

Faculty of Social and Life Sciences Biology

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DISSERTATION

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Abstract

In boreal catchments, stream water chemistry is influenced and controlled by several landscape factors. The influence of spatially distributed variables is in turn dependent on the hydrological scale. Headwater streams, with catchments smaller than 3-4km², have greater variability of water chemistry compared to major streams, and would therefore need to be taken into consideration and be included in official environmental assessments and monitoring. One objective of this study was to analyse co-variation between landscape variables and water chemistry and to determine which of the landscape variables have a major influence on the concentration of dissolved organic carbon (DOC) in headwater streams. This was done using Geographical Information Systems (GIS). Another objective was to find a simple method for predicting sources of DOC, using official map data and publically available GIS applications.

Totally 85 headwater catchments (0.1-4 km²) in the county of Värmland, western south Sweden, were used in the study. Water chemistry was analysed for water sampled at low, medium and high flows, and landscape variables were extracted from official map data sources: topographic maps, a digital elevation model (DEM, 50 m grid), and vegetation data. Statistical analyses showed that topography (mean slope and mean topographic wetness index (TWI)) and wetland cover often correlated well with DOC in headwater catchments. Official map data could satisfactorily extract landscape variables (mean slope, mean TWI) that were useful in predicting stream water chemistry (DOC).

A high-resolution elevation model, which was generated by interpolation of photogrammetric data, was used to calculate and evaluate two different wetness indices and their ability to predict the occurrence of wetlands in six catchments of different sizes and topography. The SAGA (System for Automated Geoscientific Analyses) wetness index (SWI) gave substantially better results than the TWI. The effects of resolution of DEMs on calculations of the SWI were investigated using 5, 10, 25 and 50 m grids. The results showed that SWI values increased with increasing cell size. The near linear increment of mean values for resolutions 10-50 m suggests an independence of terrain type and catchment size, which supported previous findings that indicated that mean slope and mean wetness index calculated from coarse elevation models may be used for prediction of DOC in headwater streams.

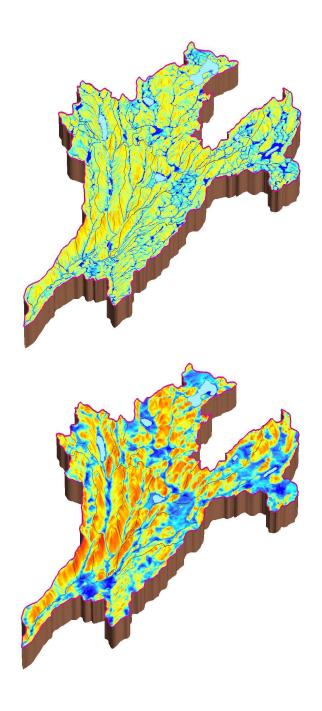


Preface

The debate on anthropogenic acidification of water and soil and its negative biological effects on the Swedish boreal landscape was initiated in 1967 by Svante Odén (1967). Until the late 1990's liming was carried out without taking into account natural acidification. The reasons were mainly a lack of knowledge of natural acidification processes, lack of available data and, perhaps foremost, the difficulty of determining how much of the acidification was caused by natural processes and how much was caused by deposition of sulphate and nitrate (e.g. Bishop *et al.*, 2000). Nevertheless, for decades scientists have been aware that organic acids may strongly influence pH in boreal forest surface.

The effects of acidification have been most severe in western south Sweden, where the decrease in pH in soil and surface water have led to increased levels of toxic aluminium, which have caused deaths of fish and other aquatic organisms (Driscoll et al., 1980). In the county of Värmland in western Sweden a comprehensive survey, called "Värmlands-undersökningen", started in 1994 with the objective of investigating different chemical flows and storages in boreal forest ecosystems. The survey started by investigating soil acidity at 180 sites (Lundström et al., 1998). The results showed clear spatial differences in soil acidification between sites, so the project proceeded to a second stage, studying the vitality of Norway spruce (Pixea abies) (Nyberg et al., 2001). A third stage investigated the acidification status of headwater streams and the influence of landscape elements in the catchments. Seventy-six small forest catchments in Värmland were sampled along a north-south gradient. It was at this stage I became involved and a result of this involvement is the dissertation you are now holding in your hands.

Jan-Olov Andersson August 2009



Contents

List of Papers	6
Introduction	
Background	7
Topography and wetness	8
Boreal forest, wetland and vegetation types	13
Natural organic matter	
Scale and resolution dependency	16
Objectives	18
Methods	20
Study area	20
Selection of streams	21
Streamwater sampling, flow and level measurement	22
Chemical analyses	22
Spatial analyses	22
Statistical analyses	24
Results	25
Paper I	25
Paper II	
Paper III	28
Paper IV	29
Paper V	33
Discussion	35
Sources of DOC	35
Available official map data	36
Wetness indices for prediction of wetlands	36
Scales and data resolution	37
Concluding remarks	39
Acknowledgements	40
References	41

List of Papers

This thesis is based on the following papers which are referred to by Roman numerals.

- I. Andersson, J-O. and Nyberg, L. 2008. Spatial variation of wetlands and flux of dissolved organic carbon concentration in headwater streams. *Hydrological Processes*, 22, 1965-1975.
- II. Andersson, J-O. and Nyberg, L. 2009. Using official map data on topography, wetlands and vegetation cover for prediction of stream water chemistry in boreal headwater catchments. Hydrology and Earth System Sciences, 13, 537-549.
- III. Nyberg, L., Andersson, J-O., Mörth, M. and Malmström, M. 2009. Influence of wetland restoration on local hydrology and DOC-leaching. *Manuscript*.
- **IV.** Andersson, J-O. and Nyberg, L. 2009. Wetness indices as predictors of boreal wetlands. *Manuscript*.
- **V.** Andersson, J-O. 2009. DEM resolution effects on the SAGA wetness index in boreal forested catchments. *Manuscript*.

The designs of the study, the water sampling and statistical analyses were performed by Jan-Olov Andersson and Lars Nyberg. Survey of catchments and GIS analyses were performed by Jan-Olov Andersson.

Paper I is reproduced with kind permission from *Hydrological Processes*. Paper II is reproduced with kind permission from *Hydrology and Earth System Sciences*.

Introduction

Background

In our global interest for a sustainable future there is an increasing need for understanding interactions in nature and the environment as a whole. In this endeavour the importance of hydrology within environmental sciences has grown during the three last decades. In hydrology, as in many other natural science disciplines, there is a mix of universal laws and complex inter-dependencies that are approached from both "upward" and "downward" perspectives. Progress has been made in many areas of hydrology during the last decades, but there is still a lack of methods to combine these two approaches (Sivapalan *et al.*, 2003), which, at catchment scales, are needed to understand the controls, influences and covariation between climate, topography, landscape elements, chemical processes and human impact.

Topography and wetlands are the focus of my dissertation since they are known to be important factors controlling stream water runoff patterns, residence and transit times and flow paths, and the variability of biogeohydrochemical processes (Merot and Bruneau, 1993). The interrelations between the factors and their influence on headwater chemistry are, however, still not fully understood.

Headwater streams, which in this thesis include first and second order streams with catchments sizes ranging from 0.1 to 4 km², have larger variability in runoff and water chemistry than streams of higher order (Wolock *et al.*, 1997). Consequently they include a greater number of habitats and have higher biodiversity than high order streams (Vannote *et al.*, 1980), and should therefore be considered important in environmental assessments. This does not necessarily mean that every single headwater stream has to be protected, but one should be aware that over 40 % of the water in large rivers and lakes originates from these small streams (Bishop *et al.*, 2001; SEPA, 2003; Bishop *et al.*, 2008).

