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Investigating the relationship between subsurface hydrology and dissolved carbon fluxes for a sub-arctic catchment

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Abstract

In recent years, there has been increased interest in carbon cycling in natural systems due to its role in a changing climate. Northern latitude systems are especially important as they may serve as a potentially large source or sink of terrestrial carbon. There are, however, a limited number of investigations reporting on actual flux rates of carbon moving from the subsurface landscape to surface water systems in northern latitudes. This study estimates dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) fluxes from the subsurface landscape for a sub-arctic catchment located in northern Sweden. Estimates are based on observed annual in-stream flux-averaged concentrations of DOC and DIC at the outlet of the 566 km^2 Abiskojokken catchment and from catchment-scale transport modeling based on advective solute travel times and their spatial distributions. We also demonstrate the importance of correctly representing the spatial distribution of the advective solute travel times along the various flow and transport pathways. For the sub-arctic catchment considered in this study, there is a relative balance between the flux of DOC and DIC from the subsurface landscape to the surface water system. This balance between DOC and DIC fluxes could shift under future climatic changes that influence the hydrological and biogeochemical system.

1 Introduction

There may be numerous climate change effects on hydrology at high-northern latitudes. These include decreasing depth and duration of snowcover (Brown and Braaten, 1998; Curtis et al., 1998), warming and thawing of the permafrost (Stieglitz et al., 2003; Walvoord and Striegl, 2007; Osterkamp, 2007), increasing precipitation frequency and amount (McCabe et al., 2001; Walsh, 2000), increasing freshwater discharge (Peterson et al. 2002) and earlier spring flood peak discharges (Déry et al., 2005). The terrestrial freshwater water cycle in the arctic and sub-arctic is often intimately connected with the presence of permafrost (White et al., 2007; Woo et al., 2008) and the depth to the permafrost largely determines the pathways of water flow through the landscape (Kane et al., 1981). In addition to influencing the hydrological response of the landscape, the location and distribution of these pathways influence the carbon and other biogeochemical cycling in northern latitude catchments (e.g., MacLean et al., 1999; McNamara et al., 2008).

Increasing precipitation and surface temperature may lead to more subsurface water flowing through the highly organic superficial soils of arctic and sub-arctic systems, promoting the transport of dissolved organic carbon (DOC) from the subsurface landscape to the surface water parts of the landscape (Dutta et al., 2006). In addition, there is the possibility that DOC is released as a direct consequence of the degradation of permafrost (Frey and McClelland, 2009). Counter to this, permafrost thawing could allow for deeper flow pathways and, as such, lead to a general reduction in terrestrial DOC export by promoting flow through deeper mineral soils (Striegl et al., 2007). With regards to dissolved inorganic carbon (DIC), deeper groundwater flow depths due to permafrost thawing would likely increase the formation of DIC due to weathering. Such shifts in DOC and DIC transport and/or production have consequences to the global C balance. Climatic-induced increases to DOC transport could increase respiration along the surface pathways of aquatic transport (Sobek et al., 2003) and have a positive feedback on atmospheric CO_2. Increases in silicate weathering and DIC production, however, consumes CO_2 and would constitute a negative feedback on atmospheric CO_2 due to climatic changes at northern latitudes (Smedberg et al., 2006).

The net effect of these opposing feedback mechanisms depends on the rates of respiration and weathering relative to the physical DOC and DIC mass transport rates along the different pathways of subsurface water flow. Quantifying the time it takes for water and solute to move along the diverse flow pathways through a catchment is essential to predicting the solute transport and fate of solutes (Destouni and Graham, 1995; Simic and Destouni, 1999; Kirchner et al., 2001; Malmström et al., 2004; Darracq et al., 2009; Persson and Destouni, 2009). Field-based identification of flow pathways and quantification of the travel time of water along such flow pathways, however, is

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difficult both in terms of collection of appropriate data and in terms of interpretation. This problem is compounded at northern latitudes as the hydrological mass transport of these regions is poorly monitored (Hannerz and Destouni, 2006; Bring and Destouni, 2009) making it difficult to identify the main solute sources and the main pathways of the waterborne transport through hydrological catchment areas (Destouni et al., 2008a, b). Still, relatively simple, physically-based modeling approaches are available such that we can estimate the distributions of solute travel times along different flow and transport pathways through catchments (e.g., Darracq et al., 2009).

In this study, we use the sub-arctic Swedish Abiskojokken catchment as a large-scale field laboratory, to which we apply a solute travel time-based modeling approach, similar to that presented by Darracq et al. (2009), for investigating physical water flow and mass transport effects on the DOC and DIC export from the subsurface landscape to the surface water system. From this modeling approach, we estimate the present-day release rate of dissolved carbon (both DOC and DIC) from the landscape.

