Landscape hydrogeochemistry of Fe, Mn, S and trace elements (As, Co, Pb) in a boreal stream network

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Abstract

The transport of elements by streams from headwater regions to the sea is influenced by landscape characteristics. This thesis focuses on the influence of landscape characteristics (e.g., proportion of wetland/forest coverage) on temporal and spatial variations of Fe, Mn, S and trace elements (As, Co, Pb) in streams located in northern Sweden, a boreal region characterized by coniferous forests and peat wetlands.

Water samples from a network of 15 streams revealed a different hydrogeochemistry in forested catchments compared to wetland catchments. The temporal variation was dominated by spring flood, when concentrations of Fe, Mn and trace elements increased in forested headwaters. However, in streams of wetland catchments concentrations decreased, but Pb concentrations were higher in comparison to other streams. Both Fe and Pb showed positive correlations with wetland area, while Co correlated with forest coverage. The anthropogenic contribution of As and Pb appear to be larger than the supply from natural sources.

During spring flood SO$_4^{2-}$ decreased in most streams, although concentrations increased in streams of wetland catchments. Concentrations of SO$_4^{2-}$ were higher in streams of forested catchments than in wetland dominated streams, the former being net exporters of S and the latter net accumulators. Isotope values of stream water SO$_4^{2-}$ ($\delta^{34}$S$_{SO4}$) were close to that of precipitation during spring flood, indicating that the major source of S is from deposition. The results show that, although emissions of anthropogenic S have been reduced, there is still a strong influence of past and current S deposition on runoff in this region.

In conclusion, wetlands are key areas for the hydrogeochemistry in this boreal landscape. The findings emphasize the importance of understanding stream water chemistry and element cycling from a landscape perspective. This may be important for predicting how boreal regions respond to environmental disturbances such as climate change.
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This doctoral thesis consists of a summary and four papers. The papers are listed below and are in the summary referred to as Paper I-IV.

**Paper I:**

**Paper II:**
Björkvald, L., Laudon, H., Borg, H. and Mörth, C. M. Landscape control on the hydrogeochemistry of As, Co and Pb in a boreal stream network. Manuscript.

**Paper III:**

**Paper IV:**
Giesler, R., Björkvald., L., Laudon., H. and Mörth, C. M. Unravelling the origin of stream water DOM using $\delta^{34}$S-DOM. Submitted to Environmental Science & Technology.

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All work in this thesis has been carried out by the author with the exception for isotope analyses, DOC and ICP-MS analyses. My participation in sampling was occasional. My contribution has been the following:
Paper I, II and III: Lead author of all papers, sample treatment and sample preparations, IC analyses and participated in ICP-OES analyses.
Paper IV: Sample preparations for isotope analysis ($\delta^{34}$S$_{\text{SOL}}$).

Stockholm, July 2008
Louise Björkvald
Vattnet från femtio kullar
dansar i hundrade bäckar,
forsar och väller och rullar,
fram under myrtenbäckar,
lyser likt mörka metaller
kyligt i månljus och faller
svalt ned i dalen, där floden går

(Gustaf Fröding, utdrag ur Stäerk och fäkar)
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Introduction

The saying “best of all things is water” (translated by R. Lattimore) expressed by the poet Pindar (ca 518-ca 446 BC) has a wider context today than during the lifetime of its author. Streams and rivers are among the ecosystems most affected by human activities and we are very dependent on this scarce resource. Surface water systems are the vessels and arteries of the continents, transporting nutrients, organic matter and mineral particles from the continents to the sea (e.g. Degens and Kempe, 1991). This transport of nutrients in streams (land sea fluxes) is essential for life, although only 0.01% of the water on the Earth’s surface is available in streams and lakes (Berner and Berner, 1996). However, stream water and soils that are unaffected by human activity no longer exist since the long-range distribution of pollutants from anthropogenic sources are widespread even in remote areas (Murozumi et al., 1969; Hong et al., 1994).

The headwater region is where precipitation meets land and the water begins its journey to the sea. The continuous movement of water through the landscape alters the water composition by interactions with geological and biological material, but also processes such as weathering, ion exchange, sorption, precipitation, organic complexation and biotic uptake/release influence the chemistry of runoff (Church, 1997; Scudlark et al., 2005). In addition, the chemistry of precipitation and the contact time with geological material and biota along sub-surface flow paths are important factors for the observed stream water chemistry (Church, 1997; Wolock et al., 1997). Consequently, the hydrogeochemistry may vary considerably spatially between streams even within small distances. In addition, the temporal variations of stream water chemistry are a result of seasonal, episodic, or diurnal variations caused by hydrological factors like discharge, water temperature, precipitation and snowmelt. In addition to natural factors, the impact of human activity on the water quality can also be a major influencing factor. Thus, the water chemistry of a specific stream is governed by a complex suite of processes that operate at spatial scales ranging from microns to kilometres and temporal scales ranging from microseconds to millennia (Johnson et al., 1997).

Although the hydrogeochemical function of even the smallest catchment results from a myriad of flow paths and biogeochemical processes (Church, 1997) one approach to unravel the complexity of stream water hydrogeochemistry is to study the hydrogeochemistry of small catchments. One advantage of the small catchment approach is that the input and output of elements can be estimated relatively precisely (Johnson et al., 2000). Several long-term headwater catchment studies (Hubbard Brook, Gårdsjön, Plastic Lake to mention a few) have increased our present knowledge on biogeochemical processes and flux of elements within forest ecosystems. However, single short-term catchment studies do not provide any information on the role of various landforms on the cycling and export of elements (Dillon and Molot, 1997). Therefore, studies which include more than one catchment can provide further insight into the dynamic relationships and processes that occur within catchments but also into how catchments of various characteristics influence the stream water chemistry of downstream regions. Management of natural resources is made at a wide range of scales and investigation of stream water chemistry from a landscape perspective can increase the overall understanding of the general condition of water resources and also aid in the planning of monitoring programmes.
In a typical boreal landscape, streams flow through a variety of interacting landscape features such as peat wetlands, moraine ridges and upland coniferous forest floors. If stream water chemistry is interpreted from landscape features, it is apparent that the chemical characteristics of the stream water will reflect catchment properties (Thierfelder, 1998). In boreal regions of Scandinavia, wetlands cover on average 10-30% of the land area and in the northern parts, up to 50% of the land area (Pakarinen, 1995). The presence of these ecosystems alters the chemical composition of the stream water draining these areas. For instance, concentrations of dissolved organic carbon (DOC) in stream water show a large variability in space and time in boreal regions (Temmerud and Bishop, 2005; Eimers et al., 2008) and are related to catchment characteristics, such as percentage of wetland coverage (Buffam et al., 2007; Ågren et al., 2007). The DOC patterns related to catchment characteristics observed at smaller catchment scale have also been observed at larger scales (Aitkenhead et al., 1999; Köhler et al., 2008). However, although it is established that peatlands are sources of DOC (e.g. Urban et al., 1989; Laudon et al., 2004a; Ågren et al., 2007), the functions that various landforms play in the temporal and spatial variation of water chemistry and export of other substances are not well understood and have only been addressed by a few studies (e.g. Dillon and Molot, 1997; Humborg et al., 2004; Inamdar and Mitchell, 2008).

To better understand processes influencing stream hydrogeochemistry in heterogeneous boreal landscapes, it is necessary to have information on how elements behave both temporally and spatially. This knowledge can be crucial since different responses to disturbances (e.g. climate change) can be expected in different landcover types. Forested catchments, for example, may respond differently in comparison to wetland dominated catchments (Köhler et al., 2008). Biogeochemical processes that occur in boreal headwaters can provide crucial information for addressing environmental issues related to element fluxes also at a larger scale. The stream length of headwaters can be considerable: the headwaters in Sweden stretch approximately ten laps around the Earth’s equator. In addition, 90% of the stream length has catchment areas <15 km² (Bishop et al., 2008). Still, the knowledge about these waters is limited as these catchments are rarely included in water monitoring programmes, although headwaters provide habitats for a rich array of species (Meyer et al., 2007). By studying the hydrogeochemistry at various spatial scales and in various landcover types, a better understanding of the complex processes that determine the stream water in boreal regions can be achieved.

**Aim of the study**

The overall aim of this study was to investigate the temporal and spatial variations in hydrogeochemistry of iron (Fe), manganese (Mn), sulphur (S) and the trace elements arsenic (As), cobalt (Co) and lead (Pb) in boreal streams in relation to landscape characteristics (e.g. proportion of forest and wetland within the catchments).

The main objectives were to address the following issues with respect to landscape characteristics:

- How does the spring flood influence the temporal behaviour of Fe, Mn (Paper I), trace elements (Paper II), S and the isotopic composition of sulphate (δ¹⁸S₅Ο₄⁻) (Paper III)? Do we observe differences in response depending on landscape characteristics?

- Is the export/retention of S controlled by landscape properties? (Paper III)

- What characterizes the isotopic composition of stream water SO₄²⁻ (δ¹⁸S₅Ο₄⁻) (Paper III) and δ¹⁸S in dissolved organic matter (δ¹⁸S-DOM) (Paper IV) in association with major landscape characteristics?

**Metals in boreal catchments and natural waters**

In this thesis the definition of minor elements and trace elements is based on their abundance in surface waters. Fe and Mn are considered minor elements, whereas As, Co, and Pb are considered trace elements. There are numerous studies regarding the behaviour of metals and trace elements in aquatic systems, where different aspects have been investigated and described. However, in this thesis the focus is not on the complete chemistry of these elements. Instead, the hydrogeochemistry is evaluated from a different perspective, i.e. the influence of landscape characteristics on the observed stream water concentrations. In this chapter the general behaviour of metals and trace elements in aquatic systems is discussed and the biogeochemistry of sulphur will be discussed in a separate section.

Elements considered to be minor elements in natural waters, such as Fe, mainly derive from natural sources by weathering of near-surface rocks and can serve as indicators of natural weathering (Erel et al., 1991). In contrast, elements such as Pb and As are often found in trace amounts in most natural systems, but as a consequence of industrial processes anthropogenic...
contribution of these elements is presently exceeding natural sources (Nriagu, 1990). Therefore, fresh waters may contain significant amounts of trace elements deriving from anthropogenic sources (e.g. Erel et al., 1990; Klaminder et al., 2006).

