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Temporal Trends in Dissolved Inorganic Carbon in a Swedish Boreal Catchment

Lukas Rehn

ABSTRACT

Temporal Trends in Dissolved Inorganic Carbon in a Swedish Boreal Catchment

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Inland waters are important systems for transforming, storing and transporting carbon along the aquatic continuum, but also by emitting carbon dioxide (CO_2) and methane (CH_4) to the atmosphere. In light of the last decades observed increase in dissolved organic carbon (DOC) in many inland waters across the northern hemisphere, a logical question arise whether other aquatic carbon species display similar trends. This study examined the measured concentrations of dissolved inorganic carbon (DIC) in a boreal catchment over a 14-year period. The objectives were to determine changes in DIC concentration over time and try to explain the causes for the observed changes. Data from 15 mostly forested sub-catchments were analyzed, both over the full time period, and grouped by season. Over the full 14-year period, only two of the sites exhibited significant trends in DIC concentration, both being negative. However, by seasonally grouping the data distinct patterns for the different seasons emerged. The autumn and winter data displayed no significant trends, whereas the spring flood data showed significant negative trends for almost all sites (14 out of 15). The summer data showed significant negative trends for seven sites, and positive for one site. The DIC concentration data were expectedly positively correlated with pH across most sites (13 out of 15). The correlation with DOC was negative for most sites (11 out of 15), possibly indicating different origins of the different carbon species. The DIC concentration was also negatively correlated with discharge for most sites (13 out of 15), suggesting a diluting effect with increased discharge. In conclusion, significant negative trends were observed during the spring flood and summer periods. Although the cause of these trends will require further investigation, the correlation analysis showed that the DIC concentration was closely related to the catchment hydrology. This suggests changes in terrestrial source areas where DIC is mobilized during spring and summer, and that these changes might continue during altered hydrometeorological conditions. The differences in DIC trends between sub-catchments further show the variability of the boreal landscape and highlight the need for local-scale process understanding when scaling to larger landscape units. We further conclude that trends in DIC concentration do not follow observed DOC changes over time, suggesting that DIC and DOC exports are mechanistically decoupled.

Keywords: Boreal catchments, carbon cycling, CO_2, DIC, headwater streams, Krycklan Catchment Study, trend analysis

Department of Earth Sciences, Program for Air, Water and Landscape Sciences, Uppsala university, Villavägen 16, SE-75236 Uppsala, Sverige.

REFERAT

Temporala trender i löst oorganiskt kol i ett svenskt borealt avrinningsområde

Lukas Rehn

Sjöar och vattendrag är viktiga system för att omvandla, lagra och transportera kol, men också genom att avge koldioxid (CO_2) och metan (CH_4) till atmosfären. Med tanke på de senaste decenniernas observerade ökning i löst organiskt kol (DOC) i flera inlandsvatten på Norra halvklotet är det logiskt att fråga sig huruvida andra akvatiska kolformer uppvisar liknande trender. Den här studien undersökte de uppmätta koncentrationerna löst oorganiskt kol (DIC) i ett borealt avrinningsområde under en 14-årsperiod. Syftet med studien var att fastställa om koncentrationen DIC hade förändrats över tid och försöka avgöra vad som hade orsakat förändringarna. Data från 15 huvudsakligen skogstäckta delavrinningsområden analyserades, dels över den fullständiga 14-årsperioden, dels med data grupperad efter årstid. Över den fullständiga perioden uppvisade endast två av mätplatserna signifikanta trender i DIC-koncentration, varav båda negativa. När datan grupperades beroende på årstid framträdde dock distinkta mönster för de olika årstiderna. Höst- och vinterdatan uppvisade inga signifikanta trender, men vårflodsdatan uppvisade signifikanta negativa trender för nästan alla platser (14 av 15). Sommardatan visade signifikanta negativa trender för sju platser, och en signifikant positiv trend för en plats. DIC-koncentrationerna var som förväntat positivt korrelerade med pH för de flesta mätplatserna (13 av 15). Korrelationen med DOC var negativ för de flesta platserna (11 av 15), vilket möjligen indikerar att de olika kolformerna har olika ursprung i avrinningsområdet. DIC-koncentrationen korrelerade också negativt med avrinning för de flesta platserna (13 av 15), vilket tyder på en utspädningseffekt vid ökad avrinning. Sammanfattningsvis observerades negativa trender under vårflods- och sommarperioderna. Även om vidare undersökningar krävs för att fastställa orsaken till de här trenderna visade korrelationsanalysen att DIC-koncentrationerna var nära relaterade till avrinningsområdets hydrologi. Detta indikerar en förändring i hur terrestra källor till DIC mobiliseras under vår och sommar, och att förändringen kan komma att fortlöpa under fortsatt ändrade hydrometrologiska förhållanden. Skillnaderna i DIC-koncentrationernas trender mellan delavrinningsområden visar dessutom på variabiliteten i det boreala landskapet, och belyser vikten av att förstå lokala processer för att kunna skala upp resultaten till större landskapsnivåer. Slutligen drogs också slutsatsen att trenderna i DIC-koncentration inte följer de observerade förändringarna över tid i DOC, vilket tyder på att de båda kolformerna inte är mekanistiskt sammankopplade.

