Macronutrient Cycling in Surface waters

Large-scale Patterns and Assessment of Global Change

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Abstract

The levels and relative proportions of macronutrients set the conditions for life in surface waters. Man-made disturbances to macronutrient cycling have caused environmental problems such as eutrophication, acidification and global change. In this thesis, macronutrient cycling was studied by performing spatial and temporal large-scale studies of aquatic, terrestrial and atmospheric national monitoring data. Trophic status was found to have a profound impact on nitrate-nitrogen (NO_3-N) concentrations in surface waters. Lakes and streams of the same trophic status displayed opposite NO_3-N patterns. These findings are of great importance when dealing with environmental assessment on the landscape scale, and an awareness of these patterns may also facilitate the design of sampling programs. Trophic status also seems important for trends in total phosphorus (TP) and total organic carbon (TOC) concentrations in boreal and alpine catchments. A temporal study of TP and TOC concentrations showed decreases in nutrient-poor catchments and increases in more nutrient-rich surface waters. Different responses of terrestrial organic matter production and decomposition to temperature increases may be responsible for the observed patterns. Consequently, continued global warming may lead to a stronger polarization between the nutrient-poor northern and the more nutrient-rich southern catchments.

Further studies showed that nutrient conditions in soils and surface waters were strongly affected by atmospheric deposition. By using large data-sets on nutrient content in soils and nutrient concentrations in lakes, it was found that carbon to nitrogen ratios (C:N) in the organic soil layer and in lakes increased from the southern to the northern parts of Sweden, resulting in a strong relationship between soil and lake water C:N. The strong relationship was primarily due to the high correlation between nitrogen (N) in organic soil layer and lake N. Large-scale variations in soil C content were not strongly linked to lake C concentrations whereas soil N seemed to leach in the form of NO_3-N to lakes. By calculating catchment soil, lake and river mouth C stocks, it was estimated that about 10 % of Sweden's total terrestrial net ecosystem production is transported through lakes annually. This indicates that the amount of C exported from soils is substantial and that boreal soils maybe less important as a C sink as previously thought. Furthermore, it was found that the colored portion of C was selectively lost and that the decrease in water color was dependent on water retention time. This implies that under conditions predicted in future climate scenarios of increased precipitation, water reaching the seas will be more colored than today.

The results from this thesis highlight the importance of atmospheric N deposition and trophic status to macronutrient cycling in both terrestrial and aquatic ecosystems.

Keywords: carbon, nitrogen, phosphorus, lakes, streams, soil, atmospheric deposition, climate

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Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Khalili, M. I., Weyhenmeyer, G. A. (2009) Growing season variability of nitrate along a trophic gradient – contrasting patterns between streams and lakes. Aquatic Sciences 71(1), 25-33.

II Khalili, M. I., Temnerud, J., Fröberg, M., Karltun, E. Weyhenmeyer, G. A. (2010). Nitrogen and carbon interactions between boreal soils and lakes. Global Biogeochemical Cycles 24(4), GB4011.

III Weyhenmeyer, G. A., Khalili, M., Fröberg, M., Karltun, E., Kothawala, D., Temnerud, J., Tranvik, L. J. (2012). Selective decay of terrestrial organic carbon during transport from land to sea. Global Change Biology 18(1), 349-355.

IV Khalili, M. I., Futter, M., Fölster, J., Lundin, L., Weyhenmeyer, G. A. Changes of phosphorus and carbon in Swedish boreal and alpine surface waters (manuscript).

Papers I-III are reproduced with the permission of the publishers.

The contribution of Maria Khalili to the papers included in this thesis was as follows:

I The respondent was responsible for the data mining and analyses, interpretation, writing and publishing.

II The respondent was partly responsible for the data mining and responsible for interpretation, writing and publishing.

III The respondent was responsible for some data preparation and for comments on the manuscript.

IV The respondent was responsible for the data mining and analyses, interpretation and writing.

Abbreviations

N	Nitrogen
P	Phosphorus
C	Carbon
S	Sulphur
NO_3-N	Nitrate-nitrogen
TP	Total phosphorus
TOC	Total organic carbon

1 Introduction

As world economies have grown, the biogeochemical cycles of macronutrients, such as phosphorus (P), nitrogen (N) and carbon (C) have been disturbed by human activities with unforeseen consequences on various types of ecosystems and their services (Chapin III et al., 2000). Global environmental problems, such as eutrophication, acidification and climate change (Oreskes, 2004; Smith et al., 1999; van Breemen et al., 1998), have emerged and are threatening the sustainability of life on Earth. Translocation of soil P to surface waters is threatening surface waters by eutrophication and food production by draining the soils of P (Childers et al., 2011). Besides causing surface water eutrophication, atmospheric deposition of N can also lead to soil and surface water acidification (Galloway, 1998). Sulphate (S) atmospheric deposition may have influenced the transport of organic C from soils to waters (Monteith et al., 2007) and it can cause severe soil and surface water acidification (van Breemen et al., 1998). Increased amounts of atmospheric C is believed to have increased temperatures globally (IPCC, 2007) and the change in climate may have contributed to an increased transport of organic C from the terrestrial to the aquatic ecosystem (Freeman et al., 2001) causing further disturbances to the C cycle. Research is therefore needed to better understand biogeochemical cycling to counteract these problems.