The atmospheric deposition of metals from anthropogenic activity dates back to the discovery of fire (Nriagu, 1990) and ever since then human activity has resulted in a significant input of metals to terrestrial and aquatic environments. The long-range transport and pollution was recognized in 1969 (Murozumi et al., 1969). Trace metal profiles in peats (e.g. Shotyk et al., 1996), lake sediments (e.g. Renberg et al., 1994), and ice cores (e.g. Hong et al., 1994) show that the anthropogenic influence of long-range pollution of trace metals has been significant for thousands of years. Even in relatively remote areas such as northern Sweden, the present Pb concentrations in the organic horizon is about 1000 times higher than natural background levels (Bindler et al., 1999), a result of anthropogenic activity during almost 4000 years (Renberg et al., 2000).

In recent decades, the concentrations of trace metals in atmospheric deposition in Europe have decreased by 30-90% (Rühling and Tyler, 2001; Harmens et al., 2008). However, there is still limited knowledge about how the accumulated pool of metals in the soils will respond to decreasing deposition. In the context of climate change the mobility of trace metals can become an important issue, especially from organic-rich environments such as the boreal regions of the world (Kaste et al., 2003; Graham et al., 2006).

In boreal regions the organic soils have a relatively high cation exchange capacity due to the numerous exchange sites upon which metal cations can interact (Steinnes and Friedland, 2006). The interactions can be via chelation, complexation and adsorption reactions, and several trace metals exhibit a strong affinity for organic matter and especially for humic acids (Warren and Haack, 2001; Steinnes and Friedland, 2006). Consequently, the binding of metals to organic matter in upper soil layers should prevent mobilization. It has long been recognized, for example, that Pb is retained in organic-rich upper soil layers (e.g. Bergkvist, 1987; Erel et al., 1990). However, it is also well established that several trace elements are complexed by dissolved organic matter (Sholkovitz and Copland, 1981; Davis, 1984), which may enhance the mobility of metal-organic compounds in the soil profile as well as through the catchment (LaZerte et al., 1989; Graham et al., 2006). The downward movement of metals through the soil profile is for Pb occurring faster than expected (Miller and Friedland, 1994; Watmough et al., 2004) and in Swedish forest soils, the Pb pollution front has migrated to depths of 20-60 cm (Brännvall et al., 2001). Therefore, the mean residence time of Pb in soils is now expected to be shorter than previously known. Consequently, there is increasing concern regarding the mobilization of previously deposited trace elements to surface waters (Miller and Friedland, 1994; Klaminder et al., 2006) and in particular from peat soils (Lawlor and Tipping, 2003; Rothwell et al., 2007).

Aquatic geochemistry of Fe, Mn and some trace elements

In natural waters, several metals can occur in more than one oxidation state, and usually exhibit different mobility, solubility, reactivity, toxicity and bioavailability for their different oxidation states. In general the free ionic form is more toxic to biota than the form complexed to organic matter or particulate matter (Hart and Hines, 1995).

Trace elements can exist in a variety of forms including (1) free (hydrolyzed) ionic forms (e.g. Cu²⁺, Fe(OH)²⁺), (2) inorganic complexes (e.g. PbCO₃), (3) organic complexes with fulvic and humic acids, (4) associated with colloidal and particulate matter (e.g. clay minerals or hydrous oxides of Fe and Mn) or with biota (e.g. phytoplankton) (Borg, 1995).

The major transport pathway for trace metals in freshwater is often through adsorption or complexation to organic molecules and reactive mineral surfaces of suspended sediment and colloids (Davis, 1984; Tessier et al., 1996). The Fe and Mn oxyhydroxides provide reactive surfaces for scavenging of trace metals and the oxyhydroxides are major carriers for trace metals in stream water (Tipping, 1981; Davis, 1984; Pokrovsky and Schott, 2002). During anaerobic conditions the reduction of Fe and Mn may be accompanied by dissolution of the solid hydroxide, whereby any adsorbed metal can be released (Drever, 2002). Thus solid-solution reactions are important for the metal partitioning between the solid phase and the solution. The metal behavior in aquatic environments is also influenced by pH which controls surface charges and speciation of elements. In general, the sorption of metals to surface ligands and solute ligands is stronger at higher pH (Stumm and Morgan, 1996). In addition, the fraction of metals complexed to organic matter usually decreases as pH decreases (Borg and Johansson, 1989; Pehlivan and Arslan, 2006).

Iron and manganese

Iron is a transition metal, essential for many organisms. As the fourth most abundant element in Earth's crust,
it is well represented in many natural environments such as the hydrosphere, where Fe minerals in igneous and metamorphic rocks are the major sources. Iron can occur in two oxidation states: ferrous iron, Fe(II) and ferric iron, Fe(III). In oxygenated surface waters Fe(III) is the thermodynamically stable oxidation state and the solubility of Fe oxyhydroxides is low in the pH range and redox potential of natural waters (Fig. 1). In anoxic waters Fe(II) is the stable oxidation state and the solubility is much greater (Faure, 1991; Drever, 2002). In most natural waters, Fe(III) usually forms strong complexes with most ligands, and especially with OH−, whereas Fe(II) in general forms weak complexes (Langmuir, 1997).

Manganese is an essential element to plants and animals and is the tenth most abundant element in the Earth's crust. Manganese is readily depleted from igneous and metamorphic rocks by the interactions of surface water and groundwater, whereby numerous oxide/hydroxide minerals are formed. Most Mn oxides display negative net surface charge in most natural waters, which is an important characteristic for adsorption processes with trace elements (Stumm, 1992). In oxygenated waters Mn(II) is thermodynamically unstable and is oxidized to Mn(III) or Mn(IV), forming solid oxides or oxyhydroxides of Mn(IV) that have very low solubility under natural conditions in aquatic systems (Davison, 1993). Like Fe oxyhydroxides, the Mn oxides tend to coexist with and coat many other minerals and organic matter. In anoxic waters manganese ions, Mn2+, are stable and present as simple hydrated ions, similar to Fe(H2O)62+ (Davison, 1993; Wedepohl, 1978).

One of the fundamental differences in the redox chemistry of Fe and Mn is that (1) the oxidation of Mn(II) to Mn(III, IV) in general proceeds more slowly (even if catalysed) in comparison to the oxidation of Fe(II) to Fe(III) and (2) the reduction of Mn occurs at a higher reduction potential than that required for reduction of Fe (Stumm, 1992).

**Arsenic, cobalt and lead**

The elements As, Co and Pb are present in trace amounts in the continental crust, (Wedepohl, 1995). Today the anthropogenic sources for these elements are greater by several orders of magnitude in comparison to their natural sources. The trace elements As and Pb do not have any known biological functions and are considered to be very toxic to biota.

The toxicity, mobility and bioavailability of As vary depending on its oxidation state. In surface waters As(V) is present primarily as deprotonated oxyanions of arsenic acid, although the more toxic form, As(III), also can be present (Sadiq et al., 1983; Pettine and Millero, 2000). The soluble As species are mainly controlled by redox conditions, pH, biological activity and adsorption reactions (Wok and Wai, 1994). Adsorption of As decreases with increasing pH because the adsorption is a result of the interaction of the negatively charged As(V) oxyanion with protonated hydroxyl sites on mineral surfaces (Smith et al., 1998; Pettine and Millero, 2000). At the pH of most natural waters As(III) occurs as a neutral, uncharged molecule and is not strongly adsorbed at any pH (Drever, 2002).

The biogeochemical cycling of Pb has been significantly changed by anthropogenic sources (Nriagu, 1990). Lead is a chalcophilic element and is a stable divalent cation, exhibiting a strong affinity for organic matter. In surface water the most important inorganic species in the pH range 4.5 to 6.5 is Pb2+. The solubility of Pb compounds in water is low and pH dependent (Lydersen et al., 2002).

Cobalt is an essential element for several organisms, and it is most often found in association with Fe and Mn oxides in oxic or suboxic environments. It is a relatively easily weathered element and the retention of Co in the soils depends primarily on the content of Fe and Mn oxides but also on the content of organic matter, Al oxides and clay silicates in the soils (Turekian, 1978). In natural waters Co is most often found as free Co2+ (Stumm and Morgan, 1996).
Biogeochemical properties of sulphur

Sulphur (S) is a ubiquitous element throughout the environment, and as a constituent of proteins it is an essential element for all forms of life. The average content in continental crustal rocks is about 0.05 to 0.06% (Hogan et al., 1998). The close association of sulphur with hydrocarbons explains why sulphur has become a dominant form of air pollution since the combustion of fossil fuels results in emissions of sulphur dioxide (SO₂). In natural environments sulphur undergoes redox changes between valencies of +6 (sulphate, SO₄²⁻) to -2 (sulphide, S²⁻) and it readily participates in oxidation-reduction processes, which can be microbially mediated. The reduction of sulphur consumes protons and hence produces alkalinity in soil solutions and waters, which can mitigate effects of acid deposition and acid mine drainage. In contrast, oxidation of sulphur produces protons and acidity (Howarth and Stewart, 1992).

Sulphur in forest ecosystems

The soil is the major reservoir of sulphur in forest ecosystems (Johnson and Mitchell, 1998) and the main sources of sulphur to forest catchments are from atmospheric deposition and mineral weathering of sulphides. However, in most forest ecosystems the contributions from mineral weathering are minor. The major outputs from forest catchments occur via biogenic gases and by runoff, although the gaseous outputs are rather small in comparison to the loss via drainage waters (Mitchell et al., 1998).

In forest ecosystems there are both inorganic and organic forms of sulphur although the organic pool dominates in forest soils, constituting about 80-90% of the soil sulphur (Mitchell et al., 1998; Likens et al., 2002). Soil organic sulphur components are carbon-bonded sulphur (C-S; amino acids) and ester sulphates (C-O-S). The inorganic sulphur in well-drained forest soils is dominated by sulphate (Mitchell et al., 1998).

The transformation of soil-sulphur can occur by biotic transformations which in general are microbially mediated and can be subdivided into the following processes (Krouse and Grinenko, 1991):

- Mineralization (conversion of organic S to sulphate)
- Immobilization (assimilatory sulphate reduction, conversion of sulphate to organic S)
- Sulphide oxidation
- Bacterial dissimilatory sulphate reduction (conversion of sulphate to sulphide)
- Sulphate assimilation by plants

The abiotic transformations processes of sulphur include ion exchange of sulphate (adsorption-desorption) and precipitation/dissolution of mineral sulphides or sulphates (Johnson and Mitchell, 1998).

Sulphur can be retained in a catchment by immobilization, bacterial dissipimilatory sulphate reduction (BDSR), uptake in biota (assimilation), mineral precipitation and adsorption. The major inorganic retention mechanism is through adsorption. These abiotic and biotic processes can result in a substantial increase in residence time of sulphur in forest soils (Mayer et al., 1995b; Alewell, 2001), which may cause a time lag in stream water response to changes in atmospheric sulphur inputs (Prechelt et al., 2001; Shanley et al., 2005). In soils with low retention capacities of sulphate, the loss via leaching can be substantial, which is of particular concern in areas that have been subjected to high atmospheric depositions of sulphur. The suggested reasons for a low sulphate sorption capacity in soils are due to all or a combination of: (i) shallow post-glacial soil development, (ii) sandy soil textures, and (iii) high humus content (Alewell et al., 2000; Alewell, 2001).