Nyckelord: Boreala avrinningsområden, kolcykeln, DIC, koldioxid, trendanalys

Institutionen för geovetenskaper, Luft-, vatten- och landskapslära, Uppsala universitet, Villavägen 16, SE-75236 Uppsala, Sverige.

PREFACE

This master thesis constitutes 30 hp and concludes my time at the Master's Programme in Environmental and Water Engineering at Uppsala University. The thesis was supervised by Marcus Wallin at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences, SLU. The subject reviewer was Thomas Grabs at the Department of Earth Sciences at Uppsala University.

I would first and foremost like to thank Marcus Wallin for his endless support in making this project happen and for letting me use his figure of the pH-dependent speciation of DIC (from his own master thesis, no less). I would also like to thank my subject reviewer Thomas Grabs, Hjalmar Laudon at SLU in Umeå, and Ryan Sponseller at Umeå University for lending me their insights on methods, results and conclusions, all of which have helped me refine the thesis considerably. Further, I would like to thank Kim Lindgren at SLU in Umeå for helping me find the right data, and Alberto Zanella, doctoral student at SLU in Uppsala, who showed me around the Krycklan catchment and made my field trip there much more enjoyable. Finally, I would like to thank my partner Agnes Wallberg, and my dog Juni, for keeping me sane with plenty of dog walks, throughout a pandemic that made work difficult. This is the end of my studies at Uppsala University, but it is the start of something new.

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Vi lever i en värld av förändring och ovisshet, inte minst när det kommer till frågor om miljön. Det rapporteras nästan dagligen om klimatförändringar, luftkvalitet och vattenföroreningar – problem som har konsekvenser för både människor och natur. Ett grundämne som ofta står i fokus i miljöfrågor är kolet. Kol förekommer i många olika former, och hur kol cirkulerar mellan olika system på jorden beskrivs av det som ofta kallas för den globala kolcykeln. Vi känner till stora delar av hur kolcykeln hänger ihop, och att de olika delarna av den påverkas av miljön på flera olika sätt. Det har till exempel konstaterats sedan flera år tillbaka att halten löst organiskt kol, kallat DOC (dissolved organic carbon), i vattendrag och sjöar har ökat i stora delar av världen. Detta kallas för brunifiering och får stora konsekvenser för vattenkvalitet, bland annat genom att göra dricksvattenrening betydligt mer kostsamt. Brunifiering är intressant eftersom det lyfter frågan: ökar halterna av andra typer av kol också i vattendrag? En form av kol som är betydligt mindre studerad än DOC är det som kallas löst oorganiskt kol eller DIC (dissolved inorganic carbon), vilket är ett samlingsnamn för löst koldioxid och de karbonat- och bikarbonatjoner som bildas när koldioxid löses upp i vatten. Det är väl känt att koldioxid i vatten kan avges till atmosfären, och att mängden koldioxid som avges från sjöar och vattendrag världen över har en betydelsefull påverkan på kolbalansen. Men något som varit i princip okänt hittills, och något som skulle kunna ha stor påverkan på klimatet, är om DIC-koncentrationerna i vattendrag har förändrats över tid på samma sätt som DOC.

