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Carbon Dioxide in Inland Waters

*Drivers and Mechanisms Across Spatial and
Temporal Scales*

ANNA CECILIA NYDAHL



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Abstract

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Inland waters are an essential component of the global carbon cycle as they are very active sites for carbon transformation processes. Much of this carbon is transformed into the greenhouse gas carbon dioxide (CO_2) and emitted into the atmosphere. The biogeochemical and hydrological mechanisms driving CO_2 concentrations in inland waters are manifold. Although some of them have been studied in detail, there are still knowledge gaps regarding the relative importance of the different CO_2 -driving mechanisms, both on a spatial and a temporal scale. The main aim of this thesis was to fill some of the knowledge gaps by studying long- and short-term effects of enhanced dissolved organic carbon (DOC) concentrations on surface water partial pressure of CO_2 ($p\text{CO}_2$) as well as to investigate both internal (i.e., within the water body) and external (i.e., catchment) drivers of $p\text{CO}_2$ in inland waters. Based on analyses of long-term data from more than 300 boreal lakes and streams and on results from two mesocosm experiments as well as a detailed catchment study, one of the main results of the thesis was that DOC concentrations were, on a temporal scale, generally uncoupled to $p\text{CO}_2$. Indeed, additions of allochthonous DOC to lake water could result in increased $p\text{CO}_2$ in waters but not as originally expected by stimulation of bacterial activity but instead by light driven suppression of primary production, at least in mesotrophic waters. Changes in the carbonate system was also found to be a main driver for surface water $p\text{CO}_2$. Finally, also external processes such as groundwater inputs contributed substantially to variations of surface water $p\text{CO}_2$. In a detailed study on carbon in groundwater, $p\text{CO}_2$ in groundwater was found to decrease with soil depth and correlated negatively with pH, which increased with soil depth. Conclusively, this thesis show that $p\text{CO}_2$ does not follow the trends of increased DOC in boreal surface waters but instead correlates with changes in primary production and shifts in the carbonate system. Additionally, the dominating mechanisms driving $p\text{CO}_2$ clearly differ between lakes and streams. Consequently, simulations of future CO_2 dynamics and emissions from inland waters cannot rely on DOC concentrations as a $p\text{CO}_2$ predictor, but rather need to incorporate several $p\text{CO}_2$ driving mechanisms, and consider the difference between lakes and streams.

Keywords: carbon dioxide, dissolved organic carbon, inland water, lake, stream, groundwater, mesocosm, carbonate system, carbon

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“If you change the way you look at things, the things you look at change.”

- Wayne Dyer

To the people I love

List of Papers

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

- I Nydahl, A. C., Wallin, M. B., and Weyhenmeyer, G. A. (2017) No long-term trends in $p\text{CO}_2$ despite increasing organic carbon concentrations in boreal lakes, streams and rivers. *Global Biogeochemical Cycles*, 31(6):985–995
- II Nydahl, A. C., Wallin, M. B., Tranvik, L. J., Hiller, C., Attermeyer, K., Garrison, J. A., Chaguaceda, F., Scharnweber, K., and Weyhenmeyer, G. A. (2019) Colored organic matter increases CO_2 in meso-eutrophic lake water through altered light climate and acidity. *Limnology and Oceanography*, 64(2):744-756
- III Nydahl, A. C., Wallin, M. B., Laudon, H., and Weyhenmeyer, G. A. (2019) Groundwater carbon within a boreal catchment – spatiotemporal variability of a hidden aquatic carbon pool. *Submitted*
- IV Nydahl, A. C., Wallin, M. B., and Weyhenmeyer, G. A. (2019) Highly variable explanations of long-term $p\text{CO}_2$ increases in boreal lakes and streams. *Submitted*

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Abbreviations

$\delta^{13}\text{C}$ -DIC	Stable carbon isotope of dissolved inorganic carbon
ANC	Acid neutralizing capacity
BCP	Bacterial carbon production
CH_4	Methane
Chl <i>a</i>	Chlorophyll <i>a</i>
C:N	Carbon to nitrogen ratio
CO_2	Carbon dioxide
CO_3^{2-}	Carbonate
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
H_2CO_3	Carbonic acid
H_3PO_4	Phosphoric acid
HCO_3^-	Bicarbonate
PAR	Photosynthetically active radiation
N	Nitrogen
$p\text{CO}_2$	Partial pressure of carbon dioxide
P	Phosphorus
POC	Particulate organic carbon
TOC	Total organic carbon
WRT	Water retention time

Introduction

Carbon is the chemical basis of all known life and by definition is present in all organic compounds. The transformation of carbon compounds, from inorganic to organic during photosynthesis or from organic to inorganic during respiration and decomposition, essentially defines the actions of living organisms and therefore play a fundamental role for life on Earth (Brown *et al.* 2015). The carbon cycle is the biogeochemical cycle by which carbon is exchanged between land, water and the atmosphere, and comprises a sequence of events that are key to make life on Earth possible. Carbon in the atmosphere exists in two main forms, carbon dioxide (CO₂) and methane (CH₄), both of which are greenhouse gases (Wigley & Schimel 2005).

Since the industrial revolution, human activities have greatly modified the exchange of carbon between land, water and the atmosphere. Atmospheric CO₂ concentrations increased from about 280 ppm before the industrial era to about 410 ppm in 2019. Only about half of the CO₂ emissions from human activities are reflected in this increase, the other half has been sequestered on land, in inland waters and in the oceans (Battin *et al.* 2009).

Carbon in inland waters

Although inland water ecosystems cover only about 1% of Earth's surface, inland waters play a major role in the global carbon cycle (Battin *et al.* 2009; Cole *et al.* 2007). Historically, inland waters have been considered passive pipes merely transporting carbon from land to the ocean (Cole *et al.* 2007). However, it is now well known that inland waters are also very active sites for transformation and storage of carbon (Aufdenkampe *et al.* 2011; Battin *et al.* 2009; Cole *et al.* 2007; Tranvik & von Wachenfeldt 2009). The most recent estimate of the terrestrial input of carbon to inland waters suggested that 5.1 Pg C is delivered to inland waters annually (Drake *et al.* 2018). Out of this 5.1 Pg C, 3.9 Pg is annually outgassed, mostly as CO₂ (Drake *et al.* 2018), which is even higher than the terrestrial carbon sink for anthropogenic emissions of 2.8 Pg C yr⁻¹ (Canadell *et al.* 2007). Inland waters also sequester as much, or more carbon as the oceans do (Clow *et al.* 2015).

Carbon compounds in inland waters can be either organic or inorganic. The organic carbon is composed of two major fractions, a dissolved and a particulate phase. These are defined based on isolation techniques using filtration

through a membrane filter with a defined pore size. Dissolved organic carbon (DOC) is typically the fraction that passes through a filter with 0.2 to 0.45 μm pore size, whereas the fraction retained by the filter is termed particulate organic carbon (POC) (Tranvik & von Wachenfeldt 2009). More than 90% of the total organic carbon (TOC) in inland waters consist of DOC (Thurman 1985). The dissolved inorganic carbon (DIC) pool in inland waters consists of dissolved CO_2 , carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). These inorganic compounds readily interconvert from one to another as a function of their relative concentration, pH and temperature, a concept which is referred to as the carbonate system. In the 1990's it was realized that the majority of lakes worldwide are supersaturated with CO_2 relative to the water-atmosphere equilibrium (Cole *et al.* 1994), and since then subsequent research has shown that inland waters effectively emit large amounts of CO_2 to the atmosphere (Raymond *et al.* 2013).

CO_2 in inland waters can originate from internal or external sources (Cole 1999; Hotchkiss *et al.* 2015; Tranvik 1992). The key internal biogeochemical mechanisms that drive CO_2 concentrations in inland waters are microbial mineralization and photochemical oxidation of DOC, primary production and distribution of carbonate system variables (del Giorgio & Peters 1994; Hope *et al.* 1994; Jansson *et al.* 2007; Lazzarino *et al.* 2009; Tranvik 1992). Furthermore, DIC can be imported directly from the surrounding terrestrial environment where it is produced via respiration or weathering in the catchment soils. Hence, catchment hydrology is also of importance for CO_2 concentrations in inland waters. Although some of the biogeochemical and hydrological mechanisms driving CO_2 concentrations in inland waters have been intensely studied, there is still some controversy regarding which processes are most important. Understanding the mechanisms driving inland water CO_2 concentrations across spatial and temporal scales is important to allow for generalizations and predictions of inland water CO_2 responses to environmental change (Seekell & Gudas 2016).

DOC quantity and quality

DOC consists of a heterogeneous mixture of different carbon compounds that vary in quality. The quality of DOC can vary greatly due to differences in origin as well as transformation processes. In inland waters, DOC can originate either from surrounding terrestrial areas (i.e., allochthonous) or from in situ release of carbon from phytoplankton, algae and macrophytes (i.e., autochthonous).