Trends in stream water sulphate

The anthropogenic sulphur emissions from combustion of fossil fuels during the twentieth century resulted in high atmospheric deposition of sulphur in Europe and North America, but during the last decades the deposition from anthropogenic sources has declined by 50-90% (Likens et al., 2001). As a result, decreasing concentrations of sulphate have been reported in runoff in North America (Likens et al., 2002; Watmough et al., 2005) as well as in Europe (Prechelt et al., 2001; Watmough et al., 2005). However, it is possible that the soil pool of sulphur, accumulated during the years of high deposition, will release sulphate to aquatic systems also in the future. Mass budget calculations for sulphur in forested ecosystems have shown that the output of sulphate by streams exceeds the input from bulk precipitation (e.g. Alewell and Gehre, 1999; Likens et al., 2002; Inamdar and Mitchell, 2008), resulting in a net release of sulphate. Five possible explanations have been attributed for this net release of sulphate from forest soils to runoff: (i) desorption of previously adsorbed inorganic sulphate, (ii) reoxidation of reduced sulphur, (iii) excess mineralization of organically bound sulphur and (iv) weathering of sulphur minerals and (v) input from dry deposition (Alewell et al., 1999; Prechelt et al., 2001; Likens et al., 2002; Watmough et al., 2005) and of course a combination of these processes (Eimers et al., 2004).
The importance of wetlands for the cycling of sulphate has received attention since it has been reported that dry periods in peatlands can result in re-oxidization of reduced sulphur, hence mobilizing sulphate (Devito and Hill, 1999; Mörtth et al., 1999; Eimers et al., 2007). In addition, studies have shown that wetlands can act as a sink for sulphate, due to BDSR (e.g. Eimers et al., 2004; Inamdar and Mitchell, 2008).

**Sulphur isotope geochemistry**

Sulphur has four stable isotopes (32S, 33S, 34S, 36S), with relative abundance averaging about 95.02, 0.75, 4.22 and 0.017%, respectively (Macnamara and Thode, 1950). The ratio between the isotopes 34S and 32S is used when reporting isotope abundance variations and is expressed as per mil (%o) differences relative to the isotopic composition of the international standard, the Cañon Diablo Troilite, using the δ34S notation.

**Isotope fractionation**

The most important isotope fractionating processes are the microbial mediated sulphur transformations, of which bacterial dissimilatory sulphate reduction (BDSR) is most important. Organic matter is decomposed by anaerobic bacteria (e.g. *Desulfovibrio* and *Desulfotomaculum*) using SO\(_4^{2-}\) as an electron acceptor to reduce SO\(_4^{2-}\), a process which consumes protons (Brown, 1985; Spratt et al., 1987).

\[
(1) \quad 2\text{CH}_2\text{O} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow 2\text{CO}_2 + \text{HS}^- + 2\text{H}_2\text{O}
\]

The lighter 32S isotope is preferred by the bacteria because it is easier to break bonds in a 32SO\(_4^{2-}\) molecule compared to 34SO\(_4^{2-}\), resulting in a depletion of 32S in the product (H\(_2\)S). Therefore, δ34S values of the product can be significantly lower in comparison to that of the reactant (SO\(_4^{2-}\)), which is enriched in the heavier isotope 34S (Krouse and Grinenko, 1991). Isotope fractionation by BDSR can be up to 45-50‰ (Canfield, 2001a; Canfield, 2001b) although the fractionation varies depending on the organism and environmental conditions.

During assimilation (an energy requiring process) sulphate is reduced to sulphide. The isotope fractionation during assimilatory reduction of sulphate by plants and animals is minor although there is some evidence that plants discriminate against 34S, resulting in lower δ34S values (Thode, 1991). The isotope fractionation during mineralization of organic sulphur to sulphate is considered to be minor (Krouse and Grinenko, 1991) and has been reported to be <1.5‰ (Norman et al., 2002). Oxidation of inorganic reduced sulphur to sulphate as a stable end product can occur by abiotic or biotic reactions. In general, these processes result in minimal isotope fractionation (Krouse and Grinenko, 1991; Canfield, 2001a). Although adsorption-desorption of sulphate is one of the major processes influencing net sulphur loss or retention within catchments, the isotopic fractionation associated with adsorption-desorption is of minor importance (Fuller et al., 1986; Van Stempvoort et al., 1990).

**Sulphur isotope variations**

The sulphur isotopic composition of an ecosystem is dependent on two major factors: the isotopic composition of the sources (i.e. atmospheric deposition and mineral weathering) and discrimination against certain isotopes during sulphur transformation (Mitchell et al., 1998). As a result there is a considerable variation in the natural abundance of sulphur isotopes with δ34S values typically ranging from -40‰ to +40‰. However, a shift in sulphur isotope ratios can only be a result of biological processes (Krouse and Grinenko, 1991).

In runoff the δ34S values typically range between -20‰ and +20‰ although the global average in rivers has been estimated to be +7‰ (Nriagu et al., 1991). There is a large variation in δ34S values in runoff due to mineralogical sources of sulphate (e.g. marine sulphate contribution, evaporates and sulphide ores). The present δ34S value of seawater is +21‰ (Rees et al., 1978) and therefore high positive values are observed in coastal areas. The anthropogenic sulphate generally has δ34S values between 0 and +10‰ (Nriagu, 1991) and several studies have reported δ34S values close to that of precipitation (e.g. Mayer et al., 1995b; Novák et al., 2000; Mörtth et al., 2008). The δ34S values in soils ranges from -30‰ to +30‰ depending on the sources of the sulphate. The terrestrial mean is considered to be 0‰. Organic soils developed under anaerobic conditions usually display depletions in 34S and hence may display negative values which are most likely due to incorporation of reduced sulphur, formed during BDSR (Krouse and Grinenko, 1991).

The variations in δ34S values of precipitation show some variation with season, caused by different oxidation mechanisms (Krouse and Grinenko, 1991). There is not a significant difference between δ34S values in wet and dry deposited sulphur, as indicated by similar δ34S values of precipitation and throughfall (Mörth and Torssander, 1995; Alewell and Gehre, 1999).
Sulphur isotopes in catchment studies

The use of sulphur isotopes has increased the knowledge about the biogeochemical cycling of sulphur in forest ecosystems considerably. The $\delta^{34}S$ values of stream water can be used to identify sources of sulphur, but also to elucidate the major pathways for sulphur transformation in riverine ecosystems (Mitchell et al., 1998). Several studies have shown that atmospheric and biogeochemical processes on a small catchment scale, and to relate these processes to the stream biogeochemistry at the landscape level. At the moment there are several research projects trying to accomplish this goal and this thesis represents one part of the work in progress.

The results and discussion in this thesis are based on stream water samples collected from a stream network in the Krycklan River Catchment (67 km$^2$), located in northern Sweden. The Krycklan catchment is situated in the mid-boreal vegetation zone, about 50 km northwest of Umeå and 30 km from the Baltic Sea, and is representative of a typical boreal catchment in northern Sweden. The Krycklan River is a free-flowing fourth order stream and a tributary of the Vindeln River, one of the last pristine rivers in Sweden. The study area comprises a stream network of 15 streams ranging from small first order streams (headwaters) to fourth order streams with catchment areas varying from 0.03 km$^2$ to 67 km$^2$ (Table 1). The Krycklan catchment includes the Vindeln Experimental Forests and the Svartrberget Research Station (64°14’N, 19°46’E), where forest research has been conducted since 1923 and climate has been monitored since 1980 (Bishop et al., 1990; Köhler et al., 2008). Several of the streams are inhabited by brown trout ($Salmo trutta$) and brook trout ($Salvelinus fontinalis$) (Buffam, 2007).

The landscape within the Krycklan catchment is characterized by coniferous forests (88%) interspersed with peat wetlands. About three percent of the Krycklan catchment is arable land. The forest vegetation is dominated by mature Scots pine ($Pinus sylvestris$) in up slope drier areas and by Norway spruce ($Picea abies$) in low-lying wetter areas, although some deciduous species ($Betula spp.$, $Alnus incana$, $Salix spp.$) are common along the riparian zones of the larger streams (Andersson and Nilsson, 2002). The peat wetlands cover about 8% of the Krycklan catchment, with the majority located in the higher reaches in the northwest. However, several of the subcatchments are influenced by a large percentage of wetlands, ranging between 0 to 76%. The wetlands (mires) are dominated by peat-forming $Sphagnum spp.$ and the mires are classified as acid, oligotrophic with varying proportions of minerotrophic and ombrotrophic patches (Sirin et al., 1998; Granberg et al., 1999). The majority of the catchments (9 of 15) are independent of one another, but the larger streams receive flow from upstream regions.

Geology

The svecofennian bedrock is dominated by migmatites (94%) (veined gneiss—metagreywacke or meta-argillite) of sedimentary origin. There are also some acid and intermediate metavolcanic rocks (granite) (4%) and basic metavolcanic rocks (amphibolites) (3%) (SGU, 1986). The topography of the region ranges from 126 to 369 m above sea level.

The region was ice free about 8900 BP and major Quaternary deposits are glacial till and peat (SGU, 1995). The glacial till is locally derived and varies in thickness up to tens of meters. However, fine-grained silty or sandy sediments deposited in a postglacial river delta are widespread in the lower reaches of the Krycklan catchment (Fig. 2), where the stream channels of the meandering streams have incised deeply into these sediments (Ivarsson and Johnsson, 1988). Well-developed iron-podzols are common in the forested areas, whereas organic-rich soils (histosols) are found in the near stream zone (Bishop et al., 1994). The highest postglacial coastline (255-260 m above sea level) transects the study area and 55% of the catchment is located below this postglacial coastline (Ågren et al., 2007).
Climate and hydrology

The climate of the region is characterized by short summers and long winters. Mean annual air temperature is +1 °C (1981-2000) and the average air temperature in January and July is -11 °C and +12 °C, respectively (Köhler et al., 2008). Mean annual precipitation is 646 mm of which about one third falls as snow. The average runoff is 323 mm, corresponding to about 50% of the precipitation (Köhler et al., 2008). The snow cover persists for 171 days on average (1980-1999) and average maximum snow depth is about 70 cm (Nyberg et al., 2001; Ottosson Löfvenius et al., 2003). The annual spring snowmelt episode during 4-6 weeks in April-May is the major hydrological event, when on average 40% of the annual streamflow occurs (Köhler et al., 2008).