För att studera trenderna i DIC undersökte jag ett avrinningsområde som kallas Krycklan och som ligger några mil nordväst om Umeå i norra Sverige. Krycklan ingår i ett miljöövervakningsprogram som är ämnat att kartlägga olika typer av miljöförändringar i Sverige. Krycklan delas i sin tur upp i flera mindre delavrinningsområden, och vattenmätningar genomförs i utloppet till varje område för att ge en bild av hur vattenkvalitet och flöden ser ut i just det området. Ett av de mått som samlats in under lång tid i de här områdena är just DIC. Genom att studera 14 år av data var planen att se om halten DIC i vattendragen hade förändrats på samma sätt som DOC hade gjort, eller om det fanns andra trender. Det finns ett visst stöd för att DOC och DIC skulle vara länkade, och därför var det tänkbart att trenderna skulle se liknande ut. Så visade sig inte vara fallet. Sett över hela 14-årsperioden fanns det nästan inga mätbara förändringar alls. I två av de 15 vattendragen syntes en minskning i DIC över åren, tvärt emot trenderna i DOC, men i de andra vattendragen syntes ingen skillnad alls. Det här resultatet var minst sagt lite förvånande, så jag bestämde mig för att gräva lite till. När datan delades upp i årstider, så att all data från vintermånaderna undersöktes för sig, vårmånaderna för sig och så vidare, så tydliggjordes spännande mönster. Även om det var få delavrinningsområden som visade trender över hela 14-årsperioden så visade det sig att de flesta områden visade en minskning i DIC under just våren och sommaren, men att hösten och vintern inte visade några förändringar över huvud taget. Det fanns alltså helt olika beteenden i datan beroende på vilken årstid som studerades. För att ta reda på vad detta berodde på behövdes en undersökning av andra faktorer som kunde tänkas påverka DIC. De troligaste kandidaterna som fanns tillgängliga var vattnets surhet i form av pH, avrinningen i området och temperaturförhållandena. Vattnets surhet påverkar vilken form DIC tar i vattnet: surare vatten innebär att mer av DIC förekommer som koldioxid, som följaktligen kan avges till atmosfären, medan mer basiskt vatten leder till att DIC tar formen av karbonat- och bikarbonatjoner som inte kan avgasas. Högre pH ger alltså mindre flyktig DIC vilket gör

att halten kan vara högre. Avrinningen har visats vara viktig eftersom DIC som rinner ut i vattendrag till stor del produceras i jorden i avrinningsområdet. Högre flöden kan ge mer vatten som rinner av ytligt, vilket späder ut DIC-halten som kommer från jorden. Temperaturförhållandena spelar också roll, men på vilket sätt är inte lika slätstruket. Å ena sidan är biologiska organismer mer aktiva när det är varmt, så att mer koldioxid kan produceras i jorden när temperaturen är högre, å andra sidan är koldioxid mer lösligt i kallare vatten, så att lägre temperaturer i vattnet gör att mer koldioxid kan hållas kvar. I Krycklan visade sig högre pH mycket riktigt vara kopplat till högre DIC-halt, och högre vattenflöden gav upphov till en utspädningseffekt som minskade DIC-halten. Temperaturförhållandena visade sig inte vara så viktiga som jag hade trott i Krycklan. Det var avrinningen som enligt datan hade störst inverkan på DIC-halterna, och även om det inte syntes någon markant ökning av avrinning i området under studiens period så verkar det som att flödesförhållandena starkt påverkade vilka koncentrationer av DIC som mättes upp.

Resultaten blev inte riktigt så tydliga som jag hade tänkt mig och det gick inte att säga att DIC ökar på samma sätt som DOC. Resultaten visade istället på den stora komplexiteten i att uppskatta hur mycket DIC som rinner ut från skogsmarker, genom vattendrag och sedan antingen rinner vidare till havet eller avges till atmosfären. Det var tydligt att vattnets vägar genom landskapet hade en inverkan, och det verkade som om ändringar i flödesmönster var en viktig påverkande faktor på de DIC-halter som mättes upp under vår och sommar. Höstresultaten var svåra att förklara, men under vintern, när området oftast låg under snö, var aktiviteten låg och avrinningen minimal, och det skulle kunna vara anledningen till att DIC inte ändrades under de månaderna. Men under vårfloden och månaderna därefter visade resultaten tydligt att DIC-halterna hade minskat över åren. Det gick inte att säga exakt vad det berodde på, men förändringar i hur vattnet flödar genom avrinningsområdet tycks vara en av orsakerna. Samtidigt visade resultaten på stora variationer inom Krycklan. En av mätplatserna låg strax nedströms en sjö, och där syntes ingen koppling mellan avrinningen och DIC alls. En annan låg nedströms en myr, och där var kopplingen mellan DIC och DOC istället positiv. Även om det fanns trender som stämde för området i stort visade resultaten att skillnaderna kan vara stora, även inom ett relativt litet område, och även om större delen av området är täckt av skog.