1.1 Eutrophication

Eutrophication is a natural process where nutrients accumulate in surface waters over long time periods. Carbon, N and P are the main building blocks of cells and poor availability of them can limit growth of all living organisms (Sterner, 2008). In the middle of the 20th century, people living close to surface waters started to notice a rapid decline in water quality. Problems with bad smell and fish kills prompted societies to act. Soon scientists found a link between these problems and excessive algal growth due to increased inputs of nutrients to the surface waters. This phenomenon is termed anthropogenic, or man-made, eutrophication and it poses a major threat to surface water quality.

In the 1970's, a number of whole-lake experiments were performed in Canada where different nutrients and combinations of nutrients were added to lakes and the response in phytoplankton production was studied (Schindler, 1977). Since the time when results from those large-scale experiments were published, P has generally considered to be the main limiting nutrient in surface waters. Recently, some argue that many lakes may have been pushed into a state of P-limitation because of anthropogenic N-deposition as phytoplankton production has been shown to be primarily limited by N in unproductive lakes receiving low amounts of N (Elser et al., 2009). Furthermore, observational and experimental data have shown greatest growth-responses after addition of both P and N (Sterner, 2008).

Another concern regarding the deposition of N is that at high concentrations, the ability of the terrestrial environment to process N is exceeded and the vegetation and soil become saturated with N with high leaching rates of N as a consequence (Aber, 1992); paper I; paper II). The increased levels of N can cause both eutrophication and acidification in surface waters.

1.2 Acidification

Trees and plants take up base cat-ions from the soil and release hydrogen ions back to the soil. The subsequent recycling of the organic matter through mineralization is incomplete (particularly for soils affected by forestry) and this leads to a natural net acidification process of soils and surface waters and a decline in pH. The base cat-ions are released from mineral particles through weathering and they buffer from changes in pH (Fernandez et al., 2003).

In the latter part of the 20th century, anthropogenic atmospheric deposition of S and N lead to a rapid acidification of waters in affected areas where the load of acidifying pollutants exceeded the buffering capacity of soils and surface waters. The effects from a low and unstable pH include species extinction and/or changes in species composition (Almer et al., 1974), an increased export of aluminum and iron (Breemen et al., 1984) and a potential decrease in organic matter export (Monteith et al., 2007; paper IV). Since the 1980's, atmospheric deposition of S and N over Sweden has decreased (Kindbom et al., 2001), but N deposition is projected to increase in the future (Reay et al., 2008).

1.3 Global Change

Since the 1950's there has been a rapid increase of fossil fuel combustion worldwide and the level of carbon dioxide in the atmosphere has been rising concurrent with an increase in global temperature (IPCC, 2007). Precipitation patterns are expected to change with changes in temperature with both increases and decreases in different regions (IPCC, 2007). So far in Sweden, no trend has been observed for precipitation (Bengtsson et al., 2010) but concurrent with the increase in temperature, levels of S and N deposition have decreased over Sweden and in the Northern Hemisphere (Kindbom et al. 2001; Fagerli and Aas, 2008).

In general, higher temperatures increase rates of microbial processes in soils and surface waters but many other factors, such as precipitation and availability of substrate, may also influence these processes (Schindlbacher, et al., 2011) and this may lead to counter-intuitive effects. For instance; warmer winters may lead to cooler winter soils due to less insulation from snow (Kaste et al., 2008) while warmer soils during summer may increase soil drought stress which in fact decreases microbial process rates (Allison and Treseder, 2008).

Furthermore, elevated temperatures may increase the release of methane as areas under permafrost warms and wetland areas increase (Nisbet and Chappellaz, 2009). In addition, enhanced mineralization rates of peat soils (Freeman, et al., 2001) and surface water sediments (Gudasz, et al., 2010) may also increase C inputs to the atmosphere and surface waters and consequently decrease C burial in surface water sediments. Other global scale changes may also interact with the changes in climate through increased levels of N deposition that may lead to increased C sequestration by forests (Högberg, 2007; Reay, et al., 2008), whereas decreased levels of S deposition may increase the release of C from catchment soils to surface waters (Monteith, et al., 2007; paper IV). Increasing levels of surface water C is problematic for the supply of drinking waters since it increases the cost of water treatment (Alarconherrera, et al. 1984) and it puts pressure on the biota in affected surface waters (paper III).

