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Accounting for instream lakes when interpolating stream water chemistry observations

Steve W. Lyon[1], Hendrik Braun[2], Johan Temnerud[3]*

Abstract: Direct monitoring of stream water chemistry is an increasingly important tool for securing stream water quality and assessing stream ecological functioning as it relates to overall ecosystem health. Such monitoring is often discontinuous in spatial extent and, thus, needs to be interpolated at unsampled locations if the desired end product is a continuous map of stream water chemistry. Recently there have been major advances in the use and development of geostatistical methods (such as kriging) for interpolating between observations of stream water chemistry within stream networks. This study investigated the influence of distance definition on interpolation of synoptically collected stream water chemistry samples. In particular, we developed a new methodology for adjusting instream distances between stream water chemistry observations such that instream lakes (which are ubiquitous in northern, boreal landscapes) are explicitly accounted for in geostatistical interpolations. The methodology developed was tested using stream chemistry data for five different constituents coming from synoptic sampling campaigns conducted across four boreal Swedish catchments during two distinct seasons. The ability of this new, lake adjusted instream distance (LAID) to produce interpolated maps of stream water chemistry was compared to that of traditional Euclidean distance (ED) and instream distance (ID). The results indicated that using LAIDs in this boreal landscape tended to improve interpolation compared to the other distance definitions considered. The grade of improvement, however, tended to vary between the constituent, watershed and season considered suggesting that the influence of instream lakes on water chemistry is quite variable in this landscape throughout the year.

Keywords: *synoptic sampling, stream networks, geostatistics, kriging, stream water chemistry*

1. Introduction

Streams are important habitats for a wide range of organisms and an important freshwater resource. Impaired stream water quality caused by pollutants from human sources can threaten the biodiversity in streams and have long ranging consequences as the pollutants are transported downstream. The importance of securing stream water quality is reflected in programs such as the Clean Water Act in the United States which established a permit system for regulating point sources of pollution into surface waters and the European Union Water Framework Directive which demands regular reports from member countries on the water quality of streams. These programs are concerned with, for example, increases in acidification due to acid atmospheric deposits (Ferrier et al., 2001) and eutrophication caused by increased inflow of nutrients (SEPA, 2000). A key component to such programs is monitoring of stream water quality. One increasingly common method to monitor and assess stream water quality is to measure the concentrations of various chemical constituents in water samples acquired through synoptic or 'snapshot' sampling campaigns. During such campaigns, a large number of water samples are taken over the whole stream network in a short time (Lyon et al., 2008). Synoptic campaigns can give insightful information on small-scale variation in stream water chemistry and they are increasingly attractive due to reduced costs associated with chemical analysis as new technology develops. While extensive, such campaigns are not continuous in their spatial extent and, thus, require some sort of interpolation or modeling to estimate values at unsampled locations.

[1]*Associate Professor, The Bert Bolin Centre for Climate Research at the Department Physical Geography and Quaternary Geology, Stockholm University, 10691 Stockholm, Sweden, *steve.lyon@natgeo.su.se*
[2]*Geographer, IVL Swedish Environmental Research Institute, 10031 Stockholm, Sweden, hendrik.braun@ivl.se*
[3]*Research Associate, Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, 75007 Uppsala, Sweden, johan.temnerud@slu.se*
*corresponding author

Numerous methods exist for estimating stream water chemistry at unsampled locations. These range from more statistical to more deterministic approaches with many approaches considered as being hybrids (Preston et al., 2009). Deterministic methods or models (e.g., the MAGIC model of Cosby et al., 1985a,b) are based on the description of physical processes governing water chemistry by mathematical equations and do not require stream sampling explicitly for estimations. Statistical methods, in their most basic form, rely on simple regressions of observations and are, thus, empirical in nature, based on a sample dataset (e.g., Caraco et al., 2003). Hybrid methods have characteristics of both statistical and deterministic methods. A prime example of a hybrid approach is the SPARROW model (Smith et al., 1997). SPARROW uses spatially referenced regression to correlate instream observations to upstream sources and watershed characteristics, such as land use or soil types (Preston et al., 2009). SPARROW includes deterministic components such as mass-conservation, but its hybrid deterministic-statistical approach allows assigning a level of uncertainty to each prediction. This model is commonly applied for identifying sources of nutrients and estimating their transport in coastal waters (e.g. Alexander et al., 2000; Howarth et al., 2002) and streams (e.g. Alexander et al., 2004; Elliott et al., 2005).

Geostatistical interpolation methods such as ordinary kriging are found on the more statistical end of the continuum for estimating stream water quality at unsampled locations (Jager et al., 1990; Preston et al., 2009). Geostatistical interpolation methods are based on the statistical analysis of the dataset considered. These methods have the advantage of linking a level of prediction uncertainty to each estimate. Furthermore, they do not require assumptions about the physical processes that govern water chemistry making the amount of required input data low. Although kriging has been used for interpolation in streams for a few decades now (e.g., Jager et al., 1990), its use in stream networks has come into recent focus due to developments of geographical information systems (GIS) and increased calculation power of personal computers. Little et al. (1997) were among the first to identify that Euclidean distance (ED), which is the straight line distance between two points and is the traditional distance definition in kriging, might be unsuitable when interpolating stream data. Little et al. (1997) assessed the use of instream distance (ID) measured along the path of the stream as a surrogate for ED. The authors interpolated a range of biological and chemical constituents in an estuary. Results showed that ID led to better results than ED in many cases. Gardner et al. (2003) extended the ID definition by adding a weighting mechanism for stream order. This led to lower uncertainties in the resulting prediction. Lyon et al. (2008) developed another approach for defining an adjusted instream distance based on similar landscape characteristics of site drainage areas. This led to improved estimations of unsampled locations in a stream network over those based on ED or ID. Peterson et al. (2006, 2007) and Ver Hoef et al. (2006) introduced asymmetric IDs to better account for flow directionality using a flow volume as a weighting mechanism to account for proportional contributions.

While these advances in geostatistical interpolation methods take different approaches, they all demonstrate the potential promise of developing meaningful methodologies for interpolating between sparse sampling locations in stream networks. However, to date, all work concerning stream networks has looked at networks where lakes are absent or present in small, non-influential numbers. In order to improve the performance of geostatistical interpolation methods in lotic environments where lakes are important, such as the lake rich boreal forests found across large parts of northern North America and Eurasia, they need to be adapted to account for the presence of lakes in the stream networks. Consider Sweden as an example: the number of lakes larger than 1 ha is around 100,000 (Fölster and Wilander, 2006) and many of these lakes are found within stream networks.

One of the most important differences between streams and lakes lies in the movement or velocity of water (Essington, 2000; Stendera, 2006). Streams are characterized by high flushing rates and turbulent mixing. Water movement in lakes is slower and influenced by factors such as stratification (Wetzel, 1983). Along with changes in water movement, a shift from processes of erosion to sedimentation can occur as streams flow into lakes with major influence on lake water chemistry (Wetzel, 1983). Boreal lakes are, for example,

potential carbon sinks due to sedimentation processes (Algesten et al., 2004; Laudon et al., 2004). Similar to carbon, nutrients such as nitrogen are lost from the flowing water during sedimentation processes (Wetzel, 1983; Howarth et al., 1996) or uptake by aquatic plants. To date, no studies have accounted for lakes in kriging interpolations of stream water chemistry.