There is not much appropriate data available on small-scale catchments, nor are resources available to survey the large number of headwater streams that would be needed to provide an adequate base for taking appropriate conservation measures. In the Swedish Environmental Quality Criteria for Land and Watercourses (SEPA, 2000), the smallest surveyed catchment is 15 km². However, the European Union's Water Framework Directive (WFD) demands assessments for all surface waters, even those smaller than 15 km². This means that Swedish water management has to adopt a strategy that includes assessment of headwater streams and catchments. Collection of spatial and hydrological data with better quality and higher resolution is probably not economically possible. An alternative approach is to develop new

methods to analyse available data and learn how to interpret and characterize the controlling landscape variables (Hooper, 2001), with hopes of being able to predict stream water chemistry.

Below, the landscape factors studied in this thesis are described and specified with reference to the biogeohydrological field. First, the influence of topography and the progress that has been made in understanding its importance in hydrological analysis of catchments is described. Second, I describe the heterogeneity of boreal forests, wetlands and vegetation types in the study area, and how they are reflected in the stream water chemistry of the catchments. The production of dissolved organic matter, which is so important in boreal forest hydrochemistry, is then discussed, followed by a discussion of hydrological scale, and how landscape analysis and modelling depend on and are complicated by data resolution.

Topography and wetness

Catchment topography can be characterized by a variety of parameters such as slope, slope length, shape, elevation, size, aspect, relief ratio, stream density and frequency (Chang and Boyer, 1977). Topography affects stream flow and influences the shape of the hydrograph through catchment storage, runoff, infiltration, and soil water content. High elevation implies low temperatures, little evapotranspiration, high rainfall, steep slope and shallow soil depth, which means more and faster runoff at high elevation than at low elevation. Slope measures the rate of change of elevation and the direction of steepest descent, and the means by which gravity induces flow of water. Thus, slope is of great significance in hydrology, affecting the soil water content, water velocity, flow paths, transit and residence times and subsequently the chemical composition of surface waters (Beven, 1986; Wolock *et al.*, 1989).

Digital topographic data have in recent years rapidly increased in importance and are frequently used by researchers and engineers for terrain analysis in many fields of science. This depends mainly on the increasing availability of data and development of computers and computer software that have made the calculation of terrain variables and indices much easier than previously. Today most GIS and a number of other scientific computer programs have tools for terrain analysis, including algorithms for the calculation of hydrological attributes and indices (Moore *et al.*, 1991; Gallant and Wilson, 1996). By using a number of these variables and indices, a catchment can be characterized in terms of geomorphology, stream network, water saturation, etc. (Beven and Kirkby, 1979; More *et al.*, 1993c).

The first algorithm for calculation of an index for water saturation was developed by Beven and Kirkby (1979), and used in TOPMODEL. The index, called topographic wetness index (TWI), is still widely used in many applications due to its simplicity. The TOPMODEL TWI combines an algorithm calculating a local contributing area (also called accumulated upslope area or specific catchment area (SCA)) per unit contour length a, which is the area flowing to a specific location, and the local slope tan β , which indicates the potential drainage from that location. A DEM grid is commonly the base for the TWI calculation but there are various algorithms for the contributing area calculation. These algorithms can be divided into two categories: single-flow-direction (sfd) and multiple-flow-direction algorithms (mfd). The earliest and simplest is a sfd algorithm called D8 (eight flowdirections), which was introduced by O'Callagan and Mark (1984). D8 means that all the area from one cell is routed into the steepest of its neighbouring cells. This causes disadvantages, arising from the discretization of flow in only eight possible directions separated by 45°. Other sfd algorithms are Rho8 (Fairfield and Leymarie, 1991), Lea's method (Lea, 1992) and D∞ (Tarboton, 1997). Mfd methods were suggested by Quinn et al. (1991) and Freeman (1991) as an attempt to solve the limitations of D8. Quinn's method, called MS or MD8, allocates the flow fractionally to each lower neighbour cell with the probability proportional to the slope. A disadvantage with the MD8 method is that the area from one cell is dispersed evenly in convergent hillslopes. Holmgren (1994) suggested using an exponent to the slope to portion out the flow. Other mfd algorithms are DEMON (Costa-Cabral and Burges, 1994) and MD∞ (Seibert and Mc Glynn, 2007).

Examples of the different methods for illustrating flow dispersion are shown below (Figs. 1-4). Depending on the hillslope characteristic, water flow differs in dispersion pattern. A hillslope can be planar, convergent, divergent or have a saddle shape.

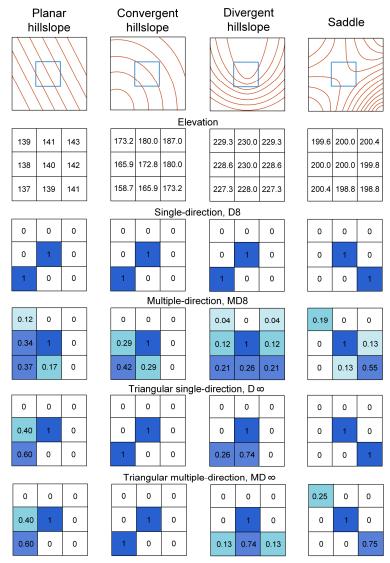


Fig. 1. Examples of synthetic data explaining the distribution of accumulated area from one cell (middle) to the eight neighbouring cells using different algorithms. The top row consists of schematic maps show the general topography of the area. The next row shows the mean elevations of the four topographic maps illustrated in the top row. The remaining four rows show different flow algorithms. The numbers (0-1) show the proportion of the flow where 1 represents 100% of the flow and 0, 0% of the flow (after Seibert and McGlynn, 2007).

It is clearly visible in the illustrations that the D8-method gives unrealistic flow dispersion, often with directions not perpendicular to the contour lines (e.g. Fig. 3A).

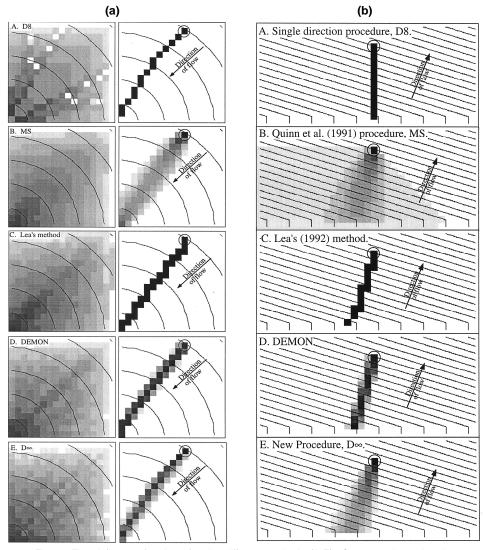


Fig. 2. Flow influence functions for the different methods (A-E). Contours show elevation. (a) Flow on an inward cone. Left panels show upslope area in grey scale and right panels show the influence from the circled pixel. (b) Flow on a planar surface. (Tarboton, 1997).

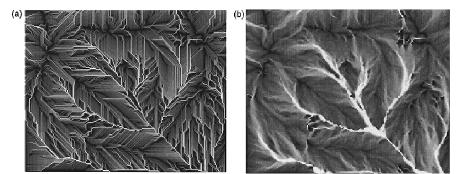


Fig. 3. Images showing upslope area calculated from a 2 m resolution DEM generated from lowaltitude stereo aerial photographs (Dietrich *et al.*, 1992). (a) D8 single-direction method; (b) MD8 multiple-direction method.