Temperature induced changes in processes and conditions that can affect the cycling of N and P may include increased rates of weathering in soils (Brantley, et al. 2011), an increase in the total demand for N and P in both soils and surface waters as growing season length increase, increased thermal stratification in lakes and shifts in lake algal community structures (Adrian, et al. 2009). Increased temperatures may cause increased problems with surface water eutrophication in nutrient-rich catchments but cause oligotrophication of lakes in nutrient-poor catchments (paper IV). Furthermore, the effect on nitrification and denitrification from increased temperature is uncertain and changes in N deposition and availablility of C substrate may be more influential than temperature. In soils, rates of nitrification and denitrification increase with deposition levels (Barnard, et al., 2005) whereas in lakes, N removal efficiency decrease with N deposition, probably because of low C availability (Weyhenmeyer and Jeppesen 2010).

2 Objectives

The main objective of this thesis was to understand large-scale patterns of macronutrient cycling in surface waters. The aim was to analyse these patterns between different types of surface water systems and how they are altered by changes in climate and atmospheric deposition. This thesis provides new insights into macronutrient cycling between the terrestrial and the aquatic ecosystems as well as between different types of surface waters. The paper-specific objectives were to:

I	compare N variability patterns between lakes and streams to identify important drivers that regulate N concentrations in surface waters
II	enhance the understanding of the connection of C and N between soils and surface waters and assess the impact from atmospheric deposition of N on soil and surface water macronutrient cycling
III	understand C quantity and quality changes during transport from headwaters to the sea
IV	compare C and P changes in undisturbed boreal and alpine surface waters in relation to changes in climate and atmospheric deposition

3 Methods

3.1 Large-scale studies

The immense complexity of ecosystems is impossible to accurately mimic in an experimental setting so most experiments are performed on much simplified and limited parts of ecosystems. Results from these experiments are then often extrapolated onto larger scales. The reasons behind this practice can be economical, related to risk assessment issues and simply practical considerations. Nevertheless, extrapolating results from smaller studies can be questionable and misleading. To reduce the risk of drawing the wrong conclusions, spatial and temporal scales should, when possible, be adjusted to include different types of ecosystems, catchment processes and different process rates (Schindler, 1998).

In the papers included in this thesis, we have put together data material from already existing data bases. This practice can be challenging since no corrections of missing data or flawed data can be made and missing or additional information can be impossible to retrieve. Still, there is much to learn from synthesizing data from large data bases and data mining often provides the only chance to study geochemical and biological changes in whole ecosystems. It also provides an opportunity to include different types of ecosystems and to analyse data over large spatial scales. The changes in climate and deposition levels that are occurring globally affect whole ecosystems in general ways but at smaller scales effects can diverge. By analysing large-scale monitoring data, the likelihood of discovering net effects increase and proper management measures can be identified.

3.2 Surface water data

The surface water data used in the studies included in this thesis were collected from surface waters within the Swedish Environmental Monitoring Programs. All surface water chemical analyzes were performed by the same laboratory accredited by SWEDAC (Swedish Board for Accreditation and Conformity) using international (ISO), European (EN) or Swedish (SS) standards (SLU, 2011) (Figure 1).

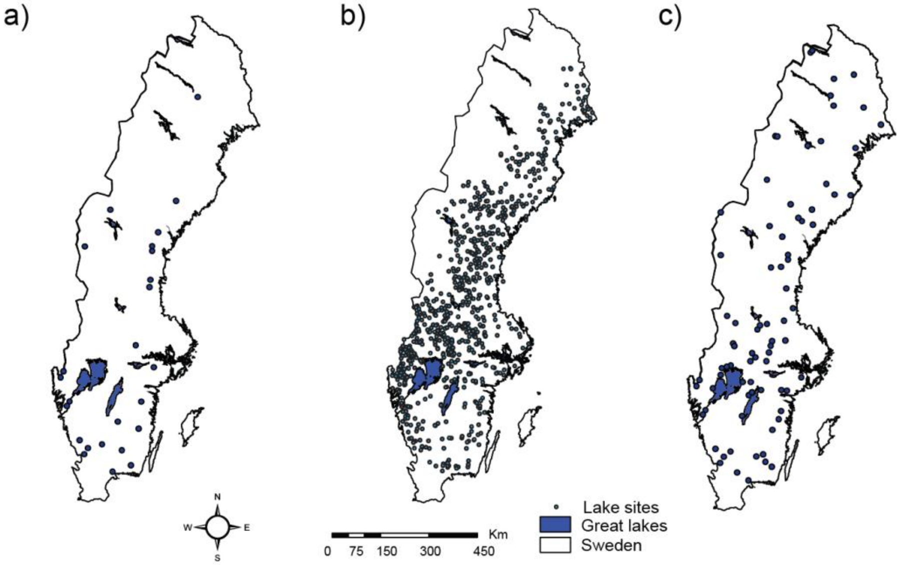

Figure 1. Location of lake data sampling sites from paper I (a), paper II and III (b) and paper IV (c).

