Intra-Annual Variability of Natural Organic Matter in Boreal Streams

Patterns and Controls

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Cover: Different types of organic matter (coarse woody debris, dissolved organic matter and the characteristic "foam") that can be found in streams. Photo from Tyresta national park, south of Stockholm, Sweden.
(photo: M. Winterdahl)

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Abstract

Natural organic matter (NOM) is a key component in aquatic ecosystems. It influences for example acidity, mobility and toxicity of metals and organic pollutants, energy input to aquatic food webs, weathering, and water light conditions. There are also considerable costs associated with removing NOM in drinking water production. Furthermore, NOM is an integral part of the carbon cycle with possible indirect effects on climate. During recent decades, there have been observations of increasing concentrations of NOM in surface waters in parts of North America and Europe. The causes of these trends are not fully understood, but are thought to be related to climate change and recovery from anthropogenic acidification. This thesis presents results from studies on intra-annual NOM cycling in more than 130 boreal streams and rivers. It also presents developments of the Riparian flow-concentration Integration Model (RIM).

Detailed studies on five forested headwater catchments revealed that stream discharge and soil temperature were the main drivers of NOM variability. In addition, a small headwater catchment at the Swedish West Coast was substantially influenced by sea-salt deposition, which suppressed NOM mobilization. A modified version of RIM with discharge and soil temperature as variables could successfully simulate NOM dynamics in all five catchments. Riparian soil organic matter content and distribution was hypothesized to be the underlying control on NOM response to discharge and soil temperature. Catchments where NOM was sensitive to discharge displayed stronger gradients in soil NOM concentrations than did catchments with weak discharge sensitivity.

A large scale study of 136 streams and rivers indicated common relationships among NOM, discharge and temperature. Conversely, there was no geographical pattern in NOM trends. Relative trends were weakly related to NOM response to flow and temperature. There were also clear relationships among intra-annual NOM dynamics, temperature, flow, and catchment landscape characteristics, indicating that catchments can be classified based on NOM dynamics. Taken together, this implies that NOM dynamics could change in ways not reflected in inter-annual trends due to climate change.

Keywords: DOC, dissolved organic carbon, NOM, modeling, soil temperature, climate change, Krycklan catchment, GLUE

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List of Publications

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

I Winterdahl, M., Futter, M., Köhler, S., Laudon, H., Seibert, J., Bishop, K. (2011). Riparian soil temperature modification of the relationship between flow and dissolved organic carbon concentration in a boreal stream. *Water Resources Research* 47, W08532, doi:10.1029/2010WR010235.

II Winterdahl, M., Temnerud, J., Futter, M. N., Löfgren, S., Moldan, F., Bishop, K. (2011). Riparian Zone Influence on Stream Water Dissolved Organic Carbon Concentrations at the Swedish Integrated Monitoring Sites. *AMBIO* 40(8), 920-930.

III Winterdahl, M., Futter, M. N., Grabs, T., Bishop K. Sensitivity of dissolved organic carbon in boreal streams to temperature and runoff (manuscript).

IV Winterdahl, M., Erlandsson, M. N., Futter, M., Weyhenmeyer, G. A., Bishop, K. Intra-annual variability of organic carbon concentrations in running waters: temporal drivers and relationship to inter-annual trends (manuscript).

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The contribution of Mattias Winterdahl to the papers included in this thesis was as follows:

I The respondent had the main responsibility of modelling, analyses, interpretations, writing and publishing

II The respondent had the main responsibility of modelling, analyses, interpretations, writing and publishing

III The respondent had the main responsibility of modelling and writing, and was partly responsible for analyses and interpretations

IV The respondent was responsible for the statistical analyses, interpretation and writing

Abbreviations

CH_4	Methane
CO_2	Carbon dioxide
Da	Dalton; atomic mass unit, where 12 Da is defined as the weight of one atom of carbon-12
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
ER	Ecosystem Respiration
FT-ICR-MS	Fourier Transform Ion Cyclotron Resonance Mass Spectrometry
GHG	Green House Gas
GPP	Gross Primary Production
IM	Integrated Monitoring
N_2O	Nitrous oxide
NEP	Net Ecosystem Production
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NPP	Net Primary Production
POC	Particulate Organic Carbon
POM	Particulate Organic Matter
RIM	Riparian flow-concentration Integration Model
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
TOC	Total Organic Carbon

1 Introduction

There are wide-spread indications of human actions altering the structure and functioning of marine, aquatic and terrestrial ecosystems. Loss of biodiversity due to habitat destruction, over-fishing, eutrophication, acidification, and pollution of ecosystems are all severe threats against the ecosystem services that the environment provides human society. Perhaps the largest current concern is about global climate change. The combustion of large amounts of fossil fuels together with extensive land-use changes has increased the atmospheric concentrations of many greenhouse gases (GHG), notably carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). GHG trap outgoing radiative heat, thereby increasing the temperature (Hartmann, 1994); rising global temperatures during the last century are thought to be caused by anthropogenic emissions of GHG.

Carbon dioxide is, besides water vapor, the most important GHG. A considerable amount of research has been devoted to the processes controlling the atmospheric content of CO_2 and the global carbon cycle (Heimann & Reichstein, 2008). Still, there are large knowledge-gaps regarding our understanding of the carbon cycle and the climate-CO_2 link, partly because of the complexity and multitude of processes controlling the carbon cycle and the feedbacks between these processes and climate.

One component of the global carbon cycle that has received considerable scientific research recently is the production, transport and degradation of organic matter in freshwater environments (Battin *et al.*, 2009; Tranvik *et al.*, 2009; Cole *et al.*, 2007). Freshwater systems have traditionally been considered to have negligible effects on global carbon cycling and that their only effect is to passively transport carbon from the terrestrial environment to the ocean. However, recent estimates indicate that the World's streams, rivers and lakes process as much carbon as the estimated terrestrial sink of anthropogenic CO_2 emissions (Battin *et al.*, 2009; Tranvik *et al.*, 2009).

One especially important area where assessment of carbon cycling is required is the boreal region covering a large part of the northern hemisphere. Forests in this area hold large stocks of carbon as biomass and soil organic carbon (SOC; Table 1; Lal, 2005; Pregitzer & Euskirchen, 2004; Dixon *et al.*, 1994) and are thought to be a large sink of atmospheric CO_2 (Pan *et al.*, 2011), although the strength of this sink is debated (Stephens *et al.*, 2007). Wetlands in this area, and nearby sub-arctic and arctic regions, hold even more carbon in peat soils (Table 1; Tarnocai *et al.*, 2009; Gorham, 1991). Gorham (1991) estimated a total carbon pool of 455 petagrams (Pg) in boreal and sub-arctic peat. A recent estimate of soil organic carbon content in northern hemisphere permafrost soils totaled 1672 Pg, almost 50 % of the entire estimated global soil carbon pool (Tarnocai *et al.*, 2009). Because these carbon reservoirs are larger or about equal to the current atmospheric carbon content, there is widespread concern about the fate of this carbon under changing climatic conditions. Ballantyne *et al.* (2012) claim that, at present, there are no signs of global carbon sinks weakening, but this is questioned, especially regarding northern areas (Hayes *et al.*, 2011). At the same time, there are observations of increasing concentrations of dissolved organic carbon in fresh-waters across central and northern Europe as well as parts of North America. Some scientists have suggested that this is evidence of climate induced destabilization of SOC stocks (Bellamy *et al.*, 2005).

Altogether, this illustrates the urgent need for research on the dynamics and fate of carbon in these systems. This thesis presents new research on the dynamics of organic carbon in boreal streams and rivers. The results have implications for the understanding and interpretation of stream carbon cycling and its effects on aquatic ecosystems.