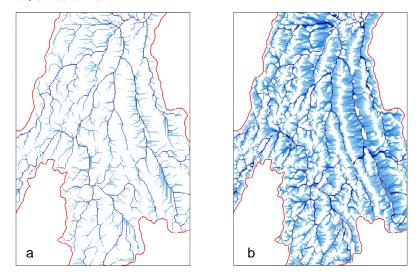


Fig. 4. Images showing upslope area calculated from a 5 m resolution DEM generated from medium-altitude stereo aerial photographs covering parts of Laskerudsbäckens catchment (Nyberg *et al.*, 2009). The tone of blue colour shows a gradient of accumulated cells. The threshold for visibility was set to 25 cells. (a) D8 (b) D^{∞} .

Figs. 3-4 show examples from of authentic flow patterns and how results of the calculations differ. The mfd-methods are likely to model the environment in a more realistic way, with water flow more evenly distributed in the terrain.

Boreal forest, wetland and vegetation types

The boreal forest is one of the most extensive biomes, encompassing approximately 14.3 million km², or 21% of the worlds forested land surface. It is estimated that wetlands store more than 37 % of the total amount of carbon in the biosphere (Whittaker and Likens, 1975). Approximately 35 % of Sweden is covered with boreal forest. The boreal forest region in Sweden starts north of the big lakes and plains (59-61°N) and continues for a thousand kilometres up to the northern mountains and arctic tundra. The boreal landscape is relatively heterogeneous and even a small catchment normally includes a number of spatially distributed topographic features, wetlands and several types of vegetation patches. These are all landscape factors that influence the runoff regime and stream water chemistry substantially, depending on proportion, location and type (Quinby *et al.*, 1995).

A common definition of wetlands is: "areas where water lies at, or slightly above or below, the ground surface at least for a large portion of the year. The term wetland also encompasses water bodies covered with a floating raft of vegetation. Wetland vegetation is mostly hydrophilous" (Löfroth, 1991).

Around 11.5 % of the land surface of Sweden is covered with wetlands, of which approximately 40 % is located in the boreal region. However, more than 1.5 million hectares or some 15 % of the peat covered (deep and shallow) land area have been drained for forestry during the last century. Some 0.6 million hectares peat-covered lands have been ditched for agricultural purposes. The latter started already in the beginning of the 17th century (Hånell, 1989). Peat has also been used as an energy resource for several hundred years. 48,000 ha of wetland in Sweden are exploited at present for energy production purposes. Extensive inventories of wetlands and protection programmes started in the early 1980's are still in progress. Especially in agricultural areas, programmes for wetland creation have been initiated to reduce nitrate transport to the sea (Arheimer and Wittgren, 2002).

Mires, divided into bogs, fens and mixed mires, are the most common wetland group in the Swedish boreal landscape. Bogs receive water only as atmospheric precipitation and are thus termed ombrotrophic. They receive no inputs from the groundwater. Bogs can be open or can have tree cover. Fens are minerotrophic, receiving at least some of their inputs from mineral groundwater. Fens may be open or have tree cover. Mixed mires are mires which possess a mixture of bog and fen elements (Löfroth, 1991).

The Swedish boreal forest belongs to the coniferous, oakless forests of the boreal region, the taiga of the northern hemisphere. The two main tree species are the Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), and occur either alone or mixed, generally also with some deciduous trees, the most common being birch

(Betula pendula) and aspen (Populus tremula). Pine prefers coarse, dry sedimentary soils, whereas spruce grows best on damp soils overlying fine-grained tills or sediments (Ebeling, 1978; Nilsson, 1990; Engelmark and Hytteborn, 1999).

Forests contain low ground-vegetation with a field layer of dwarf shrubs, herbs, ferns and grasses and a bottom layer of lichens and mosses. The plant species of both layers provide a good indication of the characteristics of the site. The plant communities are reliable indicators of soil type and suitability of the site for growing trees. Accordingly one can classify plants based on forest types. The most common types in the boreal region, based on the moisture gradient are dry, mesic, moist and wet coniferous forest, mesic, moist and wet deciduous forest, and coniferous/deciduous mire, mire of lawn, carpet and peat mud type and dwarf shrub hummock mire. Mires are also classed as bog, fen or mixed mires (Nordic Council of Ministers, 1998).

Based on these systems, vegetation maps have been produced in some counties and regions of Sweden. The most recent map includes the county of Värmland and was produced between 2000 and 2005 as a digital database including about 400 types, subdivisions and features of vegetation. The data were produced by interpreting infrared aerial photos (4600 m) digitized and classified using analytical instruments and GIS. The data are of very good quality and high resolution (LMV, 2003).

Vegetation distribution, which responds to water, light and nutrient availability, can be modelled using combinations of topographic attributes that capture much of the landscape-scale variability of these parameters (Moore *et al.*, 1993c). The circulation of water and nutrients between the vegetation and soil has a marked influence on stream chemistry, hence spatial distribution of vegetation types was therefore considered an important factor that should be included in this study.

Natural organic matter

The variability of water colour in boreal headwater streams is mainly due to the amount of dissolved natural organic matter (NOM). NOM is the sum of all organic substances in the water. Between 50 and 60 % of the NOM is organic carbon (Total Organic Carbon - TOC), which in the Nordic region varies between 10 and 200 kg C ha⁻¹y⁻¹. The brown-yellow coloured organic matter (also called aquatic humic substances) leach out to streams from the riparian zone (Bishop *et al.*, 1994) and are derived from decomposing organisms, and their secretions. TOC and humic substances are chemically very heterogeneous groups consisting of complex high molecular weight humic and fulvic acids, and low molecular weight humin, organic

acids, sugars and peptides. In boreal streams and lakes these substances are dissolved to approximately 95 %, measured as dissolved organic carbon (DOC), which is defined as all organic carbon that passes through a 0.45 µm filter (Stumm and Morgan, 1996). Different methods of quantifying the amount of organic material in surface water are used (Table 1). NOM increases the mobility of pollutants and lowers the pH and has strong effects on many biochemical processes in the environment. It is used in calculations of fluxes of carbon and macronutrients such as nitrogen and phosphorus (Kortelainen, 2003). Furthermore, NOM is the energy and nutrient source for many micro-organisms (Tranvik, 2003), but for humans NOM causes problems with drinking water quality and production. High levels of NOM cause water to taste and smell bad, and are the basis for the production of potentially hazardous chlor-organic compounds when water is disinfected with chlorine.

Table 1. Different methods of quantifying the amount of organic material in surface water (after Temnerud, 2002).

Name	ne Explanation Contents	
Humus (mg/l)	Mostly partially decomposed organic material.	Humus-, fulvic acid and humin. Definition based on different solubilities at different pH.
NOM (mg/l)	Natural organic material NOM / 2 ≈ DOC	All organic, C, N, P, S etc. Wet or dry chemical determination.
DOC (mg C/l)	Dissolved organic carbon	All organic carbon that passes through a 0.45 µm filter. Wet or dry chemical determination.
Colour (mg Pt/l)	The colour of the water is compared with a Pt Cl ₆ - ² -solution or a standard disk.	Organic material, but also iron and manganese. Poor accuracy and different scales are in use, i.e. Hazen. A subjective method.
Absorbance	420 nm and 5 cm quartz cuvette (or at 254 nm)	As above but with better accuracy.