2 Materials and methods

2.1 Site description

The Abiskojokken catchment (Fig. 1) is a sub-arctic catchment in northern Sweden (68°21′36″ N, 18°46′48″ E). It has an area of 566 km^2 and ranges in elevation from about 350 m to 1600 m above sea level. The catchment contains both alpine and sub-alpine vegetation zones. The alpine region is dominated by heath vegetation mainly as dwarf shrubs and the subalpine zone by birch forest with patches of dwarf shrubs. Wetlands and marshes can also be found in the subalpine zone and at lower altitudes in the alpine zone.

Soils at higher altitudes in the alpine zone are thin with common occurrences of exposed bedrock while soils in the low- and mid-alpine zone are generally thicker. Till soils typical of this region (e.g., Johansson et al., 2005) exhibit effective porosity and hydraulic conductivity values of 0.05 and 1.5×10^{-5} m/s, respectively, for the quaternary deposits/bedrock interface. To put these values in perspective, Clapp and Hornberger (1978) and Carsel and Parish (1988) report hydraulic conductivity values for sandy loam soils equal to 3.5×10^{-5} m/s and 1.2×10^{-5} m/s, respectively. The tills in the lower elevations and valleys of Abiskojokken catchment and nearby regions consist largely of finer material, fluvial gravels, sand and in some cases silty/clayey material (Åkerman and Malmström, 1986). The average soil depth in the adjacent headwaters of the river Kalixälven with a similar elevation range has been estimated to be about 1.7 to 5.3 m (Smedberg et al., 2006). Regionally, Smedberg et al. (2009) report median soil depth values ranging from around 9 m for mixed forest land cover to around 7 m for herbaceous land cover. In addition, the Abiskojokken catchment is in an area of discontinuous permafrost (Johansson et al., 2006) with a patchy distribution of permafrost.

2.2 Long-term observations and stream water sampling

Long-term observations have been made at the outlet of Abiskojokken in the form of 22 years (1987 through 2008) of monthly stream water alkalinity measurements. These (and other chemical measures) are available through the Swedish University of Agricultural Sciences (SLU) Department of Environmental Assessment monitoring program. Daily stream flows have also been measured and are available through the Swedish Meteorological and Hydrological Institute (SMHI) (Gage ID 957) from 1918 through 2007. The average annual flow volume based on this long-term observation record of streamflow is 4.5×10^{8} m^{3} of water per year (Lyon et al., 2009).

In addition, dissolved carbon was sampled as DOC and DIC at the outlet of the Abiskojokken catchment as part of this current study. Stream samples were collected about every fifth day for the warm (mid-April to end-July) season from 2008. During September and October of 2008, weekly stream water samples were collected and analyzed for DIC alone. This resulted in a total of 22 DOC and 30 DIC samples. The samples were collected by manual grab sampling. DOC concentration was analyzed by means of catalytic carbon combustion (Shimadsu TOC-VCPH). DIC was calculated from measured alkalinity and pH using PHREEQCI (Parkhurst and Appelo, 1999).

2.3 Shallow and deeper flow domain partitioning

A first step to determining a relevant, present-day advective transport travel time distribution for the Abiskojokken catchment is to determine the portioning of flow through shallow and deeper flow domains. To do this, we develop a simple two-component long-term hydrograph separation using long-term monthly samplings of stream water alkalinity. As alkalinity is added to surface water via the deeper pathways in this system (Humborg et al., 2004), we can use the monthly average alkalinity values to separate the observed total streamflow into water coming from the deeper versus shallow flow domain. This assumes that stream flow is primarily derived from the deeper flow domain during winter since the shallow flow domain freezes and that alkalinity levels thus provide a tracer of water from the deep flow domain.

In addition, we can check the validity of the hydraulic properties for the shallow and deeper flow domains by estimating the relative average aquifer thicknesses needed to yield the average annual flow volumes determined from the long-term hydrograph separation. The aquifer thickness can be determined for both the shallow Z_{sh} [L] and the deeper Z_d [L] flow domains as:

$$Z_{sh} = \frac{Q_{sh}}{\overline{q_{sh}}L_s} \tag{1}$$

$$Z_d = \frac{Q_d}{\overline{q_d}L_s} \tag{2}$$

where L_s is the stream length draining the catchment (approximately 520 km for the Abiskojokken catchment based on map analysis). We can compare the resulting Q_{sh} and Q_d values from the long-term hydrograph separation with the product of L_s and

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average $\overline{q_{sh}}$ and $\overline{q_d}$ values estimated from the present-day advective solute transport travel time distribution (see following section).

2.4 Advective solute travel times

The advective travel times of dissolved carbon along subsurface transport pathways to the stream network reflect the purely physical rates of advection by the variable mean pore water velocity along and among these pathways (see the travel time-based modeling approaches of both conservative and reactive solute transport in Destouni and Graham, 1995; Eriksson and Destouni, 1997; Simic and Destouni, 1999; Malmström et al., 2004; Lindgren and Destouni, 2004; Lindgren et al., 2004; Darracq et al., 2009; and Persson and Destouni, 2009).