Även om resultaten var spretiga och visade att variationen i DIC kan vara stor mellan både områden och årstider, så var det här en antydan om hur DIC-halterna har förändrats över tid. Det här arbetet väcker nya frågor: ser det likadant ut på andra platser i världen, och finns det flera förklaringar till trenderna än flödesvägarna? I framtiden förväntas stigande temperaturer föra med sig bland annat en ökad nederbörd och en längre växtsäsong, förändringar som kommer ha stor inverkan på det svenska skogslandskapet. Om trenderna fortsätter på samma sätt som de har gjort i Krycklan kommer koncentrationen av DIC-utsläppen från skogsmarken till vattendragen att fortsätta minska. Det skulle i så fall kunna göra att klimatpåverkan från de här akvatiska systemen minskar i storlek. Men det är viktigt att fortsätta undersöka vilka mekanismer som ligger bakom de här trenderna, och hur de mekanismerna kommer att förändras i framtiden. Den här studien har besvarat några av frågorna när det kommer till trender över tid i DIC-halter. Nu behövs vidare studier för att sätta in resultaten i ett större perspektiv.

CONTENTS

1 INTRODUCTION

In the face of the 21^{st} century's unprecedented environmental challenges, understanding the various stocks and flows of the carbon system is crucial in order to identify the human influence. All human activity affects this carbon balance, including our past and present land use. Carbon has accumulated in soils, peatlands and vegetation biomass both naturally and through human processes like forestry (Bradshaw & Warkentin 2015). Some of this terrestrial carbon is mobilized by water and carried as particulate or dissolved forms to streams, eventually reaching lakes and oceans across the world (Tranvik et al. 2009). One important carbon form is called dissolved inorganic carbon (DIC), a collective term referring to dissolved carbon dioxide (CO_2) in water, and its aquatic derivatives. The CO_2 efflux from inland waters globally has been estimated to be a disproportionately large source to the atmosphere in the global carbon budget, on par with the ocean carbon uptake (Raymond et al. 2013). In addition to the dire consequences of rising CO_2 levels in the atmosphere, increased concentrations of dissolved CO_2 in ocean waters pose a threat to marine ecosystems by causing ocean acidification (Doney et al. 2009), with DIC exports from inland waters contributing globally (Li et al. 2017). Despite the impacts of DIC on aquatic and terrestrial systems, DIC is still among the less studied carbon species, and many aspects of it remain unknown.

1.1 DISSOLVED INORGANIC CARBON

As carbon dioxide (CO_2) dissolves in water, it reacts with the water molecules to form carbonic acid (H_2CO_3), which in turn dissociates quickly into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions (Stumm & Morgan 2012). DIC constitutes the molecules CO_2, H_2CO_3, together with the ions HCO_3^- and CO_3^{2-} (Cole & Prairie 2014), and as such encompasses CO_2 and all of its aquatic derivatives. Usually, the quantities of CO_2 and H_2CO_3 are regarded as one entity, often simply called dissolved CO_2, since they are both uncharged molecules and function as a single chemical pool when reacting with their environment (Cole & Prairie 2014). The different DIC fractions are in constant equilibrium with each other, as detailed in equation 1.

$$CO_2 + H_2O \rightleftharpoons (H_2CO_3) \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-} \tag{1}$$

The relative prevalence of each fraction within the DIC pool is linked to the water's acidity (Stumm & Morgan 2012) (Figure 1). Higher pH values shifts the equilibrium towards the right, while lower pH values shifts it towards the left (Stumm & Morgan 2012). For example, if pH changes from 5 to 7, CO_2 shifts from being the dominant DIC species in terms of concentration, while HCO_3^- shifts to becoming dominant. Meanwhile, CO_3^{2-} remains virtually non-existent until pH rises further. This equilibrium is also temperature-dependent, as the temperature affects the solubility of the CO_2 (Stumm & Morgan 2012). A change in pH can be said to cause a shift in the DIC fractions, but the opposite is also true. If the amount of any one of the fractions is changed, equilibrium shifts away from that fraction, which in turn either liberates or consumes hydrogen ions (H^+), thus changing pH (Cole & Prairie 2014). This dynamic allows DIC to act as a buffer for small changes in pH.