Allochthonous DOC is derived from vascular plant material, root exudates and the primary and secondary metabolites of microorganisms, mostly accumulating in the organic horizon of the soil (Aitkenhead-Peterson *et al.* 2003; Mostofa *et al.* 2013). Allochthonous DOC is transported from the soil to

aquatic ecosystems through advective transport in surface- and groundwaters (Aitkenhead-Peterson *et al.* 2003). Although DOC quality can vary considerably, it can generally be divided into humic-like or protein-like components (Kothawala *et al.* 2014). Allochthonous DOC is generally structurally complex and composed of colored, aromatic, high molecular weight compounds such as humic substances (Williams *et al.* 2010) and is thus often considered to be more humic-like. Due to the high molecular weight and aromaticity of humic-like DOC, it has been regarded as recalcitrant (Miller & McKnight 2010). However, it has also been shown that high molecular weight DOC is more bioreactive than low molecular weight compounds (Amon & Benner 1996), and that the most aromatic, highly colored fractions with high molecular weight have shorter half-lives (Köhler *et al.* 2013; Weyhenmeyer *et al.* 2012a).

Autochthonous DOC is mostly produced by algae and phytoplankton, however macrophytes and autotrophic bacteria also contribute to the synthesis of autochthonous DOC (Likens 1973). Autochthonous DOC is generally more protein-like, has low molecular weight and less color (Bertilsson & Jones 2003; Guillemette & del Giorgio 2011). Protein-like DOC, is often labile and biologically reactive (Guillemette & del Giorgio 2011; McKnight *et al.* 2001). Protein-like DOC can, however, be more persistent in inland water due to constant renewal despite the loss of other components (Kothawala *et al.* 2014).

Differences in the composition of DOC, and hence its quality, e.g. driven by its origin, affect its biogeochemical functions. DOC can be transformed through processes such as microbial mineralization, photochemical oxidation, flocculation and sorption to clay, and when DOC is transformed, its quality changes. All these transformations change the quantity and the quality of the DOC pool, which subsequently influences the fate of the carbon, whether it is degraded and emitted as CO₂ or CH₄, sequestered into sediments or exported to the ocean. One of the major pathways is the emission of CO₂ to the atmosphere, which is highly influenced by microbial and photochemical degradation of DOC (Graneli *et al.* 1996; Tranvik 1992).

Microbial mineralization of DOC and its influence on CO₂ concentrations

Heterotrophic bacteria are the most abundant organisms in all ecosystems, and a great fraction of the annual primary production is metabolized by them. Consequently, they play a critical role in the carbon cycle and the largest fluxes of carbon in inland waters is that from the pool of organic matter into microorganisms (Cole 1999). Bacteria respire organic carbon to gain energy which is used to sustain cellular processes. Thereafter, the respired fraction is released as CO₂, which can subsequently be emitted to the atmosphere. Terrestrially

sourced DOC can fuel secondary production within inland waters by heterotrophic bacteria. In many inland water ecosystems, the mineralization of organic carbon by microorganisms outweighs carbon fixation by primary producers, hence these systems are heterotrophic (where respiration is greater than primary production) and are thus sources of CO₂ to the atmosphere.

Several studies have shown that, on a spatial scale, there is a positive relationship between DOC and the partial pressure of CO₂ ($p\text{CO}_2$) due to microbial respiration of terrestrial DOC (e.g. Lapierre & del Giorgio 2012; Sobek *et al.* 2003). This relationship between DOC and $p\text{CO}_2$ has been suggested to be the main reason for the CO₂ supersaturation observed in the majority of inland waters across the globe (del Giorgio *et al.* 1997; Hope *et al.* 1996; Jonsson *et al.* 2001). On a temporal scale, however, much less is known about the relationship between DOC and $p\text{CO}_2$. Surface water DOC concentrations have been increasing in the boreal region since the 1990's (Filella & Rodriguez-Murillo 2014; Monteith *et al.* 2007), suggesting that $p\text{CO}_2$ might have concomitantly increased. Therefore, assessing the long-term DOC and $p\text{CO}_2$ relationships in boreal inland waters is an important undertaking.

Photochemical oxidation of DOC and its influence on CO₂ concentrations

Solar radiation provides the primary driving force for biogeochemical cycles and is fundamental to the cycling of organic matter in inland water ecosystems. Most of the solar radiation that reaches the Earth's surface is converted into thermal energy, however a significant part is diverted into photochemical processes (Zepp *et al.* 1995). Photochemical reactions caused by solar radiation can change the physical, chemical and optical properties of water and play an important role in transforming DOC, subsequently affecting CO₂ production (Kopacek *et al.* 2003; Vähätalo *et al.* 2003). Photochemical transformations of DOC can have both direct and indirect effects on surface water $p\text{CO}_2$. Photochemical transformation of allochthonous DOC has been demonstrated to produce bioavailable substrates and increased bacterial activities, thereby also producing CO₂ through respiration, however, concurrently autochthonous DOC was converted to substances of lower microbial substrate quality during radiation, thus decreasing DOC bioavailability which could lead to decreased CO₂ production (Tranvik & Bertilsson 2001). This suggests that phototransformation of DOC can both enhance and reduce DOC bioavailability and CO₂ concentrations. Furthermore, DOC can be directly converted to DIC through photochemical oxidation (Graneli *et al.* 1996).

Primary production and its influence on CO₂ concentrations

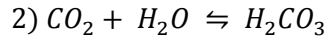
Primary production is the synthesis of organic compounds from inorganic compounds, such as CO₂ and water, through photosynthesis. Eventually, much of the primary production is converted back to CO₂ via respiration, however some carbon accumulates in biomass and organic matter. Consequently, primary production could be a strong driver of *p*CO₂ in inland waters. Primary production in inland waters is regulated by factors such as light, temperature and the supply of nutrients. The light climate in lakes and streams can be highly impacted by the water color. The water color could vary greatly depending on the DOC concentration since terrestrially derived DOC contains large amounts of colored humic-like DOC giving the water a brownish color (Roulet & Moore 2006). This browning effect has been particularly evident in surface waters across the boreal region where water color has been increasing since the 1990's (Haaland *et al.* 2010). Increased water color could lead to less light being available for photosynthesis, and subsequently less CO₂ bio-uptake (Jones 1992). However, it is still largely unknown if and how this increase in water color will alter *p*CO₂ through a change in primary production in inland waters.

The role of the carbonate system for CO₂ concentrations

Aquatic primary production is affected by the presence of dissolved carbonate species, and is thus tightly linked to the carbonate system. The carbonate system is the set of DIC species produced by the equilibria:



When CO₂ dissolves in water it exists in chemical equilibrium with H₂CO₃:



Hence, in inland waters the concentration of H₂CO₃ can be considered equivalent to the CO₂. The concentrations of the various carbonate species depend on the pH of the solution. Concomitantly, the pH in inland water is susceptible to biological influence from CO₂ consumption (photosynthesis) and CO₂ production (respiration, decomposition), which affect the ratio between CO₂:HCO₃⁻:CO₃²⁻ (Talling 2010). Hence, the pH of a solution is essentially controlled by the carbonate system (Roberts & Allen 1972). Increased CO₂ in inland waters due to reduced photosynthesis could lead to more acidic waters as pH decreases. However, inland waters have a natural protection against

acidification, a buffering capacity, referred to as alkalinity. Alkalinity is a measure of the amount of bases in a solution which can neutralize hydrogen ions from strong acids and is usually determined by titration against sulfuric acid (H_2SO_4) to the endpoint of the acid-base reaction (Mattson 2009). Alkalinity can also be referred to as a conservative property regarding the addition or the removal of CO_2 through biological activity, which respectively decrease or raise pH. A closely related term is acid neutralizing capacity (ANC), which may include any type of buffering. The major buffers in most inland waters are HCO_3^- and CO_3^{2-} . Alkalinity in inland waters is derived from several sources: weathering of rocks and soil, exchange reactions in soils, biological uptake and reduction of strong anions, evaporation and precipitation of minerals and atmospheric deposition of dust (Mattson 2009).

Influence of catchment processes on CO_2 concentrations in inland waters

It is not only the processes occurring within lakes and streams that are of importance for carbon dynamics in inland waters. Much of the DOC and DIC in inland waters originates from the surrounding catchment, hence catchment processes could be key regulators of surface water carbon concentrations. Groundwater inputs can be strong regulators of CO_2 concentrations in both lakes and streams (Hotchkiss *et al.* 2015; Leith *et al.* 2015; Marce *et al.* 2015; Weyhenmeyer *et al.* 2015; Winterdahl *et al.* 2016). Groundwater has been shown to be oversaturated in CO_2 , produced through microbial respiration of organic matter in soil and root respiration (Crawford *et al.* 2014; Leith *et al.* 2015; Macpherson 2009). Mineral weathering can also be a strong driver of groundwater CO_2 (Boerner & Gates 2015). The two key types of mineral weathering occurring in soils are carbonate weathering and silicate weathering. Both carbonate and silicate weathering consumes soil CO_2 , which is produced through soil respiration, and produces HCO_3^- . Mineral weathering can also lead to increased ANC and enhanced pH through the release of base cations and consumption of CO_2 . Hence, the carbonate system within a lake or a stream could be as important as the carbonate system in the surrounding catchment for regulating surface water CO_2 concentrations. For instance, a carbon budget for Sweden showed that CO_2 consumption through mineral weathering corresponded to 25% of the CO_2 efflux from lakes and streams (Humborg *et al.* 2010).