Table 1. Number of study lakes or streams (N) in each study and the median nitrate-nitrogen concentration (NO_3-N), total phosphorus concentration (TP) and total organic carbon concentration (TOC).

Study	N	NO_3-N (μgL^{-1})	TP (μgL^{-1})	TOC (mgL^{-1})
I	13	19	8	9
II	748	25	10	10
III	756	25	10	10
IV	82	30	8	8

3.3 Soil data

The soil data used in the studies in this thesis were collected within the Swedish National Forest Soil Inventory database. Soil samples were collected from June to September, between the years 1993 and 2002 and from more than 4000 locations from the south to the north of Sweden (Figure 2).

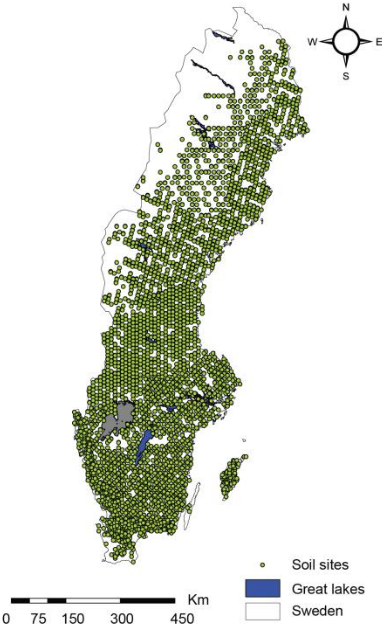

Figure 2. Location of soil sampling sites in the Swedish National Forest Soil Inventory database.

The soil samples were taken from the O horizon, B horizon (upper 5 cm of the B horizon), BC horizon (45–55 cm below the surface of the O horizon) and C horizon (55–65 cm below mineral soil surface).

3.4 Climatic and geographical data

The climatic data used in the studies included in this thesis were provided by the Swedish Meteorological and Hydrological Institute (SMHI). Data on deposition levels were downloaded from the SMHI website (SMHI, 2011) (Figure 3).

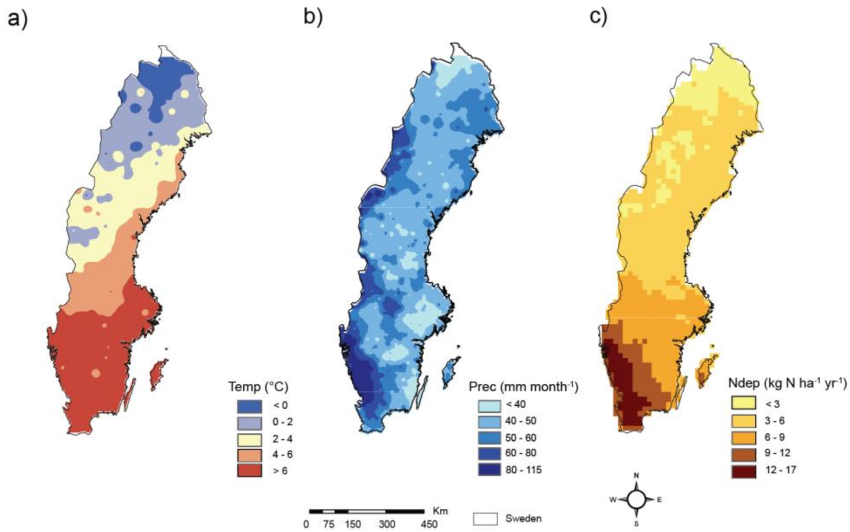

Figure 3. Data on annual mean temperature (a), monthly mean precipitation sum (b) and annual nitrogen deposition (c) in Sweden using monthly data from the years 1995, 2000 and 2005.

Data on catchment and lake characteristics were obtained from maps by using geographical information software.

4 Results and discussion

4.1 Global change impacts at the terrestrial-aquatic interface

Changes in macronutrient concentrations can result from changes in the export from the terrestrial environment or result from changes in process rates within the surface water systems. In order to understand how global change impacts macronutrient cycling in surface waters, we need to be able to assess from where these changes originate and which processes they affect. When it can be established that the cause for change can be found in the terrestrial environment, it is also important to identify from where in the landscape the change is occurring. Changes in nutrient export can result from changes in upland soils, riparian soils, catchment wetlands or a mixture of all of them.

By using large data-sets on nutrient contents in soils and nutrient concentrations in lakes, we could link C to N (C:N) ratios between boreal soil and lakes (Paper II). We found C:N ratios in the organic soil layer and in lakes to increase from the southern to the northern parts of Sweden and that the ratios were related. This was primarily due to the high correlation between N in organic soil layer and lake N. Also, the C:N ratios in lakes were lower than the C:N ratios in the organic soil layer (Figure 4).