This study was a first attempt to incorporate the existence of instream lakes into the definition of distance between observations of stream water chemistry in boreal stream networks. This was done by creating a lake adjusted instream distance (LAID) to be used in kriging applications to produce interpolated maps of stream water chemistry from unique site observations. This methodology was tested using stream water data of five different constituents (Total Organic Carbon (TOC), Total Nitrogen (TN), Total Phosphorus (TP), Potassium (K) and the calculated variable Acid Neutralization Capacity (ANC)) coming from synoptic sampling campaigns conducted across four boreal Swedish catchments sampled in two distinct seasons.

2. Materials and methods

This study developed a new lake adjusted instream distance (LAID) definition (or metric) for use in boreal stream networks. This new metric was compared with more traditional distance metrics, Euclidean distance (ED) and instream distance (ID), for geostatistical interpolation of water chemistry observations from several synoptic sampling campaigns in southern Sweden.

2.1 Catchment-scale synoptic sampling of water chemistry

Water sampling was conducted during two synoptic sampling campaigns in four catchments (Lugnån, Getryggsån, Anråse å, and Danshytteån) located in southern Sweden (Figure 1). The catchments were typical for the southern Swedish boreal landscape with Getryggsån and Danshytteån in the southern boreal biome and Anråse å and Lugnån in the boreonemoral biome. All catchments were dominated by mixed coniferous forests (Norway spruce) with mires (Table 1). Lakes also constituted a large part of the landscape for these catchments. Geologically, all sites were rather similar with granite/gneiss bedrock overlain by spodosol soils. Summaries of catchment characteristics and the sampling campaigns are provided in Table 1. Synoptic samplings were conducted in October 2007 and April 2008 during periods of no rainfall. Sampling campaigns took 2 to 3 days to complete at each catchment. The average streamflow (from the S-HYPE model of Lindström et al., 2010) during the each campaign can be used to characterize the hydrologic state of the catchment (Table 1). In general, the October 2007 sampling campaigns were conducted in hydrologically drier catchments compared to the April 2008 sampling campaigns. Readers interested in more details on the catchments, synoptic sampling design and chemical analyses are referred to Temnerud et al. (2009).

Each water sample collected was analyzed for a wide range of chemical constituents. In this current study, we consider five distinct constituents: TOC, TN, TP, K and the calculated variable ANC. ANC was calculated as the difference between strong base cations and strong inorganic acid anions (Köhler et al., 2001). These constituents were selected due to their use as ecosystem nutrients, energy sources, and indicators of overall ecosystem health (e.g., Gergel et al., 1999; Laudon and Bishop, 1999; Fölster et al., 2007).

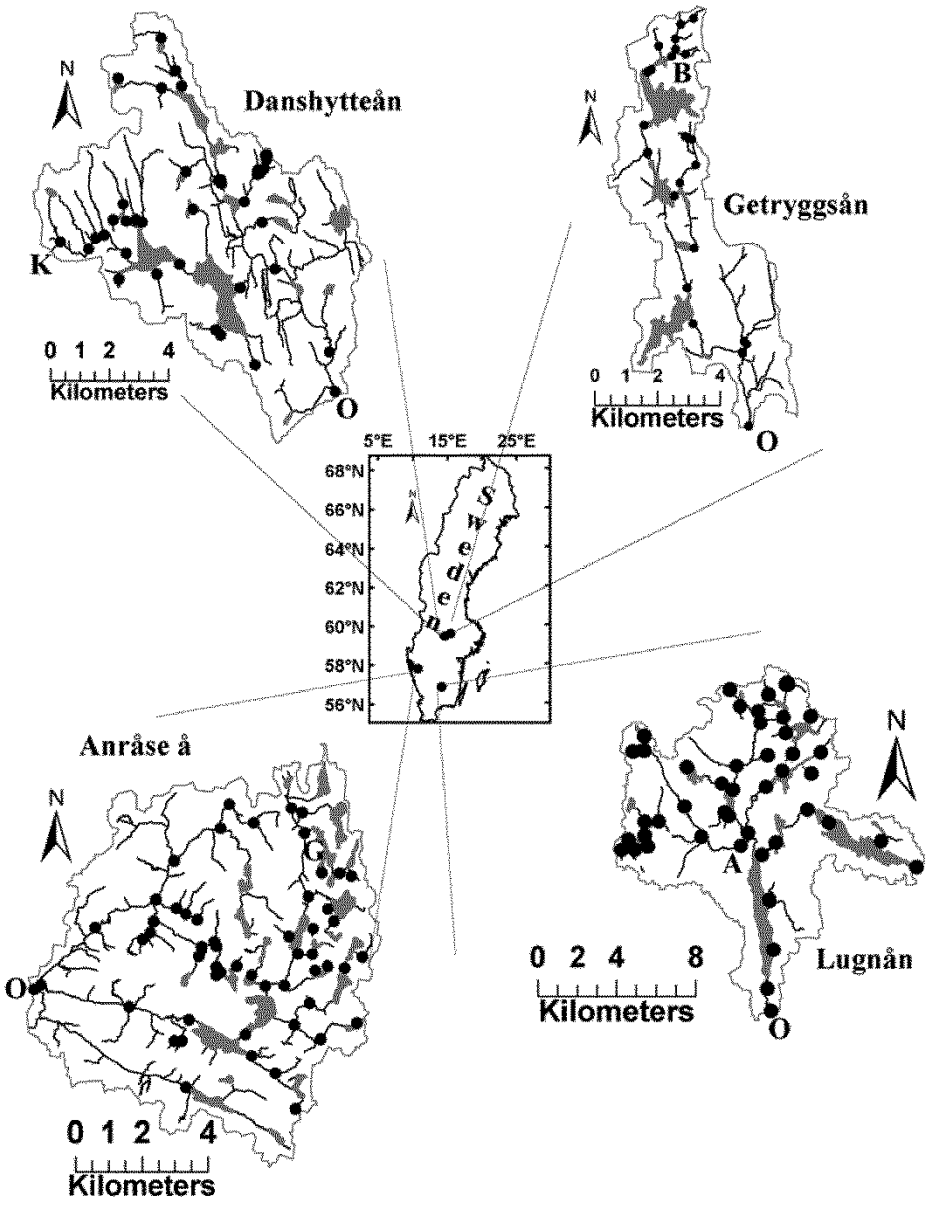

Figure 1: Site map showing the location of the four catchments sampled in the two synoptic campaigns considered in this study. The dots in each catchment show the sampling sites sampled during the synoptic campaigns and the outlet of each catchment is marked with an O.

Table 1: Catchment characterizations and general statistics for the chemical constituents measured and calculated in the two synoptic samplings considered in this study.