The importance of groundwater input for surface water chemistry can vary depending on a number of factors such as stream order, time of year, groundwater level and catchment hydrology (Hotchkiss *et al.* 2015; Peralta-Tapia *et al.* 2015). Furthermore, the relative importance of shallow and deep groundwater input for surface water chemistry can also vary depending on similar

factors (Tiwari *et al.* 2014). For instance, due to the strong hydrochemical connectivity between the catchment soil and headwater streams, the concentration of CO₂ in headwater stream water is largely dependent on the CO₂ concentration in the surrounding terrestrial areas (Vidon *et al.* 2010). Further downstream, the importance of in situ carbon transformation processes increases (Hotchkiss *et al.* 2015). Concurrently, the ratio of shallow to deep groundwater input changes towards greater influence from deeper groundwater further downstream (Peralta-Tapia *et al.* 2015). The importance of deep groundwater input to stream surface water chemistry also varies seasonally due to changes in flow rate. During spring, the contribution of deeper groundwater to surface water chemistry is diluted by increasing inputs of shallow groundwater and surface runoff, whereas during winter, at base flow, the relative contribution from deeper groundwaters increases (Humborg *et al.* 2010). Further, it has been suggested that deep groundwater inputs can be more influential at regulating stream chemistry than in-stream processes in downstream rivers (Tiwari *et al.* 2014). Despite this importance of deep groundwater, most studies on groundwater contributions to surface water chemistry have been using information from shallow depths down to ca. 1 m (i.e., Deirmendjian & Abril 2018; Grabs *et al.* 2012; Ledesma *et al.* 2016; Rasilo *et al.* 2017). Studies investigating the water chemistry of deeper groundwater are required to accurately assess how water chemistry from deeper groundwater could contribute to surface water chemistry. Consequently, there is a need for comprehensive studies and quantifications of carbon species in deeper groundwater, across both spatial and temporal scales.

Water residence time (WRT), both in the landscape and within the water body could also be a key regulator of surface water CO₂ concentrations (Algesten *et al.* 2004; Catalán *et al.* 2016). Organic carbon loss was found to increase rapidly with increasing WRT up to 2-3 years (Algesten *et al.* 2004) and CO₂ production has been shown to be more efficient in waters with long WRT due to more time available for microbial mineralization (Hanson *et al.* 2011). Runoff is predicted to decrease due to global warming, subsequently increasing WRT (Catalán *et al.* 2016) and with increasing WRT, CO₂ production may increase. Changes in precipitation can also impact WRT, and with climate change predicted to induce significant changes in many parts of the world in regards to precipitation, with increases in some areas and decreases in others (Martel *et al.* 2018), this could potentially have a large impact on CO₂ in inland waters. With decreased precipitation, WRT, and subsequently CO₂ production, may increase. Decreased precipitation would also lead to reduced discharge and consequently lead to a higher relative contribution from deeper groundwater than surface runoff and shallow groundwater to surface water chemistry (Carroll *et al.* 2018).

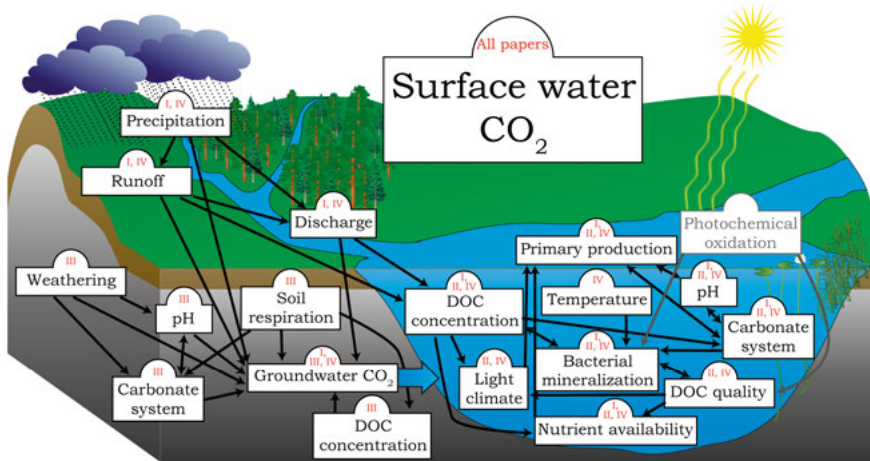


Figure 1 Conceptual figures illustrating the biogeochemical and hydrological CO₂ driving mechanisms that could be of importance for controlling CO₂ concentrations in surface water of boreal lakes and streams. Photochemical oxidation is, however, not covered in the studies of this thesis.

Aims of the Thesis

The overarching aim of this thesis was to get a better understanding of the biogeochemical and hydrological mechanisms driving CO₂ concentrations in inland waters (Figure 1). The studies on which the thesis is based upon include both internal (within lake and streams) and external (catchment) carbon transformation processes, cover a range of spatial scales, stretching from the entire Sweden, to a single catchment, to a mesocosm experiment in a lake, as well as different temporal scales ranging from four weeks to 21 years. Different spatial and temporal scales were combined to provide a comprehensive understanding of the mechanisms driving surface water $p\text{CO}_2$, which is urgently needed for the prediction of future CO₂ emissions from inland waters.

More specifically, the aims of this thesis were to:

- Investigate long-term effects of increased DOC on $p\text{CO}_2$ in boreal inland waters (Paper I).
The investigation was performed using long-term monitoring data from lakes, streams and river mouth systems distributed all across Sweden.
- Examine short-term effects of increased DOC on $p\text{CO}_2$ in lake water (Paper II).
The short-term effects of DOC on lake water $p\text{CO}_2$ were examined through two mesocosm experiments in a lake in eastern Sweden.
- Assess internal drivers of surface water $p\text{CO}_2$ (Paper II, IV)
Internal $p\text{CO}_2$ drivers were assessed through two mesocosm experiments in a lake in eastern Sweden and by investigating long-term trends in lakes and streams using monitoring data.
- Investigate external drivers of surface water $p\text{CO}_2$ (Paper III, IV)
Catchment drivers of surface water $p\text{CO}_2$ were investigated by exploring the spatial and temporal variability of organic and inorganic carbon concentrations in groundwater at intermediate depth in a catchment in northern Sweden as well as assessing long-term trends in catchment hydrology using monitoring data

Methods

Study sites

The study sites for the individual papers of this thesis ranged spatially from the national scale of Sweden (Paper I and IV), to the catchment scale (Paper III), to the mesocosm scale (Paper II) (Figure 2). In Paper I and IV, water chemical data acquired from the Swedish national freshwater monitoring program were used (Fölster *et al.* 2014). The data are made freely available by the Swedish University of Agricultural Sciences (SLU). For Paper I, an initial data set comprising 178 lakes, 86 streams and 42 river mouth systems was used. To get a complete data set with a minimum of four samples for each year for the period 1997 to 2013 a subset of the 306 waters, which resulted in a total of 71 lakes, 30 streams and 4 river mouths, was used. The same 105 water systems were initially used in Paper IV, and from these, the waters which had increased significantly in $p\text{CO}_2$ during the study period were used for further analysis, resulting in eight lakes and five streams. In Paper III, groundwater in the Krycklan catchment in northern Sweden, a boreal catchment dominated by forest and peatlands, was sampled across three seasons. For Paper II, two mesocosm experiments were conducted in the meso-eutrophic Lake Erken in eastern Sweden.

Mesocosm Experiment set-up

Two mesocosm experiments were performed, each lasting four weeks (Paper II). The first experiment was conducted in June-July (Experiment A) and the second in August-September (Experiment B) 2016. Both experiments had five replicates of four treatments (Figure 3a). In Experiment A, the four treatments were; (1) addition of DOC concentrated by reverse osmosis from a humic stream draining a forested wetland (i.e., reverse osmosis); (2) DOC from HuminFeed® (Humintech, GmbH, Grevenbroich, Germany), an alkaline extract of Leonardite (i.e., HuminFeed); (3) a mix of reverse osmosis concentrate and HuminFeed (i.e., mixed); and (4) no addition of DOC (i.e., control). Starting DOC concentrations for Experiment A were: 18.4, 18.1, 23.5 and 13.0 mg L⁻¹ for the reverse osmosis, HuminFeed, mixed and control treatments, respectively. In Experiment B the four treatments consisted of; (1) addition of reverse osmosis concentrate of DOC from the same humic stream water as in

Experiment A (i.e., reverse osmosis); (2) shading by covering of the outside of the mesocosms using black polyethylene film and on top using black chif-fon fabric (i.e., shading); (3) addition of reverse osmosis concentrate of DOC and shading (i.e., DOC-shading); and (4) no DOC addition or shading (i.e., control). Starting DOC concentrations for Experiment A were: 16.4, 12.0, 16.4 and 12.0 mg L⁻¹ for the reverse osmosis, shading, DOC-shading and control treatments, respectively.