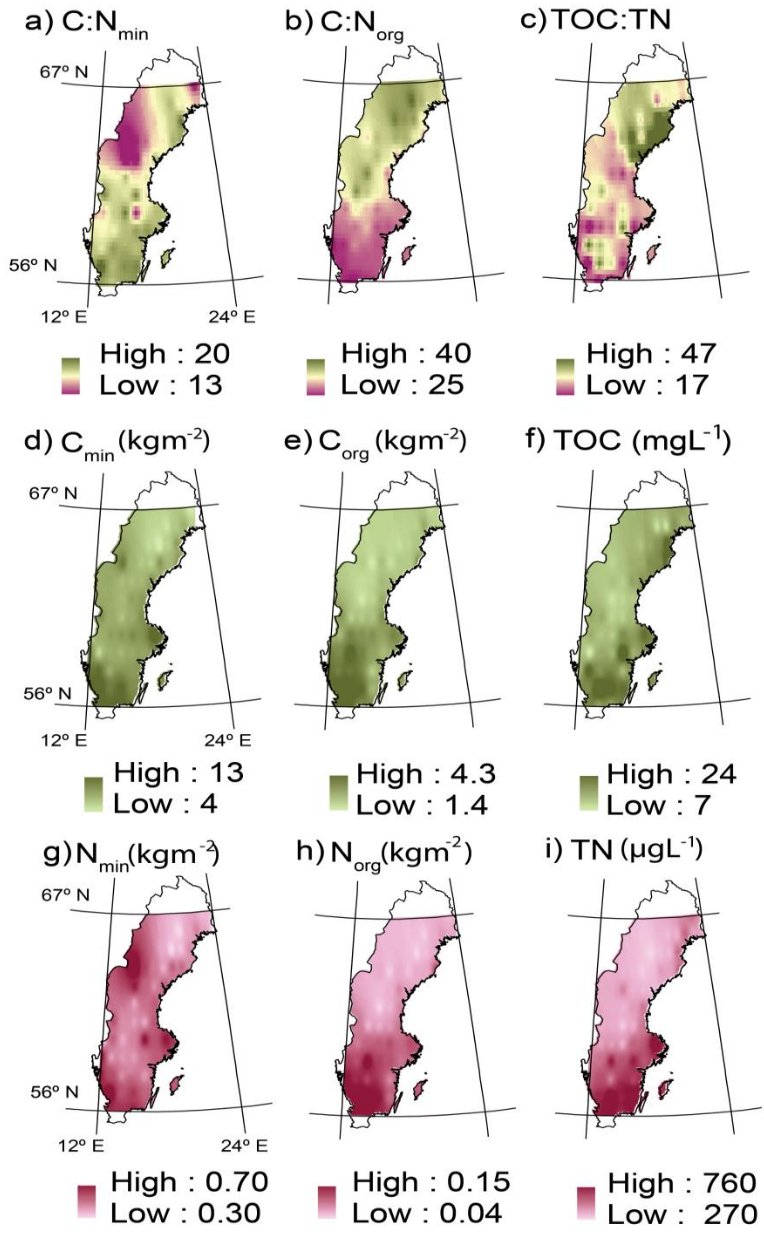

Figure 4. Organic carbon (C in kg m^{-2} for soils and TOC in mg L^{-1} for lakes) and nitrogen (N in kg m^{-2} for soils and TN in µg L^{-1} for lakes) contents in mineral (min) and organic (org) soil layers and in lake waters. For soils, gridded (1° × 1°) mean values over the whole time period 1993 to 2002 were used; for lakes, gridded (1° × 1°) median values of 1995, 2000 and 2005 were used. (a-c) C:N ratios in mineral and organic soils layers and in lake waters; (d–f) C contents in mineral and organic soil layers and TOC concentrations in lake waters; (g–i) N contents in mineral and organic soil layers and TN concentrations in lake waters.

We also found evidence of N deposition having depressed the C:N ratios in lakes more than the ones of the organic soil layers. The lake water increase in N in the south and south-western parts of Sweden was mainly in the form of NO_3-N (Figure 5).

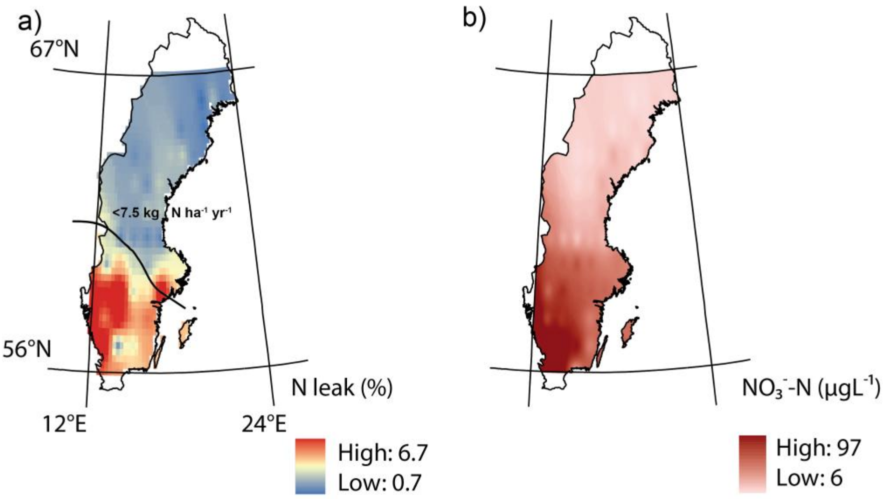

Figure 5. (a) Lake nitrate-nitrogen (NO_3-N) content in relation to direct nitrogen deposition onto the lake catchment area (Nleak). (b) NO_3-N concentrations in Swedish boreal lakes (median values of 1995, 2000 and 2005).