We conceptualize the whole subsurface flow domain of active carbon release as a shallow and deeper flow domain. The physical fractionation of water between these two domains is quantified using the above mentioned long-term hydrograph separation. This defines the fraction α_{sh} [–] of streamlines with advective solute travel times τ_{sh} [T] through the shallow flow domain and the complementary fraction 1-α_{sh} of streamlines with advective travel times τ_d [T] through the deeper flow domain. For each location at the catchment surface, a flow-weighted mean advective travel time τ [T] of waterborne carbon through the whole subsurface flow domain can then be estimated as:

$$\tau = \alpha_{sh}\tau_{sh} + (1 - \alpha_{sh})\tau_d \tag{3}$$

We evaluate the advective travel times by a simple Darcy-flow quantification, such that for the shallow flow domain (see e.g. also Darracq et al., 2009):

$$\tau_{sh} = \int_{\underline{a}}^{x_{cp}} \frac{dX_{sh}}{v(X_{sh})} \approx \int_{\underline{a}}^{x_{cp}} \frac{dX_{sh}}{\left(\frac{k_{sh}}{n_{sh}}\frac{dh}{dl}\right)_{X_{sh}}} \tag{4}$$

where n_{sh} is the local effective water content/porosity [–], k_{sh} is the saturated hydraulic conductivity [LT^{-1}] and dh/dl is the hydraulic gradient in the direction x [–], which in a moving coordinate system follows the mean water flow direction. $X_{sh}(t)$ is the position along x at time t, of a water and dissolved carbon parcel that entered the domain at input location $\underline{a}$ (vector notation). At each position X_{sh}, the local average pore water velocity $v(X_{sh})$ [LT^{-1}] advects the water-carbon parcel forward in the x-direction. The advective travel time is the total time period it takes for the water-carbon parcel to be advected from input to a control plane at $x = x_{cp}$ which here represents the interface between the subsurface system and the nearest stream or other surface water.

Similarly, for the deeper flow domain:

$$\tau_d = \int_{\underline{a}}^{x_{cp}} \frac{dX_d}{v(X_d)} \approx \int_{\underline{a}}^{x_{cp}} \frac{dX_d}{\left(\frac{k_d}{n_d}\frac{dh}{dl}\right)_{X_d}} \tag{5}$$

with analogous conceptualization and d-indexed parameter notation for this domain as for the shallow flow domain above.

Similar to Jarsjö et al. (2007), we use here a geographical information system (GIS) to estimate the flow pathway lengths and hydraulic gradients directly from the available digital elevation model (DEM), which has a resolution of 50×50 m for the entire catchment. Using the D8 flow routing algorithm as implemented in Tarboton (1997), flow pathway lengths from each non-stream network raster cell in the catchment to the stream channel network were defined. The stream channel network was defined using an accumulated area threshold set at 5 km^2. Hydraulic gradient was assumed to be equivalent to a hillslope average gradient derived from the DEM. The use of hillslope average gradient is motivated by the fact that the groundwater level and slope may be relatively unaffected by small-scale variations in surface elevation (Darracq et al., 2009). Hillslopes were delineated using the stream channel network based on the methodology outlined in Bogaart and Troch (2006).

To characterize the hydraulic parameters associated with the shallow flow domain, we adopt reported effective porosity and hydraulic conductivity values for the surface till soils in this catchment as these are in agreement with estimates made using the techniques in Clapp and Hornberger (1978) and Carsel and Parish (1988). For the deeper flow domain, we assume (as a first-order approximation) hydraulic properties are similar to those for the shallow flow domain. We can check the validity of these assumed hydraulic properties independently (and if found necessary adjust) by estimating the depth of the shallow and deeper flow domains from Eqs. (1) and (2), respectively.

2.5 Carbon flux estimates

The DOC release from the subsurface occurs at a rate r_{DOC} (mass per bulk soil volume [$\mathrm{ML^{-3}}$]) over the whole subsurface flow domain, i.e., over the shallow and the deep flow domains. Following a single flow and transport pathway (stream tube) with mean specific discharge q [$\mathrm{LT^{-1}}$] and porosity n [–] along its whole length L it is possible to estimate the local mass flux of DOC, s_{DOC} [$\mathrm{ML^{-2}\,T^{-1}}$], into the nearest surface water as:

$$s_{\mathrm{DOC}} = r_{\mathrm{DOC}} L = r_{\mathrm{DOC}} q\tau/n = r_{\mathrm{DOC}} u\tau, \tag{6}$$

where $u = q/n$ is the mean pore water velocity [$\mathrm{LT^{-1}}$] along the whole stream tube with mean travel time τ. Extending this to the whole τ population of stream tubes that receive DOC and transport it to the receiving surface water, the average mass flux $\overline{s_{\mathrm{DOC}}}$ [$\mathrm{ML^{-2}\,T^{-1}}$] into the stream network can be expressed as:

$$\overline{s_{\mathrm{DOC}}} = \int_0^\infty r_{\mathrm{DOC}} u(\tau)\tau f(\tau) d\tau \tag{7}$$

where f is the probability density function describing the spatial distribution of solute travel times τ through the whole subsurface flow domain. This average mass flux can further be related to the flux-averaged concentration of DOC $\overline{C_{\mathrm{DOC\text{-}flux}}}$ [$\mathrm{ML^{-3}}$] in the total volumetric stream flow Q [$\mathrm{L^3\,T^{-1}}$] through the stream cross-sectional area A_{s} at its outlet as:

$$\overline{C_{\mathrm{DOC\text{-}flux}}} = \overline{s_{\mathrm{DOC}}}/(Q/A_{\mathrm{s}}) \tag{8}$$