Catchment name	Lungån	Getryggsån	Anråse å	Danshytteån
Area [km^2]	127	36	86	80
Average annual temperature [^{o}C]	6	4	7	6
Average annual precipitation [mm]	750	950	1050	850
% Area as Forest	76	82	74	85
% Area as Mire/Wetland	5	6	5	5
% Area as Pasture/Arable	10	1	10	2
% Area as Lake	9	9	9	7
Total stream length [km]	108	57	262	134
# of instream lakes	18	6	24	17
Total lake area [km^2]	11	3.4	5.3	5.5
Average lake area [km^2]	0.6	0.6	0.2	0.3
# of sampling locations	63	35	90	55
# of lakes sampled at inlets and outlets	15	6	13	9
Average Q October 2007 sampling [m^3/s]	1.22	0.07	0.57	0.13
Average Q October 2008 sampling [m^3/s]	2.04	0.85	4.38	1.57
October 2007 Synoptic Campaign: Average (Standard Deviation)				
TOC [mg/L]	20.9 (9.1)	21.3 (13.0)	8.8 (3.9)	17.5 (10.0)
TN [µg/L]	574.6 (162.4)	320.6 (73.5)	415.7 (194.0)	354.5 (114.0)
TP [µg/L]	18.5 (10.1)	10.9 (6.0)	15.2 (23.4)	9.7 (6.0)
K [µg/L]	18.0 (6.5)	6.3 (2.7)	17.7 (14.4)	7.8 (4.1)
ANC [µeq/L]	253.7 (133.0)	102.0 (35.7)	190.5 (195.2)	124.5 (71.2)
April 2008 Synoptic Campaign: Average (Standard Deviation)				
TOC [mg/L]	14.0 (5.0)	14.2 (6.5)	7.7 (1.8)	12.3 (4.5)
TN [µg/L]	634.0 (175.3)	340.7 (90.7)	474.5 (144.7)	307.8 (89.0)
TP [µg/L]	15.3 (10.5)	5.9 (7.3)	8.7 (10.9)	3.5 (1.5)
K [µg/L]	19.4 (6.6)	8.7 (2.5)	14.5 (7.9)	9.0 (4.2)
ANC [µeq/L]	209.0 (74.7)	78.0 (34.2)	175.0 (107.3)	101.9 (59.2)

2.2 Defining a lake adjusted instream distance

The instream distance (ID) between locations or sites can be defined by treating the stream network as a pathway between locations. This is different from the straight lines used in a Euclidean distance (ED) framework.

Starting with symmetric ID between a set of sampling locations within a stream network, one can consider the question of how to treat ID as a stream passes through a lake. Perhaps the simplest conceptualization would be to treat streams flowing through lakes as a proportional influence relative to the total distance between two sites. By extension from Lyon et al. (2008), it is possible to represent this influence using a

scaling factor (β) to adjust sections of a stream networks flowing through lakes. This defines a lake adjusted instream distance (LAID) as:

$$LAID = d_{stream} + \beta\, d_{lake} \qquad (1)$$

Where d_{stream} is the distance between two sites in a network travelling through streams and d_{lake} is the distance between two sites travelling through lakes (treating the flow pathway through a given lake as straight lines from inlet to outlet). Note that, under this LAID definition, for β = 1 we recover the ID between any two sites.

Because no assumptions are made about the physical processes influencing water chemistry in lakes, distances through lakes can be shortened (β < 1) or extended (β > 1) under this definition of a LAID. In this study, the β term was assumed constant such that the catchment-scale influence of instream lakes was constant over these small, headwater systems. As such, this definition leads to a metric that satisfies the triangle inequality (see Lyon et al., 2010) and can be used in traditional geostatistical techniques such as semivariogram development and ordinary kriging interpolation.

2.3 Using different distance definitions for interpolations in boreal stream Networks

2.3.1 Preprocessing of spatial data and calculating distances

Preprocessing of the spatial data was carried out in ESRI ArcGIS 9.2 using standard functions, the ETGeowizard (SpatialTechniques, 2010), and the FLoWS toolbox presented in Theobald et al. (2006). FLoWS is a freely available toolbox for ArcGIS with the capability to calculate both EDs and IDs between sites within a stream network. In addition, the FLoWS toolbox was used to break the IDs between any two sampling sites into the distance travelling through streams (d_{stream}) and the distance travelling through lakes (d_{lake}). These distances were then exported to Matlab (MathWorks, 2010) to determine LAIDs.

Since the LAID has a scaling factor that must be fitted (see following section), the methodology from Lyon et al. (2008, 2010) was adopted in this study to determine the optimal LAID for each constituent at each catchment for each synoptic sampling campaign. As a first step to this process, LAID was determined for several incremental values of β from 0.1 to 2 by increments of 0.1 and from 2 to 10 by increments of 1. The factors were limited to this range and these increments as values both smaller than 0.1 and greater than 10 showed minimal differences in the interpolation results (analysis not shown).

2.3.2 Performing geostatistics and optimizing LAIDs

Development of the empirical and theoretical semivariogram and the ordinary kriging interpolations were calculated in Matlab (MathWorks, 2010) using the distance matrices for EDs and IDs exported from the FLoWS toolbox and all the unique LAIDs for the incremental values of β.

Ordinary kriging is a geostatistical method that estimates values of a random function at an unsampled location based on values at sampled sites in a defined neighborhood. It uses the spatial structure of the variance in the dataset described by a semivariogram to produce a statistically optimal estimate. In order to estimate the theoretical semivariogram ($\gamma(h)$), all site pairs with less than half the maximum separation distance of the dataset were combined into equally spaced groups or bins (Rossi et al., 1992) to create an empirical semivariogram. For ordinary kriging in stream networks, the exponential model guarantees the positive-definiteness required for ordinary kriging (Ver Hoef et al., 2006; Peterson et al., 2007). Thus, this study used an exponential model similar Cressie (1985) to represent the theoretical semivariogram for ordinary kriging:

$$\gamma(h) = c_o + c_e\left[1 - \exp\left(\frac{-h}{a_e}\right)\right] \qquad (2)$$

where h is the distance between a pair of sites. This exponential model contains three fitted parameters: c_o is the nugget, c_e is the sill, and a_e is the range. The parameters were fit using the weighted least square algorithm of Cressie (1985). After obtaining the fitted model of the theoretical semivariogram for a given dataset, ordinary kriging interpolation can be performed. The interpolated value of a given quantity at the unsampled location ($A^*(x_o)$) is estimated using:

$$A^*(x_o) = \sum_{i=1}^{n} \lambda_i A(x_i) \qquad (3)$$

where λ_i are the weighting factors for the observed value of the given quantity at each neighboring site ($A(x_i)$) of the n total neighboring sites considered. The weighting factors (which sum to unity) are chosen in a way that the variance at the unsampled location is minimized while being constrained by unbaisedness.

To optimize the LAID, $RMSE_{krig}$ was minimized over the various incremental changes in the β scaling factor. $RMSE_{krig}$ was evaluated by using a leave-one-out cross-validation (Davis, 1987; Nielsen and Wenderoth, 2003). This consists of removing one sample site at a time from the dataset and estimating the value at that location based on the remaining sample sites in the dataset. Repeating for all sampled sites, the $RMSE_{krig}$ was calculated as:

$$RMSE_{krig} = \sqrt{\frac{\sum_{i=1}^{n} (A^*(x_o) - A(x_i))^2}{n}} \qquad (4)$$

where $A^*(x_o)$ is the interpolated value of a constituent at location x_o and $A(x_i)$ the measured value at the same location. This $RMSE_{krig}$ allows for a comparison of performance between all distance measures (ED, ID, and the optimized LAID) for a given constituent and synoptic campaign.