The till soils of boreal regions have high infiltration capacities and the runoff process is dominated by flow paths in superficial soil layers, where conductivity in general is higher (Lundin 1982). During the snowmelt the groundwater rise and the superficial soil layers are saturated from below, which is especially pronounced in the riparian zones (Rodhe, 1987; Nyberg et al., 2001). The snowmelt in general generates a rise of the groundwater by 30-40 cm and the soil horizons below 90 cm are only affected in a minor way by the snowmelt event. The runoff during snowmelt in forest dominated catchments is dominated by pre-event water, i.e. water that was in the catchment prior to the snowmelt (Laudon et al., 2004b; Laudon et al., 2007).

The region has a history of forestry and many streams in northern Sweden streams were deepened during the 1920-1930s (Sirin 1998; Bishop et al., 1994). The anthropogenic deposition of trace elements has been limited in comparison to southern parts of Sweden (Rühling and Tyler, 2001. The current deposition of sulphur in the area is about 2.0 kg ha⁻¹ yr⁻¹ (Bishop et al., 2000), while the deposition was about 10 kg ha⁻¹ yr⁻¹, when it peaked during the early 1970s (Mylona, 1996).

Methods

Sampling and analyses

The results in this thesis are based on water samples collected from 15 streams in the Krycklan catchment (Fig. 2). The subcatchments are hereafter referred to as C1-C16 (note that C11 does not exist). The stream water samples were collected in 2004 and 2005, when approximately 825 samples were collected during 54
Table 1. Catchment characteristics of the studied subcatchments.

<table>
<thead>
<tr>
<th>Site No</th>
<th>Site name</th>
<th>Stream order</th>
<th>Area (km²)</th>
<th>Land cover (%)</th>
<th>Surficial sediment type (%)</th>
<th>Land cover type</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>Rishäcken</td>
<td>1</td>
<td>0.66</td>
<td>Forest 98.7</td>
<td>Wetland 1.3</td>
<td>Mixed</td>
</tr>
<tr>
<td>C2</td>
<td>Västrabäcken</td>
<td>1</td>
<td>0.14</td>
<td>Lake 100</td>
<td>Arable 0</td>
<td>Mixed</td>
</tr>
<tr>
<td>C3</td>
<td>Lillmynsbacken</td>
<td>1</td>
<td>0.03</td>
<td>Peat 0</td>
<td>Silt 0</td>
<td>Mixed</td>
</tr>
<tr>
<td>C4</td>
<td>Kallkälsmyren</td>
<td>0.19</td>
<td>0.19</td>
<td>Thin or discontinuous soil cover 59.6</td>
<td>Till 40.4</td>
<td>Mixed</td>
</tr>
<tr>
<td>C5</td>
<td>Stormjärnän Outlet</td>
<td>0.85</td>
<td>0.85</td>
<td>Sand 59.0</td>
<td>Glaciofluvial sediments 36.3</td>
<td>Wetland</td>
</tr>
<tr>
<td>C6</td>
<td>Stormjärnsbäcken</td>
<td>1.3</td>
<td>1.3</td>
<td>Glaciofluvial sediments 72.8</td>
<td>Glaciofluvial sediments 24.1</td>
<td>Wetland</td>
</tr>
<tr>
<td>C7</td>
<td>Kallkällsbäcken</td>
<td>2.05</td>
<td>2.05</td>
<td>Glaciofluvial sediments 85.1</td>
<td>Glaciofluvial sediments 14.9</td>
<td>Wetland</td>
</tr>
<tr>
<td>C8</td>
<td>Fubäcken</td>
<td>2.2</td>
<td>2.2</td>
<td>Glaciofluvial sediments 88.7</td>
<td>Glaciofluvial sediments 11.3</td>
<td>Wetland</td>
</tr>
<tr>
<td>C9</td>
<td>Nyängesbäcken</td>
<td>2.3</td>
<td>2.3</td>
<td>Glaciofluvial sediments 84.9</td>
<td>Glaciofluvial sediments 13.8</td>
<td>Wetland</td>
</tr>
<tr>
<td>C10</td>
<td>Stormmyråk</td>
<td>2.5</td>
<td>2.5</td>
<td>Glaciofluvial sediments 74.2</td>
<td>Glaciofluvial sediments 25.8</td>
<td>Wetland</td>
</tr>
<tr>
<td>C11</td>
<td>Nymyrbäcken</td>
<td>3.5</td>
<td>3.5</td>
<td>Glaciofluvial sediments 84.1</td>
<td>Glaciofluvial sediments 15.5</td>
<td>Wetland</td>
</tr>
<tr>
<td>C12</td>
<td>Långmynsbacken</td>
<td>7.2</td>
<td>7.2</td>
<td>Glaciofluvial sediments 89.1</td>
<td>Glaciofluvial sediments 9.9</td>
<td>Wetland</td>
</tr>
<tr>
<td>C13</td>
<td>Åhedsbäcken</td>
<td>14</td>
<td>14</td>
<td>Glaciofluvial sediments 90.4</td>
<td>Glaciofluvial sediments 5.1</td>
<td>Wetland</td>
</tr>
<tr>
<td>C14</td>
<td>Övre Krycklan</td>
<td>420</td>
<td>420</td>
<td>Glaciofluvial sediments 83.2</td>
<td>Glaciofluvial sediments 14.0</td>
<td>Wetland</td>
</tr>
<tr>
<td>C15</td>
<td>Krycklan</td>
<td>467</td>
<td>467</td>
<td>Glaciofluvial sediments 88.0</td>
<td>Glaciofluvial sediments 8.3</td>
<td>Wetland</td>
</tr>
</tbody>
</table>

*a Source: Swedish Geological Survey (SGU, 1995). Rare surficial sediment types (sand, gravel and glaciofluvial sediments) were excluded from this table and from statistical analyses.

*b Thin or discontinuous soil cover (<50 cm) which generally is till. Bedrock is found within 50 cm of the surface (SGU, 1995).

Land cover type defined by percent wetland coverage, where forested <2% wetland, mixed 2-30% wetland, and wetland >30% (Buffam et al., 2007).

Sampling occasions (Paper I and II). The samples for Paper III and IV were collected in 2005. The monthly sampling was intensified during the spring flood events (April-May) when samples were collected every second to third day.

For the metal and trace element studies (Paper I and II), samples were collected in thoroughly acid-washed, high density polyethylene (HDPE) bottles. After collection the samples were kept in the dark at 4 ºC until further treatment. For Paper I both unfiltered and filtered samples were prepared for analysis. The samples were filtered through polycarbonate filters (Millipore® HTTP 0.4 μm), loaded in acid-washed filter holders. All filtration was performed in a Class 100 clean air laminar flow hood in a clean air laboratory. The samples were acidified and then stored in the dark until analysis. The concentrations of major cations, Fe and Mn (Paper I), were determined using ICP-OES (Varian Vista Pro X Series 2) at the Department of Geology and Geochemistry, Stockholm University. For Paper II about 350 samples from ten of the streams were selected for analysis (C1, C2, C4-C7, C9, and C14-C16).

Dissolved organic carbon (DOC) was determined in subsamples using a Shimadzu TOC-CPH analyser (detailed methods are described in Buffam, 2007). A previous study in the area (Laudon et al., 2004a) found that the particulate organic carbon is low (<5% of total) at both low and high flow. Therefore DOC in this study is considered equivalent to total organic carbon (TOC).

For the sulphur isotope study (Paper III and IV), about 380 samples were collected during 26 sampling occasions in 2005. The samples were collected in clean HDPE bottles and all samples were analysed for the concentration of sulphate (SO₄²⁻) using ion chromatography (DIONEX-300). About 300 of the 380 samples were selected and prepared for determination of the S isotope composition in SO₄²⁻. Columns with a strong basic anion resin were used to collect dissolved SO₄²⁻ in water samples according to a method similar to that described in Andersson et al. (1992). The SO₄²⁻ was collected in columns, eluted using NaCl, acidified and then precipitated as BaSO₄ by adding BaCl₂. After filtration through a polycarbonate membrane filter (Millipore® HTTP 0.4 μm) and drying over night, the BaSO₄ was collected in small glass vials until analysis.

Each sample was analysed for the mass ratio abundance of δ³⁴S/³²S using an elemental analyser and continuous flow gas Isotope Ratio Mass Spectrometry (CF-EA-IRMS, Finnigan Delta+ and a NCS2500 elemental analyser from Carlo Erba) and reported as delta (δ) values relative to the international standard for S, the Cañon Diablo Troilite.

\[
δ^{34}S(\%) = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \cdot 1000
\]

where \( R_{\text{sample}} \) and \( R_{\text{std}} \) denote the abundance ratio of \(^{34}\text{S} / ^{32}\text{S} \) in the sample and in the standard, respectively.
For the determination of the isotope composition of sulphur in dissolved organic matter, (δ34S-DOM) (Paper IV) additional samples of 10 L were collected from nine of the streams in the Krycklan catchment (C1, C2, C4, C5, C7, C10, C13, C15 and C16). In addition, a tenth wetland-dominated catchment located outside the Krycklan catchment was also included.

The DOM in stream water samples was concentrated using cross-flow filtration and the retentate was frozen and freeze-dried. The δ34S-DOM value was calculated from the δ34S value of the freeze-dried retentate (δ34S_TOT) and the δ34S_SO4 value in the stream water, using a mixing model.

**Catchment characteristics**

Catchment characteristics and catchment area were obtained from previous work by Buffam (2007) and Ågren (2007). Gridded elevation data (DEM) with a grid resolution of 50 m was used to calculate the catchment area contributing to each sampling site (Buffam 2007). The proportion of wetland, forest, lakes and agricultural cover within each catchment was determined using a 1:50 000 scale digital land cover map (Lantmäteriet, Gävle, Sweden) (Buffam et al., 2007). A digital soil map of Quaternary deposits (1:100 000 scale) was used for determining the proportions of surface sediment types in the catchments (Geological Survey of Sweden, Uppsala, Sweden). In addition, catchment boundaries and land cover types were updated by field surveys (Buffam, 2007). For the evaluation of the results from the analyses of stream water samples, the catchments were subdivided into land cover groups depending on the percentage of wetland coverage: forested, mixed, and wetland with wetland coverage of 0-2%, 2-30%, and >30%, respectively.