Similarly to the above, the release of DIC into the subsurface water occurs at the rate r_{DIC} (mass per bulk soil volume). With analogous parameter notation to the result above, we can express the DIC mass flux as:

$$s_{DIC} = r_{DIC}L = r_{DIC}q\tau/n = r_{DIC}u\tau \tag{9}$$

$$\overline{s_{DIC}} = \int_0^{\infty} r_{DIC}u(\tau)\tau f(\tau)d\tau \tag{10}$$

$$\overline{C_{DIC\text{-flux}}} = \overline{s_{DIC}}/(Q/A_s) \tag{11}$$

Using the above expressions, it is possible to link the observed flux-averaged concentrations of DOC and DIC to their associated average mass flux from the subsurface system and the corresponding release rates using spatial distributions of advective solute travel times. To show the effect of the spatial variability in the advective solute travel time distribution, we can also estimate homogenous mass fluxes of DOC $\overline{s_{DOC}}(\overline{\tau})$ and DIC $\overline{s_{DIC}}(\overline{\tau})$ by replacing the distribution of travel times in Eqs. (7) and (10), respectively, with the catchment-average travel time and taking a catchment-average flow velocity. Similar, we can also estimate the homogeneous local release rates $r_{DOC}(\overline{\tau})$ and $r_{DIC}(\overline{\tau})$ by replacing the distribution of travel times in Eqs. (7) and (10) respectively with the catchment-average travel time. This is similar to assuming that the catchment-average travel time represents a homogeneous or a lumped characteristic travel time for the entire catchment.

3 Results

3.1 Hydrograph separation

Using 22 years of monthly observations of alkalinity as a tracer for water originating from the present-day deeper flow domain, we can separate the average annual hydrograph (Fig. 2). Based on this separation, 52% of the average annual flow from the Abiskojokken catchment originates from the deeper flow domain. It follows that the remaining 48% is derived from the shallow flow domain. This gives a long-term estimate of $\alpha_{sh} \approx 0.48$ for the Abiskojokken catchment. Based on the total long-term average annual flow for Abiskojokken, this yields $Q_{sh} \approx 2.16 \times 10^8$ m^3 per year and $Q_d \approx 2.34 \times 10^8$ m^3 per year as the flow contribution from the shallow and the deeper flow domain to the stream network, respectively.

3.2 Advective solute travel times

Adopting the above estimated value of α_{sh}, a spatially-distributed mapping of the flow-weighted average travel time τ, considering both the shallow and the deeper flow domain can be developed for each landscape location in the Abiskojokken catchment (Fig. 3). The estimation of τ is sensitive to the α_{sh} value, as this parameter controls the fractionation of flow pathways between the shallow and the deeper flow domains and to the hydraulic properties adopted to represent each of the zones. We can use the estimated aquifer thicknesses from Eqs. (1) and (2) to test and validate these estimates. Taken together, we obtain a aquifer thickness of about 4 m for the deeper flow domain and 4 m for the shallow flow domain, yielding depth for the whole subsurface flow domain of 8 m.

These estimated advective travel times (Fig. 3) vary among the different land surface locations over the whole catchment. The influence of using a hillslope-average hydraulic gradient can be seen in the relative travel time uniformity across hillslopes. This is compared to the greater travel time variability when moving along hillslopes, from flow divides to the stream channel. Shorter travel times result nearer to the stream network due to the decreased flow pathway length. To statistically characterize the spatial distribution of advective travel times in the Abiskojokken catchment, we can compute this distribution for the entire catchment area (Fig. 4) and from it calculate several summary statistics. The mean advective travel time from the statistical distribution is then 0.9 years, the median travel time is 0.6 years, and the standard deviation is 0.8 years. This shows that the present-day travel time distribution is highly skewed towards smaller travel times and exhibits a long tail of large travel times.