1.1 The Carbon Cycle

Carbon is found in varying amounts in all major compartments on Earth (Table 1). Most of the carbon is contained in bedrock and sediments, but the fluxes from these reservoirs are small compared to fluxes between the atmosphere, biosphere, soils, freshwaters, and ocean (Battin *et al.*, 2009; Falkowski *et al.*, 2000; Siegenthaler & Sarmiento, 1993; Sundquist, 1993). On geologic timescales, global atmospheric carbon content is controlled by the interplay between volcanic CO_2 outgassing, contact metamorphism, tectonic uplift, erosion, and silicate weathering (Schaller *et al.*, 2011; Berner & Kothavala, 2001; Berner, 1999; Raymo & Ruddiman, 1992). Inorganic carbon transformations thus dominate long-term carbon dynamics. However, most

Table 1. *Estimates from the literature on carbon pools, fluxes with the atmosphere, and source/sink numbers in some of the different compartments on Earth. Negative values in sink/source column represent carbon sink and positive values represent carbon source. 1 Pg =* 10^{15} *g.*

Compartment	Pool (Pg C)	Flux (Pg C $year^{-1}$)	Sink/source (Pg C $year^{-1}$)
Atmosphere	720-750[1,2]		-4.1 ± 0.1[9]
Aquatic environment	1-2[2]	1.2[8]	
Permafrost soils	1 672[3]		
Boreal & sub-arctic wetlands	455[4]		
Wetlands	743[5]		
Boreal forest	395-559[5,6]		-0.50 ± 0.08[9]
Temperate forest	159-292[5,6]		-0.78 ± 0.09[9]
Tropical forest	428-553[5,6]		-1.02 ± 0.47[9]
Terrestrial veg. & soils	2 000-2 160[1,2,7]	60-120[1,7,8]	
Marine biota	3[1]		
Ocean surface	670-1 020[1,2,7]	70-92[1,7,8]	-2.3 ± 0.4[9]
Deep ocean	36 400-38 100[1,2,7]		
Ocean, organic C	700-1 000[1,2]		
Marine sediments	3 000[7]		
Fossil fuels	4 000-4 130[2,7]		7.6 ± 0.4[9]
Sedimentary carbonates	>60 000 000[2]		
Kerogens	15 000 000[2]		
Earth's crust	90 000 000[7]	0.2[7,8]	

1. Siegenthaler & Sarmiento, 1993.
2. Falkowski *et al.*, 2000. Numbers for ocean surface and deep ocean relate to inorganic carbon.
3. Tarnocai *et al.*, 2009.
4. Gorham, 1991.
5. Lal, 2005.
6. Dixon *et al.*, 1994.
7. Sundquist, 1993.
8. Battin *et al.*, 2009.
9. Pan *et al.*, 2011. Estimates are for the years 2000-2007.

present-day carbon cycles through the biosphere where inorganic carbon is transformed to organic carbon (Reich, 2010). Some of this organic carbon is further re-mineralized back to inorganic carbon, but considerable amounts of organic material are stored in long-term deposits such as soil organic matter (SOM) in mineral soils, peat, and as lake and ocean sediments (Schlesinger, 1997). Consequently, contemporary carbon cycling is dominated by biological transformations.

The most fundamental chemical process for biogeochemical cycling on Earth is without doubt photosynthesis. Organisms are commonly separated into autotrophic and heterotrophic; the former have the capability of synthesizing chemical energy, either from sunlight (photoautotrophic organisms) or from reduced chemical compounds (chemoautotrophic organisms), while the latter need external organic compounds as an energy source. Autotrophs are therefore the basis of almost all biological food webs on Earth and photosynthesis the most important process for the diversity of life.

Photosynthesis is the process where CO_2 and water is combined into chemical energy (glucose) and oxygen through the use of light as energy source (*hv*). It is commonly summarized in the simplified formula (Campbell *et al.*, 2008):

$$6CO_2 + 6H_2O + hv \rightarrow C_6H_{12}O_6 + 6O_2$$

where *hv* is light energy. However, not all carbon captured through photosynthesis is used for production of biomass. Respiration, i.e. the reverse of photosynthesis where organic matter is converted back to CO_2, water and energy, while simultaneously consuming oxygen, through the metabolism of organisms is an equally fundamental process for carbon cycling:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Energy$$

Many, if not most, organisms on Earth today use oxygen as the oxidation agent in respiration but there are other respiration pathways where e.g. nitrate or sulphate is used as electron acceptor.

On an organismal level, the difference between photosynthesis and respiration is called net primary production (NPP; Chapin *et al.*, 2006; Schlesinger, 1997) and is an approximate measure of biomass growth. However, some biomass is lost to heterotrophic organisms (heterotrophic respiration) or through death or loss of tissue (litter fall in terrestrial systems). The difference between ecosystem gross primary production, GPP, and total ecosystems respiration (ER) is called net ecosystem production (NEP). In terrestrial systems it is often assumed that NEP indicates if the system is a source or a sink of carbon. As recognized by Chapin *et al.* (2006) there are, however, other pathways of carbon input and output. These pathways can be substantial, e.g. in aquatic systems, which commonly are subsidized by considerable amounts of carbon from the terrestrial environment.

A substantial part of NPP is delivered to the soil as dead organic matter (detritus; Schlesinger, 1977). Some of this detritus is decomposed by heterotrophic organisms into CO_2 that leaves the ecosystem either vertically in the gaseous phase or laterally dissolved in groundwater. However, a considerable part of the detritus is retained in the soil as soil organic matter

(SOM). The amount of organic matter stored in the soil is dependent on e.g. redox conditions, nutrient availability, temperature, availability of adsorbing mineral phases, and substrate availability (Schmidt *et al.*, 2011; Limpens *et al.*, 2008; Marschner *et al.*, 2008; Kaiser & Guggenberger, 2000). However, some of the organic matter found in soils is solubilized through successive oxidation (Kleber & Johnson, 2010), which allows export of SOM to the groundwater and nearby aquatic environments (Aitkenhead-Peterson *et al.*, 2003; Kalbitz *et al.*, 2000).

The focus of this thesis is on temporal dynamics of natural organic matter (NOM) concentrations in boreal streams and rivers, and on possible drivers of this NOM variability. Here I will use the term NOM to represent all dead organic matter derived from non-anthropogenic sources both in soil and water. There is a huge array of man-made organic compounds such as plastics, pesticides and pharmaceuticals, but these are excluded in this definition (though it needs to be acknowledged that the most common analytical techniques currently used to estimate NOM do not differentiate between man-made and natural substances). There is sometimes a need to distinguish between different fractions of NOM and I will then use terms like dissolved organic matter (DOM) and particulate organic matter (POM) to indicate the different fractions.

1.2 Composition and Structure of NOM

Natural organic matter includes well-defined organic substances, e.g. carbohydrates, amino acids, carboxylic acids and proteins, but the majority of the organic molecules in NOM have been uncharacterized and often called humic substances or humus. These compounds have been considered to be large heterogeneous macromolecules (Schulten & Schnitzer, 1993) that are recalcitrant, i.e. highly resistant, or even inert, to microbial degradation (Kleber & Johnson, 2010; Drever, 2002; Tipping, 2002). The classical classification of NOM has been operational and humic substances have commonly been separated into three different types: fulvic acids, which are soluble in water at any pH; humic acids, which are insoluble at pH ≤ 2 but soluble at higher pH; and humin which is insoluble in water at any pH (Drever, 2002; Tipping, 2002). Inferences based on this operational model of humic substances have indicated that NOM mainly consists of macromolecular polymers, i.e. covalently bonded carbon skeletons with associated functional groups, with masses up to at least 10 kDa (Drever, 2002; Schulten & Schnitzer, 1993; Thurman *et al.*, 1982).

New analytical techniques, such as Fourier Transform-Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) and multidimensional Nuclear Magnetic Resonance spectroscopy (NMR), have revealed new insights into the structure and properties of NOM (Lam *et al.*, 2007; Mopper *et al.*, 2007). Based on these results there is an emerging paradigm shift in the view of NOM (Sutton & Sposito, 2005). Instead of being covalently bonded macromolecules, the different organic compounds constituting NOM seem to be small, in general less than 1000 Da (Sleighter *et al.*, 2009; Tremblay *et al.*, 2007), organic molecules forming supra-molecular associations via hydrogen bonds or hydrophobic interactions (Kleber & Johnson, 2010; Sutton & Sposito, 2005; Kerner *et al.*, 2003; Piccolo, 2002; Piccolo, 2001). Some authors have even argued that humic substances are artefacts formed via the different extraction methods employed in the classical separation into humin, fulvic and humic acids (Kleber & Johnson, 2010). This may further be corroborated by recent findings where 2D NMR was used to conclude that most of the soluble organic matter from Ah horizons under a Aspen forest soil and a grassland soil consists of different identifiable biomolecules, e.g. lignin, carbohydrates and proteins (Kelleher & Simpson, 2006). Kelleher and Simpson (2006) acknowledge that polymeric humic macromolecules may exist, but then only in trace amounts (< 1 %) not detected in their NMR analyses.