In contrast to N, C was much weaker correlated between soils and lakes. Lake C concentrations were also strongly related to lake and catchment characteristics. Lake C concentrations were not strongly linked to large-scale variations in soil C concentrations whereas soil N seems to leach in the form of NO_3-N to catchment lakes.

In view of the last two decades global trend of increasing boreal surface water total organic carbon (TOC) concentrations (Evans, et al., 2005) the reports of concurrent decreasing total phosphorus (TP) concentrations (Eimers, et al., 2009) in undisturbed catchments are surprising, considering that both TOC and TP in these surface waters originate from terrestrial organic matter. To understand these contrasting trends, we analyzed changes in TP and TOC in 82 boreal and alpine surface waters and related them to changes in climate and sulfate deposition during 1996 to 2008 (Paper IV).

We found that reduced acidity was related to increased TP and TOC concentrations in surface waters regardless of catchment soil nutrient conditions, whereas increased temperatures were related to decreased TP and TOC in surface waters situated in northern nutrient-poor catchments but was related to increased TP and TOC in surface waters of more nutrient-rich catchments.

We suggest that the different responses to temperature increases between systems of different nutrient conditions may be due to the relation between terrestrial organic matter production and decomposition. Coûteaux and others (2001) showed that the heat required to achieve the same C losses was lower for northern soils and that rates of decomposition showed greater increases with temperature in northern compared to southern boreal soils in Sweden.

Changes in temperature may thus influence catchments in southern and northern parts of Sweden in different ways. In nutrient-poor northern catchments, a greater portion of the organic matter may be decomposed compared to more nutrient-rich southern systems. Meanwhile, increases in organic matter production may be lower in northern parts of Sweden due to N-limitation (Figure 6).

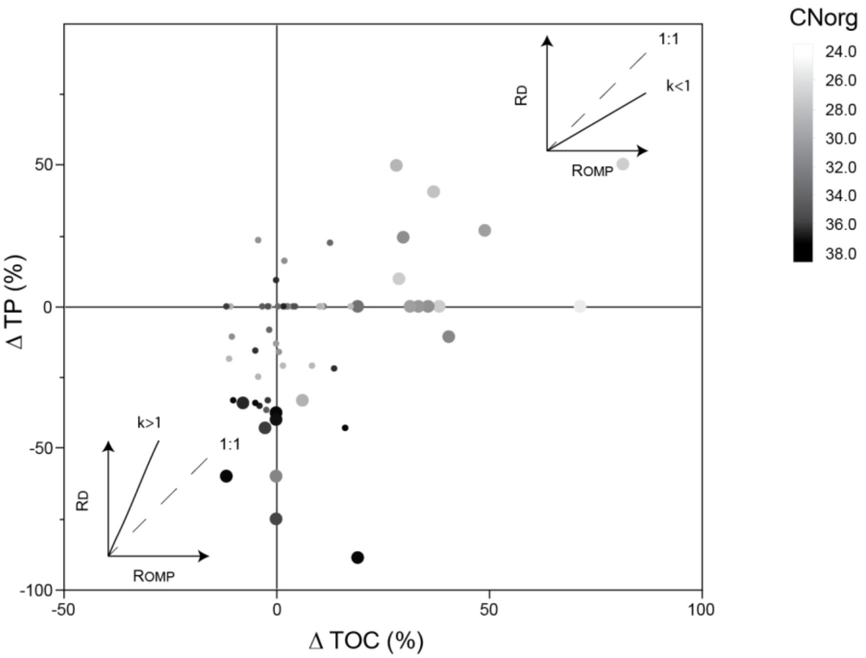

Figure 6. A conceptual figure showing the relation between relative changes in total phosphorus and total organic carbon (significant changes in large font). The two inset graphs show how the rate of organic matter production (ROMP) and decomposition (RD) changes with an increase in temperature depending on the nutrient status of the surface water catchment organic soil layer (CNorg). The graph in the left corner at the bottom depicts the conditions in the northern part of Sweden and the upper graph in the right corner depicts the conditions in the southern part of Sweden.

The different responses of these microbial processes to increases in temperature may provide an explanation for the large-scale patterns of change in TP and TOC surface water concentrations that we observe in the boreal region globally.