3.3 DOC and DIC observations and flux estimates

The time series of DOC and DIC concentrations show seasonal trends (Fig. 5). DOC concentrations peak at 3.9 mg/L around mid-May 2008 coinciding to spring thaw. DIC concentrations show the opposite pattern as they decrease moving from winter through to summer. DIC reaches a minimum concentration of 1.8 mg/L around the end of June 2008. This DIC concentration pattern in 2008 corresponds to the long-term average pattern seen for alkalinity (Fig. 2a). Based on this sampling, the annual average DOC concentration for 2008 is 1.9 mg/L and the annual average DIC concentration for 2008 is 3.0 mg/L. Using the observed stream flow for 2008 (Fig. 5), the flow-weighted DOC concentration is 2.0 mg/L and the flow weighted DIC concentration is 2.8 mg/L for 2008. Using these flow-weighted average concentrations, it is possible to estimate the corresponding average mass fluxes of DOC ($\overline{s_{\mathrm{DOC}}}$) and DIC ($\overline{s_{\mathrm{DIC}}}$) into the stream network and the release rates of DOC (r_{DOC}) and DIC (r_{DIC}) (Table 1). The estimated homogenous mass fluxes of DOC ($\overline{s_{\mathrm{DOC}}}(\overline{\tau})$) and DIC ($\overline{s_{\mathrm{DIC}}}(\overline{\tau})$) and corresponding homogeneous local release rates for DOC ($r_{\mathrm{DOC}}(\overline{\tau})$) and for DIC ($r_{\mathrm{DIC}}(\overline{\tau})$ are given for comparison.

4 Discussion

4.1 Estimation and validation of advective travel times

This study has invoked a practical and easily applicable framework analogous to the flow modeling methodology outlined in Jarsjö et al. (2007) and the travel time-based mass transport methodology outlined in Darracq et al. (2009) for determining the spatial distribution of advective travel times. This approach is advantageous particularly in ungauged or data limited environments. Often, only topographic and minimal soil

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data are available at the catchment-scale. This makes the modeling of solute transport and reactive mass transfer/transformation difficult, not least with respect to creating a physically-meaningfully representation of how solutes are physically transported through the catchment. By invoking a physical (advective) travel time-based methodology, we can clearly represent the interaction between physical and biogeochemical processes that affect solutes in their transport through the landscape in process-based transport models. As more information becomes available in data limited environments, such as Abiskojokken catchment, estimations of the spatial distributions of advective travel times that represent the physical solute transport can be more constrained.

We have here assumed that Darcy's law is locally applicable to describe the flux of water along single flow and transport pathways (stream tubes). In addition, we have assumed that, in the absence of observed hydraulic gradients, the surface topography gradient can be used to approximate the water table gradient. Moreover, owing to limited data availability and resolution, we have assumed that hydraulic parameters are spatially homogeneous over the entire extent of the Abiskojokken catchment. This, however, is not a necessary condition. If detailed mapping of for instance hydraulic conductivity and its variability were available across the catchment, this type of information could and would be used in the estimation of the advective travel time distribution. In addition to hydraulic properties, the value adopted for α_{sh} is a key parameter for the estimation of the spatially distributed travel times for Abiskojokken. As such, its value needs to be constrained based on independent hydrologic measurements and theory. Here, it was possible constrain this α_{sh} value based on independent hydrologic measurements and theory using alkalinity as a long-term tracer of water originating from the deep reservoir (Fig. 2). Other methods may be available to estimate this weighting parameter for water flow fractionation between shallow and deep aquifers (e.g., Eriksson and Destouni, 1997). While the present assumptions are typical to many hydrological models and need to be considered, we can adopt the modeled spatially distributed travel times as a first-order approximation.

Confidence is given to the modeled distribution by independent corroboration with field-based aquifer thickness observations and by comparison with previous empirical estimates of catchment-scale travel time made in this region. In the current study, the estimated aquifer thickness of 8 m for the whole subsurface flow domain, which is based entirely on observed and modeled hydrology, agrees well with observed depths of deposits ranging from 1.7 m to 5.3 m in a nearby catchment (Smedberg et al., 2006) and regionally-based median values for herbaceous and mixed forest land covers of 7 m and 9 m, respectively (Smedberg et al., 2009). As such, we can accept the hydrological characterizations assumed for both the shallow and deeper flow domains in generating the advective solute travel time distribution (Fig. 3). Further, the mean advective travel time modeled for the Abiskojokken catchment is 0.9 years. This is in general agreement with regional estimates on water transit times inferred from 10 years of ^{18}O isotope signatures by Burgman et al. (1987). Water mean transit times were empirically estimated to be about 1.1 years (Burgman et al., 1987) in the 6000 km^2 Torne älv catchment located near the Abiskojokken catchment. The slightly larger Torne älv catchment is subjected to a similar climate and has a similar geological setting as the Abiskojokken catchment.