**Discharge measurements**

The Krycklan catchment site C7 (0.5 km²), where runoff has been measured since 1980, was used as a reference site for hydrological measurements. The runoff is monitored continuously (every 10 seconds and stored as hourly averages) using a 90° V notch weir in a heated shelter. The specific discharge at C7 was used to estimate the discharge for the other subcatchments assuming the same specific runoff for all subcatchments. This assumption was justified by previous discrete measurements of discharge at the other streams. From these comparisons, the inter-site differences in annual discharge have been calculated to ±12% and the inter-site differences in flow regimes ("flashiness") have been calculated as a ±12% maximum error during spring flood (Ågren et al., 2007).

**Summary of results**

**Paper I: Hydrogeochemistry of Fe and Mn in small boreal streams: The role of seasonality, landscape type and scale**

Organic matter and Fe and Mn oxyhydroxides are important carriers for several trace metals in stream water, and hence it is important to evaluate the temporal and spatial variation of these carriers prior to trace element studies.

Water samples from the 15 streams were collected and analysed (ICP-OES) for unfiltered (total) and filtered (<0.4 μm) concentrations of Fe and Mn during 2004-2005. The purpose was to investigate the temporal and spatial variations of Fe and Mn and their relation to landscape characteristics, for example, the proportion of wetland coverage, but also to dissolved organic carbon (DOC).

The temporal variations of Fe and Mn during the spring flood were characterized by increasing concentrations in headwater streams of forested catchments (wetland coverage <2%), whereas concentrations decreased in headwater streams with wetland coverage >30%. In the forested catchments the concentrations increased by a factor of 2-4, whereas the concentrations decreased in the wetland catchments by a factor of 10. The different responses in the contrasting catchments in Fe and Mn concentrations were consistent with temporal variations of DOC in these streams (Buffam, 2007).

In the forested headwater streams Fe correlated significantly with DOC. High concentrations of soluble Fe were related to high concentrations of organic compounds in the upper soil layers, which during the spring flood were flushed into the stream by rising water tables. However, Mn did not show any significant correlation with DOC, which can be attributed to the fact that Mn does not form organic complexes with DOC to the same extent as Fe does.

At the catchment outlet (C16), there was a significant difference between unfiltered and filtered concentrations of Fe and Mn, especially during spring flood, when Fetot and MnTot increased by a factor of 15 and 8, respectively. The concentrations of Fe34s and Mn34s only increased by a factor of 2. No significant correlation was found between DOC and either Fe or Mn.

In this study, the hydrogeochemistry of Fe was dependent on the proportion of wetlands within the catchments; total concentrations of Fe showed a significant positive correlation with wetland coverage ($r^2=0.89$, p<0.001). In contrast, no significant correlation was observed for Mn, which instead was more dependent
on the supply of minerogenic particulates, especially during high discharge (i.e. spring flood) and especially in the lower reaches of the Krycklan catchment where the stream banks are characterized by silt deposits. The results from Paper I show that wetlands, DOC, and particulates are important factors governing the concentrations of Fe and Mn in stream waters within the Krycklan catchment.

**Paper II: Landscape control on the hydrogeochemistry of As, Co and Pb in a boreal stream network**

This paper is related to Paper I, but in this study the major focus is on the trace elements arsenic (As), cobalt (Co) and lead (Pb). However, as in the other papers in this thesis, one of the main objectives was to investigate the influence of the landscape characteristics (proportion of wetland and forest coverage) on the stream water concentrations. The spring flood was the major period of study and filtered samples (<0.4 μm) from ten of the streams in the Krycklan stream network (~350 samples) were analysed on ICP-MS to determine the concentrations of As, Co and Pb during 2004-2005.

Since the behaviour of trace elements in stream water is considered to be influenced, for example, by DOC, pH and the occurrence of Fe, the correlation between these stream water variables and the concentration of As, Co and Pb in stream water was evaluated. Enrichment factors (EF) were calculated to evaluate if these elements were enriched in stream water in relation to the lithogenic source composition. The EF was calculated by normalizing the concentration in the stream water to that of Al in the till (mineral soil, C-horizon).

There was a significant difference in stream water concentrations of Co and Pb between headwater streams draining forested (<2% wetland coverage) and wetland dominated catchments (>30% wetland coverage). Average concentrations of Co were 10-15 times higher in headwater streams draining forested catchments, compared to wetland dominated streams (Fig. 3). However, concentrations of Pb were highest in wetland dominated streams and a significant correlation was observed between percentage of wetland coverage and Pb concentrations in stream water ($r^2=0.79$, $p<0.001$). In contrast, Co correlated with percentage of forest coverage ($r^2=0.46$, $p<0.05$) whereas As did not show any significant correlation with land cover type.

The temporal variation of the trace elements in the headwaters of forested and wetland dominated catchments (2-30% wetland coverage) increased during spring snowmelt, whereas concentrations decreased in streams of wetland dominated catchments (Fig 3). This result is in concordance with the observations of Fe and Mn from Paper I, and in the forested catchments is most likely due to the activation of flow paths in upper organic-rich soil horizons, where As and Pb have accumulated and Co is released by weathering processes. Decreasing concentrations in the wetlands were due to dilution with snowmelt.

Enrichment factors were calculated for a forested headwater stream (C2), a wetland dominated stream (C4), and at the outlet (C16). The enrichment factors, which estimate the tendency of a trace element to be enriched in relation to the lithogenic source (i.e. till), showed that there was an enrichment of As, Co and Pb in stream water by a factor of about 5-50, 5-10 and 2-50, respectively. The enrichment was most pronounced at C4 during the spring flood event. This result suggests that wetlands in the Krycklan catchment can be potential sources for some metals and that the contributions from anthropogenic sources are greater than from natural sources.
The export of As and Co from the streams was in general higher than the input from atmospheric deposition by a factor of 2-3 and 2-20, respectively. However, the transport of Pb via runoff was lower by a magnitude of 10 in comparison to the atmospheric input. Although the present input of Pb from atmospheric deposition is relatively low and the streams show enrichments of Pb in comparison to the lithogenic sources, the Pb is retained in the catchments.

The results from Paper II highlight the importance of studying the hydrogeochemistry of trace elements from a landscape perspective.

**Paper III: Anthropogenic S - still important for sulphur dynamics in small boreal streams**

The objective of Paper III was to study the hydrogeochemistry of sulphur (S) by analyzing stream water sulphate (SO\textsubscript{4}\textsuperscript{2-}) and the isotopic composition of sulphate (\ensuremath{\delta^{34}S_{\text{SO}_4}}) in 15 of the streams in the Krycklan catchment during 2005. The isotopic composition was analysed in an attempt to trace sources of SO\textsubscript{4}\textsuperscript{2-} from various landscape components and to evaluate if there were significant differences in \ensuremath{\delta^{34}S_{\text{SO}_4}} values between various land cover groups (forested, wetland and mixed catchments). The purpose was also to investigate the influence of the proportion of wetland and forest coverage on stream water SO\textsubscript{4}\textsuperscript{2-} and to estimate mass balances of S to evaluate if the catchments in the Krycklan region act as sinks or sources of S. Previous studies from forested catchments have shown that the stream export of S can exceed the input of S from atmospheric deposition, and there is still some uncertainty in how streams in boreal regions will respond to decreased deposition rates.

Stream water SO\textsubscript{4}\textsuperscript{2-} concentrations were significantly higher in streams of forested catchments than in wetland dominated streams of similar size. A significant negative correlation was observed between stream water SO\textsubscript{4}\textsuperscript{2-} and percentage of wetland coverage (\(r^2=0.77, p<0.001\)), indicating that bacterial dissimilatory sulphate reduction (BDSR) occurs in wetland areas. Fractionating during BDSR processes was confirmed in catchments with a wetland coverage >30% by a negative relationship between \ensuremath{\delta^{34}S_{\text{SO}_4}} values and SO\textsubscript{4}\textsuperscript{2-} concentrations. This was especially pronounced during the summer when high \ensuremath{\delta^{34}S_{\text{SO}_4}} values and concomitant low SO\textsubscript{4}\textsuperscript{2-} concentrations were observed in streams draining wetland catchments.

The annual average \ensuremath{\delta^{34}S_{\text{SO}_4}} values in streams draining forested, wetland and mixed catchments were +6.7‰, +7.6‰ and +6.9‰, respectively. Hence, there were small differences in annual average \ensuremath{\delta^{34}S_{\text{SO}_4}} values between the various land cover groups. The small difference indicates that anaerobic conditions in the riparian zones also can be of importance in the forested and mixed catchments thus altering the stream water \ensuremath{\delta^{34}S_{\text{SO}_4}} values.

During spring flood episodes, the SO\textsubscript{4}\textsuperscript{2-} concentrations decreased by about 50% in all streams, except in the wetland dominated streams, where SO\textsubscript{4}\textsuperscript{2-} concentrations increased. The \ensuremath{\delta^{34}S_{\text{SO}_4}} values decreased in all streams by 1 to 5‰ during the spring flood. The \ensuremath{\delta^{34}S_{\text{SO}_4}} values in the stream waters were higher at all times during the sampling period than the \ensuremath{\delta^{34}S_{\text{SO}_4}} value of precipitation (i.e. snow, +4.7‰).

The anthropogenic influence on the stream water SO\textsubscript{4}\textsuperscript{2-} dynamics was evaluated by two-component end member mixing analysis (EMMA) at the catchment outlet, C16, using isotopic values and SO\textsubscript{4}\textsuperscript{2-} concentrations for the forested sites and snow. The result revealed that at peak spring flood about 75% of the S derives from deposition, i.e. anthropogenic sources, of which half was estimated to derive from snowmelt and the other half originating from previously deposited S.

The mass balances of the catchments show that only the wetland dominated catchments retain the input of S through deposition, in all other streams there is a net export of S by the streams. Despite reduced emissions of anthropogenic S, there is still a strong influence of past and current deposition of SO\textsubscript{4}\textsuperscript{2-} on runoff in this northern boreal region, and anthropogenic S is still the major source in the Krycklan catchment. The results also demonstrate that large discrepancies in S-export can be expected from small geographic regions depending on the characteristics of the catchment that is being drained. Therefore it is crucial to include landscape characteristics when studying the dynamic features of SO\textsubscript{4}\textsuperscript{2-} in boreal ecosystems.

**Paper IV: Unravelling the origin of stream water DOM using \ensuremath{\delta^{34}S}\textsubscript{DOM}**

In this paper, the focus is on the isotopic composition of organic sulphur in stream water. The spatial and temporal variations of \ensuremath{\delta^{34}S} in dissolved organic matter (\ensuremath{\delta^{34}S}\textsubscript{DOM}) in ten streams were studied in an attempt to identify different sources of DOM in the landscape. The index streams for a forested catchment (C2), a wetland catchment (C4) and the outlet of the Krycklan catchment (C16) were sampled more frequently than the other streams.

