
				Up (mg l <sup>-1</sup> )	Down (mg l <sup>-1</sup> )		
O1	2	7.6	1458	7.9	7.5	-4.1	-0.26
O1	2	1.0	569	8.4	8.1	-3.6	-15
O1	2	4.9	195	8.1	8.3	2.5	7.9
O1	2	1.8	709	8.3	8.3	-0.072	2.9
O1	3	0.37	344	8.3	8.5	1.7	-3.8
O1	3	8.0	655	8.4	8.3	-0.65	-11
O1	3	2.2	661	8.3	8.5	2.1	26
O1	2	146	1750	14	14	-0.77	-35
O1	3	22	3612	8.6	11	33	94
O1 <sub>Ave</sub> <sup>h</sup>	2.4	22	1106	8.9	9.2	3.4	7.4
O2	2	1.2	310	31	32	5.0	-34
O2	2	4.7	490	24	32	35	98
O2	3	3.4	400	35	36	4.1	61
O2	3	3.1	1405	36	21	-42	-23
O2	3	17	578	21	25	19	29
O2	2	112	902	16	24	54	188
O2	3	7.7	1691	25	22	-15	48
O2 <sub>Ave</sub> <sup>h</sup>	2.6	21	825	27	27	8.7	52
O3	4	2.4	1853	15	15	-4.4	1.7
O3	4	9.3	96	15	15	-1.6	-5.0
O3	4	0.73	962	15	15	0.89	-0.29
O3 <sub>Ave</sub> <sup>h</sup>	4.0	4.2	970	15	15	-1.7	-1.2
O <sub>Ave</sub>	2.7	19	981	16	17	4.5	23

Sites not in O1 or O2 are O3.

<sup>a</sup> Str is stream order.

<sup>b</sup> Percentage difference in catchment size between sites, sites along the same stream and with no incoming streams visible on map.

<sup>c</sup> The stream distance (m) between the sites.

<sup>d</sup> The upstream site.

<sup>e</sup> The downstream site.

<sup>f</sup> Percentage difference in TOC-concentrations, and does not take into account any differences in discharge between the two tributaries. Down-up.

<sup>g</sup> Percentage difference in TOC-fluxes, Down-up.

<sup>h</sup> The mean values for respective parameter. No significant differences were detected at  $p = 0.05$ .

The downstream pattern in volume-weighted concentrations from headwaters compared to downstream was generally similar to that for median TOC and specific discharge (Table 1), but the downstream decline along O1 was less pronounced than for median TOC. The difference between volume-weighted TOC-concentration above stream junctions compared to the observed value below the junction is also smaller than for the arithmetic averages above the junction. These differences between volume-weighted and median/mean TOC-concentrations result from the negative correlation between specific discharge and TOC-concentration. This means that when calculating the contribution of headwaters to what is observed downstream, variations in specific discharge between headwater catchments need to be accounted for.

While these results provide some basic information about headwater/downstream TOC patterns, more fundamental questions are raised by spatial patterns concerning the processes that create them. The observed TOC-concentration patterns of both declines along O1 and a more stable concentration along O2 could be explained by assuming conser-

vative mixing of headwaters and inflowing downstream groundwater with TOC-concentrations between 10 and 12 mg l<sup>-1</sup> (Table 1) which are reasonable values for the region (Bishop et al., 2004).

Thus, it does not appear necessary to invoke in-stream losses or sources of TOC on the basis of the overall landscape TOC patterns, so the hypothesis stated in the Introduction seems to be valid, namely that headwater/downstream differences can be reasonably explained solely by conservative mixing of headwaters with downstream catchment inputs. However, just because in-stream processes are not needed to explain the overall spatial pattern does not mean that they can be ruled out as also contributing to the pattern. The character of organic matter might also change even though the TOC-concentrations remain the same (Gadmar et al., 2005; Pettersson et al., 1994). Preliminary results indicate that the character of organic matter was stable and did not change significantly between headwater and downstream sites (Temnerud, 2005).