4.2 Carbon flux in relation to flow pathways

For the Abiskojokken catchment, there exists a relative balance between the flux of DOC and DIC from the subsurface landscape to the surface water system (Table 1). DIC constitutes about 58% and DOC about 42% of the total flux of dissolved carbon through the landscape and into the stream network. This differs from the larger flux of DOC observed in many other northern landscapes. For example, boreal landscapes tend to have a direct connection from wetlands rich in organic matter and large amounts of DOC in stream systems (Kortelainen, 1993; Laudon et al., 2004). For example, in the well studied Krycklan catchments (located about 600 km southeast of the Abiskojokken catchment), DOC comprises about 81% of the total dissolved carbon export while DIC makes up 19% (Wallin et al., 2010). Looking over the whole of Sweden, Humborg et al. (2010) estimated that organic carbon comprised the majority of the carbon flux

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from the terrestrial environment to the aquatic system. However, in contrast to the Swedish rivers where DOC concentrations are higher than DIC concentrations, most large Siberian rivers are richer in DIC than DOC. On average, DIC comprises 56% of the total dissolved carbon export (Gordeev et al., 1996), which is very similar to the Abiskojokken watershed. These various estimates, along with the present results, demonstrate the fundamental differences that arise due to variation in both ecosystem processes and subsurface materials with respect to the carbon transport through and from the subsurface landscape into the surface water system. As such, there is a need to represent an appropriate level of interaction between the terrestrial environment and hydrology to capture the real nature of carbon transport along and among the aquatic conduits (Cole et al., 2007).

In the current study, this can be seen by the comparisons of release rates based on spatially-distributed travel times with those estimated from a single, lumped travel time (Table 1). Lumping to create a mean travel time value will generally led to underestimation of the release rates of both DIC and DOC (Table 1). For the present-day Abiskojokken catchment, the local DIC release rate is underestimated by 22% and the local DOC release rate by 19%. The differences found here between DIC and DOC release rates (and mass fluxes) when considering spatially distributed travel times over a single lumped travel time are similar to previous findings considering other types of, or more general, solute transport (e.g., Eriksson and Destouni, 1997; Malmström et al., 2000; Lindgren and Destouni, 2004). Such differences in how we represent the movement of water through the catchment subsurface will greatly affect interpretations and predictions of the CO_2 sink or source functioning of the landscape within hydrological catchments. The first approximation given in this study elucidates the role of hydrological flow and transport and the need for more process-based studies that consider this role and its possible climate feedbacks. This role may be even more important under future climate conditions, when the balance between DOC and DIC in taiga and tundra catchments (such as Abiskojokken) may be become even more sensitive to the hydrologic regimes.

4.3 On the potential effects of changes to flow pathways in the sub-arctic

Localized (Åkerman and Johansson, 2008) and catchment-scale (Lyon et al., 2009) permafrost thawing has been documented in Abiskojokken. This thawing has already led to changes in the storage-discharge dynamics of the catchment (Lyon et al., 2009) and could also influence future shifts in the hydrologic flow pathways at the catchment scale. Fluvial and ground water exports of dissolved carbon may be affected by such climate change-induced (or land-use induced) changes in hydrology (Cole et al., 2007). Evidence for this has been found for the Yukon River Basin where decreasing DOC concentrations during summer has been explained by increased flow path and travel times in combination with increased microbial mineralization of DOC in the soil active layer and groundwater (Striegl et al., 2007). A general increasing trend in the groundwater contribution has also been observed across the Yukon River Basin as a result of changed hydrological flow paths due to permafrost thawing and this alteration of flow paths is believed to further decrease DOC exports and increase DIC exports (Walvoord and Striegl, 2007; Lyon and Destouni, 2010). Accordingly, Hinzman et al. (2005) observed increasing DIC concentrations (together with Mg, Ca and K) in Toolik Lake, Alaska, suggesting deeper infiltration of runoff water and increased weathering. For systems where the exports of DOC and DIC are currently in a relative balance (such as the Abiskojokken catchment), such large-scale changes in flow pathways could ultimately shift this balance. This may led to an altering of the CO_2 production and consumption within the subsurface landscape thereby having feedback (i.e., reinforce or shift) to climatic changes.

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Table 1. Observed concentrations and estimated carbon fluxes and release rates for the Abiskojokken catchment.

Measure	Parameter	Units	Values
Flux-averaged DOC concentration in the stream	$\overline{C_{\text{DOC-flux}}}$	mg m^{-3}	2000
Average DOC mass flux into the stream	$\overline{s_{\text{DOC}}}$	$\text{mg m}^{-2}\,\text{s}^{-1}$	571
DOC release rate based on spatially distributed travel time	r_{DOC}	$\text{mg m}^{-3}\,\text{s}^{-1}$	0.36
Homogeneous DOC mass flux, based on the above release rate with a lumped, single travel time and flow velocity	$\overline{s_{\text{DOC}}}(\overline{\tau})$	$\text{mg m}^{-2}\,\text{s}^{-1}$	726
DOC release rate calculated from observed average mass flux with a lumped, single travel time	$r_{\text{DOC}}(\overline{\tau})$	$\text{mg m}^{-3}\,\text{s}^{-1}$	0.29
Flux-averaged DIC concentration in the stream	$\overline{C_{\text{DIC-flux}}}$	mg m^{-3}	2800
Average DIC mass flux into the stream	$\overline{s_{\text{DIC}}}$	$\text{mg m}^{-2}\,\text{s}^{-1}$	799
DIC release rate based on spatially-distributed travel time	r_{DIC}	$\text{mg m}^{-3}\,\text{s}^{-1}$	0.51
Homogeneous DIC mass flux, based on the above release rate with a lumped, single travel time and flow velocity	$\overline{s_{\text{DIC}}}(\overline{\tau})$	$\text{mg m}^{-2}\,\text{s}^{-1}$	1016
DIC release rate calculated from observed average mass flux with a lumped, single travel time	$r_{\text{DIC}}(\overline{\tau})$	$\text{mg m}^{-3}\,\text{s}^{-1}$	0.40