The organic sulphur was enriched in relation to SO\textsubscript{4}\textsuperscript{2-} by ultrafiltrating 10 L of stream water sample, and \ensuremath{\delta^{34}S}-
DOM was then determined as the difference between $\delta^{34}$S$_{TOT}$ and $\delta^{34}$SO$_4$$^2$ in the freeze-dried retentate using a simple mixing model. The average stream water $\delta^{34}$SO$_4$$^2$ value was significantly higher than the $\delta^{34}$S$_{TOT}$ and $\delta^{34}$S-DOM values. The $\delta^{34}$SO$_4$$^2$ ranged between +5.3‰ and +9.5‰, whereas the range for $\delta^{34}$S$_{TOT}$ and $\delta^{34}$S-DOM was +7.8‰ to -2‰, and -5.2‰ to +9.6‰, respectively.

In general the variations in $\delta^{34}$S-DOM values ranged between +3‰ and +5‰, which is close to the $\delta^{34}$S value of the deposition in the area. The average $\delta^{34}$S-DOM in the stream waters was +4.0±0.6‰ (N=62) although large temporal variations were observed in stream water $\delta^{34}$S-DOM. In the wetland dominated stream C4 a shift of more than 10‰ occurred just after spring peak flow. The decrease in $\delta^{34}$S-DOM coincided with low stream water DOC concentrations, although there was a lag in the decrease in $\delta^{34}$S-DOM values compared to the decrease in DOC concentrations. During the rest of the sampled period, the $\delta^{34}$S-DOM values ranged between +2.9‰ and +5.7‰. The negative values were observed at the wetland headwater stream after peak spring flood and interpreted as associated with the incorporation of SO$_4$$^2$ that had been subjected to bacterial dissimilatory sulphate reduction (BDSR). This process is strongly fractionating and results in a product enrichment of $^{34}$S (sulphides) in comparison to the SO$_4$$^2$ source which is enriched in $^{34}$S.

In the headwater stream of a forested catchment (C2), $\delta^{34}$S-DOM decreased at spring flood, from +5.5‰ during winter base flow to +0.3‰ at the start of the spring flood and thereafter increased again during the melt event to +4.5‰. During winter base flow, a higher $\delta^{34}$S-DOM value of +10‰ was observed at the catchment outlet compared to the small (<1 km$^2$) headwater forested and wetland streams, where winter base flow values were about +6‰ and +4‰, respectively. The $\delta^{34}$S-DOM values in streams of mixed catchments were in the same range as the forested headwaters. The higher $\delta^{34}$S-DOM values at the catchment outlet indicate that isotopically heavier DOM from deeper soil layers, possibly derived from an increasing degree of mineralization of organic S with depth, can be important in the larger catchments.

The spatial and temporal variation in $\delta^{34}$S-DOM within this boreal catchment illustrate that $\delta^{34}$S-DOM potentially can be used as a tracer to generate new insights about terrestrial DOM sources in the boreal landscape.

**Discussion**

Peatlands cover about 4% of the Earth’s surface (Shotyk, 1988) and in boreal regions of Scandinavia they cover 10-50% of the land area (Pakarinen 1995). The presence of these waterlogged ecosystems (wetlands) in the forested landscape alters the chemistry of water leaving these catchments. The wetlands are important for the biogeochemical cycling of elements since they can provide potential sources or sinks for various elements. For example, Fe and Mn are expected to be mobilized in the reducing environment of wetlands (Shiller, 1997) (Paper I). However, the organic-rich low pH environment of wetlands can also contribute to mobilization of Pb (Shotyk, 1988; Eimers et al., 2008) (Paper II) and wetlands can increase the retention of SO$_4$$^2$ (Devito, 1995) (Paper III).

In boreal forest ecosystems, streams and rivers undergo characteristic hydrological cycles due to the annual snowmelt episode. In the Krycklan catchment the spring floods can result in a 50-fold increase in stream flow. The chemical response in stream water is usually characterized by increased concentrations of DOC (Buffam et al., 2007, Eimers et al., 2008), but also by increasing concentrations of Fe and Mn (e.g. Andersson et al., 2006, Dahlqvist et al., 2007). The increase in DOC concentrations in boreal streams during spring flood is due to activation of upper organic-rich soil horizons, where DOC is accumulated (Laudon et al., 2004a; Ågren et al., 2007), by rising groundwater levels (Bishop et al., 1994; Rodhe, 1987). This increase in DOC is a major factor governing the temporal and spatial behaviour of other elements, e.g. Fe and Mn (Paper I), but also the behavior of some trace elements (Paper II). As a result of increased transport of organic acids to the streams and a dilution of acid neutralization capacity there is a characteristic pH decline during spring in boreal regions (Laudon et al., 1999; Buffam et al., 2007).

During spring flood events, stream water in forested catchments in Krycklan is dominated by pre-event water (70-85%), namely water that was in the catchment prior to the melting (Rodhe, 1987; Laudon et al., 2007). In contrast, according to $\delta^{18}$O studies, about 50% of the stream water at spring flood in wetland dominated catchments derives from meltwater (Laudon et al., 2007). The frozen peat prevents infiltration of meltwater whereby meltwater is rapidly delivered to the stream mainly by over land flow (Laudon et al., 2007; Rodhe 1987) diluting the stream water. At the wetland site (C4), an additional preferential pathway at a depth of 200-250 cm is also active during snowmelt (Laudon et al., 2007). These hydrological patterns in forested and wetland
catchments have consequences for all elements in this study.

The concentrations of DOC in streams of forested catchments increase with increasing proportion of wetland area (e.g. Dillon and Molot, 1997; Buffam et al., 2007; Eimers et al., 2008). In this study, it has also been shown that concentrations of Fe and Pb increase in stream water as the proportion of wetland area increases.

Laudon et al. (2004a) showed that DOC increased in stream water draining a forested catchment at spring flood, but decreased in a wetland catchment. The different seasonal patterns of DOC in forested catchments indicate different sources and flow paths in forest dominated versus wetland dominated catchments (Laudon et al., 2004a; Laudon et al., 2007; Eimers et al., 2008). The results from this study show that Fe, Mn and trace elements exhibit similar seasonal pattern as DOC during the spring melt, hence highlighting the importance of hydrology and DOC for their hydrogeochemistry.

Iron and manganese

The dynamic behaviour of Fe and Mn in natural waters and their crucial role as essential elements in biota have led to extensive research of these elements during recent decades. However, relatively limited focus has been devoted to the occurrence of Fe and Mn in natural waters in relation to the landscape properties within catchments (Dillon and Molot, 1997). In general Fe and Mn concentrations in stream water are considered to correspond to natural levels since their major source is from mineral weathering (Erel et al., 1991). However, the occurrence of Fe and Mn also plays a central role in the geochemical behaviour and fate of trace elements (Paper II).

The significant correlation between Fe and DOC is probably attributed to colloidal organic matter since Fe is mainly transported as colloidal Fe associated with DOC (Andersson et al., 2006; Ingri et al., 2006). During the spring flood organically complexed Fe compounds are flushed from the upper organic-rich soil horizons to the stream (Bishop et al., 1994; Lydersen et al., 2002). Mn does not form complexes with organic matter to the same extent as Fe, which may explain why Mn did not show significant correlation with DOC in the headwater streams (Laxen et al., 1984; Young and Harvey, 1992). Most likely the pH drop during the spring flood also contributes to an increase in solubility of both Fe and Mn.

During base flow conditions higher concentrations of Fe and Mn were observed in headwater streams draining wetlands than in forest dominated headwater streams. This result is most likely due to the anaerobic environment providing suitable conditions for the reduction of Fe and Mn which mobilize these elements.

It was hypothesized that Fe and Mn would correlate with wetland coverage, and the significant correlation between Fe/Al and wetland coverage is in agreement with a previous study (Dillon and Molot, 1997). Hence, in this boreal stream network the mobility of Fe appears to be enhanced by organic matter and/or reducing conditions (Dillon and Molot, 1997). However, no correlation between wetland coverage and Mn concentrations was observed, which is enigmatic since previous studies in larger streams in northern Sweden have attributed increased Mn concentrations to mires within the catchment (Ponté et al., 1990; Ponté et al., 1992). However, those studies encompassed larger catchments where the contribution from groundwater and processes in upstream lakes may have contributed to a different response in Mn concentrations in stream water. Instead, in this study, PCA analysis showed that Mn was associated with surficial silt deposits in the downstream regions of the stream network. During spring flood, both Fe and Mn were mainly transported as particulates in the larger silt influenced streams. The silt fraction has previously been reported to be important for the transport of Mn in stream water (Shafer et al., 1997; Morrison and Benoit, 2005).

In this thesis, little attention has been placed on the influence of biota on stream water chemistry. This can be an important factor for elements that are cycled through the vegetation, e.g. Mn. The biological contribution of Mn to stream water is still uncertain. Studies of Mn in precipitation and throughfall have shown that Mn is enriched in throughfall from coniferous forests showing 70 times higher Mn concentration in comparison to precipitation. (Andersson, 1991; Skrivan et al., 1995). These studies indicate that biogeochemical cycling of Mn in coniferous forests and release of Mn from trees may be of great importance for concentrations observed in runoff.

Trace elements

During recent decades, the long-range deposition of pollutants such as As and Pb has decreased significantly (Rühling and Tyler, 2001). In the Krycklan region the content of As and Pb in moss have decreased by 56 and 84%, respectively since 1985 (http://www.ivl.se). Still, there is most likely a large pool of trace elements in the
upper soil layers and the fate of these elements is not fully understood. In Paper II trace metal concentrations (As, Co and Pb) in ten of the streams were evaluated in order to investigate the influence of wetland coverage, on the stream water concentrations of these elements, but also to investigate the importance of Fe, DOC and pH. During the spring flood episodes, the temporal patterns of As, Co and Pb were similar to those of Fe and DOC. in both forested and wetland dominated streams. This result emphasizes the importance of Fe and DOC for the observed trace element concentrations but also the importance of the hydrology, i.e. surficial shallow flow paths in headwater streams of forested catchments (Rodhe, 1987; Nyberg et al., 2001) and the overland flow in wetland dominated headwater streams (Laudon et al., 2007; Rodhe, 1987).