2.3.3 Kriging interpolations and performance measures

In addition to quantifying $RMSE_{krig}$ associated with each distance metric, continuous maps of stream water chemistry were produced using ED, ID and the optimal LAID for TOC, TN, TP, K, and ANC in the Lugnån catchment for the 2007 synoptic campaign. This allowed for visualization of the ordinary kriging interpolation values at unsampled locations in this stream network. For this purpose, the stream network was split into 250 m long line segments represented by sites positioned at the centre of each line segment.

Along with the interpolated values, the kriging variance was calculated and mapped along the stream network. Kriging variance is a measure for the suitability of the spatial configuration of neighboring sites (Nielsen and Wenderoth, 2003; Chilès and Delfiner, 1999) and often interpreted as a level of uncertainty for the interpolation (e.g. Gardner et al., 2003; Skøien et al., 2006). Kriging variance ($s^2(x_o)$) at an unsampled location is given as:

$$s^2(x_o) = \sum_{i=1}^{n} \lambda_i \gamma(x_i - x_o) + \mu \qquad (5)$$

where $\gamma(x_i\text{-}x_o)$ is the semivariance estimated between a sampled and an unsampled site and μ is the kriging Lagrangian multiplier. In the special case of a flat semivariogram defining a pure nugget model, equal interpolation weighting factors are assigned to all neighboring sites and the kriging variance is calculated as (Armstrong and Boufassa 1988):

$$s^2(x_o) = (n+1)c_o / n \qquad (6)$$

where n is the number of neighboring sites and c_o is the nugget of the theoretical semivariogram. In addition to mapping the kriging variance of a subset of constituents, Eq. (5) and Eq. (6) were applied to each sampling site in a leave-one-out routine (similar to that outlined above) to calculate an average kriging variance over all constituents and synoptic campaigns.

The mean squared deviation ratio (*MSDR*) was also defined for each interpolation as:

$$MSDR = \frac{1}{N}\sum_{i=1}^{N}\frac{(A^*(x_o) - A(x_i))^2}{s^2(x_o)} \quad (7)$$

Where *N* is the total number of observation locations. The *MSDR* provides a measure of the bias associated with a kriging interpolation with values over 1 implying under estimation of the residuals by the kriging variance and values over 1 implying over estimation. MSDR is, therefore, a performance diagnostic of a kriging model's prediction uncertainty accuracy in a global-sense.

3. Results

3.1 Comparison of the distances

Adopting a Euclidean distance (ED) between sampling sites in a stream network led to smaller separation distances on average between the sites in the stream network compared to using an instream distance (ID) (Table 2). This was expected due to the meandering nature of stream networks. The optimal lake adjusted instream distance (LAID) had much variability (Table 3); however, most optimal LAIDs were longer than the corresponding IDs for a given catchment. This is because, for the most part (31 out of 40 cases), β scaling factors were larger than 1 (Table 4) indicating that the distance through lakes was increased during interpolation. Looking at the two synoptic campaigns (October 2007 vs. April 2008), there was some consistency in the changes in the optimal β scaling factor. TOC was the only constituent that showed a constant decrease in β scaling factor from October 2007 to April 2008 across all catchments. On average, the β scaling factor increased for plant nutrient constituents (TN, TP, and K) from October 2007 to April 2008 while ANC stayed about the same.

Table 2: General statistics of Euclidian distance (ED) and instream distance (ID) values calculated for each of the catchments considered in this study.

Catchment name	Lungån	Getryggsån	Anråse å	Danshytteån
ED: Average (Standard Deviation) [km]	5.8 (3.2)	4.6 (3.7)	4.1 (2.1)	4.6 (2.6)
ID: Average (Standard Deviation) [km]	10.7 (5.8)	6.8 (5.4)	11.7 (7.5)	8.3 (4.7)
Ratio total length in lakes to length in stream	0.27	0.18	0.13	0.22

Table 3: General statistics for the optimal lake adjusted instream distance (LAID) for each chemical constituent over each catchment considered.

Catchment name	Lungån	Getryggsån	Anråse å	Danshytteån
October 2007 Synoptic Campaign: Average (Standard Deviation)				
LAID for TOC [km]	30.9 (16.8)	9.2 (7.3)	25.4 (16.3)	13.8 (7.8)
LAID for TN [km]	9.3 (5.0)	8.0 (6.4)	10.3 (6.6)	13.8 (7.8)
LAID for TP [km]	25.1 (13.6)	7.4 (5.9)	10.3 (6.6)	6.8 (3.9)
LAID for K [km]	11.0 (6.0)	7.4 (5.9)	14.7 (9.5)	21.1 (11.9)
LAID for ANC [km]	11.3 (6.1)	17.8 (14.1)	22.3 (14.3)	9.2 (5.2)
April 2008 Synoptic Campaign: Average (Standard Deviation)				
LAID for TOC [km]	19.4 (10.5)	6.2 (4.9)	17.8 (11.4)	8.7 (4.9)
LAID for TN [km]	11.0 (6.0)	6.2 (4.9)	13.2 (8.5)	21.1 (11.9)
LAID for TP [km]	9.3 (5.0)	5.7 (4.5)	22.3 (14.3)	12.0 (6.8)
LAID for K [km]	13.6 (7.4)	8.0 (6.4)	14.7 (9.5)	21.1 (11.9)
LAID for ANC [km]	30.9 (16.8)	10.5 (8.3)	22.3 (14.3)	7.4 (4.2)

Table 4: Scaling factor (β) optimized for defining the lake adjusted instream distance (LAID) for each chemical constituent over each catchment considered. The change in these scaling factors between the October 2007 and the April 2008 synoptic campaigns ($\Delta\beta$) is listed.

Catchment name	Lungån	Getryggsån	Anråse å	Danshytteån	Average (All catchments)
October 2007 Synoptic Campaign					
β for TOC	8	3	10	4	6.3
β for TN	0.5	2	0.1	4	1.7
β for TP	6	1.5	0.1	0.2	2.0
β for K	1.1	1.5	3	8	3.4
β for ANC	1.2	10	8	1.5	5.2
April 2008 Syntopic Campaign					
β for TOC	4	0.5	5	1.2	2.7
β for TN	1.1	0.5	2	8	2.9
β for TP	0.5	0.1	8	3	2.9
β for K	2	2	3	8	3.8
β for ANC	8	4	8	0.5	5.1
$\Delta\beta$ from October 2007 to April 2008					
$\Delta\beta$ for TOC	4.0	2.5	5.0	2.8	3.6
$\Delta\beta$ for TN	-0.6	1.5	-1.9	-4.0	-1.3
$\Delta\beta$ for TP	5.5	1.4	-7.9	-2.8	-1.0
$\Delta\beta$ for K	-0.9	-0.5	0.0	0.0	-0.4
$\Delta\beta$ for ANC	-6.8	6.0	0.0	1.0	0.0

3.2 Comparison of ordinary kriging performance

Kriging root mean squared error ($RMSE_{krig}$) cross-validation helps indicate the best performing distance measure of the three distance measures (ED, ID, and LAID) considered (Table 5). In 31 of 40 cases considered, kriging based on the LAID led to the lowest $RMSE_{krig}$. Of these 31 cases, the distance in lakes had been increased (i.e., the β scaling factor was larger than 1) in 25 cases. The Lugnån and Anråse å catchments were the only two catchments where either using EDs or IDs led to the lowest $RMSE_{krig}$. The high frequency of LAID producing the lowest $RMSE_{krig}$ may be related to the fitting procedure that explicitly optimizes $RMSE_{krig}$ (Lyon et al., 2008). Next to LAID, the ID gave the lowest $RMSE_{krig}$ in 27 of the interpolation cases while ED gave the lowest $RMSE_{krig}$ in only 13 cases. Thus, ID generally outperformed ED for these systems.