High concentrations of humic substances occur mainly in peat and forest with few lakes, i.e. areas with large pools of carbon and short retention times. Climatic factors, such as precipitation and temperature, regulate the carbon pool and fluxes, including the dynamics of NOM. Research results have shown that there is a strong covariance between precipitation and DOC concentration in headwater streams, and hypotheses that wetlands and riparian zones are the major sources for dissolved humic substances were first reported by Hemond (1990) and later confirmed by Bishop *et al.* (1994) and Fölster (2001). Some of their ideas were questioned by Hongve (1999). Andersson and Nyberg (2008) did not find evidence for the riparian wetland sources of DOC in headwater catchments.

Within the last 10-15 years a significant increase of the concentration of NOM has been seen. Theories of the causes include reduced acid rain (Monteith et al.,

2007), changes in land use and forestry practices (Rosén et al., 1996; Lundin, 1999), and climate change (Clair et al., 1994; Freeman et al., 1995, Tranvik et al., 2002; Worrall et al., 2003; Löfgren et al., 2003). Whatever the causal factor is, more research is needed, and it can be stated that headwater chemistry is of highest concern in Sweden, where more than 50 % of the households' drinking water comes from lakes and streams (Fritzdotter et al., 1984; Löfgren et al., 2003).

Scale and resolution dependency

It is widely recognized that terrain analysis is sensitive to the resolution of the elevation data used. This affects all topographic attributes, but in varying ways. The resolution-dependence of slope and specific catchment area has been intensively studied because of its regular application in hydrological modelling (Moore *et al.*, 1993b; Zhang and Montgomery, 1994; Quinn *et al.*, 1995; Wise, 2000 Kienzle, 2004; Aryal and Bates, 2008).

An important factor affecting stream chemistry at any location is the size of the catchment defined by that location (Beven et al., 1988; Fan and Bras, 1995). The "representative elementary area" (REA) concept (Blöschl et al., 1995) for stream flow response to precipitation suggests that the variability between small catchments is large and between large catchments small. This means that as the catchment size increases, the variability tends to decrease (Wood et al., 1990). The size of the REA is, in theory, related to catchment topography and soil characteristics (Wolock, 1995). Depending on the landscape and soil type, flow situation and the measured variable, the REA size will vary. For runoff, evapotranspiration and infiltration REA was estimated to be about 1 km² (Wood et al., 1988), for soil moisture 5-10 km² (Wood et al., 1990), and for chemistry about 3 km² (Wolock et al., 1997). The downstream change is due to in-stream chemical and biological stream processes, change in soil type and land use, whereas the downstream reduction of variability between different streams depends on the addition and mixing of a diversity of tributaries and dilution by "old" groundwater (Rademacher et al., 2005).

The conclusion based on theories of mentioned scale dependency is that it is difficult to make general and reliable models and predictions for stream chemistry. Out in the field it is quite obvious to the observer that the rich diversity of the spatial arrangements of flow paths and processes change with scale. To fully capture this diversity, complex model building is necessary. Blöschl (2001) suggested that instead of trying to capture everything when upscaling it would be better to develop methods to identify dominant processes that control hydrological response in different environments and at different scales, and then develop models to focus on

these dominant processes. The aim of this dissertation is a step along the lines of Blöschl: a landscape perspective, or downward approach, towards an understanding of the influence of those landscape elements and factors in boreal forest environments that control stream water chemistry at the headwater scale.

Objectives

The overall objective of this dissertation was to investigate how different spatial landscape factors in boreal forest catchments influence the variability of headwater chemistry, to test if available map data can be used to determine these landscape factors with satisfactory results, and to find a simple and fast method, using GIS, for prediction of water chemistry in boreal headwater streams.

The five papers in this thesis address different parts of the conceptual model (Fig. 5). In this conceptual model the relationships between climate and geology on one hand and topography, wetlands and vegetation and headwater chemistry on the other are visualized. Geology and climate have an overriding influence, shaping the topography and controlling the precipitation and distribution of water in the landscape. In turn the characteristics of topography and water distribution give different conditions for wetlands and vegetation. Finally, all together those factors form the basis for the streams' water chemistry. The main objectives of the papers were to answer the following questions:

- I. Do occurrence, spatial variation and location of wetlands influence DOC-concentrations in stream water in boreal headwater catchments?
- II. Is it possible to use existing official map data and available GIS applications for prediction of DOC in headwater streams?
- III. What impacts do wetland restorations have on boreal stream hydrology and DOC-leaching?
- IV. Can wetness indices be used as predictors of wetlands?
- V. What effects has the resolution of elevation data on the SAGA wetness index?

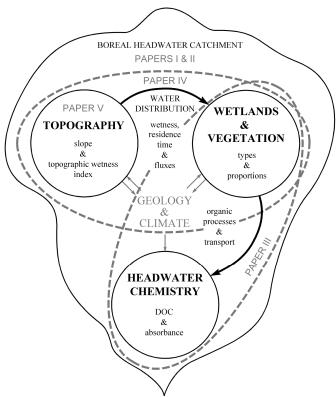


Fig. 5. A conceptual model showing relationships in a headwater catchment. Papers I-II deal with topography, wetland, vegetation and headwater chemistry, Paper III wetlands and headwater chemistry, Paper IV topography and wetlands, and Paper V topography.

Methods

Study area

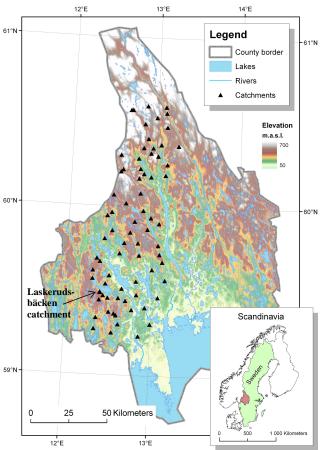


Fig. 6. The study area with 85 catchments within a $150 \times 50 \text{ km}$ region, including the Laskerudsbäcken catchment in the county of Värmland, Sweden.

The studied catchments are located in a 150×50 km region in the county of Värmland, western south Sweden, between 59-61°N and 12-13°E (Fig 5). The region is situated within the southernmost area of the boreal forest region, in a landscape that is dominated by a hilly relief with occurrence of faults and bare rocks, and includes a large number of lakes and mires. The bedrock is mainly of pre-Cambrian age and consists of grey gneisses in the west and red gneisses and granites in the north and east. In the south mylonized and schistose Åmål quartzite and Åmål-

Kroppefjäll granites occur. In the area with red gneiss numerous hyperite bodies occur (Lundqvist, 1958; Lundegårdh, 1995). The dominant soil types are till (>65 %) and peat (~20 %), and there are occurrences of small areas covered with layers of other quaternary deposits, such as sand and silt. The average elevation is approximately 200 m a.s.l., and the highest marine shoreline lies between 170 and 210 m a.s.l. (Lundqvist, 1961). The mean annual temperature is 3-5°C, precipitation 800-900 mm, runoff 400-450 mm and evapotranspiration 400-450 mm, all with a gradient from south to north and with increasing elevation. Precipitation occurs as rain between April and October and as rain or snow between November and March. The peak runoff normally occurs during the snow melt in April (Raab and Vedin, 1995). Coniferous forest (*Picea abies* and *Pinus sylvestris*) dominates the area. The major impact of humans is in the form of forestry and acid deposition (Lundström *et al.*, 1998)

The catchments range in size from 0.1 to 4 km², in outlet elevation from 55 to 420 m a.s.l., in mean elevation from 93 to 448 m a.s.l., and in elevation difference from 30 to 260 metres.