The spatial variation in stream chemistry is different between high and low flow (Zielinski et al., 2003). In a nearby

**Table 4** Lake influence on stream TOC in O, with branches O1 and O2

Catchment	Stream order <sup>a</sup>	Area Diff. <sup>b</sup>	TOC-concentrations (mg l <sup>-1</sup> )		% Diff. <sup>e</sup>	TOC-fluxes (g s <sup>-1</sup> )		% Diff. <sup>g</sup>
			Up <sub>Ave</sub> <sup>c</sup>	Outlet <sup>d</sup>		∑Up <sup>f</sup>	Outlet <sup>d</sup>	
O1	2	473	25	11	-58	0.46	0.84	84
O1	2;1;1	8	11	8.1	-6.7	1.1	1.2	15
O1	2;1	33	13	7.9	-41	1.3	2.2	69
O2	2	74	15	12	-21	0.12	0.26	115
O3	3;1	64	20	17	-14	2.8	15	459
O <sub>Ave</sub> <sup>h</sup>		131	17	11	-28	1.1	4.0	148

Sites not in O1 or O2 are O3.

<sup>a</sup> The sequence of numbers indicate the stream order of inflowing streams to the lake, for example 2;1;1 where the first number is stream order 2 while the others are stream order 1.

<sup>b</sup> Percentage difference in catchment size between inflowing streams and outlet.

<sup>c</sup> Mean TOC value of inflowing streams to the lake.

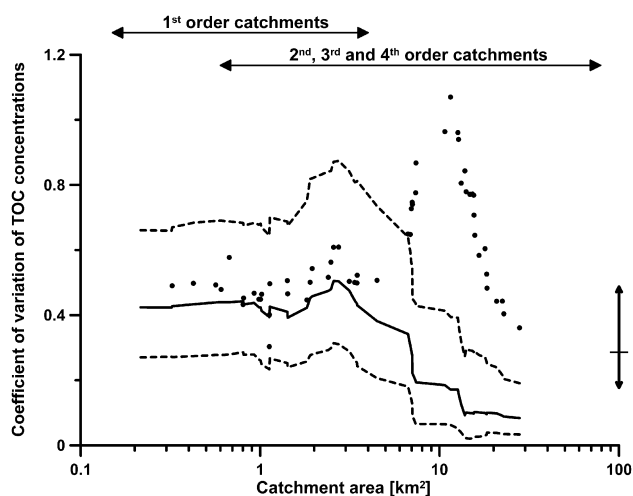
<sup>d</sup> TOC value for lake outlet.

<sup>e</sup> Percentage difference between outlet and mean inflowing TOC-concentrations.

<sup>f</sup> The sum of TOC-fluxes for inflowing streams to the lake.

<sup>g</sup> Percentage difference between outlet and mean inflowing TOC-fluxes.

<sup>h</sup> The mean values for respective parameters. No significance test was performed.



**Figure 4** Observed variation in TOC-concentrations (mg l<sup>-1</sup>) as a function of catchment size predicted with a Monte Carlo model of random inputs from the subcatchments. Coefficient of variation calculated on a 10-value window moving along the sample points sorted by area plotted against median area for each window. The circles represent the values computed from the observations. The solid line is the median of the Monte Carlo runs of the mixing model (10000 realizations), the dotted lines show the 10th and 90th percentiles. The line on the right indicates the coefficient of variation for 10 larger catchments, the "River Öre data" (median as well as 10th and 90th percentiles).

and similar catchment, the spatial variation in organic carbon was shown to be larger during low flow than during spring flood (Buffam et al., 2007). For Ottervatnsbäcken though, there has been no sampling conducted at high flow. This study was a first attempt to make a synoptic investigation of a Fenno-Scandian mesoscale catchment. Thus we have not sought to draw conclusions about annual patterns,

instead restricting ourselves to the situation at low flow conditions which are what the biota experiences during most of the year. During low flow, water retention time are longer, and summer low flow, with high temperatures as well as much sunlight also provides the best possibility for observing any transformations in OC along the stream network that may be occurring.

### Stream reaches

One place that in-stream TOC losses due to in-stream processes might be evident is along stream reaches, in the form of consistent downstream decreases in TOC-concentration. The stream reach data revealed a scatter of TOC changes, with losses on some reaches, but a mean overall increase (Table 3) in both concentration (4.5%) and flux (23%). It is not surprising that only a few stream reaches had a decreasing TOC given the low rates of TOC mineralization from both biotic and abiotic processes reported in the literature (Bertilsson et al., 1999; Fisher et al., 2002; Köhler et al., 2002) relative to the in-stream residence times in this landscape, even at the low flow conditions of summer. The maximum calculated in-stream residence time, excluding lakes, did not exceed one day. The residence times are even shorter at higher flow rates, so it is reasonable that in-stream biotic and abiotic mineralization processes are a minor factor in downstream TOC losses. Hyporheic process contributions to TOC losses have yet to be quantified in a similar way (cf. Boulton et al., 1998; Clinton et al., 2002; Gomi et al., 2002), but based on Table 3, TOC losses due to hyporheic processes do not appear to be manifested along the stream reaches in a consistent fashion.