Natural organic matter is mainly carbon (mass basis), but it also contains significant amounts of oxygen, hydrogen, nitrogen, sulphur and phosphorous (Drever, 2002; Schulten & Schnitzer, 1993). In addition, there may be trace amounts of other elements, e.g. chloride, iron and mercury, either within the structure or associated with functional groups in NOM, e.g. through adsorption. Due to the predominance of carbon, NOM is often approximated with the amount of organic carbon in soil or water. In water, organic carbon is usually divided into dissolved (DOC), particulate (POC) and total organic carbon (TOC). This is an operational definition and DOC is usually defined as the fraction passing a filter with a pore size between 0.2 and 0.7 µm. The fraction that is contained on the filter is considered to be particulate and TOC is the sum of dissolved and particulate fractions. However, it is important to recognize that the fraction passing the filter is not necessarily truly dissolved, but can be colloidal (Gustafsson & Gschwend, 1997). Colloidal phases may have large effects on e.g. the cycling of metals and organic pollutants (Schwarzenbach *et al.*, 2003). Furthermore, there is evidence of both biotic and abiotic formation of colloids and particles from dissolved organic carbon phases (Kerner *et al.*, 2003), probably due to the structure and composition of NOM. Pranzas *et al.* (2003) estimated the molecular sizes of organic compounds in natural waters and their results showed that NOM molecules generally are in the order of a few nanometres across. This is considerably smaller than the pore sizes of commonly used filters to separate dissolved organic matter from particulate fractions.

1.3 Ecological, Societal and Biogeochemical Significance of NOM

Natural organic matter has profound effects on aquatic biogeochemistry and ecosystem functioning. The complex structure and composition of NOM bring several fundamental functions. Due to the ubiquitous presence of carboxylic groups (Lam *et al.*, 2007; Hertkorn *et al.*, 2006), NOM displays acid-base properties and acts as a pH buffer (Tipping, 2002; Hruska *et al.*, 2001; Köhler *et al.*, 2000; Driscoll *et al.*, 1994; Hemond, 1990; Driscoll *et al.*, 1989; Eshleman & Hemond, 1985; Oliver *et al.*, 1983). Research indicates that organic acids in NOM have buffered anthropogenic acid deposition in central and northern Europe and parts of North America (Erlandsson *et al.*, 2011; Evans *et al.*, 2008; Krug & Frink, 1983) and that recent increases in stream and lake NOM may simply be a result of these systems returning to "natural" conditions (Winterdahl *et al.*, 2012; Monteith *et al.*, 2007; Evans *et al.*, 2006). In addition, NOM affects toxicity, bioavailability and transport of metals (Ravichandran, 2004; Tipping, 2002) and organic pollutants (Smith *et al.*, 2011; Niederer *et al.*, 2007; Yang *et al.*, 2006; Schwarzenbach *et al.*, 2003) as well as pharmaceuticals (Gu *et al.*, 2007). This is partly a result of the ubiquitous presence of various functional groups in NOM, making it a potent adsorbent. The inherent acidity and adsorption potential of NOM is also thought to affect weathering rates in vegetated environments (Oliva *et al.*, 1999; Lundström, 1994).

There is increasing awareness of the role of NOM in other biogeochemical cycles. A recent report hypothesizes that access to highly bioavailable NOM drives denitrification across diverse ecosystems, from soils to the ocean (Taylor & Townsend, 2010). This has been corroborated in later studies where the coupling between NOM quality and denitrification rates was investigated in a mountainous stream in Colorado, USA (Barnes *et al.*, 2012). Some scientists have also suggested that observed decreasing trends in stream nitrate concentrations are caused by increases in dissolved organic matter (Goodale *et al.*, 2005). Furthermore, it is known that NOM has important effects on e.g. sulphur (Strickland & Fitzgerald, 1984) and chloride cycling (Bastviken *et al.*, 2009; Bastviken *et al.*, 2007). Organic material is also thought to have indirect effects on the hydrological cycle and climate in the form of aerosols. There is e.g. increasing appreciation of the importance of organic substances for cloud formation as cloud condensing nuclei (Quinn & Bates, 2011; Pöschl *et al.*, 2010). Formation of organic aerosols takes place both at the ocean-atmosphere interface through bubble bursting and above forests through oxidation of gaseous biogenic precursors (Pöschl *et al.*, 2010; Russell *et al.*, 2010; Altieri *et al.*, 2006).

Many researchers have considered aquatic NOM to be recalcitrant, i.e. highly resistant to decomposition. Still, there is wide-spread evidence of the ecological importance of both autochthonous (formed within the aquatic environment) and allochthonous (imported from the terrestrial environment) NOM in food-web dynamics (Jansson *et al.*, 2007; Pace *et al.*, 2004; Tranvik, 1992; Wetzel, 1992). Especially in oligotrophic lakes, allochthonous NOM is the primary energy source for heterotrophic bacteria and thereby constitute the basis of lake food-webs (Carpenter *et al.*, 2005). The coloured fractions of NOM also influence light attenuation in water. The attenuation is substantial in unproductive systems with high NOM content and has been shown to limit lake productivity (Karlsson *et al.*, 2009).

The positive effect of NOM on soil fertility has been understood for centuries. Aquatic NOM has, however, been associated with detrimental effects, e.g. on drinking water production. NOM can affect both colour and smell of water leading to aesthetic problems in drinking water. Large costs in drinking water production are associated with the removal of NOM (Matilainen *et al.*, 2010). It is also known that NOM can form carcinogenic by-products e.g. during chlorination of drinking water (Krasner *et al.*, 2006).

1.4 Production, Degradation and Transport of NOM

Almost all NOM is biogenic, i.e. derived from biological activity. It may vary in age, from millions of years old organic material in sedimentary deposits, e.g. bituminous coal, to recently fixed carbon, such as root exudates. Still, there are large knowledge gaps in the mechanistic understanding of production and degradation of aquatic NOM, and the relative importance of different processes is not fully understood.

In many aquatic systems, especially in northern latitudes, most NOM is allochthonous, i.e. it originates in the terrestrial environment and is then transported to the aquatic environment via hydrological processes (Carpenter *et al.*, 2005; Pace *et al.*, 2004; Aitkenhead-Peterson *et al.*, 2003). Autochthonous sources, i.e. NOM formed within the aquatic environment, can however be significant, particularly in eutrophic systems (Bertilsson & Jones, 2003). However, our knowledge about the primary terrestrial source areas and dominating processes contributing NOM to aquatic systems is incomplete.

There is evidence that NOM in soils consists of material derived from both higher plants and microorganisms, though estimates of the relative contributions differ (Simpson *et al.*, 2007; Kögel-Knabner, 2002). The formation of DOM, which is the primary fraction delivered to the boreal aquatic environment is however uncertain. One potential pathway can be as a byproduct of the degradation of NOM by microorganisms in soils. Both saprotrophic (Osono, 2007) and mycorrhizal fungi (Talbot *et al.*, 2008) have been shown to degrade organic matter in soils through extra-cellular enzymes, e.g. peroxidases and phenol oxidases (Sinsabaugh, 2010; Sinsabaugh, 1994).

There is a traditional view that certain fractions of NOM are highly resistant to microbial degradation. It has been thought that this inherent resistance, or recalcitrance, is due to molecular structure. For example lignin, one of the structural components in woody tissue (Kögel-Knabner, 2002), has been thought to be recalcitrant. However, research on forest litter indicates that decomposition of resistant NOM may be enhanced by availability of more easily accessible organic matter (Klotzbücher *et al.*, 2011). This is also consistent with results from research on enzyme activities in relation to lignin degradation, where peroxidase activities are facilitated by simultaneous activity of saccharide-oxidizing enzymes like glucose oxidase, which reduce oxygen to hydrogen peroxide (Sinsabaugh, 2010). Some researchers even challenge the notion of recalcitrance and claim that most NOM is bioavailable (Schmidt *et al.*, 2011; Kleber & Johnson, 2010; Marschner *et al.*, 2008), which seem to be corroborated by recent reports on NOM structure and composition (Lam *et al.*, 2007; Kelleher & Simpson, 2006). The stated resistance of NOM may simply be due to soil structural causes, e.g. adsorption to mineral particles, making the organic matter inaccessible to microbial attack (Marschner *et al.*, 2008; Kleber *et al.*, 2007; Sutton & Sposito, 2005), and not a result of inherent recalcitrance.