The first study (Paper I) includes 68 catchments distributed over the region and the second study (Paper II) includes the fourteen largest catchments in the first study and four additional catchments selected from a wetland restoration project in the Laskerudsbäcken catchment (Paper III-V).

Selection of streams

When designing the study, 1:250,000 and 1:100,000 scale official maps were used to delimit an area within the western part of Värmland, where earlier studies showed soil acidification. Using 1:50,000 scale maps a random selection of spatially distributed first order streams was made according to the following criteria: 1. Catchment sizes should range between 0.1 and 4 km²; 2. No arable land or lakes within the catchments; 3. Outlets should be close to roads for fast and easy sampling. Out of totally 85 sampled streams 68 headwater catchments were selected for analyses (Paper I). Eighteen first-order and second-order catchments were selected within the same region (Paper II). The selected catchments were part of two previous studies: fourteen of the catchments were also included in Paper I. The other four were taken from a hydrological restoration project called "The Laskerud Project" (Paper III). The study in the third paper was part of a wetland restoration project, in which ditches were blocked in three wetland areas and the ecological consequences were monitored locally and in the main streams.

Streamwater sampling, flow and level measurement

Water sampling was made on four occasions at different flow situations and seasons: low flow in summer, medium flow in summer (referred to as medium flow #1), medium flow in autumn (referred to as medium flow #2) and high flow in spring (Papers I & II). The runoff was estimated using the "bucket method" at the same time the samples were taken, and pH and conductivity were measured. The sampling rounds took 3-5 days and no rain fell during these days, ensuring comparable water samples. During the low flow sampling round seven streams were dried out and during the high flow sampling 24 streams were not sampled as snow conditions made them inaccessible.

In the restoration project (Paper III) water in eleven streams was sampled for chemical analyses 38 times during the 68-month project-period. Water levels were measured both automatically and manually during water sampling occasions. Three automatic recorders were used, one in the main stream and two in groundwater tubes. The levels were recorded every hour. Data from the recorder in the main stream were transformed into water discharge using a rating curve (based on discharge measurements). Manual recordings of water level were made with help of gauging scales at the sampling points, which were used to produce rating curves for the estimations of discharge.

Chemical analyses

The water samples were collected in polyethylene bottles and stored cold and dark, for subsequent analysis or preservation the day after sampling. A large number of chemical parameters were measured but only DOC, Al, Fe and Si were included in the analyses in this study. The instrument used for DOC detection was a Schimadzu 500 carbon-analyzer. Absorbance was analysed with a Hach DR/2000 spectrophotometer (455 nm). Fe, Al and Si were analysed with ICP-OES (Varian).

Spatial analyses

In ArcInfo GIS the catchments were delineated using the contour lines. Stream and wetland layers were created and several variables associated with these were extracted, such as "wetland connected to stream", "wetland within 100 m buffer zone", "stream length connected to wetland" and "stream length not connected to wetland" (Fig. 7). These variables were analysed in relation to the catchment area. A 50 m grid digital elevation model (DEM) grid was used for deriving slope.

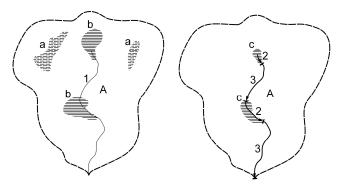


Fig. 7. Examples of analysed catchment variables: A = "catchment area"; a = "wetland not connected to stream"; b = "wetland connected to stream"; c = "wetland within a 100 m buffer zone"; 1 = "total stream length"; 2 = "stream length connected to wetland"; 3 = "stream length not connected to wetland".

GIS was also used for calculations of wetness indices (Papers II, IV & V). The percentage of each vegetation type within the catchments was calculated (Paper II). The digitized wetlands from the 1:50,000 scale maps were compared with the mire types extracted from the vegetation data. The mires were classed into fens, bogs and mixed mires. Digital data were obtained from the official "Värmland Vegetation Map Database" released in 2003 by the Swedish National Survey (LMV, 2003; LMV, 2009). The most common vegetation types covering the catchments were extracted and percentages calculated for each of them.

The six catchments studied in the restoration project ranged from 0.1-1.1 km² (Papers IV & V). A high resolution (5 m grid) digital elevation model (DEM) was generated from photogrammetric data and improved by field surveys. Two types of algorithms (available and free of charge on the internet) were used for calculation of wetness indices, which were compared to the forest (non-wetlands) and wetland distributions extracted from an official vegetation database (Paper IV). The relations between the indices and the occurrence of wetlands were then analysed by comparing the vector data for wetland with the pattern of the wetness index rasters. By comparing frequency distributions of the forest and wetland cell values, a threshold (breakpoint of the wetness value) between wetlands and non-wetlands could be defined.

In Paper V the photogrammetric data were used for interpolation and generation of four digital elevation models (DEMs) with different resolutions (5, 10, 25 and 50 meter grids). An official DEM (50 m grid) was obtained from the National Land Survey of Sweden (LMV). SAGA (System for Automated Geoscientific Analyses) was used for calculation of wetness indices (SWI), based on the DEMs. The DEMs

and wetness indices were first analysed by comparing the SWI pattern of each catchment and the differences between the four levels of resolution. Slope grids were generated for catchment characterization and for comparisons with the SWI. The LMV DEM and its derived SWI were compared to the interpolated 50 m DEM and its derived SWI.

Statistical analyses

Correlation (Pearson) and regression analyses were performed to investigate the covariation between landscape variables and water chemistry at different flow situations (Papers I & II). As a second step, multi-variate analyses (PLS) were performed to study the relation between the full set of landscape variables as explanatory variables (x-block) and DOC concentrations from the four sampling occasions as response variables (y-block). The advantage of PLS in this case was to include the full set of variables in one analysis to get an overview of the covariation both within and between blocks (Paper I). A PCA analysis including all topographic and vegetation variables was carried out to investigate the relations between the two groups of variables (Paper II). Histograms (Paper IV & V) were used for analysing the frequency distribution of wetness indices to predict wetland occurrence and how it changes with decreasing resolution of elevation data.

Results

Paper I

Analyses of spatial variation of wetlands in 68 headwater catchments showed large variation in size and location in relation to catchment latitude, location, size and stream length. The areal cover of wetlands ranged from 0 to 45 % of the total catchment area. The location within the catchments was measured in different ways in relation to the stream and its outlet. There was a significant relationship between the total percentage of wetlands and DOC-flux at two of four flow situations, while there were no significant correlations found between location of wetlands, catchment area and latitude and DOC-flux.

In the multivariate analysis, about 40-45 % of the variation in DOC (all four flow situations) could be explained by 60-70 % of the variation at the x-block, when three principal components were used (Fig. 8). The mean slope was the dominant x-variable, showing a negative covariation with DOC. The elevation and the northing coordinate showed weak covariation with DOC-flux. The contribution from other variables was of a random character, dependent upon a single low or high data point.

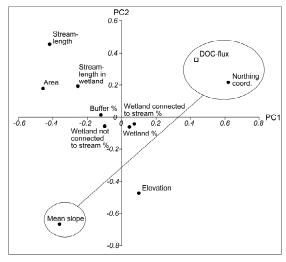


Fig. 8. Loadings from PLS-analysis of landscape variables (x-block) and DOC (y-block).

The result of this study showed that the mean slope explained variation of the DOC-flux and DOC-concentration in the streams better than the percentage and location of wetlands in a headwater catchment (Figs. 9 and 10).