Kriging variance (Table 6) may give a better measure of uncertainty for an interpolation based on different distance metrics. Looking across all cases, the optimal LAID led to the lowest kriging variance in more cases than either ED or ID (albeit slightly with only 15 of 40). Again, considering only interpolations using ID and ED, ID outperformed ED and gave the lowest kriging variance in 22 of the 40 cases considered. The mean squared deviation ratio (*MSDR*) as a performance measure (Table 7) indicates the bias inherent to interpolations using the three distance measures (ED, ID, and LAID). Looking across all cases, the ED led to the least biased interpolation in more cases than either the optimal LAID or ID (again albeit slightly with only 15 of 40). Considering only interpolations using ID and ED, ID-interpolations were less biased than ED-interpolations in 23 of the 40 cases considered. Interestingly for the *MSDR* values when considering only ED and ID interpolations, the October 2007 interpolations based on ED by and large had the least bias relative to those made using ID while during April 2008 the ID-based interpolations had the least bias.

Table 5: The kriging root mean squared error ($RMSE_{krig}$) for each constituent in each catchment from the kriging interpolations based on Euclidian distance (ED), instream distance (ID), and optimal lake adjusted instream distance (LAID). Bold numbers indicate the 'best' performer for this criterion.

Catchment name	Constituent	Using ED	Using ID	Using LAID
$RMSE_{krig}$ for October 2007 Synoptic Campaign				
Lungån	TOC [mg/L]	**7.5**	8.4	8
	TN [µg/L]	195	**185.3**	188.3
	TP [µg/L]	9.9	10	**9.9**
	K [µg/L]	8.1	7.5	**7.5**
	ANC [µeq/L]	135.5	130.5	**130.5**
Getryggsån	TOC [mg/L]	9.4	7.9	**7.8**
	TN [µg/L]	67.9	66.1	**66**
	TP [µg/L]	4.7	4.7	**4.6**
	K [µg/L]	1.4	1.4	**1.4**
	ANC [µeq/L]	25.2	28.4	**23.1**
Anråse å	TOC [mg/L]	4.6	4.6	**4.4**
	TN [µg/L]	181	182.7	**180.9**
	TP [µg/L]	**26.3**	27.9	26.4
	K [µg/L]	12.4	11.4	**10**
	ANC [µeq/L]	173.1	167	**158.4**
Danshytteån	TOC [mg/L]	10.2	10.1	**9.5**
	TN [µg/L]	116.1	117	**111.5**
	TP [µg/L]	6	5.6	**5.6**
	K [µg/L]	3.8	3.4	**3.3**
	ANC [µeq/L]	51.4	50.9	**50**
$RMSE_{krig}$ for April 2008 Synoptic Campaign				
Lungån	TOC [mg/L]	**3.3**	4	3.8
	TN [µg/L]	201.2	**200.9**	201.3
	TP [µg/L]	**10.3**	11.2	10.6
	K [µg/L]	**7.1**	7.6	7.2
	ANC [µeq/L]	79.7	82.4	**78.5**
Getryggsån	TOC [mg/L]	7	6.4	**6.3**
	TN [µg/L]	91.3	81.3	**79**
	TP [µg/L]	8.1	8.1	**8.1**
	K [µg/L]	2.8	2.8	**2.7**
	ANC [µeq/L]	32.2	32.8	**31.3**
Anråse å	TOC [mg/L]	2.2	2.1	**1.8**
	TN [µg/L]	**106.1**	107.9	107.2
	TP [µg/L]	**7.5**	8.4	8.1
	K [µg/L]	8.1	7.1	**6.4**
	ANC [µeq/L]	101.3	99.5	**87.9**
Danshytteån	TOC [mg/L]	4.7	4	**4**
	TN [µg/L]	88.1	75	**74.2**
	TP [µg/L]	1.6	1.3	**1.3**
	K [µg/L]	3.9	3.6	**3.5**
	ANC [µeq/L]	58.6	46.1	**45.9**

Table 6: The average kriging variance for each constituent in each catchment from the kriging interpolations based on Euclidian distance (ED), instream distance (ID), and optimal lake adjusted instream distance (LAID). Bold numbers indicate the 'best' performer for this criterion.

Catchment name	Constituent	Using ED	Using ID	Using LAID
Kriging variance for October 2007 Synoptic Campaign				
Lungån	TOC [mg/L]	59.7	53.4	**48**
	TN [µg/L]	**12115.5**	12617.8	13371.2
	TP [µg/L]	82.4	**74.9**	86.1
	K [µg/L]	**34.7**	44.7	45
	ANC [µeq/L]	16192.8	13654.2	**13652.9**
Getryggsån	TOC [mg/L]	**103**	106.6	135
	TN [µg/L]	3174.2	2949.1	**2943.6**
	TP [µg/L]	19	**16**	18.1
	K [µg/L]	1.8	**1.6**	1.7
	ANC [µeq/L]	938.2	1021	**896.3**
Anråse å	TOC [mg/L]	8.8	10.5	**8.1**
	TN [µg/L]	18086.6	**14102.8**	14486.5
	TP [µg/L]	282.7	**196.3**	225.7
	K [µg/L]	**100.7**	102.1	237.6
	ANC [µeq/L]	**22639.5**	22851.2	42211.2
Danshytteån	TOC [mg/L]	86.4	73.2	**67.8**
	TN [µg/L]	9535.8	9692.7	**9237.3**
	TP [µg/L]	42.7	42.5	**41.3**
	K [µg/L]	7.5	**7.1**	8.5
	ANC [µeq/L]	2143	**2091.8**	2271.3
Kriging variance for April 2008 Synoptic Campaign				
Lungån	TOC [mg/L]	16.6	**14.8**	14.9
	TN [µg/L]	16145.6	16094.4	**13303.7**
	TP [µg/L]	104.5	**102.1**	125
	K [µg/L]	23.1	24.5	**22.4**
	ANC [µeq/L]	3818	3405.6	**2273.7**
Getryggsån	TOC [mg/L]	**30.8**	31.3	32.2
	TN [µg/L]	7503.5	**6827.9**	7276.6
	TP [µg/L]	107.4	108.1	**96.9**
	K [µg/L]	**8.3**	8.6	8.8
	ANC [µeq/L]	**580.1**	614.7	594.6
Anråse å	TOC [mg/L]	**1.6**	1.8	1.8
	TN [µg/L]	**9992.1**	10548.9	10672.9
	TP [µg/L]	**76.2**	86.2	157.2
	K [µg/L]	38.5	**34.2**	80
	ANC [µeq/L]	**7171.5**	9121.9	14353.1
Danshytteån	TOC [mg/L]	17.4	**13**	13.3
	TN [µg/L]	6096.5	5202.6	**4532.3**
	TP [µg/L]	0.8	0.6	**0.5**
	K [µg/L]	13.3	8.5	**7**
	ANC [µeq/L]	**1761.8**	1782.5	1771.6

Table 7: The mean squared deviation ratio (*MSDR*) for each constituent in each catchment from the kriging interpolations based on Euclidian distance (ED), instream distance (ID), and optimal lake adjusted instream distance (LAID). Bold numbers indicate the 'best' performer for this criterion.