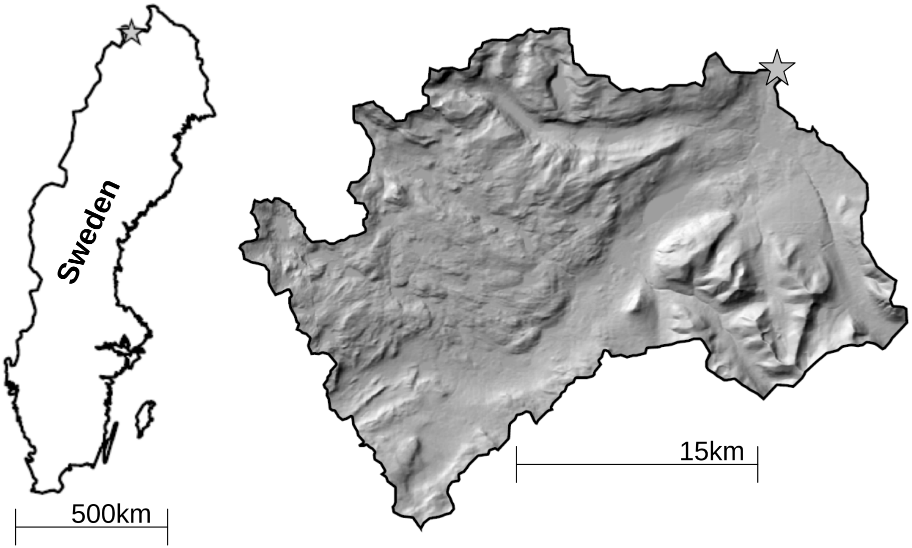

Fig. 1. Site map showing the Abiskojokken catchment in northern Sweden with the outlet (indicated by a star) at 68°21′36″ N, 18°46′48″ E.

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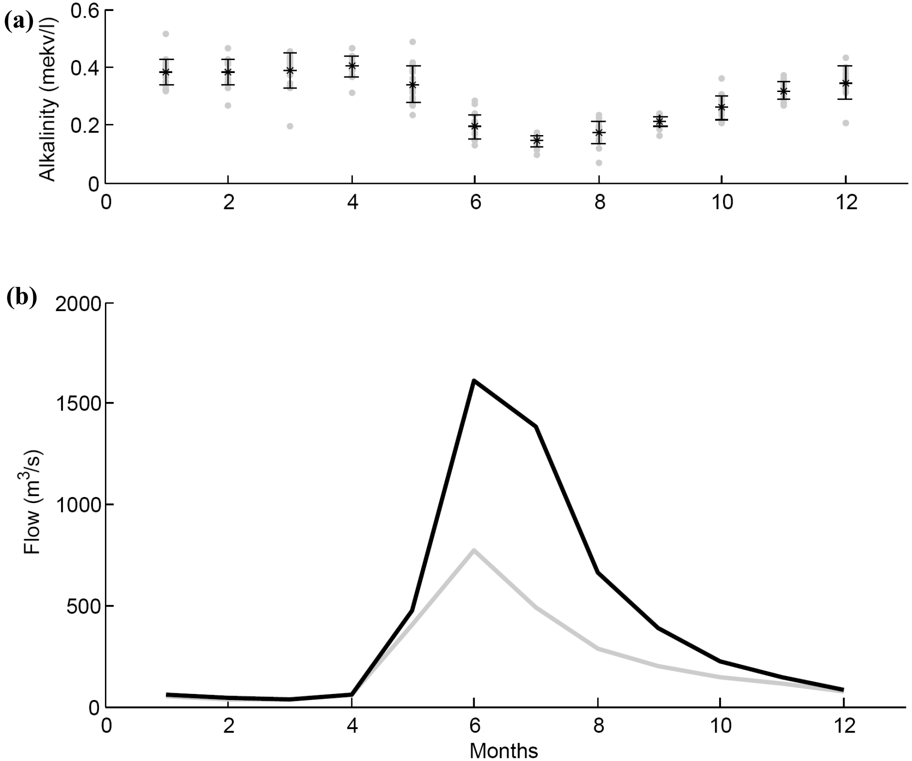

Fig. 2. (a) Long-term (22 years) observations of monthly alkalinity concentrations at the outlet of the Abiskojokken catchment and **(b)** the resultant long-term hydrograph separation between shallow and deep ground water. In (a), crosses show the mean in a given month and vertical bars show one standard deviation.