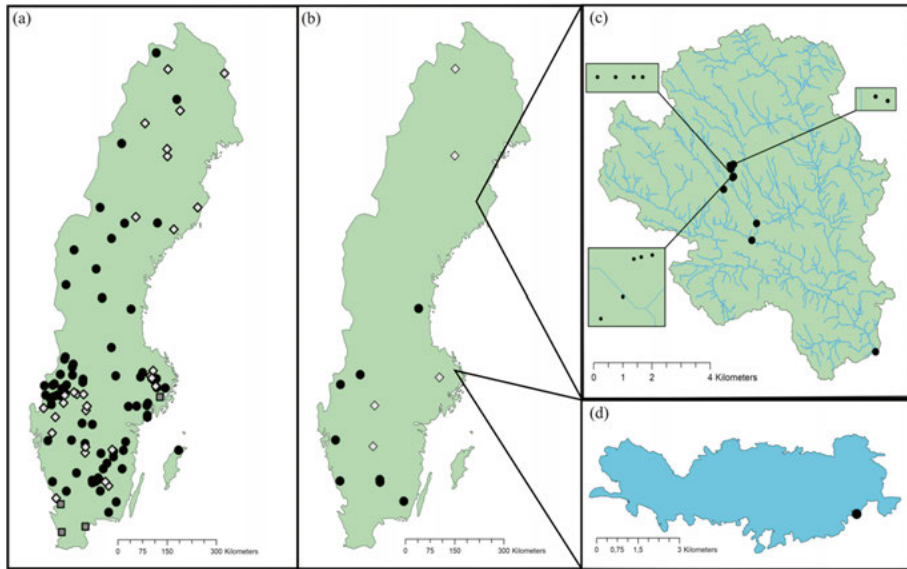


Figure 2 Study sites for each individual paper of this thesis; location of Swedish study lakes (circles, $n=71$), streams (diamonds, $n=30$), and river mouths (squares, $n=4$) (Paper I) (a), location of Swedish study lakes (circles, $n=8$), and streams (diamonds, $n=5$) (Paper IV) (b), location of groundwater wells in the Krycklan catchment in Northern Sweden (Paper III) (c), and location of the mesocosm experiment in Lake Erken (Paper II) (d).



Figure 3 Aerial photograph (photo credit: Erik Sahl  e) of the mesocosm experiment in Lake Erken (a), sampling of the mesocosms (b), and groundwater sampling in the Krycklan catchment (c, d).

Mesocosm and field sampling

Water sampling of the mesocosms were conducted weekly starting on the first day of the experiment and then four more times including the final sampling at the end of the experiment (Figure 3b) (Paper II). Sampling of $p\text{CO}_2$ was performed first at each sampling occasion to avoid outgassing due to turbulence and disturbance from water sampling. Water samples for $p\text{CO}_2$ analysis were taken with a syringe directly below the surface whereas water samples for all other analyses were collected using a tube sampler (1.5 m long, ~ 3 liter volume).

Sampling of groundwater was carried out in June (summer) and September (autumn) 2017 and in May (spring) 2018 (Figure 3c, d) (Paper III). Water was sampled from 16 groundwater wells with depths ranging from 3.4 to 19.5 m. The total volume of water in the well was determined before sampling and at least three times the volume of the well of water was removed prior to sampling to ensure collection of only the new infiltrating water. In a few wells the water refilled at such a slow rate that sampling took several days. Water temperature and $p\text{CO}_2$ were measured directly in the field while samples for analysis of DOC, DIC, the stable carbon isotope of DIC ($\delta^{13}\text{C}$ -DIC), CH_4 , pH and total nitrogen (N) were stored in the dark at 4°C for a maximum of seven days until analysis. Water samples collected for DIC and CH_4 analysis were collected in the same vial and acidified directly using phosphoric acid (H_3PO_4).

$p\text{CO}_2$ analyses

All samples for $p\text{CO}_2$ measurements collected for this thesis (Paper II and III) were analyzed directly in the field using the headspace equilibration method (described in Sobek *et al.* (2003)) as modified by Kokic *et al.* (2015). Bubble-free water samples of 30 mL were taken with a 60 mL polypropylene syringe equipped with a three-way stopcock. A 30 mL headspace of ambient air was then introduced and the syringe was vigorously shaken for one min to equilibrate the dissolved gas from the water into the headspace. The equilibrated air was then transferred into another syringe before being analyzed on a portable infrared gas analyzer (IRGA, EGM-4). All gas samples were analyzed within 5 min of sampling. The $p\text{CO}_2$ of ambient air was also measured to correct for the $p\text{CO}_2$ in the equilibrated air samples. The $p\text{CO}_2$ was calculated according to Weiss (1974) using Henry's law constant, correcting for temperature, atmospheric pressure and added ambient air CO_2 .

For Paper I and IV, CO_2 was calculated based on water temperature, alkalinity and pH according to Weyhenmeyer *et al.* (2012). From this, $p\text{CO}_2$ was calculated using Henry's law corrected for temperature and atmospheric pressure (Weiss 1974).

Additional chemical analyses

All chemical analyses for Paper I and IV were performed in an accredited laboratory at the Swedish University of Agricultural Sciences (SLU) following standard limnological procedures. Analytical methods are published online on SLU's website. TOC concentrations were considered equivalent to DOC concentrations since the particulate fraction of organic carbon generally is less than 1% in boreal inland waters (Laudon *et al.* 2011).

For the mesocosm experiment (Paper II), additional chemical analyses were performed by members of the KAWater team. Filtered water samples were analyzed on a Sievers M9 TOC analyzer for DOC concentrations while DIC concentrations were measured on a Sievers 900 TOC analyzer. Bacterial carbon production (BCP) was analyzed using the 3H-leucine incorporation method by Smith & Azam (1992). Ethanol extractions were performed with subsequent spectrophotometry analysis to establish chlorophyll *a* (chl *a*) concentrations following standard techniques (Kutser *et al.* 2005). The pH was measured directly in the mesocosms using a YSI multiprobe. Light was measured at seven depths in each mesocosm with a light meter. Total N and total phosphorus (P) were analyzed on unfiltered samples on a SEAL AutoAnalyzer. Water color was measured as absorbance at 420 nm (abs₄₂₀) using a Lambda 40 UV/VIS spectrophotometer (Paper II).

Additional groundwater chemical analyses were performed by laboratory staff at the Department of Forest Ecology and Management at SLU (Paper III). The DOC was measured as TOC on a Shimadzu TOC-VCPh. For DIC and CH₄ determination, a headspace method was used and headspace CO₂ and CH₄ concentrations were analyzed by gas chromatography (GC) (Wallin *et al.* 2010; Wallin *et al.* 2014; Åberg & Wallin 2014). Concentrations of DIC and partial pressure of CH₄ (*p*CH₄) were then calculated using temperature-dependent equations for the carbonate equilibrium (Gelbrecht *et al.* 1998) and Henry's Law (Weiss 1974). The $\delta^{13}\text{C}$ -DIC was analyzed from the CO₂ headspace using an isotope ratio mass spectrometer. Total N was measured on a Shimadzu TNM1 whereas the pH was measured with a Mettler Toledo Digi117-water combined pH meter.

Catchment hydrology

In addition to the water chemical data acquired from the Swedish national freshwater monitoring program, hydrological data downloaded from the Swedish Meteorological and Hydrological Institute (SMHI)'s website was used for Paper IV. Data acquired were monthly average precipitation, discharge and groundwater for the catchments of the study lakes and streams.

Statistics

In this thesis a variety of different statistical approaches were used, i.e., Mann Kendall trend tests, one way analyses of variances (ANOVAs), repeated measures ANOVAs, linear regressions and partial least squares regressions (PLS). Assumptions of normality and heteroscedasticity were tested prior to statistical analyses. If necessary, transformations of data or non-parametrical methods were applied in order to test significance. To identify long-term changes, non-parametric Mann Kendall trend tests were performed on yearly median water chemical and hydrological values (Paper I and IV). To find influential variables on lake and stream surface water $p\text{CO}_2$ PLS were used (Paper IV). One way ANOVAs were used to evaluate the direct effects of DOC additions in the mesocosm experiments whereas repeated measures ANOVAs, with mesocosm as a random effect, were performed to test for differences in $p\text{CO}_2$ and $p\text{CO}_2$ drivers between mesocosm treatments (Paper II). One way ANOVAs were used to test for differences in groundwater chemistry between seasons (Paper III). Linear regressions were performed on the mean of the values measured at the different seasons to investigate relationships between groundwater chemistry and depth as well as between groundwater $p\text{CO}_2$ and other groundwater carbon species (Paper III).