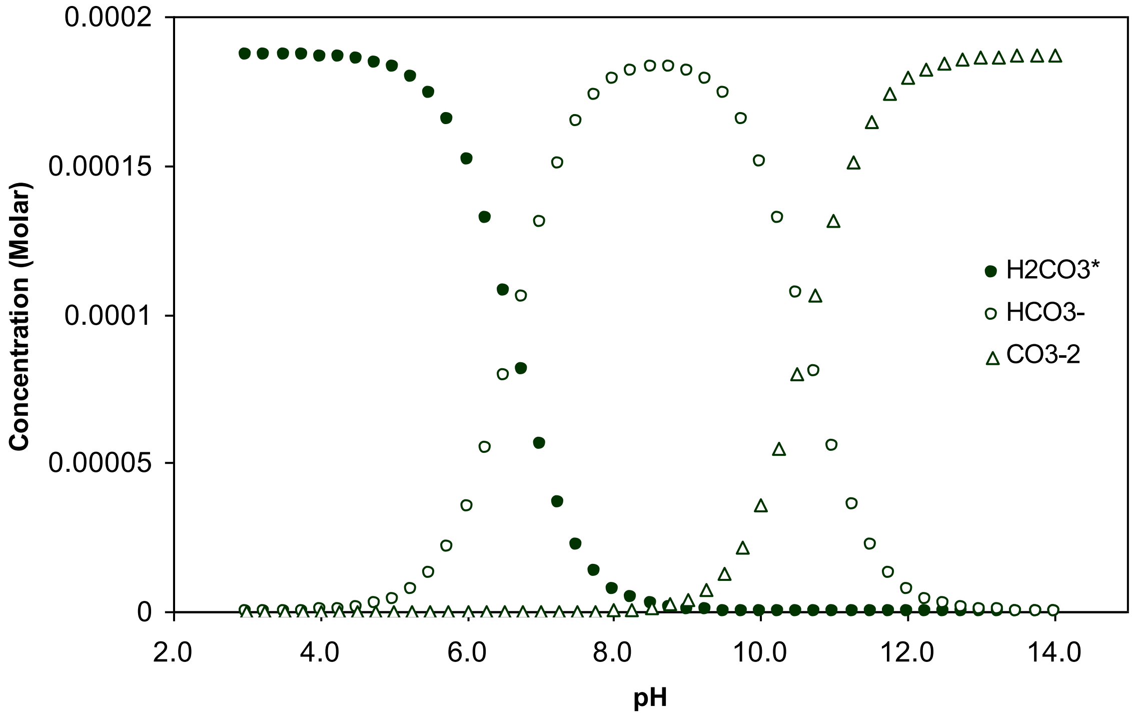

Figure 1: Example of the relative prevalence, in this case molar concentration, of H_2CO_3* (CO_2 and H_2CO_3 combined), HCO_3^- and CO_3^{2-} at different pH (Marcus Wallin, n.d.).

1.2 SOURCES OF DIC IN STREAMS

DIC can either be of biogenic (produced through biological processes) or geogenic (produced through abiotic processes) origin, often with one of the DIC fractions as the direct outcome. Through weathering processes, for example, HCO_3^- and CO_3^{2-} ions are released from bedrock to soils (Riebeek 2011). For regions with lime-rich bedrock and soils, this process can cause a high influx of DIC as CO_3^{2-}, even when the biological production of CO_2 is low (Hutchins, Prairie, & Giorgio 2019). In regions where calcareous rock is rare, silicate minerals can also contribute to an influx of HCO_3^- as weathering by carbonic acid consumes CO_2 and generates HCO_3^- (Stumm & Morgan 2012). This process notably does not change the overall DIC concentration but instead the relative prevalence of the fractions.

On the other end of the DIC equilibrium, CO_2 is commonly generated from biological processes like respiration and decomposition of organic matter (Mackenzie & Lerman 2006). This CO_2 can be produced in the surrounding catchment soils and transported via groundwater to surface waters, or produced in-situ in the lake or stream (Winterdahl et al. 2016). Alongside biological degradation processes like respiration, another considerable process of generating DIC in the stream is photo-oxidation. Photo-oxidation is the breaking down of organic compounds by sunlight, which can, based on the lighting conditions, create a substantial influx of DIC on par with in-stream respiration (Granéli, Lindell, & Tranvik 1996). Several studies have found that the external input of CO_2 from the surrounding catchment generally outweighs in-stream production in headwater streams (Humborg et al. 2010; Hutchins, Prairie, & Giorgio 2019; Winterdahl et al. 2016). This external dominance lessens gradually along the stream, however, as upstream CO_2 emits to the atmosphere while in-situ processes have more time to produce new CO_2 (Hotchkiss et al. 2015). In a study of carbon isotopes in four Swedish catchments, all four were found to be dominated by soil respiration, but the different catchments also showed some variability in the importance of other DIC sources (Campeau et al. 2017).