4.2 Global change impacts during transport from land to sea

Once macronutrients have reached the surface waters, they regulate aquatic productivity and surface waters in the landscape serve as important nutrient sinks during the transport of nutrients from land to sea. Primary production is limited by the concentrations of P and N but is also regulated by dissolved organic C since it regulates autotrophic production through determining the availability of light. This means that there is a tight link and many overlaps between the aquatic cycles of P, N and C (Figure 7).

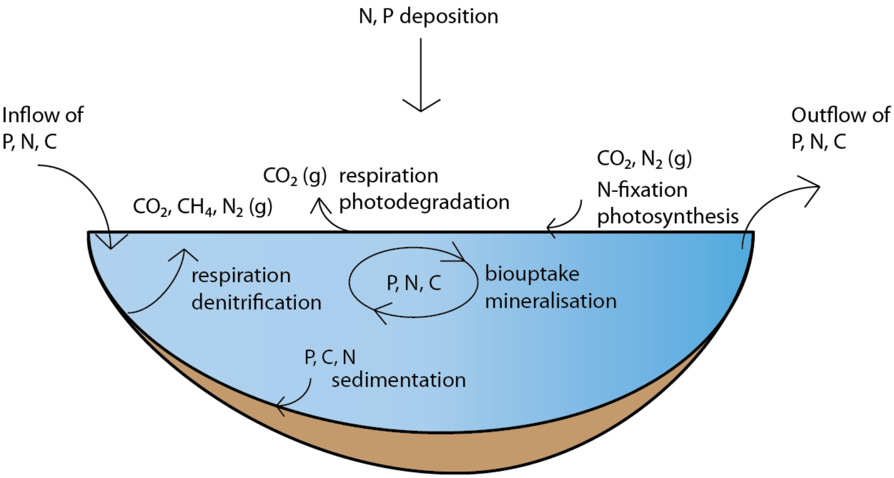

Figure 7. Processes and flows affecting the concentration of carbon (C), nitrogen (N) and phosphorus (P) in surface waters.

The results from Paper I highlight the relation between growing season variability of NO_3-N and trophic status in lakes and streams. In oligotrophic lakes, growing season variability of NO_3-N is low and NO_3-N concentrations are high. The opposite is true for oligotrophic streams. In eutrophic lakes, growing season variability of NO_3-N is high and NO_3-N concentrations are low whereas the opposite holds true for eutrophic streams.

Table 2. *Nitrate-nitrogen coefficient of variation (NO_3-N CV) and nitrate-nitrogen concentration (NO_3-N conc) according to type of surface water and trophic status, where oligo is for oligotrophic and eu is for eutrophic.*

Trophic Status	Surface water type	NO_3-N CV	NO_3-N conc
Oligo	Lake	Low	High
Oligo	Stream	High	Low
Eu	Lake	High	Low
Eu	Stream	Low	High

The high NO_3-N levels in nutrient-poor lakes may be a result of low levels of denitrification and P is often the limiting nutrient which allows for NO_3-N to accumulate. In oligotrophic streams, low levels of NO_3-N result from loss by denitrification or rapid incorporation into biomass. The low NO_3-N levels in nutrient-rich lakes result from high levels of biological uptake and denitrification. The high NO_3-N levels in eutrophic streams result from high mineralization rates and saturated uptake processes. (Figure 8).

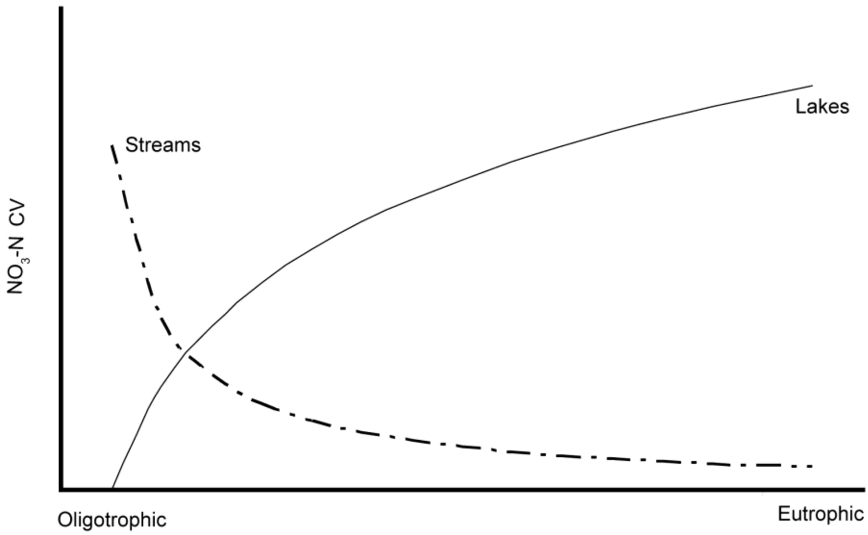

Figure 8. A conceptual graph depicting how the seasonal variation of NO_3-N changes with trophic status in lakes and streams.