Results and Discussion

Long-term effects of increased DOC on surface water $p\text{CO}_2$

Over the past 20 years, DOC concentrations have been increasing in surface waters across the boreal region (Evans *et al.* 2005; Filella & Rodriguez-Murillo 2014; Monteith *et al.* 2007). On a spatial scale, high DOC concentrations have been shown to correspond to high levels of surface water $p\text{CO}_2$. However, the effect of a long-term DOC increase on $p\text{CO}_2$ in inland waters are still unknown. In Paper I, the long-term relationship between DOC and $p\text{CO}_2$ in boreal inland waters was investigated. In more than half of the 105 study waters, DOC was found to have increased significantly during the period 1997 to 2013, however, only a few of those showing a DOC increase also increased in $p\text{CO}_2$ (Figure 4). Overall, long-term water chemistry trends in 71 lakes, 30 streams and four river mouth systems were investigated. Out of the 39 lakes that had increased in surface water DOC concentrations during the 17-year study period, merely four had also increased in $p\text{CO}_2$. Half of the 30 streams had increased in DOC and of those 15 streams, only two had also increased in $p\text{CO}_2$. While all four river mouths had increased in DOC during the period 1997 to 2013, none of them showed an increase in $p\text{CO}_2$. These results relate to a previous study of long-term $p\text{CO}_2$ trends in lakes of the Adirondack park in northeastern U.S, where only six out of 31 lakes had increased in $p\text{CO}_2$ (Seekell & Gudas 2016). Contradicting the results of this thesis, Seekell & Gudas (2016) did, however, also observe a significant increase in DOC in the six lakes with enhanced $p\text{CO}_2$. Due to the established spatial relationship between surface water DOC and $p\text{CO}_2$ and the results from the six study lakes of Seekell & Gudas (2016), enhanced $p\text{CO}_2$ levels were expected in most of the waters that had increased in DOC. It was expected that either in situ CO_2 production through bacterial mineralization of allochthonous DOC would have increased or the inflow of catchment produced CO_2 would have increased in conjunction with the increased DOC input. However, this was not the case in the majority of the study waters in Paper I. Both in situ CO_2 production and CO_2 input from the catchment may indeed have increased, however other processes, that at the same time draw down the $p\text{CO}_2$, must have been stimulated to a greater extent. The lack of long-term DOC- $p\text{CO}_2$ relationship could potentially have been due to a change in hydrological patterns. Although precipitation has decreased in some areas of Sweden, in many

areas precipitation, and therefore also runoff, have increased since the 1990's (Bengtsson & Rana 2014; Chen *et al.* 2015; Weyhenmeyer *et al.* 2016). This increase in precipitation could have resulted in a dilution effect of the CO₂-rich groundwater input, leading to the observed uncoupling of DOC-*p*CO₂ trends on a temporal scale. In addition to hydrological changes, the lack of DOC-*p*CO₂ relationships could potentially be explained by a change in alkalinity or DOC quality for some of the systems (Kothawala *et al.* 2014; Seekell & Gudas 2016).

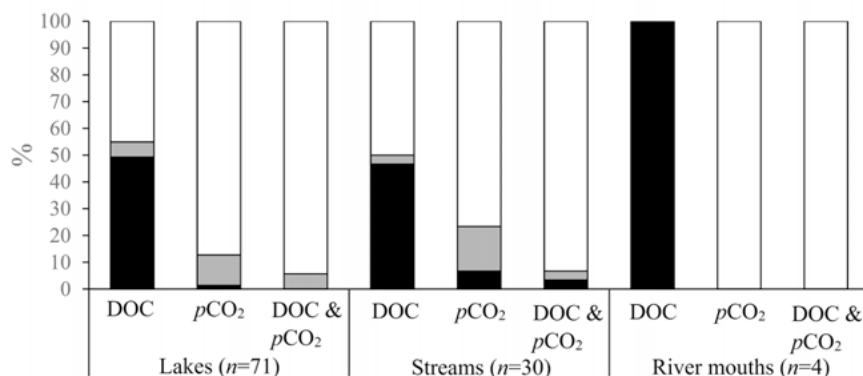


Figure 4 Percentage of surface waters of Swedish boreal lakes ($n=71$), streams ($n=30$) and river mouths ($n=4$) that had increased significantly in dissolved organic carbon (DOC), partial pressure of carbon dioxide (*p*CO₂) and both DOC and *p*CO₂. The black and grey parts of the bars combined refer to the systems investigated in Paper I with significant increases during the period 1997 to 2013. The grey part of the bar alone refers to the systems investigated in Paper IV during the period 1997 to 2017.

Short-term effects of increased DOC on lake water *p*CO₂

After discovering that DOC and *p*CO₂ were uncoupled through time, I wanted to investigate the short-term effect of increased DOC on surface water *p*CO₂. The effect of enhanced allochthonous DOC input could be three-fold (Figure 1). Firstly, allochthonous DOC may function as a carbon source to heterotrophs, stimulating CO₂ production. Secondly, DOC could contribute to water color, hence increasing light attenuation and potentially hampering CO₂ consumption by primary producers. Thirdly, DOC may have an acidifying effect, which can lead to decreased pH with a subsequent increase in CO₂ as the distribution within the carbonate system shifts. In Paper II, two mesocosm experiments were performed in a meso-eutrophic lake. In the first mesocosm experiment, DOC concentrations were manipulated, whereas in the second ex-

periment both DOC concentrations and light climate were manipulated. During the four-week durations of the experiments, a significant $p\text{CO}_2$ increase was observed in all treatments relative to the control (Figure 5). Hence, there was a clear short-term response of $p\text{CO}_2$ to the allochthonous DOC input. Additionally, $p\text{CO}_2$ also increased during the four-week experiment due to a change in light climate. Generally, the $p\text{CO}_2$ increases were most pronounced during the first one to two weeks of the experiments, further emphasizing how quick the responses to DOC additions were. Also, the first $p\text{CO}_2$ measurements were performed about 18 hours after DOC additions, and already then, a clear increase in $p\text{CO}_2$ could be seen in the majority of the treatments. The lack of long-term $p\text{CO}_2$ -DOC relationship and the clear short-term $p\text{CO}_2$ -DOC relationship could be related to the quality of the DOC. This has previously been shown in a study comparing short-term and long-term bacterial carbon consumption (Guillemette & del Giorgio 2011). The labile carbon is quickly consumed leaving behind the more recalcitrant carbon, hence the microbial response to enhanced allochthonous DOC input might be more pronounced in the short-term. However, there was no difference in bacterial production between any of the treatments in either of our mesocosm experiments despite the increased $p\text{CO}_2$. Lennon (2004) performed a mesocosm experiment with DOC additions where he measured the CO_2 response and, similar to our mesocosm studies, found a significant increase in CO_2 in response to enhanced DOC concentrations. However, contradicting to the results of this thesis, Lennon (2004) also found a significant increase in bacterial productivity. Two of the key differences between ours and Lennon's (2014) mesocosm experiments are the length and sampling strategy. Our experiments were performed for four weeks, sampling on a weekly basis whereas Lennon's (2014) experiment was performed for 10 days with daily sampling. The short-term effect of DOC on bacterial production may indeed be short, and the increase of the bacterial activities during the first week in response to the added allochthonous DOC might have been missed. However, there are several mechanisms other than bacterial mineralization affecting $p\text{CO}_2$ in inland waters, some closely related to DOC, others independent of DOC.

Internal drivers of surface water $p\text{CO}_2$

Our mesocosm experiments (Paper II) allowed me to get a better mechanistic understanding of the effect increased DOC input could have on lake water $p\text{CO}_2$ and to further explore the internal drivers of surface water $p\text{CO}_2$. To test the results on a broader scale, a study which included field observations was performed. In Paper IV, long-term monitoring data were used to investigate reasons behind significantly increasing $p\text{CO}_2$ in eight lakes and five streams, distributed all across Sweden that had increased in $p\text{CO}_2$ during the 21-year period of 1997 to 2017. In the mesocosm experiments (Paper II), the DOC

additions as well as the shading had a strong effect on the light climate decreasing the amount of light available for photosynthesis. There was a negative relationship between $p\text{CO}_2$ and light climate (Figure 6a, b). The increased light attenuation must have had a negative impact on primary production, decreasing CO_2 bio-uptake and subsequently increasing the $p\text{CO}_2$ in the mesocosms. In Paper IV, there was also a potential negative effect of shading through darkening of the waters on primary production. Of the eight study lakes, four had increased in water color (i.e., absorbance at 420 nm), which was used as a proxy indicator for primary production, and this could have been a reason for the observed $p\text{CO}_2$ increase. These results relate to previous studies showing a negative effect of shading on primary production caused by allochthonous DOC (Ask *et al.* 2009; Carpenter *et al.* 1998). The large natural variation in water color due to differences in DOC concentrations and DOC sources could potentially be a reason for variation in primary production (Carpenter *et al.* 1998). In the mesocosms, *chl a* had increased in all treatments, which was a bit surprising as *chl a* often has been used as a proxy indicator for primary production (Huot *et al.* 2007; Michelutti *et al.* 2005; Roehm *et al.* 2009), and should thus have decreased with increased shading. However, primary producers are able to produce more chlorophyll to compensate for the lack of light (Richardson *et al.* 1983), hence water color may be a more suitable proxy indicator for primary production in this context.

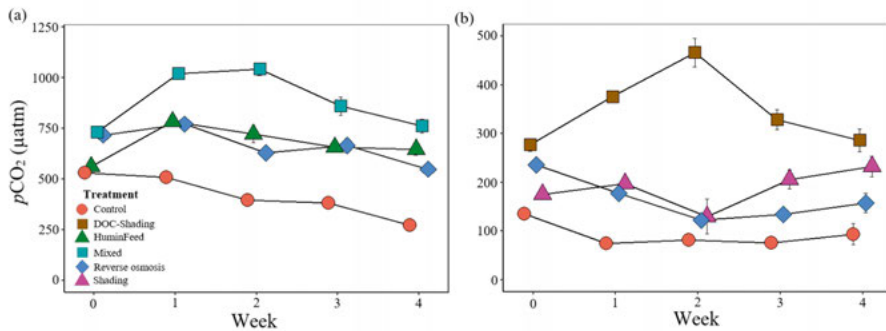


Figure 5 Weekly variations in the partial pressure of carbon dioxide ($p\text{CO}_2$) under four treatments (see legends in figure) during two four-week mesocosm experiments, Experiment A (a) and Experiment B (b), with dissolved organic carbon (DOC) additions and/or changed light climate through shading. Values are mean ($\pm\text{SE}$, $n=5$). Error bars are sometimes so small that they are hidden within the symbols.