Catchment name	Constituent	Using ED	Using ID	Using LAID
Kriging variance for October 2007 Synoptic Campaign				
Lungån	TOC [mg/L]	**0.94**	1.32	1.33
	TN [µg/L]	3.14	2.72	**2.65**
	TP [µg/L]	1.19	1.34	**1.14**
	K [µg/L]	1.89	1.26	**1.25**
	ANC [µeq/L]	**1.13**	1.25	1.25
Getryggsån	TOC [mg/L]	**0.86**	0.59	0.45
	TN [µg/L]	**1.45**	1.48	1.48
	TP [µg/L]	**1.16**	1.38	1.17
	K [µg/L]	**1.09**	1.23	1.15
	ANC [µeq/L]	0.68	**0.79**	0.60
Anråse å	TOC [mg/L]	2.40	**2.02**	2.39
	TN [µg/L]	**1.81**	2.37	2.26
	TP [µg/L]	**2.45**	3.97	3.09
	K [µg/L]	1.53	**1.27**	0.42
	ANC [µeq/L]	1.32	**1.22**	0.59
Danshytteån	TOC [mg/L]	**1.20**	1.39	1.33
	TN [µg/L]	1.41	1.41	**1.35**
	TP [µg/L]	**0.84**	0.74	0.76
	K [µg/L]	1.93	1.63	**1.28**
	ANC [µeq/L]	1.23	1.24	**1.10**
Kriging variance for April 2008 Synoptic Campaign				
Lungån	TOC [mg/L]	0.66	1.08	**0.97**
	TN [µg/L]	2.51	**2.51**	3.05
	TP [µg/L]	**1.02**	1.23	0.90
	K [µg/L]	**2.18**	2.36	2.31
	ANC [µeq/L]	**1.66**	1.99	2.71
Getryggsån	TOC [mg/L]	1.59	1.31	**1.23**
	TN [µg/L]	1.11	**0.97**	0.86
	TP [µg/L]	0.61	0.61	**0.68**
	K [µg/L]	**0.94**	0.91	0.83
	ANC [µeq/L]	1.79	1.75	**1.65**
Anråse å	TOC [mg/L]	3.03	2.45	**1.80**
	TN [µg/L]	1.13	1.10	**1.08**
	TP [µg/L]	0.74	**0.82**	0.42
	K [µg/L]	1.70	**1.47**	0.51
	ANC [µeq/L]	1.43	**1.09**	0.54
Danshytteån	TOC [mg/L]	1.27	1.23	**1.20**
	TN [µg/L]	1.27	**1.08**	1.21
	TP [µg/L]	3.20	**2.82**	3.38
	K [µg/L]	**1.14**	1.52	1.75
	ANC [µeq/L]	1.95	1.19	**1.19**

3.3 Visual comparison of selected results

The absolute errors at each sampling site (Figure 2) are the values obtained by a leave-one-out cross-validation that are averaged to compute the $RMSE_{krig}$. These errors compare the ordinary kriging interpolation to the observed value of the chemical constituent. It should be noted that while results are presented for only three of the cases considered in this study, these cases highlight scenarios where $RMSE_{krig}$ was lowest for an ED-based interpolation (e.g., TOC), an ID-based interpolation (e.g., TN) and a LAID-based interpolation (e.g., ANC) within a given catchment (e.g., Lugnån) and synoptic campaign (e.g., October 2007). It is obvious that for all three constituents (TOC, TN, and ANC), high absolute errors tended to stay high when changing between the distance metrics. There was a tendency that the absolute errors were higher towards the headwaters of streams and lower along the main stem of the network. The spatial patterns in the kriging variance (Figure 2) from the different distance measures were similar. For TOC, however, there was marked difference in the kriging variance for the interpolation based on an optimal LAID which shows considerably lower kriging variances. As with the absolute error, the kriging variance tended to be higher towards the headwaters of streams.

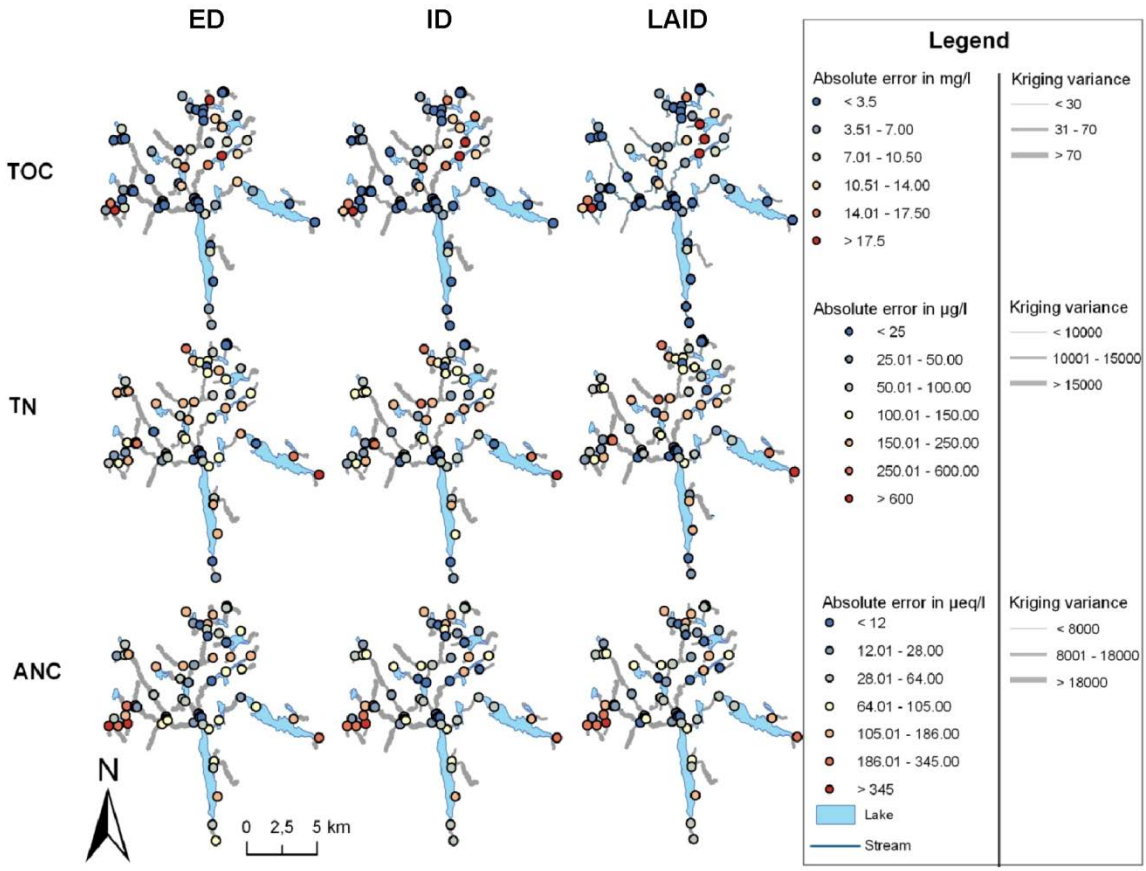

Figure 2: Map showing the absolute error comparing Total Organic Carbon (TOC), Total Nitrogen (TN), and Acid Neutralizing Capacity (ANC) compared to the kriging interpolated value using Euclidean distance (ED), instream distance (ID) and optimal lake adjusted instream distance (LAID) at each sample site in the Lugnån catchment for the October 2007 sampling campaign. The size of the line representing the stream is proportional to the kriging variance.