The study provided a new understanding of how different processes affect NO_3-N in lakes and streams of different status. Due to the suggested mechanisms, NO_3-N variability may differ between lakes and streams located in the same catchment. This may be of great importance when dealing with environmental assessment on the landscape scale. Awareness of these patterns may also facilitate the design of sampling programs as variability is highly related to sampling error and size.

In Paper III, by using organic soil C stock data, lake C flux data and river mouth C flux data, we could estimate that a minimum of 0.03 to 0.87 % of the organic soil C stock is exported to lakes annually in the boreal landscape in Sweden. About 10 % of Sweden's total terrestrial net ecosystem production is transported through lakes annually and the corresponding annual flux at river mouths is 50 % less than the lake flux. This indicates that the amount of C exported from soils is substantial and that boreal soils maybe less important as a C sink as previously thought (Figure 9).

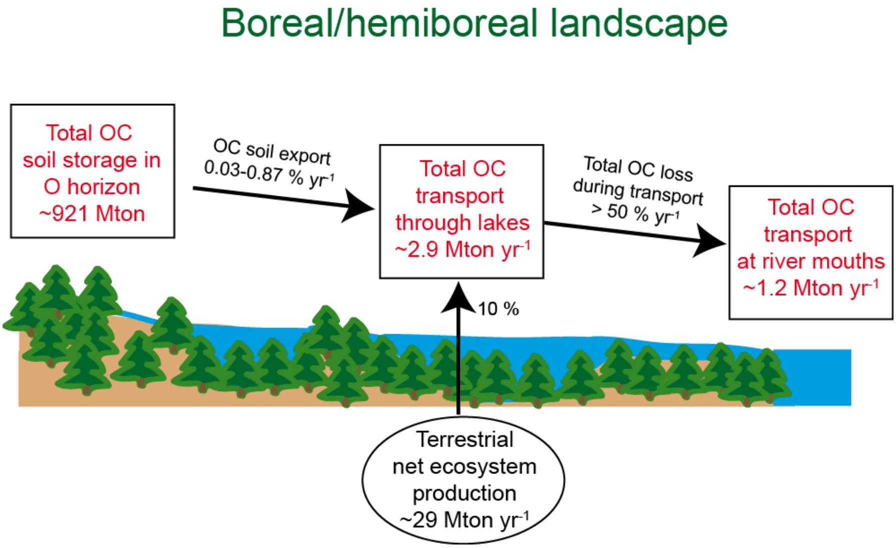

Figure 9. Conceptualization of the storage and transport of organic carbon (OC) through the Swedish boreal and hemiboreal landscape, comprising an area of almost 500 000 km^2. Indicated are the percentage of soil OC imported into surface waters, and the percentage of OC loss during passage through inland waters prior to export to the sea. The export of OC through inland waters has been placed in context with the terrestrial net ecosystem production.

Furthermore, we found that both C and water color loss followed a simple exponential decay function and that water color was lost about twice as fast as C. This selective loss of the colored portion of the soil-derived C was dependent on water retention time. This suggests that during dry years when water flows through the landscape at a slower pace, more color is lost and river mouth water is clearer than during wetter years. This also implies that under conditions predicted in future climate scenarios of increased precipitation, water reaching the seas will be more colored than today.

5 Synthesis

This thesis concerns macronutrient cycling in and between different surface waters, the connection of macronutrients between soils and surface waters and how surface water macronutrient cycling may change along with changes in atmospheric deposition, precipitation and temperature. The results in the thesis show that the atmospheric deposition of N has influenced nutrient conditions in soils and surface waters throughout Sweden at a very large scale. The results also highlight the profound impact that trophic status has on the cycling of macronutrients in surface waters and show the importance of water residence time and catchment properties on macronutrient cycling.

If air temperatures continue to rise, the results from this thesis suggest an increase in the geographical polarization of Swedish surface waters. Northern, oligotrophic surface waters may become even more nutrient-poor while already nutrient-rich southern surface waters may become more eutrophic. The adverse effects from the nutrient increase in the south include algal blooms and more expensive drinking water treatment and these problems may exacerbate if precipitation also increases.

If the atmospheric deposition of N would start to increase over Sweden, the results from this thesis suggest that forest soils would increase in N content and that the leaking of NO_3-N from forest soils to surface waters would increase. This may increase both the terrestrial and aquatic biomass production and cause problems with eutrophication and acidification.

The interactions between the cycles of C and N are tightly linked in the terrestrial ecosystem but there is a shortage of data on P from soils. Similarly, data on N and P from aquatic systems are abundant due to the relation to eutrophication, but data on C are usually not available to the same degree. This thesis show that synthesizing results from analyses of C, N and P from both terrestrial and aquatic ecosystems can provide new hypothesis and explanations for observed patterns and changes in macronutrient cycling in surface waters.

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