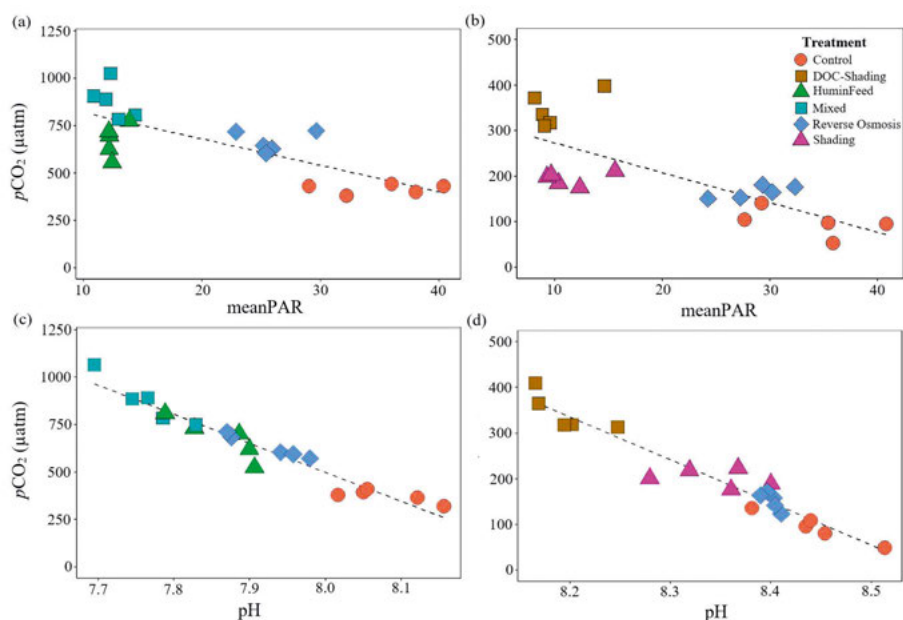


Figure 6 Relationships between partial pressure of carbon dioxide ($p\text{CO}_2$) and average photosynthetically active radiation (meanPAR) throughout the entire water column in the mesocosm (a, b) and time-weighted averaged pH (c, d) from two four-week mesocosm experiments with dissolved organic carbon (DOC) additions and/or changed light climate through shading (see legend in figure for treatments). The left panel refer to result from the first experiment and the right panel refer to the second experiment.

Nutrient limitation can also be an important factor controlling primary production and thus regulating $p\text{CO}_2$ (Figure 1). In Paper II, the DOC additions led to higher concentrations of total P, which is another proxy indicator of primary production since P often is the limiting nutrient for primary production in inland waters. If the primary producers in the mesocosms were nutrient limited, this enhanced total P should have led to increased primary production, and consequently decreased $p\text{CO}_2$. However, the opposite pattern was observed. In Paper IV, total P was used as a proxy indicator for primary production, in addition to light climate, and no evidence for nutrient-limited primary production being the reason for the observed $p\text{CO}_2$ increase in the lakes during the period 1997 to 2013 was found. In regards to the streams in Paper IV, three of the five study streams had decreased significantly in total P during the 21-year study period and it is possible that this hampered primary production, which resulted in the $p\text{CO}_2$ increase. Overall, there were high variations in the relationships between changes in $p\text{CO}_2$ and total P, suggesting that in some waters nutrient limited primary production could be driving factor for $p\text{CO}_2$, whereas in other waters this process would be less important.

In the mesocosm experiments (Paper II), there was also a strong relationship between $p\text{CO}_2$ and pH (Figure 6c, d). Allochthonous DOC can be quite

acidic due to humic acids. In the first experiment there were two different sources of DOC, and one of these, which was extracted from humic stream water (i.e., the reverse osmosis treatment) had a pH of 3.4. This reverse osmosis DOC was also used in the second experiment. All reverse osmosis DOC addition treatments showed a significant increase in $p\text{CO}_2$ already on the day after DOC additions. This acidic DOC input probably resulted in an instant shift in the carbonate system with decreased pH and a subsequent increase in $p\text{CO}_2$. The reduced primary production due to changes in the light climate could also have led to a reduced pH, adding on to the observed negative relationship between $p\text{CO}_2$ and pH. This was particularly apparent in the second experiment in the treatment with added DOC and changed light climate due to shading as this treatment had a much higher $p\text{CO}_2$ than the treatment with only DOC addition, despite having the same DOC concentrations. In Paper IV, two of the five streams decreased in pH, hence it is possible that the observed long-term $p\text{CO}_2$ increase was due to distribution changes within the carbonate system in these two waters. The importance of the carbonate system on surface water $p\text{CO}_2$ has recently been demonstrated (Marce *et al.* 2015; Stets *et al.* 2017) and the results from this thesis further emphasize the need of acknowledging the carbonate system in research of CO_2 dynamics in inland waters and subsequent gas exchange with the atmosphere.

Paper IV also allowed us to explore the factors affecting DOC mineralization within lakes and streams, such as DOC concentration, water temperature and DOC quality (Figure 1). Of the eight lakes and five streams, four lakes and two streams had increased significantly in DOC during the 21-year study period (Figure 4). Despite the general uncoupling of long-term DOC- $p\text{CO}_2$, it is still possible that in these four lakes and two streams, the long-term $p\text{CO}_2$ increase was due to enhanced microbial mineralization resulting from increased DOC concentrations. Temperature can also affect microbial mineralization of DOC as enhanced temperatures have been shown to lead to higher mineralization rates in lake sediments (Gudas *et al.* 2010). Increased temperature was found in only one of the 13 study waters in Paper IV, hence there was no strong trend suggesting temperature would be a key internal driver of surface water $p\text{CO}_2$. The quality of DOC could also be an important driver of surface water $p\text{CO}_2$ (Bodmer *et al.* 2016) and in five of the eight lakes and in three of the five streams changes in at least one of the DOC quality proxy indicators, $\text{abs}_{420}/\text{DOC}$ and C:N (i.e., the ratio between DOC and dissolved organic N) were observed. The most pronounced DOC quality change was a significant increase in C:N, which occurred in five lakes and two streams. An increased C:N suggests that the proportion of humic-like DOC has increased (Kothawala *et al.* 2014). There is however, some disagreement regarding the reactivity of humic-like DOC. While it has been argued in some studies that humic-like DOC can be considered recalcitrant (Hosen *et al.* 2014; Miller & McKnight 2010), in other studies, bioreactivity of DOC has been found to increase with increased proportions of humic-like DOC (Amon & Benner

1996; Bodmer *et al.* 2016). Larger and more complex organic compounds have also been shown to be associated with elevated CO₂ levels (D'Amario & Xenopoulos 2015). The results of this thesis are in line with the findings of Amon & Benner (1996), Bodmer *et al.* (2016) and D'Amario & Xenopoulos (2015), however, more research into the reactivity of DOC of different quality and how this changes through time is needed.

External drivers of surface water $p\text{CO}_2$

External (i.e., catchment processes) drivers can be as, or even more, important as internal drivers for regulating inland surface water $p\text{CO}_2$ (Figure 1) and this was further explored in Paper III and Paper IV. In Paper III, dissolved and gaseous carbon species in groundwater at 3 to 20 m depth in a boreal catchment were quantified. The aim was to get a better understanding of the carbon biogeochemistry of intermediate groundwater since this water can be an important contributor to surface water chemistry in downstream rivers, particularly during base flow, and in lakes (Hagedorn *et al.* 2000; Hood *et al.* 2005; Maberly *et al.* 2013). The groundwater sampled from all 16 wells was supersaturated with CO₂ relative to the atmosphere. This finding is in agreement with previous studies investigating CO₂ concentrations in groundwater in the U.S (Boerner & Gates 2015; Macpherson 2009). A relationship between $p\text{CO}_2$ and depth of the well, with decreasing $p\text{CO}_2$ with depth, was also observed (Figure 7a). It is quite possible that soil respiration decreases further down the soil profile and this could be the reason for the negative $p\text{CO}_2$ -depth relationship. There was also a negative relationship between $p\text{CO}_2$ and pH (Figure 7c) as well as a positive relationship between pH and depth (Figure 7b). The negative relationship between $p\text{CO}_2$ and pH was not a surprise, as they are tightly linked and can control each other. Consequently, the negative $p\text{CO}_2$ -depth relationship could be a result of the positive pH-depth relationship, which could be due to increased silicate weathering with depth. Higher silicate weathering and subsequent increased pH in deeper groundwater has previously been shown for groundwater down to 4.3 m depth (Klaminder *et al.* 2011). Whether the $p\text{CO}_2$ and pH relationships with depth are due to changes in soil respiration or silicate weathering cannot for certain be determined from the results of this thesis. Both processes are most probably very important in the soils of this catchment and it is likely that they change with depth. Hence, the observed $p\text{CO}_2$ and pH relationships with depth are likely due to a combination of both processes. Due to the tight link between $p\text{CO}_2$ and soil respiration as well as silicate weathering, these processes can be important external drivers for surface water $p\text{CO}_2$.