The spatial variability of the landscape complicates the flow paths and appearance of DIC considerably. The effects of large- and small-scale heterogeneity play an integral part in influencing the biogeochemical flows in a catchment (Laudon & Sponseller 2018). It has been shown that the spatial variability of DIC can be large even within smaller catchments (Kokic et al. 2015; Wallin et al. 2010), greatly complicating the prediction of DIC based on catchment characteristics. Some broad patterns have been suggested by previous studies, however. Soil type, for example, has been shown to influence DIC influx to streams. Leith et al. (2015) showed that the importance of riparian soils in supplying DIC was greater than uphill mineral soils, probably because of the higher water table limiting vertical diffusion of CO_2 in riparian soils, and the greater accumulation of organic material compared to the uphill slopes. Mires are also important landscape features in controlling carbon fluxes, but their impact on DIC concentrations appear more complex. Some studies (e.g. Rantakari et al. 2010) have found a positive relationship between mires and DIC, indicating that mires contribute more to DIC concentrations than some other landscape types, whereas others (e.g. Huotari et al. 2013) have found a negative relationship. One proposed explanation for the diverging results was suggested by Rantakari et al. (2010) to be whether the peatland was drained or not, with drained mires contributing less because CO_2 can be emitted to the atmosphere more easily while undrained mires constrain the vertical flux, similar to the results found for riparian soils by Leith et al. (2015).

In addition to spatial variations due to landscape types, DIC varies vertically with soil depth within a catchment. Soil characteristics play an integral role by impacting the hydrological pathways in the catchment (Novák & Hlaváčiková 2019), in turn affecting where DIC accumulates and where it can flow. The vertical distribution of DIC is not yet widely studied, but some examples exist. In one study of a soil transect next to a stream in a small boreal catchment, the highest concentrations of DIC were found at a depth of 40–60 cm, while concentrations were lower both below and above that soil depth (Öquist et al. 2009). Another study of CO_2 exports from riparian soils found that more than 70% of the CO_2 entered the stream at a depth of 30–50 cm, while the deeper soil horizons provided a lower, steady input of DIC (Leith et al. 2015). Both studies linked the influx of DIC to the water table, suggesting that DIC concentrations were highest just below the groundwater table. Winterdahl et al. (2016) also suggested that DIC from soil respiration supplied by groundwater was the dominating source of DIC in a stream.

1.3 SINKS FOR DIC AND THE STREAM–ATMOSPHERE EXCHANGE

The ionic fractions of DIC are transported along the aquatic continuum, eventually reaching the ocean (Carlson et al. 2001). An important quality of CO_2 that sets it apart from the other DIC fractions is that it is gaseous, and as such, CO_2 can diffuse across the stream surface to and from the atmosphere (Cole & Prairie 2014). This means that, in addition to the lateral transport of CO_2 through the stream network, there is a vertical exchange with the atmosphere. Though the extent of this water-atmosphere exchange is not entirely known, it has been estimated that inland waters make up an integral part of the global carbon cycle, contributing as a net-source of CO_2 to the atmosphere (Raymond et al. 2013). Several studies over the last decade have found streams to be supersaturated with CO_2, and subsequently emitting CO_2 to the atmosphere (Butman & Raymond 2011; Crawford et al. 2013; Giesler et al. 2013; Huotari et al. 2013; Hutchins, Prairie, & Giorgio 2019; Rawlins et al. 2014; Wallin et al. 2011). It has been estimated that most of the CO_2 in boreal waters emits to the atmosphere within the first few hundred meters of the stream network (Öquist et al. 2009), giving further importance to the small headwater streams. Lakes are important nodes in the stream network, where a vast number of processes convert, sequester and free up different carbon species in the water column and sediments (Tranvik et al. 2009). Longer retention times in lakes compared to streams give CO_2 more time to degas, while respiration processes in the lake have more time to convert organic carbon to CO_2 (Humborg et al. 2010). This shifts the relative importance of DIC-producing processes in the water compared to the surrounding catchment. Studies of Swedish lakes have indicated that terrestrial sources of DIC are still generally dominant, but that the contribution of aquatic processes can be considerable (Einarsdottir, Wallin, & Sobek 2017; Weyhenmeyer et al. 2015). The CO_2 that is not degassed to the atmosphere along the stream network can either be consumed by primary producers in the streams, lakes and oceans and incorporated into the aquatic food webs, or sequestered in the deep ocean together with the other DIC fractions (Carlson et al. 2001).