The results from Paper II indicate that As, Co and Pb are mobilized from surface soil layers to the streams, especially during spring flood events. Most likely there is a redistribution of the elements within the catchments (Watmough and Dillon, 2007). The mobility and export of Pb are governed by DOC concentrations (e.g. Watmough and Dillon, 2007; Dillon and Molor, 1997). The increase in Pb concentrations during spring flood shows that Pb is related to organic matter deriving from the upper soil horizons, but also related to Fe in the forested headwater streams (Kaste et al., 2005). The mobility of As and Co does not show the same dependence on organic matter. In all catchments Pb appears to be retained in the soils since the input from the atmosphere exceeds the export by streams, whereas the exports of As and Co exceed the input from atmosphere. The retention of As in the forest floor is considered to be low in a long-term perspective (Gustafsson and Jacks, 1995) and a previous study has also reported low retention of As in forest soils (Lawson and Mason, 2001).

The significantly higher Pb concentrations in runoff from wetlands in comparison to runoff from upland forest soils have also been reported from other areas (Watmough and Dillon, 2007). It is generally believed that the organic soils in wetlands are net sinks for Pb due to the high affinity of Pb for organic matter (Vile et al., 1999). However, organic acids are effective leaching agents for Pb in peat (Kalmykova et al., 2008) and since wetlands release large amounts of DOC, high concentrations of Pb can be expected in waters draining wetlands. In addition, since the sorption of metals on the surface of humic acids decrease with decreasing pH, Pb can be considerably mobile in the low pH environment in the wetland (Tipping et al., 2003; Pehlivan and Arslan, 2006). The significant correlation between Pb and wetland coverage emphasizes the importance of wetlands for the geochemical cycling of Pb in this boreal forest ecosystem.

The sources for trace elements in streams are most likely several, and may be active during various parts of the year. In addition, the relative contribution of each source probably varies depending on the element studied. During base flow conditions, the influence of chemical weathering of bedrock and soil is most likely larger than at spring flood. However, the input of trace elements by weathering has not been considered in this study. Yet, even in the relatively remote areas of the Krycklan catchment, there is a large pool of anthropogenic Pb in the soils (Klaminder et al., 2006) and possibly also As. During high discharge episodes the contribution from anthropogenic deposition can be significant (Lindberg and Turner, 1988) and the enrichment of As, Co and Pb in stream water during spring flood indicates that anthropogenic sources in the Krycklan catchment are larger than the natural sources. This has been confirmed for Pb by studying Pb isotopes (Klaminder et al., 2006). Natural contribution of Co by weathering is most likely the major source in the forested headwater catchments as the concentrations in these headwaters were significantly higher than in the other streams.

In summary, the results from Paper I and II show that DOC is a major factor governing the hydrogeochemistry of Fe and Pb. In addition, major hydrological events (spring flood) contribute to the temporal variation in stream water concentrations of Fe, Mn and trace elements. The response to the spring flood varies depending on the composition of the landscape, that is increasing concentrations were observed in streams of forested and mixed catchments whereas concentrations decreased in wetland dominated headwaters. Also, the geochemistry of the bedrock and the till most likely influences the stream water chemistry during low flow periods although the importance of the input from weathering in Krycklan needs to be investigated further. The chemistry of the upper soil layers appears to determine the hydrogeochemistry of the headwater streams in the Krycklan catchment. Enrichment of Fe and Mn in the upper soil layers (B-horizon) is a natural part of the podsolization process and the close association between the Fe and Mn oxyhydroxides with trace elements contributes to the accumulation of trace elements in the soil profile. However, the anthropogenic contribution of trace elements to stream water is evident as observed in the enrichment of As, Co and Pb in comparison to the contribution from the local till. In summary, the major controls on metal and trace element release to the streams appear to be DOC, hydrological conditions, pH and redox. All these factors are influenced by the landscape type and are interconnected by the composition of the landscape.
The dynamic cycling of sulphur in the Krycklan catchment

The importance of wetlands for the biogeochemical cycling of S is emphasized by the results of Paper III (and IV). In wetlands, and most likely also in the riparian zone, BDSR occurs. This is in particular evident during periods of low discharge, when low SO\textsubscript{4}\textsuperscript{2-} concentrations were accompanied by high δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values in stream waters draining wetland areas (Eimers et al., 2004). This result can only be achieved by microbial organisms which discriminate against \textsuperscript{34}S, hence enriching the residual stream water in \textsuperscript{34}S (Krouse and Grinenko, 1991). However, the δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values in stream water of forested catchments were only 1-2‰ lower than in streams of wetland-dominated catchments. A larger difference would have been expected due to the anaerobic conditions in the wetlands, thus favouring microbial sulphate reduction, which can be as large as 30‰ to 50‰ (Canfield, 2001a). However, lower temperatures, in combination with relatively low SO\textsubscript{4}\textsuperscript{2-} concentrations in the wetland areas, may explain the small isotope fractionations in this study (Canfield, 2001b). Furthermore, in forested and mixed catchments the organic-rich riparian zones can provide suitable anoxic environments for BDSR, which can be important for S cycling. High δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values were observed in some of these streams during parts of the year, indicating BDSR. In addition, it is possible that reoxidation of reduced S (enriched in \textsuperscript{32}S in comparison to the source SO\textsubscript{4}\textsuperscript{2-}) in the wetlands generates SO\textsubscript{4}\textsuperscript{2-} with lower δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values (Mörth et al., 1999).

The mass balance calculations showed that, with the present deposition of about 1.8 kg S ha\textsuperscript{-1} yr\textsuperscript{-1}, all catchments, except the catchments with a wetland coverage >24% (C3, C4, C5 and C6), are exporting more S than the input from atmospheric deposition. Hence, the wetlands in the Krycklan catchment are net sinks for S, most likely because BDSR in the anaerobic part of the peat retains S (Alewell and Gehre, 1999; Eimers et al., 2004). In forested and mixed catchments the input of S from atmospheric deposition was not retained and these catchments were sources of S to the stream water and up to about 50% were exported during the spring flood event. Soils in formerly glaciated areas generally have low adsorption capacity of SO\textsubscript{4}\textsuperscript{2-}, which can contribute to a more rapid SO\textsubscript{4}\textsuperscript{2-} leaching to surface waters (Alewell et al., 1999; Alewell, 2001). Another contributing factor can be that the SO\textsubscript{4}\textsuperscript{2-} that earlier was retained in the soil now is mobilized, resulting in a net loss of SO\textsubscript{4}\textsuperscript{2-} (Löfgren et al., 2001; Wilander, 2001). Mineralization of organic S can be an important additional source of SO\textsubscript{4}\textsuperscript{2-} (Alewell et al., 1999; Mörth et al., 2005). To elucidate the role of mineralization in this catchment it is necessary to analyse δ\textsuperscript{18}O in the SO\textsubscript{4}\textsuperscript{2-}. Previous studies have demonstrated that atmospherically derived S is cycled through the organic soil pool before it is released to the streams (Mayer et al., 1995a, Mörth et al., 2005). Analysis of δ\textsuperscript{18}O in the SO\textsubscript{4}\textsuperscript{2-} would give further insight into the cycling of S in this boreal system.

The SO\textsubscript{4}\textsuperscript{2-} concentrations in stream water depend to a large extent on the relative coverage of forested areas and wetland areas, since they affect S cycling in different ways. Yet, from a landscape perspective, the relative importance of wetlands does not seem to be major, as the average δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} value at the catchment outlet was similar to that of the forested catchments. However, this is not surprising since the wetland coverage of the Krycklan catchment is only about 8% of the total area. In this boreal stream system the influence of wetlands on the stream water chemistry of S is more apparent in small headwater areas and when wetland coverage is >30%. At spring flood, the temporal variations of SO\textsubscript{4}\textsuperscript{2-} and δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} in the wetland dominated headwater streams were characterized by increasing concentrations and a concomitant decrease in δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} a result that was interpreted as a contribution of SO\textsubscript{4}\textsuperscript{2-} from the snow. This can be argued since the δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} value of the snow was lower (+4.7‰) than the δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values in the streams, and a previous study has shown that 50% of the stream water in the wetland stream C4 derives from meltwater at spring flood (Laudon et al., 2007).

During spring flood, δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values decreased in all streams, but were always higher than the δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} value of +4.7‰ in the precipitation (snow). Compared to precipitation, stream water enriched in \textsuperscript{34}S has been shown to indicate continuous BDSR in catchments (Alewell and Gehre, 1999). However, precipitation in the area has been reported to have δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values between +5‰ and +7‰ (Novak et al., 2003; Mörth et al., 2008) and the average value of +6.7 ‰ in streams of forested catchments probably reflects the δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} value of a small influence of BDSR superimposed on current and past deposition. The mineralogical influence of S is most likely minor (Mörth et al., 2008) since this would have been reflected in lower δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values and higher SO\textsubscript{4}\textsuperscript{2-} concentrations. This assumption would benefit from a more detailed and frequent sampling of groundwater in the Krycklan catchment. The low δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values in combination with high SO\textsubscript{4}\textsuperscript{2-} concentrations in the groundwater indicate that the influence of groundwater can be important during periods of low flow. However, base flow δ\textsuperscript{34}S\textsubscript{SO\textsubscript{4}} values are high and thus indicate minor influence from this sulphur.

Two-component end member mixing analysis revealed that about 75% of the S at the catchment outlet at peak
spring flood derives from deposition. In addition, of the 75% deriving from deposition, it was estimated that 50% was recently deposited (snow) SO₄²⁻ and the remaining 50% derived from previously (recent years) deposited SO₄²⁻. Although the deposition of anthropogenic S has decreased in the area, there is still a strong influence of past and current deposition of SO₄²⁻. Michel et al. (2002) found that about 75% of the SO₄²⁻ at spring flood derived from deposition during previous years, using ³⁵S as a tracer. However, to more accurately estimate the contribution from recent and previously deposited S in the Krycklan catchment it is necessary to use some kind of tracer, e.g. the radioactive isotope ³⁵S, which has revealed that the residence time for atmospherically derived SO₄²⁻ exceeds one year (e.g. Shanley et al, 2005).

Organic S - the use of δ³⁴S-DOM to trace the origin of DOM

The δ³⁴S value in dissolved organic matter (δ³⁴S-DOM) was determined in order to gain insight into processes and sources governing the nature of DOM in the Krycklan catchment (Paper IV). The δ³⁴S-DOM showed a large spatial and temporal variation. In particular, the δ³⁴S-DOM values from the wetland dominated stream C4 showed high variability, with negative values after spring flood. As the upper part of the frozen peat melts during spring flood, release of DOM may contribute to the shift to lower δ³⁴S-DOM values. This is because BDSR has resulted in an enrichment of ³⁴S in DOM in comparison to the SO₄²⁻ source, and DOM therefore exhibits low δ³⁴S values.