### Stream junctions

Another potential explanation for in-stream TOC losses is flocculation/precipitation when water with different chem-

istries mix at stream junctions (Benda et al., 2004). At most stream junctions, volume-weighted averaging of the concentrations in the two tributary streams predicted downstream concentrations only slightly below those observed below the junction. Considering all stream junctions, i.e., including those with large calculated TOC losses/gains, the mean TOC loss was  $-9.0\%$  (Table 2). The largest apparent loss of TOC ( $-56\%$ ) was observed for a site where discharge at the downstream site was much higher than the sum of the upstream sites, suggesting an upwelling of groundwater at that junction. Still, the fact that 3 of 4 remaining deviations greater than 10% were losses of TOC raises the possibility that there may in fact be losses at some junctions. Correlations, were also found in PCA-analysis between TOC loss and other chemical parameters (aluminum, iron and pH), as well as the magnitude of the differences in catchment size between the tributary waters mixing at the junction.

### Lake effects

Lower concentrations of TOC were observed at the outlets of the lakes compared to the volume-weighted mean of the inflow concentrations. These lakes and possibly some specific junctions comprise a set of discrete loci in the landscape where TOC-concentration decreases downstream. A lake's influence on the TOC-concentration of downstream sites depends largely on lake residence time. Meili (1992) found that the inflowing streams to 18 boreal lakes had higher TOC-concentrations than observed at the lake outlets. Kling et al. (2000) found similar lake effects in the arctic.

Since water flow out of the lakes was larger than inflow, however, the flux of TOC from the lakes was larger than the fluxes into the lakes (mean increase 148%). This is due to groundwater inflows to lakes with some TOC, as well as any autochthonous TOC production (Table 4). Higher TOC-concentrations in Swedish boreal headwaters than in downstream catchments could be due to the lack of lakes in most headwaters (Pers et al., 2001) and a greater percentage of mires in headwaters.

In O1, with lower TOC-concentrations downstream from headwaters, there are three lakes from which large amounts of low TOC-concentration water flow to 2nd and 3rd order streams (Table 4). In the downstream part of the catchment there is also less mire area. In O2, where TOC-concentrations downstream were similar to those in headwaters, there is only one lake, and the portion of mire area in the headwaters is similar to that in the downstream catchments.

Lakes and possibly some specific junctions comprise a set of discrete loci in the landscape where TOC-concentration decreases downstream. A similar view of loci of TOC loss as opposed to more gradual, evenly distributed losses was suggested by Minshall et al. (1985) in a proposed revision of the River Continuum Concept, and Naiman et al. (1987).

### Discharge

While the pattern of concentrations itself is of ecological importance, one can also ask how important the headwaters are for water resources and ecosystems further downstream

where much of the value to society is found, as well as how to assess waters at a landscape scale (cf. Stieglitz et al., 2003). It is the flux and character of TOC rather than just the concentration in the water contributed by a landscape element that determines the influence of that element on downstream concentrations and fluxes (Aitkenhead-Peterson et al., 2005; Aumen, 1990; Carey et al., 2005; Clark et al., 2000; Dillon and Molot, 1997; Ford et al., 1990; Gadmar et al., 2005; Hillman et al., 2004; Thomas et al., 2004; Walling and Webb, 1980). Therefore the variation of specific discharge is of importance for the headwater influence on downstream TOC.