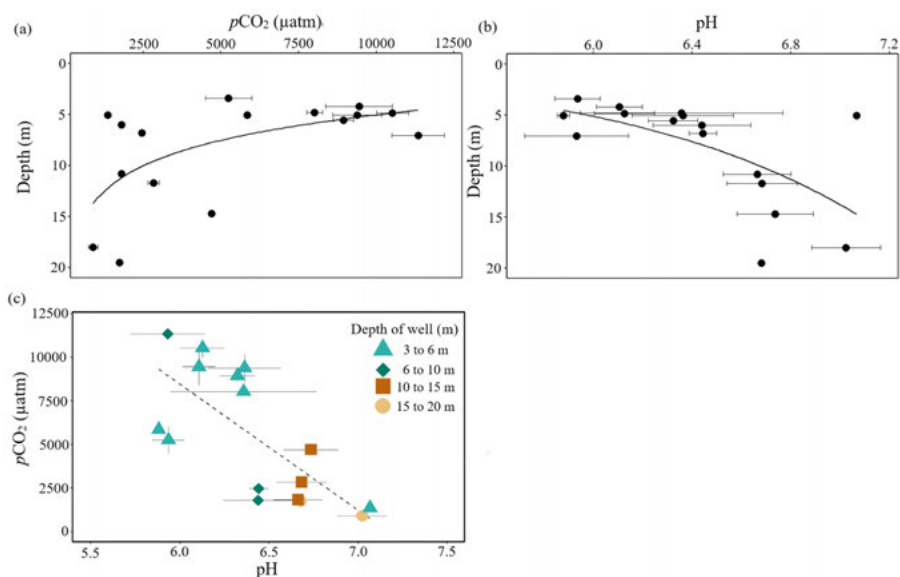


Figure 7 The partial pressure of carbon dioxide ($p\text{CO}_2$) (a) and pH (b) in groundwater wells at different depths and the relationship between $p\text{CO}_2$ and pH (c) in the groundwater of the Krycklan catchment. The symbols in panel c are color coded according to the depth of the sampled well. For all variables, data are presented as mean values \pm standard error ($n=3$, SE).

Although it was hypothesized that the observed long-term $p\text{CO}_2$ increase could have been due to increased groundwater level, since groundwater can be an important source of CO_2 to surface water, no support for this hypothesis was found in Paper IV. During the 21-year study period from 1997 to 2017, groundwater levels had remained the same in all 13 study catchments, except the catchment of the stream Bergmyrbäcken, where groundwater levels had decreased. Since precipitation can affect the ratio of surface runoff to groundwater input to lakes and streams, and thus surface water $p\text{CO}_2$, long-term trends in precipitation were also investigated. As with groundwater, very little change had occurred in precipitation during the period 1997 to 2017 in the study catchments. Precipitation had remained the same in all study catchments, except the catchment of Fräcksjön where precipitation had decreased. Since a decrease in precipitation could lead to lower surface runoff to groundwater input, and thus more CO_2 -rich groundwater entering the lake, the observed decrease in precipitation could potentially be the reason to the observed $p\text{CO}_2$ increase in Fräcksjön. Overall, very little long-term changes in the hydrological processes in the study catchments were found. Likewise, the conditions were stable across seasons in all measured organic and inorganic carbon species in the study catchment investigated in Paper III. This suggests that below ground conditions are generally stable through time and although groundwater can be an important regulator of surface water chemistry, internal

processes appeared to more strongly regulate $p\text{CO}_2$ of the study waters of Paper IV than external processes.

Conclusions and Future Perspectives

The role of inland waters in the carbon cycle, particularly the transport and transformation of carbon along the land to ocean aquatic continuum, through river systems, lakes, estuaries and coastal waters, to the open ocean must be considered in climate change mitigation schemes. In the most recent report of the Intergovernmental Panel on Climate change (IPCC), alarming information on accelerated global warming can be found (IPCC 2014). Global warming is to a large extent induced by greenhouse gas emissions, and more than one quarter of the total annual CO₂ emissions is emitted from inland waters (Drake *et al.* 2018; IPCC 2014). Consequently, inland waters play an important role for greenhouse gas emissions, hence future estimates of CO₂ emissions from inland waters are needed. Additionally, understanding the turnover of carbon in inland water ecosystems and integrating these fluxes into the global carbon cycle are important steps toward appropriate CO₂ management. One important step towards better predictions of future CO₂ emissions from inland waters and better management practices towards CO₂ mitigation is to better understand the biogeochemical and hydrological mechanisms regulating inland water CO₂ concentrations, which was the main goal of this thesis. Overall, the complexity of the drivers of CO₂ dynamics in inland waters is demonstrated and several mechanisms that are at play concomitantly are highlighted (Table 1, Figure 8). On a spatial scale, there is a positive DOC-*p*CO₂ relationship and therefore DOC concentrations are often used to predict *p*CO₂ and thereby CO₂ emissions from inland waters. Consequently, it was expected that the observed increase in surface water DOC concentration across the boreal region over the past 20 years had resulted in an increase in *p*CO₂, however a positive relationship on a temporal scale could not be established. Furthermore, in our mesocosm study no support for the hypothesis that increased allochthonous DOC input stimulates bacterial activities was found. Instead, addition of DOC to lake water in our mesocosm experiments resulted in a reduction of light available for photosynthesis thus reducing the photosynthesis to respiration ratio, which turned out to be the main driver of the increased *p*CO₂. Another key driver of the increased *p*CO₂ was an increase in pH due to decreased photosynthesis as well as addition of acidic DOC. If the input of colored DOC to inland waters increase in a warmer and wetter climate, the light conditions may change sufficiently to suppress primary production and lead to enhanced CO₂ emissions. In the fourth paper, it was shown that reasons behind *p*CO₂ increases are rather site-specific with complex interactions of drivers that

clearly differed between lakes and streams. The dominating mechanism in lakes was stimulation of microbial mineralization by increased DOC and/or changed DOC quality or suppressed primary production due to light limitation by increased water color. In streams, the dominating mechanism was either carbonate system distribution changes due to decreased pH or a possible decreased primary production due to nutrient limitation. Such site-specific patterns show the importance of including several $p\text{CO}_2$ driving mechanisms, and of recognizing the difference between lakes and streams, when aiming to predict future CO_2 emissions from inland waters. Consequently, simulations of future CO_2 emissions from inland waters need to consider the findings of this thesis.

Table 1. Summary of the key hydrological and biogeochemical surface water CO_2 driving mechanisms found in the studies of this thesis.

<i>System</i>	<i>Mechanism</i>
<i>Lakes</i>	
Internal	Light limitation/decreased photosynthesis (Paper II, IV) Increased acidity/decreased pH (Paper II) Increased DOC concentration (Paper IV) Changed DOC quality (Paper IV)
<i>Streams</i>	
Internal	Increased acidity/decreased pH (Paper IV) Nutrient limitation/decreased photosynthesis (Paper IV)
<i>Lakes & Streams</i>	
External	Surface runoff (Paper I) Groundwater input (Paper I, III) <ul style="list-style-type: none"> • Soil respiration (Paper III) • Weathering/pH (Paper III)

For future studies one important topic to investigate is the relationship between DOC quality and $p\text{CO}_2$. Both the quality of DOC within inland waters and in the catchment soils as both could have an effect on surface water $p\text{CO}_2$. Moreover, food web processes were not covered in this thesis, but could potentially also be strong regulators of CO_2 emissions from inland waters and should therefore be considered in future studies. Furthermore, in Paper III, concentrations of both organic and inorganic carbon species in groundwater were shown to vary greatly on a spatial scale. This information is critical when aiming to upscale carbon concentrations in groundwater to regional or larger scale since it shows the importance of multiple sampling locations as well as sampling at different depths. Groundwater can be an indirect source of CO_2 emissions due to the influence of groundwater on surface water chemistry, therefore more studies into the carbon dynamics of groundwater are needed.

It could be particularly useful to model groundwater movement and investigate the connectivity between groundwater at different depths and surface water.

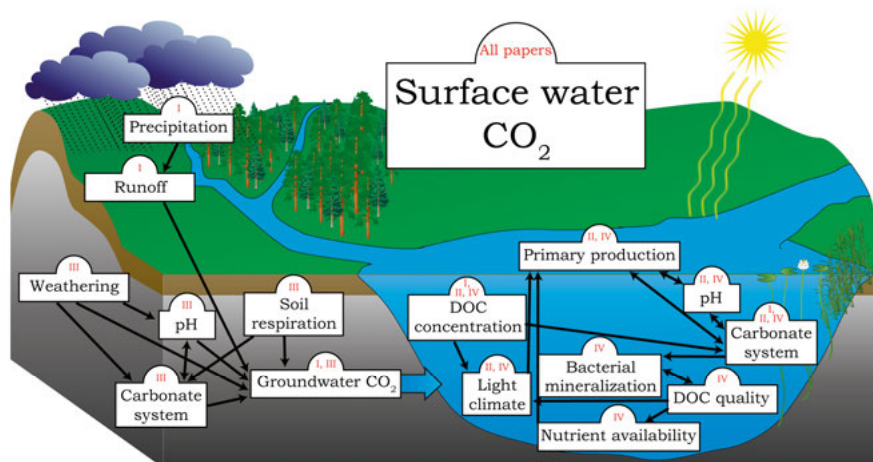


Figure 8 Conceptual figure showing the key biogeochemical and hydrological mechanisms driving CO₂ concentrations in surface waters of boreal lakes and streams, which are discussed in this thesis. The mechanisms that are shown in figure 1, but not in figure 8 were found not to be important for CO₂ concentrations in the boreal lakes and streams included in this thesis. Photochemical oxidation was however removed as it was not investigated in the studies of this thesis. The different roman numbers refers to the papers of this thesis where the processes were found to be dominating.