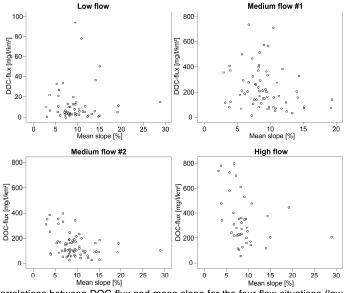


Fig. 9. Correlations between DOC-flux and mean slope for the four flow situations (low flow: r = 0.04, n.s.; medium flow #1: r = -0.24, n.s.; medium flow #2: r = -0.35, p < 0.01.; high flow: r = -0.32, p < 0.05).

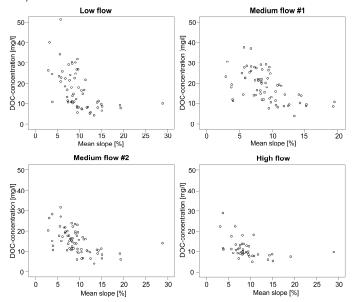


Fig. 10. Correlations between mean slope and DOC-concentration for the four flow situations (low flow: r=-0.43, p<0.01; medium flow #1: r=-0.55, p<0.01; medium flow #2: r=-0.52, p<0.01; high flow: r=-0.43, p<0.01).

Paper II

In 18 headwater catchments (1.0-3.8 km²), mean slope, mean TWI and percentages of wetland and 15 vegetation types were calculated to identify the major landscape factors influencing water chemistry (DOC, Al, Fe and Si). Official topographic 1:50,000 scale maps and vegetation data were used for extraction of the spatial variables.

A PCA (Fig. 11) including all topographic, wetland and vegetation variables was carried out to investigate the relations between those three groups of variables. The first principal component explained 40% of the total variation, and captured primarily the slope-related variation. The second component explained 22 % of the variation, and described the variation related to elevation.

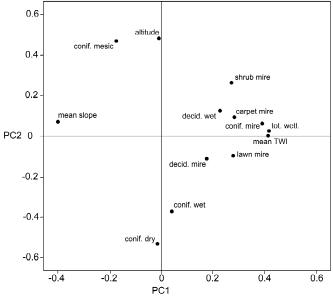


Fig. 11. PCA analysis of topographic and vegetation variables. The axes represent loadings for PC1 and PC2. The topographic variables included were mean altitude, mean slope and mean TWI. The vegetation variables included total wetland area and vegetation types.

There were very strong relationships between mean slope and mean TWI vs. absorbance and iron at the medium and high flow situations. Mean slope showed an even stronger negative relationship with water chemistry than in Paper I. The levels of significance decreased with decreasing flow. At the high flow situation the relationship between mean TWI and DOC-concentration was very strong ($r^2 = 0.93$) (Fig. 12).

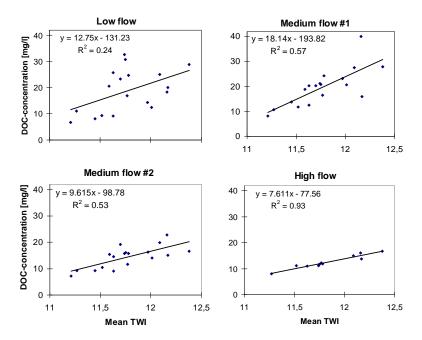


Fig. 12. Regressions between mean TWI and absorbance at the four flow situations. Low flow: $r^2 = 0.24$, p < 0.05; Medium flow #1: $r^2 = 0.57$, p < 0.01; Medium flow #2: $r^2 = 0.53$, p < 0.01; High flow: $r^2 = 0.93$, p < 0.01.

There were also significant relations between Fe and coniferous forest mire, which was interpreted as an effect of chemical bonding of Fe to the dissolved organic carbon in soils and streams. This was confirmed by strong a correlation between Fe and DOC-concentration (r = -0.81 in the high flow situation).

Si was the only chemical constituent that correlated negatively with elevation and dry coniferous forest. This can be explained by the geology and topography of the area: the soil layer is thin (large areas with bare rocks exposed to weathering) in the southern part of the region where the hills are low.

Paper III

This paper reports on the hydrological and hydro-chemical response to restoration measures in the 4.8 km² "Laskerud" catchment. The damming of ditches led to a substantial rise of the groundwater levels in the restored areas. Typically the levels

rose with 1-2 dm in the center of the areas. In one of the areas, a 12.6 ha fen, the change in DOC-concentration was followed, and a substantial increase in concentration after the damming was found.

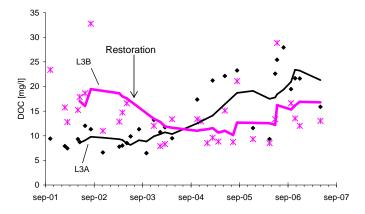


Fig. 13. DOC [mg/l] in water downstream Ängmyren at sampling points L3A and L3B. The solid lines are moving averages (period of 5).

There was no significant impact of the restoration on the main stream hydrology or DOC, likely because only 1.6% of the entire catchment was affected by the restoration measures. There were, however, local scale effects in the restored subcatchments. To some extent, at the local scale, the restoration was a success. Because of the importance of wet areas for the ecosystem as a whole, the restoration consequences can have ecological impacts on a large scale.

Paper IV

Various algorithms for calculation of wetness indices give different results for the spatial saturation pattern. We compared two different indices available on the internet: topographic wetness index (TWI) and SAGA wetness index (SWI).

There was an overlap in the frequency distribution of wetness index values between forest (non-wetland) and wetland cells for both TWI and SWI, but the SWI showed a clearer separation of the distributions. There was also some variation in the difference between the six catchments, L3-L11 (Fig. 14). The bimodal shape of the frequency distribution for TWI can be explained by the "stream" pattern of cells with high values. The SWI cells frequency are more normal distributed than the TWI cells.

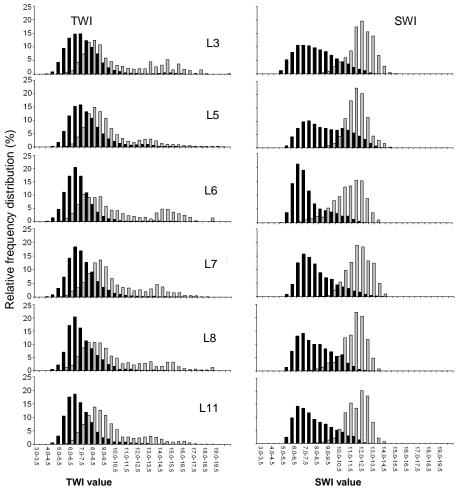


Fig. 14. Forest (black) and wetland (grey) relative frequency distributions for TWI and SWI in the six catchments.

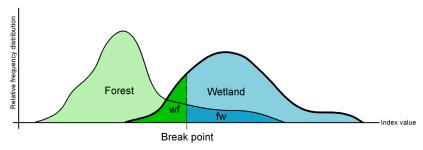


Fig. 15. Overlapping frequency distributions of wetness index cell values. The break point (threshold) index value is found where wf = fw.

The threshold for wetland occurrence was calculated by identifying the index value where the percentage of cells for forest above the threshold equals the percentage of cells for wetland below the threshold for each subcatchment (Fig. 15). The mean threshold index value was 7.6 for TWI and 10.0 for SWI. The overlap for SWI was half of the overlap of TWI (13.7 % vs. 26.0 %). SWI was then tested further by making comparisons to the vegetation map.

Table 2. Predicted and mapped wetland percentages.