At the same time, there is substantial evidence that trees together with associated ectomycorrhizal fungi produce considerable amounts of DOM in forest soils. Högberg & Högberg (2002) found that almost half of all DOC in a Scots pine soil was produced by ectomycorrhizal fungi and associated roots. This was corroborated in a later study (Giesler *et al.*, 2007) where a tree-girdling experiment resulted in a fast 40 % reduction in DOC in the humus layer of a forest soil, indicating that photosynthesis drives much of below-ground DOM production, e.g. through production of root exudates. Moreover, Giesler *et al.* (2007) found that many of the low-molecular weight organic acids involved in the citric acid cycle decreased substantially. It is further hypothesized that recent tree photosynthate drives soil respiration (Högberg *et al.*, 2001). This would suggest a coupling between respiration and DOM production. However, studies on CO_2-DOM relationships in soils are equivocal (Klotzbücher *et al.*, 2011; Neff & Hooper, 2002).

The carbon cycling in upslope areas within a catchment may, however, not be relevant for carbon cycling in streams and rivers. Several studies in boreal and temperate areas have indicated that there may be partial de-coupling between aquatic NOM dynamics and organic matter production in upslope areas, which usually dominate catchment areal coverage (Bishop *et al.*, 2004; Hinton *et al.*, 1998; Bishop *et al.*, 1994; Dosskey & Bertsch, 1994; Fiebig *et al.*, 1990). While NOM production in organic soil layers in upslope soils can be substantial (Fröberg *et al.*, 2006), much of this is mineralized or effectively immobilized through adsorption to iron and aluminum oxides in the mineral soil (Jardine *et al.*, 1989; McDowell & Wood, 1984). There is also successive degradation of NOM along groundwater flow pathways from upslope areas to aquatic environments (Klaminder *et al.*, 2011). NOM in forested catchments rather seems to originate in hydromorphic organic soils in the riparian zone (Bishop *et al.*, 2004; Bishop *et al.*, 1994; Dosskey & Bertsch, 1994; Fiebig *et al.*, 1990).

Organic soils, especially in wetlands, seem to be particularly important for NOM cycling in running waters. There is wide-spread evidence that wetlands have considerable impacts on NOM concentrations and export in streams and rivers (Creed *et al.*, 2008; Laudon *et al.*, 2004; Mulholland, 2003). Vonk *et al.* (2008) studied lipid biomarkers in surface sediments from the Bothnian Bay and found evidence of *Sphagnum* moss species as primary sources of sediment organic matter. Similar results were found in a later study on surface sediments and POC along a transect from the Kalix River into the Bothnian Bay (Vonk *et al.*, 2010).

Little work has been done to quantify the delivery of NOM through atmospheric deposition. However, there are indications that this source can have substantial influence on catchment carbon cycling, at least in alpine areas (Mladenov *et al.*, 2012).

In areas dominated by deciduous forest, autumn leaf fall can have considerable effects on stream NOM cycling (Mulholland & Hill, 1997). Meyer *et al.* (1998) estimated that about 30 % of stream DOC export in a temperate stream was due to instream production from leaf litter. In-stream production in boreal streams is generally thought to be small.

Several studies have found wide-spread supersaturation of CO_2 in freshwater systems (Wallin *et al.*, 2012; Butman & Raymond, 2011; Humborg *et al.*, 2010; Koprivnjak *et al.*, 2010; Kosten *et al.*, 2010; Duarte & Prairie, 2005; Richey *et al.*, 2002). There is also evidence of considerable degassing of CO_2 from boreal headwaters (Wallin *et al.*, 2012; Koprivnjak *et al.*, 2010), which constitute the majority of all flowing waters (Benstead & Leigh, 2012; Bishop *et al.*, 2008). One common interpretation is that this is due to mineralization of organic carbon by microorganisms (Battin *et al.*, 2008; Jonsson *et al.*, 2003), specifically bacteria (Robarts & Carr, 2009). Nevertheless, studies on microbial breakdown of aquatic NOM in boreal and temperate areas indicate that only a few percent is degraded at timescales comparable to stream residence times (Ågren *et al.*, 2008a; Wiegner *et al.*, 2006; Köhler *et al.*, 2002). There are however differences in bioavailability of NOM from different sources. NOM originating from forests seem to be more bioavailable than NOM from wetlands (Ågren *et al.*, 2008a; Berggren *et al.*, 2007). This would also explain the observed predominance of wetland derived NOM in shallow sediments in coastal areas (Vonk *et al.*, 2008).

Photochemical transformations can mineralize NOM, but also enhance its bioavailability (Bertilsson & Tranvik, 2000; Bertilsson *et al.*, 1999). However, the net effect of irradiation on NOM bioavailability seems to depend on NOM source (Tranvik & Bertilsson, 2001). In addition, photooxidation has been shown to be considerably larger than microbial degradation in a boreal catchment (Köhler *et al.*, 2002).

The bioavailability of different organic compounds differs considerably. Wiegner *et al.* (2006) found that dissolved organic nitrogen, i.e. nitrogen rich organic compounds, were preferentially taken up by microorganisms in nine rivers along the east coast of United States. Seitzinger *et al.* (2005) used high-resolution electrospray-ionization mass spectrometry to characterize NOM from two streams in eastern United States on a molecular level, and 12-day incubations to investigate microbial NOM degradation. They found that a majority of compounds did not change in abundance during the incubation. Still, a substantial part of all molecules decreased in abundance due to microbial degradation, and results were consistent between the two streams. This indicates that molecular composition ultimately controls relative bioavailability of NOM.

2 Objectives

The overall main objective of this thesis was to further our understanding of the processes controlling short-term temporal variability of NOM concentrations, approximated with DOC, in boreal streams and rivers. Moreover, the aim was also to further develop and analyse the Riparian flow-concentration Integration Model (RIM), which is a mathematical model of stream water chemistry dynamics. The paper specific objectives were to:

I investigate processes, besides water discharge, that control the dynamics of DOC in a boreal stream and conceptualize this by modifying RIM

II resolve and compare controlling processes responsible for DOC dynamics in the four Integrated Monitoring sites

III investigate and quantify the sensitivity of DOC to changes in water discharge and temperature by using RIM

IV quantify and characterize intra-annual DOC dynamics on a national scale, relate it to recent DOC trends, and seek underlying causes of this within-year variability

3 Methods and Material

3.1 Study Area and Data

Long-term data sets are invaluable information in environmental research, although sometimes accused of being inefficient and too costly (Lovett *et al.*, 2007). This work had not been possible without access to several long-term data series on stream water chemistry, stream flow and weather related variables. The work presented in this thesis has focused on boreal streams (papers I, II, III and IV) and rivers (paper IV) all across Sweden (Figure 1). In papers I and III data on chemical variables, discharge and climatic variables from sites within the well-studied Krycklan Catchment Study were used (Laudon *et al.*, 2011). Data from the Integrated Monitoring (IM) sites were used in papers II, III, and IV (Löfgren *et al.*, 2011). The data used in paper IV were from the regular monthly sampling within the Swedish Environmental Monitoring Program. Stream water chemistry in the IM and SEMP data sets was analysed at the same laboratory (at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences), which is accredited by the Swedish Board for Accreditation and Conformity (SWEDAC) using national and international standardised methods. The Swedish Meteorological and Hydrological Institute (SMHI) provided data on water flow for paper IV.

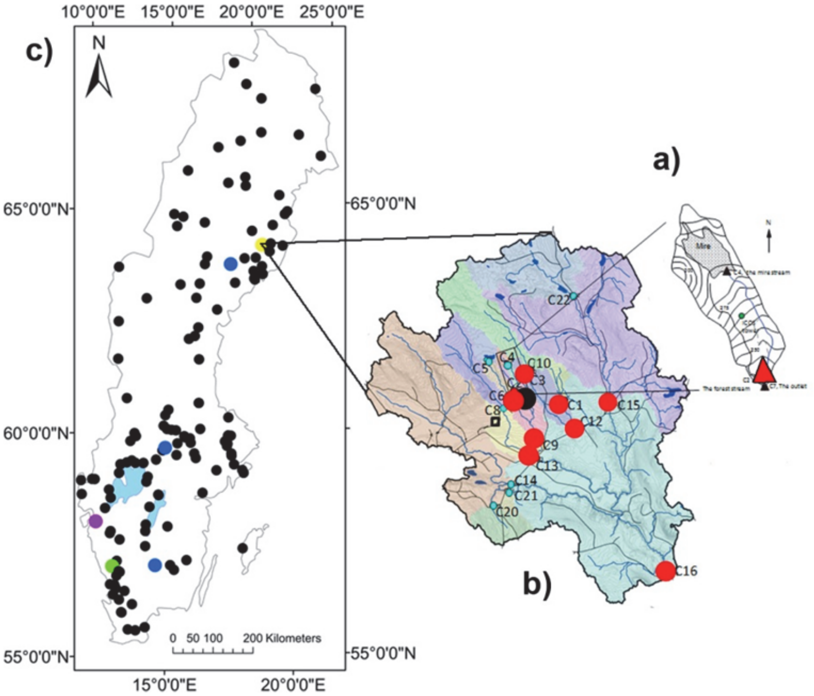

Figure 1. Location of study sites. Red triangle in a) is Västrabäcken (papers I and III), red circles in b) are Krycklan sites in paper III, blue circles in c) are Aneboda, Kindla and Gammtratten (papers II, III and IV), green circle in c) is Berg (Pipbäcken Nedre; papers III and IV), and purple circle in c) is Gårdsjön (paper II). Black circles are study sites in paper IV.