1.4 DIC IN BOREAL SYSTEMS

The boreal region stretches from approximately 40° to 60° N, encompassing a large part of North America and Eurasia (Hall et al. 2004). The region is typically characterized by an organogenic top soil and vast swaths of coniferous forest, with long, cold, snow-covered winters and short, warm summers (Hall et al. 2004). The snowmelt event constitutes a swift transition from winter to summer, radically impacting the hydrological pathways through the landscape (Hall et al. 2004). The boreal region is estimated to contain about one third of the world's terrestrial carbon pool, predominantly stored in soils and peatlands (Bradshaw & Warkentin 2015). Simultaneously, it is a region highly sensitive to even small changes in climate (Bradshaw & Warkentin 2015; Hall et al. 2004). The United Nations' Intergovernmental Panel on Climate Change (IPCC) has predicted that both abiotic disturbance factors like forest fires, and biotic disturbance factors like invasive pests, could come to considerably alter boreal ecosystems in the near future (Jia et al. 2019). There are historic examples of the vulnerability of these systems, such as the many decades of anthropogenic acidification following industrial emissions of sulfur and nitrogen, from which many inland waters in the Nordic countries are still recovering (Arvola et al. 2010). As the boreal region contains perhaps the single largest terrestrial carbon stock in the world (Bradshaw & Warkentin 2015) while also being susceptible to alterations because of current and future environmental shifts, mapping and understanding the carbon fluxes within the region is of utmost importance.

The DIC concentrations found in waters across the boreal landscape varies greatly. In a study of several catchments of different sizes and characteristics, encompassing 190 streams and rivers, in Quebec, Canada, the values ranged from median 1.9 mg/L in one catchment to median 6.9 mg/L, with considerable variability within and between catchments (Hutchins, Prairie, & Giorgio 2019). Two studies on Finnish stream networks reported total inorganic carbon (TIC, comprised of DIC plus particulate inorganic carbon) and DIC concentrations, respectively; one for several catchments in eastern Finland (Rantakari et al. 2010), and one for the sub-catchments to lake Pääjärvi in the south of Finland (Huotari et al. 2013). Rantakari et al. (2010) found TIC concentrations ranging from

0.8 to 6.9 mg/L while Huotari et al. (2013) found DIC concentrations between 2.5 and 7.8 mg/L. Rantakari et al. (2010) also displayed a great temporal variability in measurements collected during different times of year. In the inlet to the central Swedish lake Gäddtjärn, Einarsdottir, Wallin, & Sobek (2017) measured DIC concentrations of between 0.8 and 1.6 mg/L; on the low end of the other studies. DIC concentrations have also been studied in the Degerö mire, northwest of Umeå, Sweden, where Leach et al. (2016) reported DIC concentrations between approximately 0 and 20 mg/L for the period 2003–2014, further showing the temporal and spatial variability of DIC.