			Percentage
	Cells	Area (m²)	of total area
Mapped wetland	15189	379725	14.9%
Predicted Wetland	22254	556350	21.8%
Predicted NOT Mapped wetland	10224	255600	10.0%
Mapped AND Predicted wetland	11921	298025	11.7%
Mapped NOT Predicted wetland	3268	81700	3.2%
Total wetland	25413	635325	24.9%
Forest	76680	1917000	75.1%
Total area	102093	2552325	100.0%

The success rate of the wetland prediction was assessed by comparing the percentage of the predicted and the mapped wetland areas (Fig. 16). The total area was 2.55 km², the predicted wetland area was 0.56 km² and the mapped wetland area was 0.38 km². There was a surplus of 6.9 % predicted wetlands, and 3.2 % of the areas that were classed as wetlands were not predicted (Table 2).

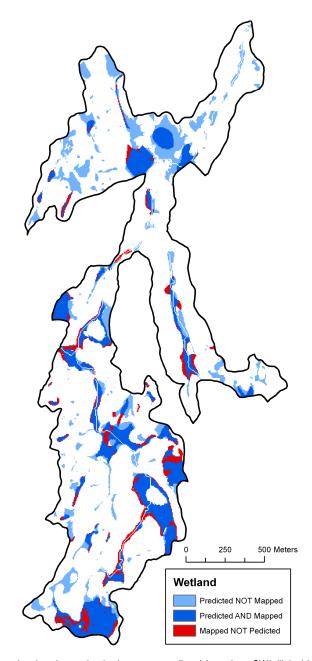


Fig. 16. Map showing the wetlands that were predicted based on SWI (light blue), wetlands included in the vegetation map but not predicted (red) and both predicted and mapped (blue).

Paper V

The 5, 10 25 and 50 m grid SAGA wetness indices were analyzed and compared. The histograms showed how the distribution of grid cells moved towards higher SWI values (Fig. 17). There is a step of about one unit from the 5 m grid to the 10 m grid, and the shape of the distribution is more or less preserved, with the peak at lower values. The next step, however, to the 25 m grid, is more than two units, and the shape is completely altered, with a less skewed distribution. The 50 m grid values shift more than five units for the lowest values and show random shapes. When comparing mean values for 10, 25, 50 m grids we found a near linearity in SWI value increment changes between the six catchments (Fig. 18).

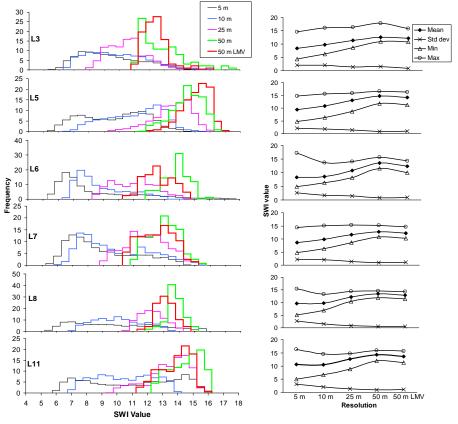


Fig. 17. Histograms showing relative frequency distributions (%) of SWI values (left) and diagrams showing the trend for five statistical measures for SWI values changing with increasing grid cell size for each catchment L3-L6 (right).

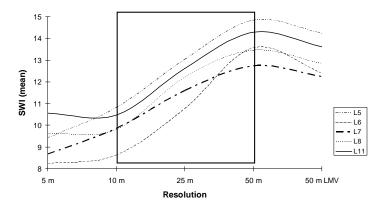


Fig. 18. Near linear increase of SWI mean values for 10, 25 and 50 m resolutions.

Discussion

The five papers in this thesis focus on headwaters, headwater catchments, landscape elements and, what were found to be the most important factors influencing streamwater chemistry: topography and wetlands. These are tightly related to each other and in boreal forests, wetlands are almost always found in flat areas with thin soils and low hydraulic conductivity. Headwater streams exhibit a large natural variability in water chemistry and should therefore be considered in environmental assessments. There are several ongoing research projects on headwaters and their importance for environmental assessment, e.g. Bishop *et al.*, 2008. Monitoring of these streams is, however, not realistic due to their large number. Hence, a fast and simple method for predicting headwater chemistry needs to be developed and adopted in assessment of surface waters.

Sources of DOC

In flat areas, water is moving slowly and close to the ground surface, where many biological and chemical processes take place (Mulholland and Kuenzler, 1979; Hemond, 1990; Likens and Buso, 2006). Thus, wetlands contribute substantially to the amount of organic substances released into streams. In our studies we found strong relations between the areal cover of wetlands (as shown on official maps) in the catchments and DOC in the streams. We did not find evidence that riparian wetlands were main sources of DOC based on the proportion of "wetlands-connected-to-streams" in the catchments. One hypothesis we investigated was that unmapped wetlands and peat cover may contribute substantially to DOC leakage. The assumption was that these are located on flat ground. We used slope models and wetness indices to reveal these areas (Papers I & II). In the statistical analyses mean values for the catchments correlated strongly with DOC. In the wetland restoration project the blocking of ditches resulted in a local decrease of DOC in the streams, which supports the theories that a major part of the DOC is produced in peat and released to streams when groundwater levels rise (Paper III).

Several similar studies have concluded that wetlands are the major sources for DOC (e.g. Bishop *et al.*, 1994) and our results support them. However, there is still uncertainty in exactly where, how and when these processes take place (e.g. Hongve, 1999; Köhler, *et al.*, 1999 and 2008; Buffam *et al.*, 2008).

Available official map data

Surveying and creation of large-scale spatial data sets are expensive and time consuming and appropriate maps are therefore seldom available in scientific or assessment projects covering many small study areas. The problem of using available official map data is often that it is too coarse and/or is of questionable quality (Harrie, 2008). In our studies of small catchments we used official 1:50 000 and 1:20 000 scale maps for extraction of landscape variables. These maps are produced by the Swedish Land Survey (LMV) using stereo instruments and 4 600 m aerial photographs and thus the maps are limited in detail richness and accuracy. Especially elevation (contour lines) and wetland boundaries are difficult to trace from high altitude photos in boreal forest landscapes. The official maps have therefore a high degree of topographic generalisation (NFS, 1993; Arnberg and Wästfelt, 2005; LMV, 2006 and 2009). We used the LMV official 50 m DEM for calculation of slope (Paper I-II), and TWI (Paper II) was generated using different methods, originally designed for production of orthophotos. A 50 m resolution DEM with a mean elevation error of 2.5 m would not be useful for spatial analyses of small areas (Rodhe and Seibert, 1999). One would not expect that the methods using these data would reveal any relationships in small catchments. Nevertheless, the fact that we found a strong correlation between DOC-flux and mean slope and a very strong relationship between mean TWI and DOC-concentration indicates the contrary.

A new official elevation model is under production in Sweden (Klang and Burman, 2006). The model is based on air-borne laser scanned points with an elevation accuracy of a few dm. The DEM interpolated from these points will have a resolution of 2 m and a mean elevation error of 0.5 m. This model gives us new possibilities for hydrological analyses and modelling.

Wetness indices for prediction of wetlands

There exists a range of more or less sophisticated algorithms to calculate wetness indices (e.g. Grabs et al., 2009). We compared two different wetness index algorithms that are available, free of charge and rather easy to use: The TWI, a single-direction (D8) based index, in the form of a script to use in ArcView GIS, and the SWI, a multi-direction (MD8) based index that is included in the freeware SAGA. Seibert and McGlynn (2007) suggest that the algorithm MD ∞ for wetness index calculations is more appropriate and gives better results than other existing algorithms. The MD ∞ algorithm was, however, not available at the time of the study and would probably not be easy to use.