3.2 The Riparian Flow-Concentration Integration Model

Mathematical models are common tools in biogeochemical research. The benefits with using models include e.g. the ability to experiment or test the response of a variable of interest to changes in forcing factors on temporal or spatial scales that preclude physical experiments, or to formulate scientific understanding into a consistent form (Beven, 2009; Wainwright & Mulligan, 2004). Maybe the largest advantage with models, however, is the ability to use them as hypotheses that can be tested with data (Buytaert & Beven, 2011; Beven, 2010; Beven, 2001a).

Mathematical models are commonly classified into empirical, conceptual or physically based models based on how system functioning is formalized in the model structure (Wainwright & Mulligan, 2004). Empirical models relate model input to output without explicit consideration to mechanistic principles. Physically based models on the other hand are derived from established physical principles. Conceptual models fall in between empirical and physically based models and commonly include elements of both of these endmembers. In reality it is, however, difficult to distinguish models based on these ideal concepts. What counts as a physically based model at one scale or in one discipline may be regarded as an empirical model at another scale or in another discipline (Brutsaert, 2005).

Several different models of catchment NOM dynamics exist in the scientific literature (Xu *et al.*, 2012; Jutras *et al.*, 2011; Yurova *et al.*, 2008; Futter *et al.*, 2007; Michalzik *et al.*, 2003; Neff & Asner, 2001; Boyer *et al.*, 1996; Grieve, 1991). They differ in structure, purpose, and applicable spatial and temporal scales. In paper I, II and III the Riparian flow-concentration Integration Model (RIM) was used as a hypothesis of system functioning regarding mobilization and transport of NOM. RIM is a conceptualized interpretation of the combined effects of water flow pathways across the riparian soil and solute concentrations along those flow pathways (Figure 2; Seibert *et al.*, 2009; Bishop *et al.*, 2004). This is formalized as the depth integrated combination of a function describing the flow at different levels in the soil ($q_i(z)$) with a function describing the solute concentration variability with depth in the soil ($C_i(z)$):

$$E_i = C_{stream,i}Q_i = \int_{z_0}^{z_{1,i}} C_i(z)\frac{dQ_i(z)}{dz}dz = \int_{z_0}^{z_{1,i}} C_i(z)q_i(z)dz \qquad (1)$$

where E_i is the total stream export of NOM, $C_{stream,i}$ is stream NOM concentration, Q_i is stream flow, $z_{1,i}$ is the ground water table at time i, and z_0 is

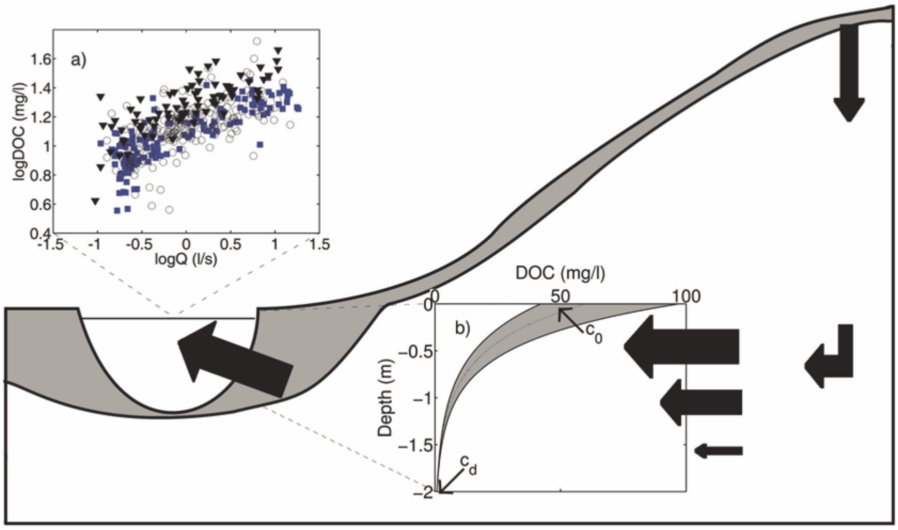

Figure 2. a) Schematic of the Riparian flow-concentration Integration Model (RIM) where the dynamics in stream NOM concentration is the result of a combination of b) the soil solution concentration profile in the riparian soil c) and lateral flow across that profile at different depths in the soil. Black block arrows represent water flow and are sized relative to the volume of flow.

the lower integration limit, which is the deepest soil layer contributing stream flow. Several studies have found strong relationships between stream discharge and groundwater table depth in the near-stream zone (Seibert *et al.*, 2003; Fölster, 2001; Nyberg, 1995; Rodhe, 1989). Saturated hydraulic conductivity increases exponentially towards the ground surface in these systems, resulting in large variations in flow with changes in groundwater table position. This mechanism has been conceptualized in the transmissivity feedback hypothesis for runoff generation in these systems (Bishop, 1991), which commonly are dominated by till soils. This relationship, $Q_i(z)$, is generally exponential or a power-law and can be derived from Darcy's law (Grabs *et al.*, 2012). It is easily incorporated into the structure of RIM and if the soil solution NOM profile also can be modelled with a power-law or exponential function, simple analytical solutions to Equation 1 can be produced (Winterdahl *et al.*, 2011; Seibert *et al.*, 2009). Seibert *et al.* (2009), who used exponential functions, arrived at:

$$\mathrm{C}_{stream} = \frac{c_0}{\left({}^{a}/_{b}\right)^{\frac{f}{b}}\left(\frac{f}{b}+1\right)} Q^{\frac{f}{b}}$$

This is basically a rating curve, which has long been used to estimate load and concentration of different solutes in running waters (Godsey *et al.*, 2009; Cooper & Watts, 2002; Walling, 1977). The slope of this relationship, i.e. *f/b*, reveals information about the sensitivity of solute mobilization to flow. A negative slope of unity indicates dilution, whereas a slope close to zero indicates chemostatic behaviour, i.e. concentrations do not change with flow (Godsey *et al.*, 2009). RIM could be interpreted as a vertical array of chemostats.

Every model is an abstraction of the real system under study (Wainwright & Mulligan, 2004). It is therefore necessary to make some simplifying assumptions about the system. These assumptions will be a fundamental part of the model chosen to accomplish the purpose(s) of the model, and are among other things dependent of the scale of observation. It could e.g. be a valid assumption to regard the Earth as a perfect sphere, or even a particle, in astronomical studies but doing the same thing in geographic information science will cause serious errors. When analysing any shortcomings of a model it is therefore useful, as one of the primary steps, to go back to the fundamental assumptions of the model in question and analyse their validity. The assumptions underlying RIM include (Seibert *et al.*, 2009):

1. both the flow-groundwater table relationship and the soil solution concentration profile are constant in time

2. lumped catchment behaviour, i.e. no spatial variability
3. groundwater flow is kinematic (Beven, 2001b)
4. lateral flow only occurs in the saturated zone below the groundwater table
5. all flow crosses the riparian zone before entering the stream
6. water traversing the soil instantaneously receives the chemical signature of the soil solution profile

This thesis has focused on investigating assumption 1 (papers I and II). Seibert *et al.* (2009) recognized that the soil solution concentration profile is not static during the year. In addition, field studies have shown that stream NOM-flow relationships can vary over the year (Dawson *et al.*, 2011; Dawson *et al.*, 2008; Ågren *et al.*, 2008b).