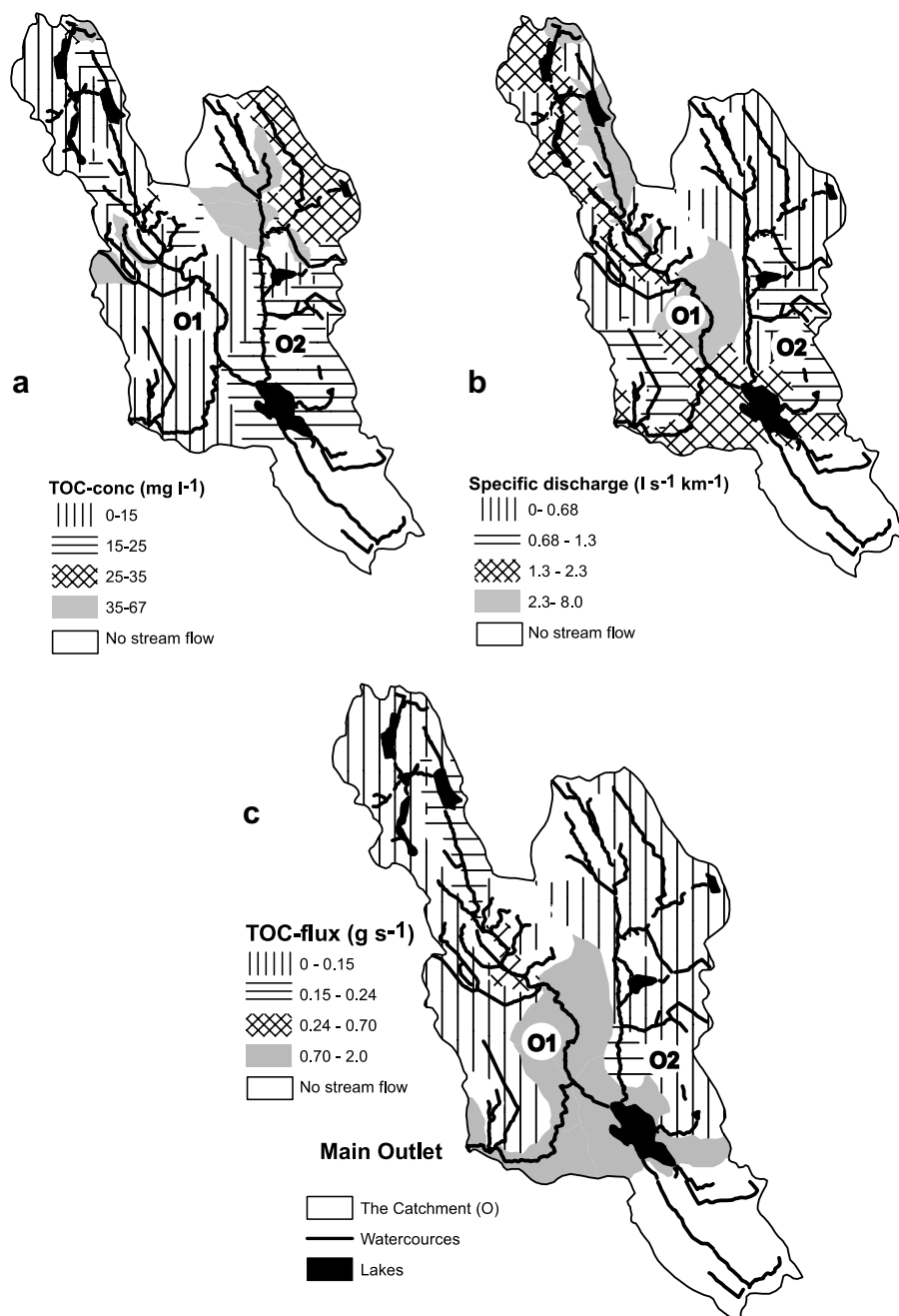
The measurements of discharge at many locations revealed a variation in specific discharge almost as large as in TOC-concentrations (Fig. 2). Despite the order of magnitude variation in specific discharge and concentration, and a median downstream TOC-concentration over twice as high in O2 than in O1 – the specific TOC-fluxes were almost twice as high on the downstream reaches of O1 compared to O2 ( $0.016$  vs.  $0.0087$   $\text{kg ha}^{-1} \text{day}^{-1}$ ).

These results emphasize that the discrepancy between concentration and flux of TOC is related to the negative correlation observed between specific discharge and TOC-concentrations. If a uniform specific discharge is used for the whole catchment when calculating fluxes, the importance of headwaters will be overestimated compared to using spatially distributed  $q$  for O and O1, but not for O2 (Fig. 3b). For instance, using a uniform specific discharge gives a headwater percentage contribution to the outlet flux of water for O of 32%, compared to 18% using a spatially distributed  $q$ .