The influence of the distance definition on predicting chemical constituents in the stream network can be seen explicitly in Figure 3. These maps highlight the differences in how distance was represented in each case. For example, using ED, the TN concentration was lower in the northern part of the stream segment (marked with Arrow 1 in Figure 3). Around the middle section of this stream segment, a sample site with a higher TN concentration can be found on a non-connected stream reach north-east of the marked stream segment. Using an ED definition, this unconnected site had much influence on the stream segment; whereas, with ID or an optimal LAID there was no influence. The differences between ID and LAID tended to be less pronounced for the selected results presented here. Those differences identified easily through visual inspection occurred mainly upstream of lakes (marked with Arrow 2 in Figure 3).

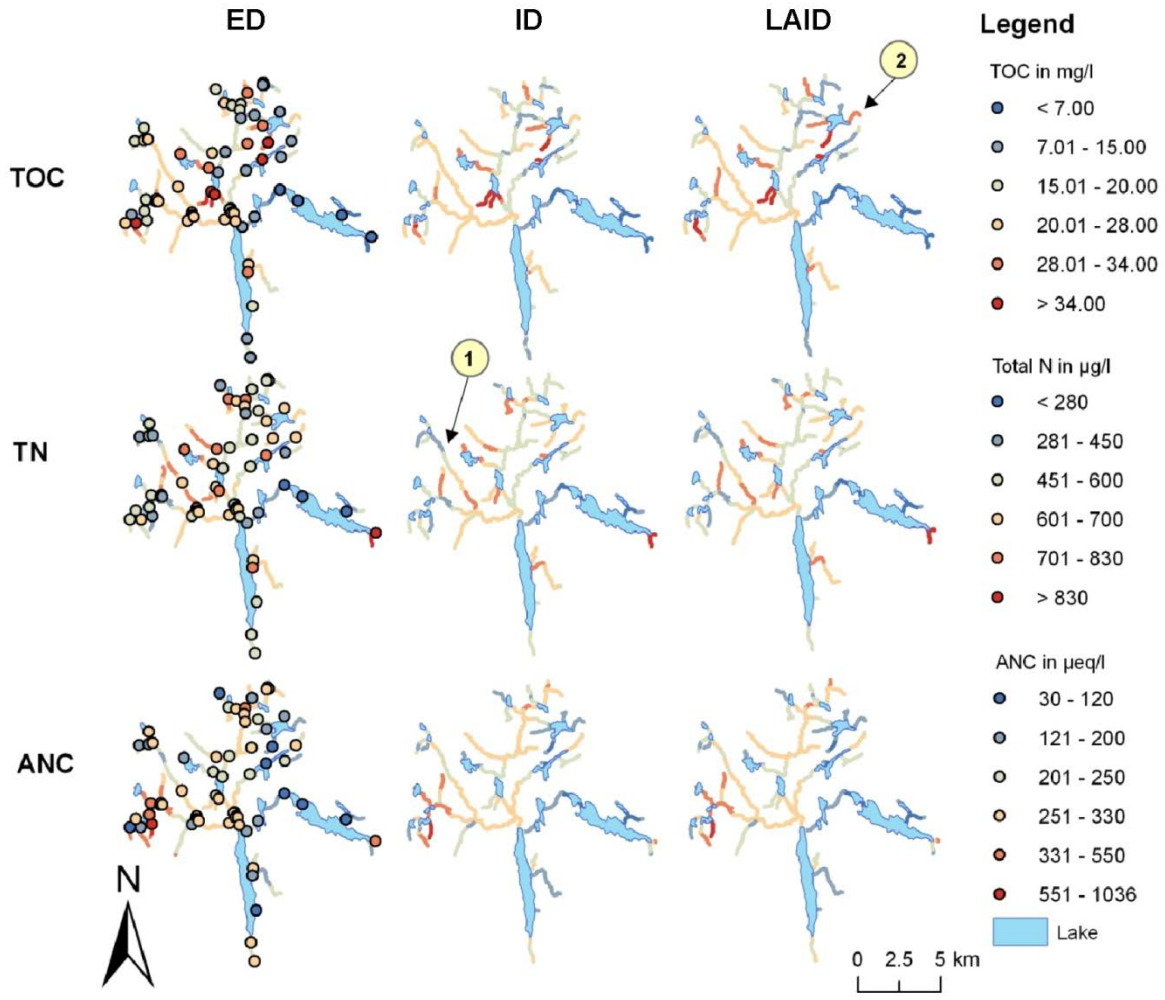

Figure 3: Map showing the Total Organic Carbon (TOC), Total Nitrogen (TN), and Acid Neutralizing Capacity (ANC) at each sample site in the Lugnån catchment for the October 2007 sampling campaign and the related kriging interpolations using Euclidean distance (ED), instream distance (ID) and optimal lake adjusted instream distance (LAID).

4. Discussion

4.1 The influence of distance definitions in geostatistics

Adjusting instream distances by changing the length of stream segments in lakes increases the performance of ordinary kriging interpolation of stream water chemistry in southern Sweden in most cases considered in this study. Distance altering approaches similar to the one used here have been applied by Gardner et al. (2003) and Lyon et al. (2008). These studies demonstrated more improvement in the interpolations when altering instream distances than was achieved in this current study. This could be attributed to distance altering based on more temporally consistent first-order controls on water chemistry in other studies. For example, the influence of landuse characteristics on water chemistry in the non-boreal landscape considered in Lyon et al. (2008) was likely more pronounced than the influences of lakes in this current study. Lyon et al. (2008) considered samples from a catchment with a clear and heavy influence of agricultural lands, primarily pastures and corn fields, over large parts of the catchment on water chemistry (Lyon et al., 2006). In this current study, while lakes clearly influence stream water chemistry in these systems (Temnerud and Bishop, 2005; Temnerud et al.,2007), this influence is rather temporally variable and potentially complicated by landscape transport processes and groundwater-surface water interactions which also influence stream water chemistry. As such, only a minor improvement was brought about when interpolation based on LAID and there was much variability in which distance definition performed 'best'.

Another potential reason for the rather small improvement seen using LAID could be due to the use of symmetric ID. Symmetric ID that allows for both flow connected and flow unconnected sites might not be so 'realistic' a representation of passive movement in streams (Peterson et al., 2006; Peterson and Urquhart, 2006; Peterson et al., 2007). This could lower the potential performance of a LAID in interpolations of water chemistry. Peterson and Urquhart (2006) worked around this potential 'unrealistic' nature of the symmetric ID by using an asymmetric ID weighted by flow volume to predict dissolved organic carbon in a stream network. Adopting asymmetric IDs, however, greatly reduces the number of sites available for a kriging interpolation as it limits the number of connected sites. In addition, pure asymmetric IDs produce singular matrices that cannot be inverted to solve for kriging weights (Peterson et al., 2007). As such, the advantages offered with asymmetric ID may not outweigh the potential shortcomings. More pragmatically speaking, as the symmetric IDs considered in this study tended to outperform EDs based on the $RMSE_{krig}$ (Table 5), variance (Table 6), and bias (Table 7), there is some support for adopting symmetric ID definitions.