RIM, as used in this work, is a lumped, conceptual model, i.e. it does not account for spatial variability in soil solution gradients or groundwater table positions (assumption 2). However, promising developments of RIM integrate topographic landscape information into the model (TRIM), allowing spatial variability in e.g. simulated groundwater table position (Grabs *et al.*, 2012).

3.3 Model Conditioning and Uncertainty Analysis

Some model parameters in RIM can in theory be estimated from observed data (Seibert *et al.*, 2009). However, environmental models generally require parameters that are valid at the spatial and temporal scales imposed by the studied issue (Brutsaert, 2005). These effective parameters are difficult or impossible to measure in some cases (Beven, 2009). Modellers are therefore often forced to estimate model parameters from observed behaviour of the variable under study, the so called inverse modelling problem (Tarantola, 2006). This process, commonly referred to as calibration or model conditioning, may, however, bring considerable parameter uncertainty (Duan *et al.*, 2003). In addition, there are uncertainties in model structure, observed data, and boundary conditions, which may combine in non-linear ways (Beven, 2009; Beven, 2006). Together this shows the necessity for methods of estimating the total uncertainty involved in the modelling process.

In papers I, II and III the Generalized Likelihood Uncertainty Estimation (GLUE) was used to estimate RIM parameters and modelling uncertainty (Beven, 2009; Beven, 2006; Beven & Freer, 2001; Beven & Binley, 1992). GLUE uses Monte-Carlo simulations to randomly sample parameter values within pre-defined limits. The number of parameter sets generally needs to be large, here 100 000 or more, to cover the parameter space well. Parameter sets are then classified as behavioural or non-behavioural based on informal likelihood measures, e.g. the Nash-Sutcliffe efficiency index, which is a common measure of model performance in hydrology. Non-behavioural models are rejected as working hypotheses for the studied system. Recent work proposes limits of acceptability, which were used in paper II, as a less subjective basis for model rejection compared to informal likelihood measures (Blazkova & Beven, 2009; Beven, 2006).

4 Results and Discussion

4.1 Short-Term Temporal Variability of NOM in a Boreal Headwater Stream (Paper I)

Stream discharge has been shown to be strongly related to NOM dynamics and is the first-order driver of NOM variability in many systems (Raymond & Saiers, 2010; Dawson *et al.*, 2008; Eimers *et al.*, 2008; Finlay *et al.*, 2006; Mulholland, 2003; Hope *et al.*, 1994; Grieve, 1984). It is also known that this relationship varies through the year (Seibert *et al.*, 2009; Dawson *et al.*, 2008; Ågren *et al.*, 2008b; Grieve, 1984). The aim of this study was to investigate the relationship between DOC and possible second-order drivers of DOC variability in Västrabäcken, a forested boreal headwater catchment in northern Sweden. The investigated variables included air and soil temperature, soil moisture, precipitation, antecedent flow, and concentrations of stream sulphate.

We conditioned the original static version of RIM (Seibert *et al.*, 2009) to stream DOC concentrations and then correlated RIM residuals to the potential variables. We found that soil temperature and antecedent flow accumulated over the preceding 159-168 days displayed the strongest correlations to model residuals. However, antecedent flow and soil temperature covaried considerably, indicating that the antecedent flow effect could be an artefact caused by a seasonal flow signal coinciding with soil temperature.

RIM was modified to account for changes in soil temperature or antecedent flow by linearly varying the modelled shape of the DOC-depth relationship in the riparian soil. We tested five different implementations. The model where only soil temperature was included had the highest performance when simulating stream DOC concentrations. Simulated DOC concentrations in the riparian soil solution also corresponded well with observations from the riparian soil.

Discharge and temperature were the first and second-order drivers of DOC dynamics in Västrabäcken. A modified version of RIM, where the shape of the soil solution DOC concentration profile varied seasonally, was able to simulate stream DOC considerably better than the static version of RIM (Figure 3).

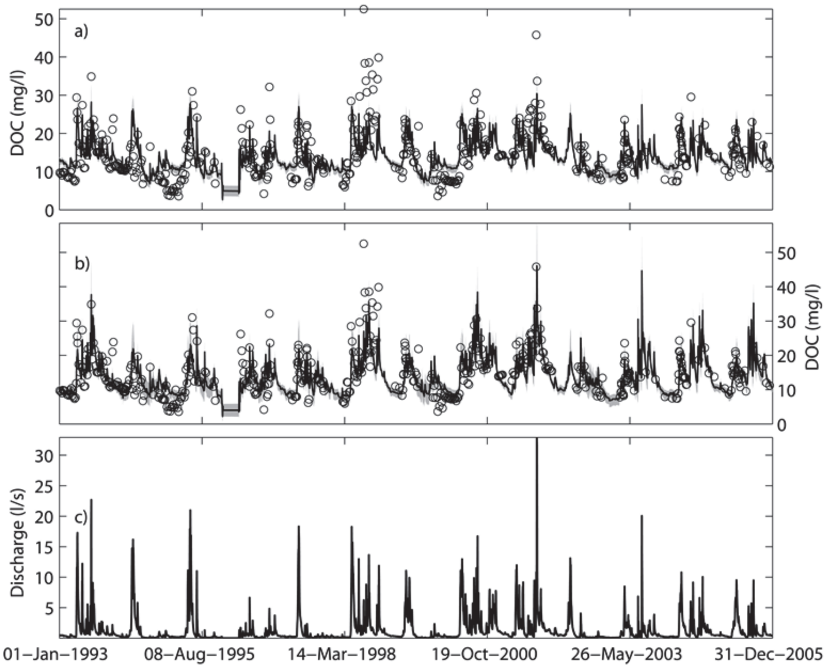

Figure 3. Time series plot of observed and simulated DOC concentrations in Västrabäcken using a) the original RIM and b) the modified dynamic RIM. c) Time series plot of observed discharge in Västrabäcken.

4.2 Different Drivers of Short-Term Temporal NOM Dynamics at the Integrated Monitoring Sites (Paper II)

The response of NOM to changes in discharge varies among catchments with different landscape structure (Laudon *et al.*, 2011; Mulholland, 2003). Forested catchments often display positive relationships between NOM concentrations and discharge (Dawson *et al.*, 2008; Hinton *et al.*, 1998) whereas the relationship commonly is negative in streams in wetland dominated catchments (Eimers *et al.*, 2008; Clark *et al.*, 2007; Schiff *et al.*, 1998). In addition, there are other variables affecting NOM dynamics, e.g. soil temperature (Clark *et al.*, 2009; Fröberg *et al.*, 2006; Clark *et al.*, 2005), soil moisture (Christ & David, 1996), and atmospheric deposition (Moldan *et al.*, 2012; Monteith *et al.*, 2007). The objective of this study was to investigate probable causes of intra-annual

NOM variability in the four IM sites Gårdsjön, Aneboda, Kindla and Gammtratten.

As in paper I, we used an analysis of RIM residuals. We explored possible drivers of DOC variability through a partial least squares (PLS) analysis with model residuals as response variables and concentrations of major cations and anions, pH, air and soil temperature, precipitation, and instantaneous change in discharge as explanatory variables.

Flow was the primary driver of DOC variability in Gammtratten and Gårdsjön. Conversely, flow was weakly related to DOC in Aneboda and Kindla, which displayed strongly seasonal DOC variability. Soil temperature and sulphate concentration were significant predictors of RIM residuals in all catchments (Figure 4). Sea-salt deposition had a particularly large influence on DOC dynamics in the Gårdsjön catchment, which is close to the Swedish west-coast.

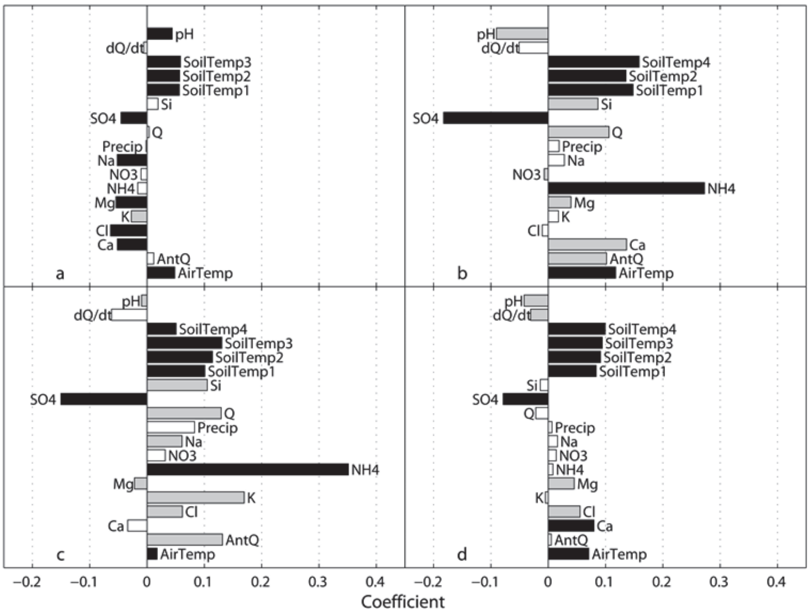

Figure 4. Partial Least Squares coefficients (first component) for the explanatory variables in predicting RIM residuals in a) Gårdsjön, b) Aneboda, c) Kindla, and d) Gammtratten. The different colors of the bars indicate importance with black variables being the strongest predictors of RIM residuals.