The shift in DOM sources in stream water of forested catchments appeared to occur at the onset of the spring flood, which indicates that a small change in hydrology activates and connects a DOM source to the stream. In the forested headwater streams the riparian zones most likely are important areas for BDSR, hence lowering the δ³⁴S-DOM values in stream water when the soil water in these zones are activated.

The δ³⁴S-DOM values were in general close to the deposition value of +4.7‰ (Paper III). Therefore, the δ³⁴S-DOM values in aerobic conditions can reflect the δ³⁴S SO₄²⁻ value of deposition. It has been shown that incorporation of SO₄²⁻ into the organic S pool (by immobilization) is a rapid process (Novak et al., 2003; Giesler et al., 2005) with limited isotope fractionation, thus explaining the δ³⁴S-DOM values being close to the deposition value.

The SO₄²⁻ is subjected to transformations between organic and inorganic S, a process which complicates the biogeochemical cycling of S in boreal forest systems. Since organic S is the dominant S pool in forested ecosystems it is important to elucidate the temporal and spatial variation of δ³⁴S in dissolved organic matter. This study (Paper IV) suggests a method that can trace sources of terrestrial DOM.

Key areas for biogeochemical processes

It is important to identify biogeochemical key areas that influence the cycling of elements in boreal catchments. The identification of key areas can only be accomplished when considering the hydrogeochemistry from a landscape perspective. In this context the wetlands in the Krycklan catchment can be considered to be key areas for the biogeochemical cycling of DOC, Fe, SO₄²⁻ and Pb. In addition, the spring flood and possibly also extreme precipitation events can be considered as key events for the export of Fe, Mn, trace elements and SO₄²⁻ from boreal catchments. The findings from this study also demonstrate that large differences in hydrogeochemistry are observed within small geographic regions depending on the characteristics of the catchment that is being drained. Therefore it is crucial to include landscape characteristics when studying the hydrogeochemistry in boreal ecosystems.

Conclusions

Have the results from this study contributed to further insights into the controls on the complex hydrogeochemistry of Fe, Mn, S and trace elements (As, Co and Pb)? Yes, the results from this study, carried out in a boreal catchment (67 km²), reveal that the temporal and spatial variations in the hydrogeochemistry of these elements are influenced by landscape characteristics and that that wetlands are key areas in the landscape.

Temporal variations

The response in stream water concentrations to the annual snowmelt in forested (<2% wetland coverage) and mixed catchments (2-30%) was significantly different from that in wetland dominated catchments (>30% wetland coverage).

• In headwater streams of forested catchments, concentrations of Fe, Mn and trace elements increased in response to snowmelt. In headwater streams of wetland catchments, the opposite response was observed, i.e. decreasing concentrations. In streams of mixed catchments the temporal patterns were similar to those observed in forested headwaters.
• In forested catchments, the increasing concentrations were a response to activation of surficial organic-rich flow paths by rising groundwater levels, flushing Fe, Mn and trace elements to the streams. The decreasing concentrations in wetland headwater streams were due to dilution with meltwater.

• The response in stream water concentrations of SO$_4^{2-}$ was characterized by decreasing concentrations in headwater streams of forested and mixed catchments (dilution). In headwater streams of wetland catchments increasing concentrations of SO$_4^{2-}$ were observed, due to a contribution of SO$_4^{2-}$ from the melting snow, reaching the streams by overland flow.

• The isotope composition of stream water SO$_4^{2-}$($\delta^{34}$S$_{SO4}$) decreased in all streams in response to snowmelt.

• During base flow conditions, concentrations of Fe and Mn were, in general, higher in headwater streams of wetland catchments than in other streams. However, concentrations of SO$_4^{2-}$ were in general lower in streams of wetland catchments, due to bacterial dissimilatory sulphate reduction (BDSR) occurring in the anaerobic environments of the wetland areas.

**Spatial variations**

The analyses of the influence of landscape on spatial variations, in terms of varying coverage of forest and wetlands within the subcatchments, reveal that:

• Stream water concentrations of Fe and Pb were significantly correlated with wetland coverage. This result indicates that wetlands are potential sources of Fe and Pb, for Fe by providing a reducing, low pH environment which enhances the mobility of Fe and for Pb by the organic-rich, low pH environment enhancing the mobility of Pb.

• Concentrations of Co were significantly higher in streams of forested catchments, most likely due to a combination of local minerogenic influence and association with Fe oxyhydroxides. However, concentrations of Pb were significantly higher in wetland dominated streams. This was attributed to large pool of Pb in these environments in combination with increased mobility when associated with DOC. The significant correlation between wetland coverage and both Fe and Pb emphasize the importance of wetlands for the geochemical cycling of these elements.

• The spatial variation in the concentrations and export of SO$_4^{2-}$ in forested catchments was different in streams of forested catchments in comparison to headwater streams of wetland catchments. The former showed significantly higher annual stream water SO$_4^{2-}$ concentrations than in wetland dominated streams. The forested catchments were net exporters of SO$_4^{2-}$. In contrast, SO$_4^{2-}$ concentrations were negatively correlated with wetland area and the wetland acted as net sinks for SO$_4^{2-}$.

• In wetland catchments, BDSR altered the $\delta^{34}$S$_{SO4}$ value and higher $\delta^{34}$S$_{SO4}$ values were observed in headwater streams of wetland catchments.

**Anthropogenic influence**

Even in the relatively remote area of the Krycklan catchment, the influence of human activity on the hydrogeochemistry is present. Although the deposition of anthropogenic S has decreased in the area and the current deposition of SO$_4^{2-}$ is relatively low, there is still a large influence of past and current deposition on stream water SO$_4^{2-}$.

Enrichment factors show that there was an enrichment of As, Co and Pb in stream water in comparison to lithogenic contribution from the till. The enrichment was especially pronounced for the wetland dominated catchment, and particularly during spring flood. The enrichment in stream water indicates that a major part of these elements derives from anthropogenic sources. These results show that wetlands are potential sources for some trace elements (e.g. Pb).

It can be concluded that the influence of wetland area on stream water chemistry is significant for Fe, Pb and SO$_4^{2-}$. Positive correlation was observed between wetland coverage and both Fe and Pb but negative with SO$_4^{2-}$ (and Co).

In summary, the major factors governing the temporal and spatial variations in hydrogeochemistry of Fe, Mn, trace elements and the dynamic cycling of S appears to be: hydrological conditions, DOC, redox conditions, pH and to some extent the geological setting, although this does not seem to be of major importance for the trace elements in this study. However, the key control on the stream water chemistry appears to be the landscape components since all the mentioned factors are governed by the major landscape components and are interconnected by the composition of the landscape. Furthermore, anthropogenic sources are also important and affect stream water concentrations of SO$_4^{2-}$, Pb and As.
Implications and future research suggestions

It still remains to evaluate if the temporal and spatial patterns in stream water chemistry observed in the Krycklan catchment also will be observed in other parts of the boreal region. Can the results from this study be implemented in other regions and on larger catchments? The temporal and spatial patterns of TOC observed in the Krycklan catchment have also been observed at larger scales in Sweden (Köhler et al., 2008). However, it remains to evaluate if the temporal and spatial patterns observed for the elements studied in this thesis also are observed at a larger scale. In addition, this study only encompasses two years, and the results would benefit from confirming with results from long-term studies. Moreover, it is crucial to sample major hydrological episodes and in particular, peak flow events. During base flow conditions less frequent sampling is required.

Several intriguing questions remain unanswered after conducting this study and there are several suggestions for future research. A challenge for future research is to further investigate the intricate processes and influencing factors that control the complexity of hydrogeochemistry in boreal regions. The Fe and Mn study (Paper I) would benefit from a follow-up on the distribution of these elements between the particulate phase and the dissolved phase. The results from Paper I showed that the particulates are important, and moreover, suspended particulate material is important for the transport of trace elements.

The trace element study (Paper II) could be extended to include several elements and the link to the hydrogeochemistry of Fe and Mn could be further investigated. To better understand the geochemical behaviour of the trace elements, speciation of the elements would be valuable. The use of isotopes (e.g. Fe and Pb isotopes) can provide further insight into sources and pathways through the catchment.

The input of elements by weathering has not been considered in this study. Specifically it would be interesting to investigate the contribution of Co from weathering. It would also be interesting to evaluate the influence of biota and in particular the role of vegetation for the cycling of elements. For example, Mn is cycled through the vegetation and it has been shown that the biogeochemical Mn pump is of great importance in coniferous forests. In addition, decomposition of vegetation and litter releases elements to the forest floor and to the streams and these processes may be of importance for stream water chemistry during parts of the year.

The results from the studies with stable S isotopes (Paper III and IV) show their usefulness in environmental studies. However, a study encompassing several years and also more accurate deposition data from the Krycklan region would improve a future study. To further disentangle S dynamics it is also necessary to use some kind of tracer, for example the radioactive isotope $^{35}$S which could be useful for estimating the residence time of S in the soil before it enters the stream. In addition, analysis of $^{18}$O in SO$_2$\textsuperscript{2-} can also provide insight into pathways and cycling mechanisms for S in the system. To further study the cycling of S in the area, the $\delta^{34}$S values in different soils and soil solutions should be determined as well as the isotopic signal of S from the underlying bedrock. The study would also benefit from additional groundwater samples within the Krycklan catchment and during different parts of the year.

The metal and trace element studies could be linked to the sulphur studies by investigating the relationship between the S hydrogeochemistry and that of Fe and Mn and other trace elements. The organic sulphur is probably involved in the transport and mobilization of trace elements and this should be investigated.

The wetlands appear to be key areas for the cycling of for example Pb. Peat samples and peat pore water samples from various depths would provide further information on where the major pool of Pb is located. This in combination with the use of stable Pb isotopes in the wetlands could provide more information on the cycling of Pb in the wetlands in this region. In the same manner, soil water samples from various depths in the riparian zone will also provide more information on which soil horizons are the most important for the stream water chemistry and during what parts of the year.

The predicted climate change for Scandinavia is warmer and wetter climate (Graham, 2004; Hanssen-Bauer et al., 2005). This will probably alter the amount and character of DOC exported from the boreal landscape (Köhler et al., 2008), which may also influence the mobility and transport of elements from boreal regions to the sea. Since headwater streams are most likely more sensitive to disturbances in comparison to downstream regions, it may be possible that small streams (<10 km$^2$) can serve as early indicators to disturbances such as climate change.

The landscape is a product of continuous processes, and the hydrogeochemistry that we observe today will not be the same tomorrow. Fresh water resources are continuously altered by natural processes and will continue to be altered by human activity in the future. Thus, continued research of the complex processes...
changing and influencing the stream water chemistry from headwater regions to the sea will be important to address present and future environmental issues. Let us hope that also in the future, water will still be best of all things.

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**References**