The separation of wetland from non-wetland cells in the wetness indices was done by overlaying the vector polygons for wetlands included in the vegetation map and extract the SWI cells inside the polygons (wetland cells) and outside the polygons (non-wetland or forest cells). There was an overlap in the frequency distribution between forest and wetland for both of the indices, but the SWI showed much clearer separation of the distributions. The threshold for wetland occurrence was calculated by identifying the index value where the percentage of cells for forest above the threshold equals the percentage of cells for wetland below the threshold for each of the six catchments. The mean threshold index value was 7.6 for TWI and 10.0 for SWI. The overlap for SWI was half of the overlap of TWI (13.7 % vs. 26.0 %). SWI was then tested further by comparison to the vegetation map. The comparison showed that SWI gives a more realistic wetness pattern, especially in large flat areas since the algorithm includes a variable for the cells vertical distance to the stream. Compared with the vegetation map this method of wetland prediction resulted in 7% higher areal wetland cover.

We did not take soil or geology into account but earlier research has shown that these factors are of comparatively little use for predictions (Güntner *et al.*, 2004). Forest ditching, however, proved to be one factor that can affect the predictions.

Our method of calculating a threshold for distinguishing between wetlands and non-wetlands may be a useful way of identifying DOC sources. However, a high resolution DEM (5-10 m grid) is needed, which is still not available in forested landscapes in Sweden.

Scales and data resolution

Methods of using high resolution elevation data and wetness indices algorithms for wetland prediction were tested (Paper IV). The index using a multiple-direction flow method was singled out as the most useful. We concluded that wetness indices are sensitive to the DEM cell size, but also that mean values were scale-independent (Paper V) in terms of similar increments of mean values independent of catchment size and terrain type. Similar results have been discussed by e.g. Laudon *et al.* (2007) and Gong *et al.* (2009) for other hydrological processes. This is an interesting result that has to be further investigated using a larger number and greater topographical variation of catchments than is this study. This should be possible with the new elevation data mentioned above.

Several recent studies have developed complex, distributed, physically based models to predict hydrological response (e.g. Beven and Kirkby, 1979; Moore *et al.*, 1991). These models are either based on theories of small scale processes, large data

and computer requirements, or else are lumped conceptual models. The lumped conceptual models are fast in set up times and modest in terms of data requirements, but are fraught with difficulties associated with calibration and the lack of a sound physical basis (Bergström and Graham, 1998; Sivapalan *et al.*, 2003). Nevertheless, the extensive work with all of these models has only led to minor steps towards an understanding of the interactions and co-variations in the landscape. A different approach is needed to override the problems of scale dependencies.

Wolock *et al.* (1997) identified a scale upper limit for DOC variation at a catchment size of about 3 km², which seems to be supported in this study (Paper I). Additional catchments larger than 2 km² need, however, to be analysed to corroborate this result. This scale limit can be explained by dilution from groundwater and precipitation, degradation by bacteria and sunlight, and sedimentation due to complex binding (Dawson *et al.*, 2001).

Today, faced with climate changes and more frequent extreme weather situations, we need concepts for upscaling the models, which so far only work reasonably well at small scales and under certain circumstances. Scaling problems are found in almost all kinds of systems (Schulze, 2000) but perhaps are most evident in hydrological sciences. Water issues have grown dramatically in importance along with rapid population growth, accelerating pollution and other environmental problems in different parts of the world. All together these facts have led to an appreciation that scaling is an important issue. Thus this thesis may give new insights into how geographical data can be used in a scale independent way to predict stream water chemistry in the boreal landscape.

Concluding remarks

I conducted an analysis of stream water chemistry from a landscape perspective and at a headwater catchment scale. The hypothesis that there may be dominant landscape factors controlling the variability in small catchments was confirmed by strong correlations between slope and wetland and DOC-concentration (Paper I), topographic variables and absorbance (Paper II). These results confirm the hypothesis about temporal and spatial variability of DOC (e.g. Creed et al., 2003; Driscoll et al., 1987; Hope et al., 1994; Kortelainen, 1999; Laudon et al., 2004; Moore et al., 1993a, Temnerud et al., 2007). The study also indicates that available official map and elevation data can be used to analyse and predict headwater chemistry in Swedish boreal forest landscapes.

Papers III-V highlight the difficulty of measuring, analysing, characterizing and predicting hydrological status and processes in nature. The question of scale makes it difficult to select the best way of measuring hydrology. However, the results indicate that scale-independence occurs for the relation between resolution, topography and mean wetness index value. Moreover, terrain analysis proved to be a useful predictive method in hydrological research.

There is still a lack of reliable hydrological data (Silberstein, 2006). Data on precipitation and stream runoff may be extensive at large scales but often poorly characterized at small scales, and most of these data are generally project-specific, poorly achieved and often only available for the collecting research teams (Soulsby et al., 2008). Thus development of methods for hydrological analyses and predictions, using the new high resolution topographical data and GIS, will be a cornerstone for the increasing global need for understanding and solving many water-related problems in the world.

Hopefully, this thesis will contribute to the development of combined upward and downward approaches, based on existing data and knowledge as well as on imagination and intuition, all needed in the understanding of hydrological responses. To put it in a broader Earth Sciences context, a citation by Harte (2002) summarizes the problems I deal with in this dissertation: "Physicists seek simplicity in universal laws. Ecologists revel in complex interdependencies. A sustainable future for our planet will probably require a look at life from both sides".

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A GIS-based landscape analysis of dissolved organic carbon in boreal headwater streams

In boreal catchments, stream water chemistry is influenced and controlled by several landscape factors. The influence of spatially distributed variables is in turn dependent on the hydrological scale. Headwater streams, with catchments smaller than 3-4 km², have greater variability of water chemistry compared to major streams, and would therefore need to be taken into consideration and be included in official environmental assessments and monitoring. One objective of this study was to analyse co-variation between landscape variables and water chemistry and to determine which of the landscape variables have a major influence on the concentration of dissolved organic carbon (DOC) in headwater streams. This was done using Geographical Information Systems (GIS). Another objective was to find a simple method for predicting sources of DOC, using official map data and publically available GIS applications.

Totally 85 headwater catchments (0.1-4 km²) in the county of Värmland, western south Sweden, were used in the study. Water chemistry was analysed for water sampled at low, medium and high flows, and landscape variables were extracted from official map data sources: topographic maps, a digital elevation model (DEM, 50 m grid), and vegetation data. Statistical analyses showed that topography (mean slope and mean topographic wetness index (TWI)) and wetland cover often correlated well with DOC in headwater catchments. Official map data could satisfactorily extract landscape variables (mean slope, mean TWI) that were useful in predicting stream water chemistry (DOC).

A high-resolution elevation model, which was generated by interpolation of photogrammetric data, was used to calculate and evaluate two different wetness indices and their ability to predict the occurrence of wetlands in six catchments of different sizes and topography. The SAGA (System for Automated Geoscientific Analyses) wetness index (SWI) gave substantially better results than the TWI. The effects of resolution of DEMs on calculations of the SWI were investigated using 5, 10, 25 and 50 m grids. The results showed that SWI values increased with increasing cell size. The near linear increment of mean values for resolutions 10-50 m suggests an independence of terrain type and catchment size, which supported previous findings that indicated that mean slope and mean wetness index calculated from coarse elevation models may be used for prediction of DOC in headwater streams.