We tested a new version of RIM, where the shape of the depth-DOC relationship was allowed to vary non-linearly based on the van't Hoff equation:

$$\mathrm{C}_{stream} = \frac{\gamma_0 e^{\kappa T_{soil}}}{\alpha^{\Gamma_0 e^{\eta T_{soil}}}\left(\Gamma_0 e^{\eta T_{soil}+1}\right)} Q^{\Gamma_0 e^{\eta T_{soil}}} \qquad (2)$$

where C_{stream} is stream DOC concentration, Q is stream discharge, T_{soil} is soil temperature, and α, γ_0, Γ_0, κ, and η are model parameters. This dynamic version of RIM was successful in simulating DOC dynamics in all four IM sites and performed substantially better than the original version of RIM with static depth-DOC relationships. The dynamic RIM was able to explain 36-61 % of DOC variability in the IM streams.

We suggested that the different DOC variability displayed in the IM streams was due to differences in riparian soil organic matter distribution with depth. Observations, as well as RIM simulated soil solution DOC profiles, indicated the existence of relatively thick organic soil layers in Aneboda and Kindla, whereas the organic soil layers in Gårdsjön and Gammtratten seemed to be shallower.

4.3 NOM Sensitivity to Flow and Temperature in Boreal Forested Catchments (Paper III)

There are observations of increasing trends in stream and lake DOC in several areas in central and northern Europe as well as in North America (Monteith *et al.*, 2007; Vuorenmaa *et al.*, 2006; Evans *et al.*, 2005; Skjelkvale *et al.*, 2005; Hongve *et al.*, 2004; Worrall *et al.*, 2004; Driscoll *et al.*, 2003). Several hypotheses have been put forward to explain these trends, e.g. higher temperatures (Freeman *et al.*, 2001), higher atmospheric CO_2 content (Freeman *et al.*, 2004), increased precipitation (Hongve *et al.*, 2004), increased N deposition (Findlay, 2005; Pregitzer *et al.*, 2004), decreases in acid atmospheric deposition (Monteith *et al.*, 2007; Evans *et al.*, 2006), decreases in ionic strength (Hruska *et al.*, 2009), or combinations of these (Erlandsson *et al.*, 2008). It is likely that several of these processes act simultaneously in affecting NOM dynamics. However, as acid deposition is declining in these regions and areas previously influenced by acidification are recovering, climate related drivers will probably be the main drivers of NOM trends in the future (Futter *et al.*, 2009). To assess potential future NOM trajectories it is therefore important to understand the sensitivity of NOM to changes in temperature and flow. In this paper we estimated DOC sensitivity to flow and temperature under current winter and summer conditions in thirteen boreal streams by using RIM.

The simple structure of RIM (Equation 2) allows for analytical solutions of the partial derivatives with respect to flow (Q):

$$\frac{\partial C}{\partial Q}=\frac{\Gamma_0\,\gamma_0\,e^{(\eta+\kappa)T_s}}{\alpha^{\Gamma_0\,e^{\eta T_s}}\left(\Gamma_0\,e^{\eta T_s}+1\right)}Q^{\Gamma_0\,e^{\eta T_s}-1}$$

and temperature (T_s):

$$\frac{\partial C}{\partial T_s}=\frac{\kappa+\Gamma_0 e^{\eta T_s}\left(\kappa+\eta\left[\log\frac{Q}{\alpha}-1\right]+\Gamma_0\eta\,e^2\left[\log\frac{Q}{\alpha}\right]\right)}{\Gamma_0 e^{\eta T_s}+1}\cdot\frac{\gamma_0 e^{\kappa T_s}}{\alpha^{\Gamma_0 e^{\eta T_s}}\left(\Gamma_0 e^{\eta T_s}+1\right)}Q^{\Gamma_0 e^{\eta T_s}}$$

We assumed that the partial derivatives, $\partial C/\partial Q$ and $\partial C/\partial T_s$, represent DOC sensitivity to flow and temperature. At each site we estimated $\partial C/\partial Q$ and $\partial C/\partial T_s$ at representative summer and winter conditions, which were estimated from observed joint probability distributions of flow and temperature.

We found varying sensitivity to flow and temperature among the study sites. The different streams could roughly be divided into three groups: 1) streams where DOC dynamics are flow driven, 2) streams with temperature driven DOC dynamics, and 3) streams with low sensitivity to both flow and temperature. Sensitivity to temperature was generally higher in summer than in winter, whereas the opposite was seen for flow sensitivity. At sites with soil solution data, flow sensitivity was strongly related to soil solution DOC gradients (Figure 5). DOC was more sensitive to flow in areas with large soil DOC gradients. In addition, $\partial C/\partial T_s$, was related to stream DOC seasonality in areas with high temperature sensitivity.

To conclude, the response of stream DOC dynamics to climate change will depend on current catchment characteristics, especially soil organic matter content and distribution.

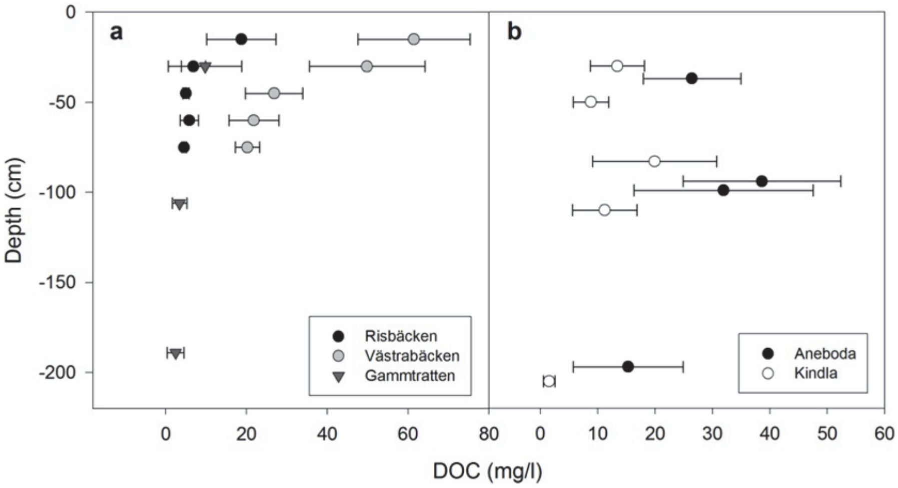

Figure 5. Observed soil solution and groundwater DOC concentrations in a) three strongly flow driven catchments (high $\partial C/\partial Q$ and low $\partial C/\partial T_s$), and in b) two temperature driven catchments (low $\partial C/\partial Q$ and high $\partial C/\partial T_s$). Symbols show average values and whiskers represent standard deviation.

4.4 Spatial Variability in Intra-Annual NOM Dynamics and Its Relationship to Temporal Trends in NOM (Paper IV)

Temporal trends in NOM concentrations have received considerable scientific interest during the last decade. However, intra-annual NOM variability is often orders of magnitude larger than year-to-year trends and unravelling the controls on intra-annual NOM dynamics likely hold the key to understanding long-term changes. The aim with this paper was to quantify and characterize intra-annual DOC variability and compare it with DOC trends in 136 Swedish streams and rivers. We also aimed at investigating the coupling among DOC, discharge and temperature as well as seeking explanations in catchment characteristics for these patterns.

We found different patterns in intra-annual DOC variability among the 136 sites. Annual DOC trends did not show any geographical pattern (Figure 6), and these were generally much smaller than intra-annual DOC variability. In contrast, the relationships among DOC, discharge, and temperature differed between northern and southern Sweden. Flow, temperature, and seasonality were shown to be significant predictors of intra-annual DOC variability in a majority of sites. Those sites where these variables were poorly related to intra-annual DOC dynamics were mainly large catchments or areas with large upstream surface water areas, i.e. lakes or reservoirs.