Sammanfattning på svenska

Inlandsvatten är en essentiell resurs för liv på jorden. Förutom det självklara att inlandsvatten används som dricksvatten, förser inlandsvatten mänskligheten med många viktiga funktioner som produktion av mat och energi, transport och rekreation. Trots att inlandsvatten endast täcker ungefär 1% av jordens yta så har de stor betydelse i jordens kretslopp av kol. Kol är en av livets byggstenar och förekommer i alla levande organismer. Kol förekommer som organiska och oorganiska föreningar och kan genom ett antal olika biokemiska processer lätt omvandlas från den ena föreningen till den andra. Omvandlingen av organiskt kol till oorganiskt kol sker genom respiration och nedbrytning medan omvandling av oorganiskt kol till organisk kol sker via fotosyntes. Dessa processer definierar huvudsakligen levande organismer och spelar därför en grundläggande roll för livet på jorden. Kol ingår i växthusgasen koldioxid som har ökat markant i atmosfären genom mänsklig påverkan och lett till påtagliga klimatförändringar.

Inlandsvatten kan innehålla stora mängder kol och koldioxid. Mycket av kolet i inlandsvatten kommer från omgivande skog och mark och tidigare trodde forskare att inlandsvatten endast transporterar kol vidare till haven. Numera vet man att en stor del av kolet som kommer från omkringliggande mark omvandlas i sjöar och vattendrag till koldioxid genom mikrobiella processer. Grundvatten kan genom nedbrytningsprocesser i jorden också bestå av höga mängder koldioxid. En stor del av koldioxiden i sjöar och vattendrag har producerats direkt i marken och tillförs till vattnet via grundvatten. Det finns även andra viktiga processer som kan leda till ändrade koldioxidhalter i inlandsvatten, som bland annat fotosyntes av växtplankton och alger och förändringar i pH genom t.ex. försurning. Fotosyntes av växtalger leder också till att organiskt kol produceras inom sjöar och vattendrag. Organiskt kol från terrestra miljöer består till stor del av humus, vilket övervägande utgörs av nedbrutna växtdelar, och är brunsvart till färgen. Detta gör att inlandsvatten med höga mängder organiskt kol är brunaktigt. Ökad brunhet i vatten på grund av höga mängder organiskt kol kan leda till minskad produktion av växtalger eftersom den bruna färgen på vattnet gör att mindre ljus finns tillgängligt för fotosyntes. Humus har också lågt pH, vilket gör att en ökad mängd organiskt kol kan leda till försurning. Organiskt kol kan vara av olika kvalitet, dels på grund av var det har producerats och dels på hur det har bearbetats, vilket gör det lättare eller svårare för bakterier att bryta ner det och omvandla det till koldioxid.

Genom alla de processer som kan leda till ökade koldioxidhalter i inlandsvatten är många av jordens sjöar och vattendrag övermättade i koldioxid. Detta gör att många inlandsvatten avger koldioxid till atmosfären. Trots svårigheten att få fram exakta siffror på hur mycket koldioxid som avges från jordens alla sjöar och vattendrag så visar ny forskning tydligt på att det handlar om mer koldioxid än alla terrestra ekosystem tillsammans tar upp ifrån atmosfären av de utsläpp som människan orsakar. För att kunna förstå och förutspå hur koldioxidnivåer i sjöar och vattendrag ändras i förhållande till miljöförändringar är det viktigt att förstå processerna som reglerar koldioxidhalterna i inlandsvatten. Det främsta syftet med denna avhandling var därför att undersöka både de koldioxidreglerande processer som verkar inom sjöar och vattendrag och de koldioxidreglerande processer som verkar i marken som omgärdar våra inlandsvatten. Det andra syftet med denna avhandling var att studera de lång- och kortsiktiga effekter ökad organisk kolmängd har på koldioxidhalter i inlandsvatten.

I den första studien undersöktes vattenkemin i över hundra Svenska sjöar, vattendrag och flodmynningar för att identifiera hur koldioxidhalterna påverkats av ökad tillförsel av organiskt kol under en 17-årsperiod. I den andra studien undersökte vi hur en ökad tillförsel av organiskt kol kortsiktigt påverkar koldioxidhalten i sjövattnet. Detta gjordes genom två mesokosm experiment i sjön Erken i östra Sverige där vi manipulerade mängden organiskt kol samt ljusklimatet. I det tredje projektet studerade vi mängden organiskt och oorganiskt kol i grundvattnet i ett avrinningsområde i norra Sverige. Vi tog prover från 16 grundvattenbrunnar som var mellan 3 och 20 m djupa. Detta gjordes på våren, sommaren och hösten för att se om det var någon skillnad mellan de olika säsongerna. I den fjärde studien återgick vi till de sjöar och vattendrag från första studien som hade ökat i koldioxidhalt för att undersöka orsaken till ökningen.

Eftersom bakterier bryter ner organiskt kol och då bildar koldioxid förväntade vi oss att den ökade mängden organiskt kol i ytvattnet skulle leda till ökade koldioxidhalter i vår första studie. Dock visade våra resultat att de flesta vatten som visade på ökade mängder organiskt kol inte hade fått högre koldioxidhalter under de 17 år som studien täckte. Även om den ökade mängden organiskt kol skulle ha lett till en ökad bakteriell nedbrytning så märktes ej detta på koldioxidhalterna. Det kan vara så att den ökade nederbörd som observerats över stora delar av Sverige de senaste 20 åren har lett till att en större del av vattenkemin i sjöar och vattendrag påverkas av ytavrinning än av grundvattentillförsel. Vatten som tillförs till inlandsvatten genom ytavrinning består av större mängder organiskt kol och mindre mängder koldioxid, medan förhållandena är det motsatta för grundvattnet. Att grundvattnet kan ha höga halter av koldioxid men små mängder organiskt kol var något vi visade i den tredje studien. Den ökade nederbörden kan därför leda till en ökad mängd organiskt

kol i ytvatten utan att koldioxidhalten höjs. Samtidigt kan ökad nederbörd resultera i brunare vatten, vilket i sin tur leder till ett ändrat ljusklimat som kan påverka växtplankton.

Resultaten från de två mesokosmexperimenten visade tydligt att den ökade mängden organiskt kol ledde till en ökad koldioxidhalt, och detta var till följd av minskad fotosyntes av växtalgerna på grund av det ändrade ljusklimat som det organiska kolet medförde. Tillsättning av det organiska kolet gjorde att mängden ljus i vattnet minskade markant, vilket medförde att växtalgerna tog upp mindre koldioxid eftersom det fanns mindre ljus tillgängligt för fotosyntes, vilket ledde till ökade koldioxidhalter. Tillsättningen av organiskt kol ledde också till en försurning som gjorde att koldioxidhalterna ökade. Resultat från den fjärde studien, där vi undersökte orsaken till varför koldioxidhalten i några svenska sjöar och vattendrag hade ökat markant under en 21-års period, visar också på hur ändrat ljusklimat och försurning kan leda till högre koldioxidhalter i inlandsvatten. Resultaten från den fjärde studien visade också på att kvalitén på det organiska kolet kan ha stor betydelse för hur mycket som omvandlas till koldioxid.

Eftersom processer i omgivande mark också kan ha stor betydelse för koldioxidhalter i ytvatten undersökte vi hur koldioxidhalterna i grundvatten kan variera på olika djup i marken. Genomgående fann vi höga mängder koldioxid på alla uppmätta djup över hela avrinningsområdet vi studerade. Överlag så minskade koldioxidmängden med djup vilket tyder på att de bakteriella aktiviteterna också minskade med djup. Samtidigt kan silikatvittringen ha ökat på djupare nivåer, vilket också leder till lägre koldioxidhalt.

Sammantaget visar resultaten från denna avhandling att det är stor variation i vilken koldioxidreglerande process som har störst påverkan på koldioxidhalten i inlandsvatten. Vi fann inget samband mellan koldioxidhalt och mikrobiell aktivitet, varken på kort eller på lång sikt. Istället visade våra resultat att brunare vatten på grund av ökat organiskt material gjorde att växtplankton och alger hade mindre ljus tillgängligt för fotosyntes vilket ledde till minskat upptag av koldioxid och därmed högre koldioxidhalt i vattnet. Förändringar i pH på grund av försurning från organiskt material och från minskad fotosyntes gjorde också att koldioxidhalten höjdes. Vilka koldioxidreglerande processer som är viktigast kan skilja mellan sjöar och vattendrag, vilket våra resultat tydligt visade. Mängden organiskt material och ljusklimatet visades vara av stor vikt i sjöar, medan i vattendrag så var surhetsgrad och mängden näring för växtplankton och alger viktiga koldioxidreglerande processer. Tidsperspektivet kan också ha väldigt stor betydelse. Därför är det viktigt att undersöka processer både på kort och på lång sikt. En stor del av jordens sjöar och vattendrag kommer fortsätta vara koldioxidkällor i ett ändrat klimat. Ett ändrat klimat kommer sannolikt att påverka våra inlandsvatten, men hur de påverkas kan vara väldigt individuellt.

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