Further, the relative performance of ID compared to ED between the October 2007 and April 2008 samplings may indicate a shift from a dominance of landscape-transport process to instream-transport processes for these systems. ID-interpolations tended to be more biased during the relatively drier October 2008 samplings compared to the ED-interpolations (Table 7). This pattern switched for the wetter April 2008 samplings. This potentially indicates that during relatively lower flow conditions (i.e., October 2007) there is a stronger connection between landscape processes and stream water chemistry such that the ED leads to a less biased interpolation. This is consistent with Yuan (2004) who demonstrated that ordinary kriging in stream networks using ED can be more appropriate than using ID for certain variables when they are governed by external factors on a larger scale. As the landscape is in general drier during these lower flow, late autumn conditions, lateral subsurface flow pathways (and the inherent variability therein across the landscape) are likely responsible for moving nutrients and biogeochemical from the landscape into the stream network (e.g., Lyon et al., 2011). As such, ED might be more representative of the spatial patterns of watershed biogeochemistry in this boreal landscape under such conditions. During spring periods (i.e., April 2008), the landscape is in a wetter state and, thus, biogeochemical movement from the landscape is no longer transport limited (Basu et al, 2010). During such periods, IDs allows for a less biased representation of the stream water chemistry compared to EDs (Table 7).

4.2 Trends in kriging errors and variance

The maps of the cross-validation absolute errors (Figure 2) show that interpolation errors tend to be higher towards the headwaters than along the main channels. This is due to the higher variation in water chemistry in the headwaters than in streams of higher order as described by Temnerud and Bishop (2005) and Bishop et al. (2008). Gardner et al. (2003) presented higher kriging standard errors in headwaters because they were farthest away from the sampling sites. Skøien et al. (2006) showed that cross-validation errors were generally higher on tributaries than on the main channel when interpolating 100-year flood events. Predicting water chemistry in unsampled headwaters by ordinary kriging interpolation is problematic and, although incorporating lakes into the interpolation increased the overall performance of the interpolation, the problem of unsampled headwaters are not solved by this approach. This was especially problematic in Sweden, where about 90% of the country's total stream length is found in catchments smaller than 15 km^2 (Bishop et al. 2008).

The maps of kriging variance (Figure 2) show small differences in variance between the distance measures for TN and ANC. For TOC, however, the differences between distance measures are more pronounced. These findings are congruent with those by Gardner et al. (2003), showing that distance adjustment by stream order leads to lower kriging standard errors. Generally, extending distances between sample sites as considered in this study often leads to theoretical semivariograms with larger ranges but equal sills (analysis not shown). This implies that the same inter-site distances have lower assigned semivariances for the adjusted distance cases compared to other distance metrics. This highlights a potential disadvantage of using the kriging variance as a measure of interpolation performance as it relies on the theoretical semivariogram and the spatial configuration of the sample sites, but not on the data values at the sample sites (Chilès and Delfiner, 1999). The kriging variance can be used to identify which configuration of sample sites is more suitable compared to another, but it is not an absolute measure for the accuracy of the prediction.

4.3 Interpreting the lake adjusted instream distance methodology

The method of distance adjustment presented here is rather generic in its development. As such, the β scaling factor is fitted as a constant over all lakes in each catchment for each constituent. If we can assume some deterministic processes influencing constituents within lakes, approaches that account for these processes (i.e., fitting/assigning of unique β scaling factor for each lake) might lead to better interpolations. Such process-driven approaches are not within the scope of this initial geostatistical-based work to incorporate the existence of instream lakes into the definition of distances in stream networks. Even though processes are not explicitly defined in the formation of the LAID, the mechanisms influencing the β scaling factor can be hypothesized in the context of existing understand of these boreal Swedish systems.

Extending lake distances ($\beta > 1$) may be related to the simulation of longer water renewal time in lakes compared to streams. Studies by Essington et al. (2000) and Stendera et al. (2006) showed that the differences in renewal time between lakes and streams can explain some of the variation in water chemistry between both systems. An extension of the distance in lakes could hence lead to a more mechanistically accurate representation of flow of water between a lake's inlet and outlet. For shortening of the distances ($\beta < 1$), on the other hand, major inflows of the chemical constituent into lakes by groundwater might be a reasonable explanation. Another explanation for distance shortening might be processes of sedimentation or atmospheric exchange (Howarth et al., 1996, Algesten et al., 2004, Laudon et al., 2004), which could justify shorter distances through lakes. As such, the relative magnitude of β across a catchment represents how mechanistically 'lake-like' versus 'stream-like' lakes behaved for a given synoptic campaign.

This is consistent with the results of this study. Here, lakes were more 'lake-like' with optimized β scaling factors different than 1 for all synoptic campaigns considered (Table 4). Further, since there is no explicit process representation associate with the development of the LAID, it is possible to use the β scaling factors

to gauge the relative influence of lakes between the different synoptic campaigns (October 2007 vs. April 2008). Looking at TOC between the October 2007 and April 2008 campaigns (Table 4), there was a consistent decrease in fitted β scaling factors across all catchments. In these systems, the catchments are in general wetter during the spring periods relative to late autumn periods (Table 1). As such, it is likely that the renewal time in lakes was shorter during the April 2008 sampling than in October 2007. This leads to less time in-lake for TOC and less time for the occurrence of photoreaction leading to TOC decay or sedimentation (Laudon et al., 2004). As such, lakes were a more important factor for influencing stream water TOC during October 2007 relative to April 2008.

Counter to this, there is on average across all catchments an increase in fitted β scaling factors between the October 2007 and April 2008 campaigns (Table 4) for the TN, TP, and K interpolations (e.g., the plant nutrient constituents). This may indicate an increased uptake of nutrients via aquatic plants in lakes during the April relative to October in these systems. This increased uptake would coincide with the onset of rapid aquatic plant growth occurring in spring relative to the die off that would be expected during the late autumn at the onset of winter. This would be consistent with an effective lengthening potentially represented via the increased β scaling factors for the TN, TP, and K interpolations. This potentially indicates a greater relative importance of lakes for influencing stream water TN, TP, and K concentrations during April 2008 relative to October 2007.

5. Concluding remarks

It is not entirely clear how all the complexities of instream lakes, catchment wetness, and other landscape factors come together to influence either the processes determine stream water chemistry in these networks. As such, the variability in the fitted β scaling factors of the LAID and in the relative performance of the different distance definitions considered in this study suggests that the influence of geological setting, hydrology and instream lakes on water chemistry is quite variable in this landscape. This is in agreement with more mechanistic studies in this and other boreal landscapes. Regardless, the success of the LAID presented here likely alludes to some inherent process representation captured during certain conditions by accounting for lakes in the definition of distance in a stream network. And, while the overall improvement gained using a LAID is relatively small, such a distance definition allowed for some hypothesis development and estimates of the relative importance of lakes under different seasons.

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