The difference in downstream patterns of TOC-concentrations on the two branches, including the stable downstream TOC observed on O2, points to the importance of patterns in the different landscape elements (Fig. 5) for creating the landscape scale patterns. This means that with different arrangements of elements in the landscape (lakes, mires, forests, etc.), the downstream change in TOC-concentration is not necessarily a large decrease (Tables 2 and 3), or even a decrease, because it is the inputs from different landscape elements and the distribution of loci for TOC-loss, rather than consistent in-stream processes, that determines downstream TOC-concentrations in this catchment (Table 4). In other words, our results suggest that interdependent processes associated with landscape elements, including lakes, wetlands and specific combinations of tributary waters, control catchment-scale patterns of solute distribution (Fig. 5). This investigation represents an initial step toward quantifying those associations in boreal catchments.

### REA – Monte Carlo simulations

If the landscape scale TOC patterns were created largely by conservative mixing of the TOC-flux from different landscape elements (Karlsson et al., 2005; Palmer et al., 2005), then downstream decreases in concentration variability from mixing of tributary streams could create an REA, a scale at which landscape signals emerge from small scale variation (Uchida et al., 2005). The variability of observed concentrations decreased with subcatchment area, which could be interpreted as support for the existence of



**Figure 5** Map of Ottervattsbäcken, with branches O1 and O2: (a) TOC-concentrations ( $\text{mg l}^{-1}$ ) on upper left map, (b) specific discharge ( $\text{l s}^{-1} \text{ km}^{-2}$ ) on upper right map, (c) TOC-fluxes ( $\text{g s}^{-1}$ ) lower middle map. Gray is highest values, checkered next highest, horizontal lines next lowest and vertical lines the lowest class of each representative parameter. Black are lakes and watercourses.

an REA (Fig. 2). This was tested by simulating the effect of conservative mixing using a Monte Carlo approach.

The measured concentrations indicate that the spatial variability decreases rapidly for catchments larger than  $10 \text{ km}^2$ , but they also show a clear increase in variability from the smallest catchments to a catchments area of  $\sim 10 \text{ km}^2$ . The mixing model does not reproduce this increase and predicts a faster decrease than the one seen in the observations. It is interesting to note that in one of the few places where an REA has been calculated for flow and chemistry, the flow REA appeared at  $3 \text{ km}^2$  and the chemical REA at  $1 \text{ km}^2$  (Shaman et al., 2004).

The average coefficient of variation for the observations in the larger catchments of the River Öre also had a larger value than the mixing model for the largest catchments in the study area. These catchments are one order of magnitude smaller than the River Öre catchments. In other words, even for larger catchments there still is variability larger than that corresponding to a random field and conservative mixing.

The complexity of the observed inter-stream variability of TOC-concentrations at different scales indicates that important landscape features vary at different scales (Fig. 4). Thus, while a decrease of inter-stream variability

could be observed while moving downstream to larger catchments, this decrease is smaller than what could be expected from our simulation of conservative mixing. This suggests that the landscape is not a mix of randomly arranged elements, but rather a structured mosaic (cf. Pringle et al., 1988), and that this also applies at larger scales.

## Conclusions

- On the catchment as a whole there was a downstream decrease in TOC-concentration, but looking at the two major branches separately there was a downstream decrease along only one of the branches. The inter-stream variability of TOC-concentrations as well as other chemical parameters and specific discharge was larger for headwaters than for downstream sites.
- Knowledge of the specific discharge was essential for defining the role of headwaters for downstream TOC-concentration and flux, as reported by others.
- The hypothesis that headwater/downstream differences can be explained solely by conservative mixing of headwater and downstream catchment inputs was not disproven.
- In-stream processes were not identified as major factors in shaping the pattern of downstream TOC, but loci of TOC-concentration decrease were identified at some stream junctions and in lakes.
- In this study, the landscape signal stabilized at approximately 5 km<sup>2</sup> for both flow and chemistry. This applied to both branches (O1 and O2) despite the difference between them. However, the spatial variability was higher than expected from conservative mixing of a random field.
- Even if mixing of tributaries, inflows of groundwater, and localized zones of TOC loss from surface waters summarizes the way downstream patterns are created, this is not a simple random mixing, but rather mixing from a structured mosaic. Understanding that structure, potentially through GIS, would be a major step forward in assessing such landscapes from the standpoint of water chemistry and aquatic ecology.

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