We suggested a coarse qualitative classification of the studied streams and rivers based on observed DOC dynamics and its response to flow, temperature and landscape characteristics (Figure 6): 1) areas where DOC dynamics was strongly related to stream flow; 2) areas with high DOC seasonality where DOC was strongly correlated to temperature, but with weak relationship to flow; 3) snow-melt dominated areas with high DOC seasonality, where DOC is strongly and positively correlated to both flow and temperature; 4) mainly large catchments or systems with large upstream lakes or reservoirs experiencing non-seasonal DOC dynamics and where DOC is weakly related to both flow and temperature.

A full understanding of the controls on intra-annual DOC variability is needed to assess possible future trajectories of aquatic DOC dynamics and ecosystem functioning under the pressure of expected global change. We found clear differences in relationships among DOC, temperature and flow between northern and southern areas in this study. These relationships are likely to change with a warming climate in ways not shown in inter-annual trends.

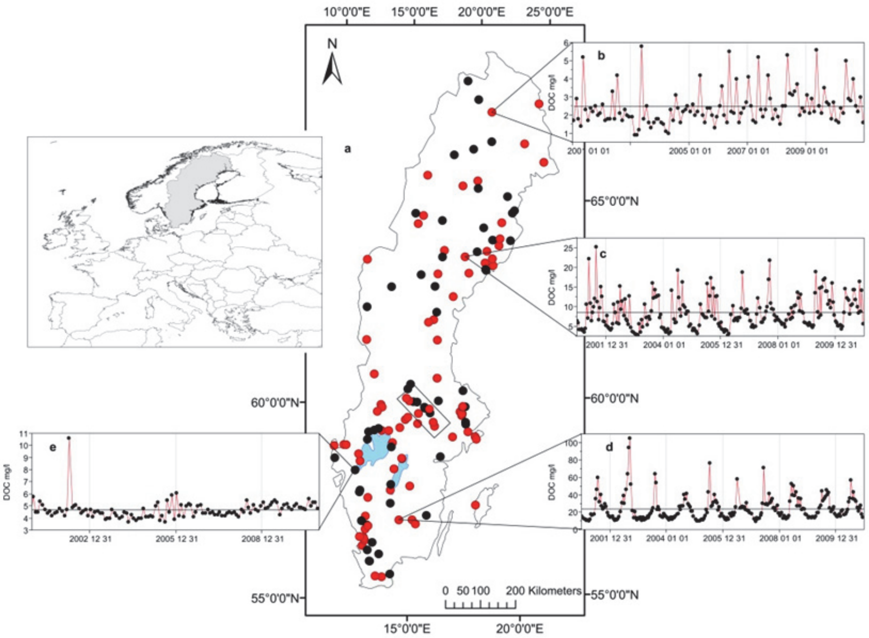

Figure 6. a) Map with sampling stations. Red points indicate sites with significant positive DOC trends while black points indicate sites without significant trends. Inlet show four typical time series of DOC and arrows indicating position: b) the Killingi stream with high seasonality and high DOC-flow correlation; c) the Gammtratten stream with non-seasonal DOC dynamics and high DOC-flow correlation; d) the Aneboda stream with high seasonality and high DOC-temperature correlation; and e) the Göta Älv river at Vargön, which is located downstream Sweden’s largest lake.

5 Conclusions

Discharge and soil temperature are primary drivers of intra-annual NOM variability in many running waters in the boreal region. Results presented in this thesis suggest that the underlying causes of these relationships are combinations of soil organic matter content and distribution, and water flow pathways across the soil. Lakes and reservoirs further regulate downstream NOM dynamics through substantial reworking of NOM due to long water residence times. A better understanding of intra-annual NOM dynamics is required for estimating the sensitivity of NOM cycling to global change.

RIM is able to simulate NOM dynamics properly in many boreal streams. Previous work has emphasized the importance and effects of flow pathways on solute flux and concentrations in surface waters. However, this has often been done by discrete divisions of the terrestrial environment into a shallow and a deep zone, or possibly into three different compartments (see e.g. Lyon *et al.*, 2010; Mulholland & Hill, 1997; Hornberger *et al.*, 1994). Also, mathematical biogeochemical models in use today commonly divide the terrestrial environment into a small number of "boxes" where each box represents different horizons in the soil with varying physical and biogeochemical properties (Futter *et al.*, 2007; Michalzik *et al.*, 2003). Contrarily, the RIM concept offers a simple yet powerful conceptual explanation for the effect of flow pathways on stream solute variability without imposing strong assumptions about the structure of the terrestrial environment, notably the soil.

6 Future Research

Natural organic matter plays an important role in aquatic biogeochemistry and ecology. Still, much is unknown or uncertain when it comes to the production, transport and degradation of NOM in the landscape. This work has provided new insights in only a small part of the entire cycling of NOM, but a great deal of future research is needed for a better understanding of its dynamics and fate. I think there are three main issues that require further research: 1) where do NOM come from, i.e. what are the dominant sources of NOM and how is it formed; 2) what happens to NOM when it gets dissolved in water, i.e. how is it degraded and what is the coupling to stream CO_2 dynamics; 3) what is the connection between NOM and other substances, e.g. inorganic nitrogen, sulphur and metals. In addition, I see the need for future research on RIM as a model and concept.

6.1 NOM Sources

There has been excellent research done on identifying sources of NOM. However, there is still much to do and I especially think there are two approaches that need further exploration. One is the identification of dominating flow pathways in the landscape to elucidate the movement of NOM between different landscape elements. Studying aquatic biogeochemistry will almost always require a good understanding of the hydrology within and between systems, both for source apportionment and for estimation of water transit times. The other approach is to characterize the composition and structure of NOM. Do different sources imprint distinct biochemical signatures in NOM that are possible to map out? The combination of different isotopic signatures with high-resolution biochemical screening will probably help in understanding the character of different possible sources.

6.2 Fate of NOM

Determining NOM sources is uncertain, but ascertainment of the fate of NOM is equally difficult. Supersaturation of CO_2 in streams and rivers seem to be wide-spread, but the cause of this oversaturation is not fully understood. One source is thought to be mineralization of NOM, but estimates of the degradability of this material differ. Once again may the combination of hydrology, isotopic and high-resolution analytical techniques be important tools to study NOM dynamics. In addition, different sensor techniques, e.g. field-deployable photospectrometry and laser spectrometers, may allow scientists to get unprecedented high-frequency datasets that will bring new exciting insights into the temporal variability of NOM, CO_2, isotopic signatures and the coupling among these.

6.3 Interaction With Other Substances

It is well-known that NOM interacts, affects and is affected by other substances, e.g. metals and mineral particles. The exact mechanisms controlling these interactions are, however, not fully understood. New analytical techniques, like FT-ICR-MS, could give clues on these controls, but the low content of e.g. NOM associated metals, may prove too difficult to detect with the sensitivity of current techniques.

6.4 RIM

RIM is a fairly new model, although the concept has qualitatively been applied for longer. As shown in this work, the model has proved successful in simulating DOC dynamics in boreal streams, but this work has also identified a couple of short-comings with current implementations and possible improvements.

The functions used for the soil solution DOC concentration profile in this work have proven insufficient in some cases. This has identified the need for more flexible functions, e.g. functions based on the log-normal or gamma distribution. However, such functions may complicate or even preclude an analytical solution.

In the first paper outlining the technical description of RIM it was tested on calcium, magnesium and chloride, besides TOC (Seibert *et al.*, 2009). However, this has not been pursued further, although the model should be suitable for other substances than NOM. Also, using RIM for all major cations and anions could allow for improved identification of model parameters while simultaneously preserving charge balance.

Another interesting issue is regionalization of model parameters. Would it be possible to regionalize RIM parameters from landscape and climatic characteristics? The first step here would be to decide suitable spatial scales on which RIM is applicable and meaningful.

6.5 Model Uncertainty Estimation

Changes in analytical techniques are necessary when collecting long-term data series, though it is important to note that these changes may bring inconsistencies to the data series. There is considerable scientific interest in estimating data and model uncertainty, especially within the hydrology community. There are, however, at present few attempts in accounting for censored data or differences in data uncertainty in model conditioning and uncertainty estimation. Methods accounting for variable data uncertainty are thus essential for full use of the information contained in long-term data series in environmental modelling.

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