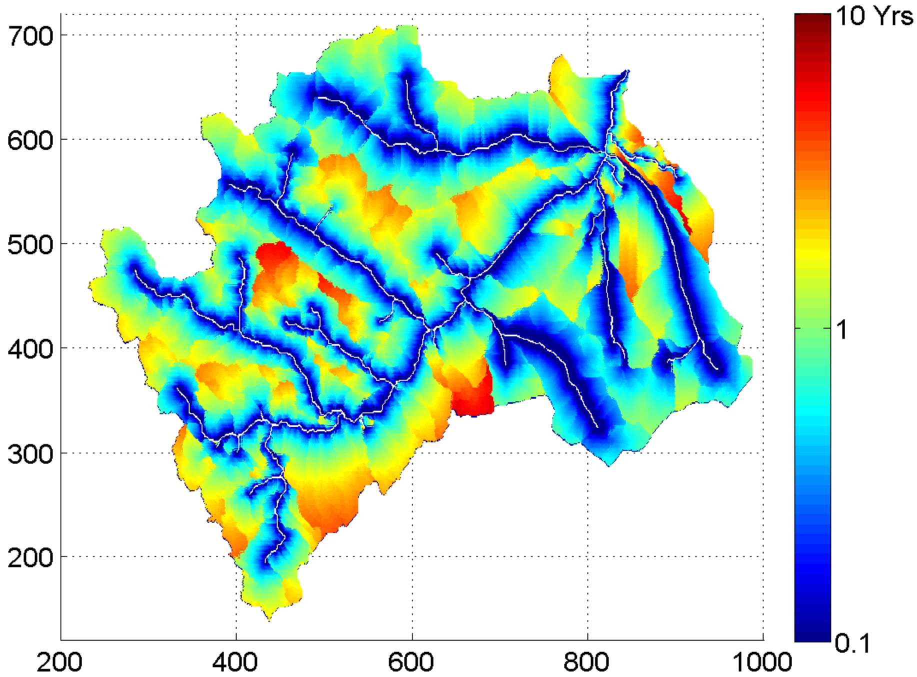

Fig. 3. Present day spatially distributed travel times for each point in the Abiskojokken catchment through the subsurface landscape to the stream network. Note that the color bar has a log scale to show the variability in the spatial distribution. The axes for the map of spatially distributed travel times are labeled in kilometers of linear distance.

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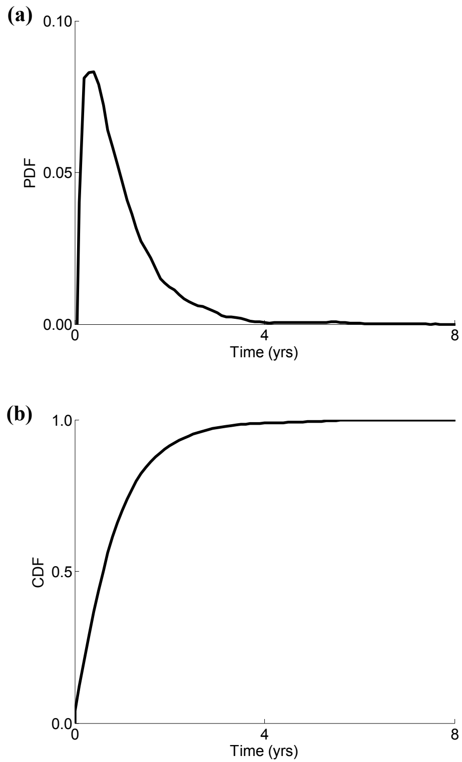

Fig. 4. Characteristic distributions summarizing **(a)** probability density function (PDF) and **(b)** the cumulative distribution function (CDF) of the spatially distributed travel times given in Fig. 2.

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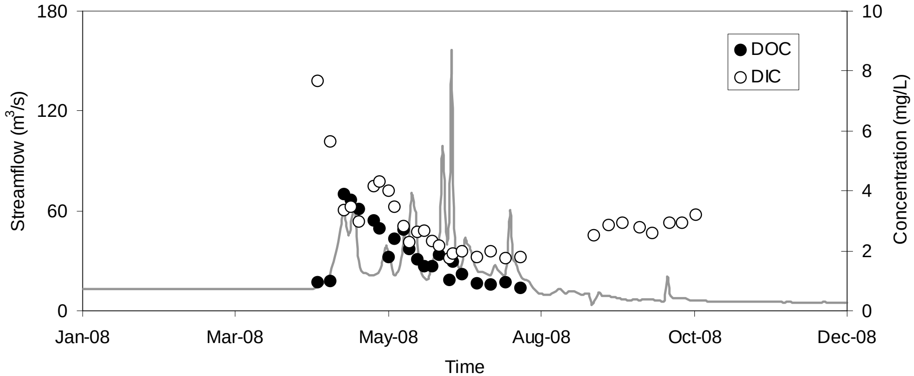

Fig. 5. Time series of observed concentrations of **(a)** DOC (open symbols) and **(b)** DIC (closed symbols) at the outlet of the Abiskojokken catchment along with observed hydrograph for 2008.