During recent decades an increase in the concentration of another important form of carbon, dissolved organic carbon (DOC)[1] has been observed, in surface waters across much of the boreal region (Porcal et al. 2009). Many potential causes for this have been suggested, including alterations of precipitation and hydrology, decreased sulfur depositions and increasing air temperatures (Porcal et al. 2009). The temporal changes and patterns in DOC have been studied across various landscape scales, from single catchments (e.g. Fork, Sponseller, & Laudon 2020, Laudon et al. 2011) to entire regions (e.g. Wit et al. 2016). Meanwhile, the corresponding trends in DIC remain largely uncharted. Some properties of DIC have been examined, for example what causes influxes of DIC to streams (Giesler et al. 2013; Hutchins, Prairie, & Giorgio 2019; Smits et al. 2017), and the mechanics and patterns in CO_2 efflux from streams and lakes to the atmosphere (Huotari et al. 2013; Wallin et al. 2011), but the long-term trends in DIC concentrations, how they relate to climate change and the repercussions of these changes, are all areas where little is known. At time of writing, the author is not aware of any long-term studies of DIC data in boreal systems. Furthermore, a positive spatial relationship between DIC and DOC in boreal waters has been suggested (Lapierre et al. 2013; Sobek et al. 2003), possibly due to DOC being a direct source of CO_2 through respiration and photodegradation (Lapierre et al. 2013). The validity of this relationship across the temporal scale has been questioned, however. In a study of several lakes, streams and river mouths across the Swedish landscape, significant increases in DOC were found in a majority of the water bodies while a significant increase in the partial pressure of CO_2 was only reported in a few of the sites (Nydahl, Wallin, & Weyhenmeyer 2017). Humborg et al. (2010) proposed that organic carbon and weathering-induced HCO_3^- and CO_3^{2-} ions in Swedish lakes and streams followed different hydrological pathways. Organic carbon was located mostly in the top layer of soil while the DIC fractions were found in deeper horizons, indicating that the carbon species followed different patterns of hydrological mobilization. Both DOC and DIC, as well as the interactions between them, make up important parts of the global carbon cycle, with impacts on water chemistry, ecosystems and atmospheric CO_2 levels. Studying if DIC follows similar or different trends as DOC, and why, is therefore an important part in our understanding of how boreal systems function today and how they will function in the future.

[1]DOC constitutes the carbon component of dissolved organic matter.

1.5 OBJECTIVES

The purpose of this study was to examine how DIC concentrations have changed within a typical boreal catchment, the Krycklan catchment, during a 14-year period (2006–2019). The aim was further to investigate differences in the data between 15 sub-catchments, to analyze which trends, if any, are present in the data, and to identify the causes of the observed trends in DIC. In order to do this, three main objectives were devised:

- Determine the spatial variability in DIC concentrations among the sub-catchments within the Krycklan catchment.
- Analyze the temporal trends in DIC concentration for each sub-catchment, both on an annual scale and for specific seasons, and examine how the trends differ between different sub-catchments.
- Examine the temporal trends in other chemical and physical variables, and how these variables relate to DIC.

2 METHODS

2.1 SITE DESCRIPTION

The study was conducted within the Krycklan catchment, which is located ca 50 km northwest of Umeå in Sweden, at 64°14′N, 19°46′E (Figure 2). The 68 km^2 catchment ranges in elevation from 114 to 405 meters above sea level (a.s.l.), and is predominantly covered by forest, mires and stream-lake networks. Due to the highest postglacial sea level being 257 m a.s.l., soils above that level are predominantly characterized by till and peat, whereas soils below it are mostly made up of postglacial sediments (Laudon et al. 2013). Almost 87% of the catchment area is forested, populated by Scots pine (*Pinus sylvestris*), and Norway spruce (*Picea abies*) in varying amounts, with a smaller population of Birch (*Betula ssp.*) (Laudon et al. 2013). The mean annual air temperature for the period 1981–2010 was 1.8 °C, with monthly means ranging from –9.5 °C in January to 14.7 °C in July. The mean annual precipitation was 614 mm and the mean annual runoff 311 mm (Laudon et al. 2013). These values should be treated with caution, however, as the climate conditions in Krycklan have changed drastically over the last three decades, with increasing temperatures and an increase in the number of extreme weather events, such as droughts and torrential rains (Laudon & Sponseller 2018).

The Krycklan catchment is divided into sub-catchments based on their topography (Ågren et al. 2007) (Figures 2 and 3). The areas of each sub-catchment, their respective land cover and soil characteristics were outlined by Laudon et al. (2013). The outlet of each sub-catchment, where sampling is conducted, is instrumented for hydrological monitoring (see example, Figure 4). The Strahler stream order[2] for the monitoring sites has been determined by Ågren et al. (2007). The sub-catchments span four stream orders and range in size from 12 to almost 6800 ha. Though the primary land use is forest, some of the sub-catchments, especially 4 and 5, also have a high percentage mire or peatland (Table 1).

2.2 DATA DESCRIPTION

All of the data used in the analyses of this study were downloaded on 2020–09–01 from the Svartberget data portal, which can be accessed through the Krycklan Catchment Study website[3]. Along with DIC, data for five other variables were downloaded – DOC, pH, air temperature, discharge and water temperature (Table 2). Data for different sub-catchments and different variables were not always collected on the same dates, and the sampling frequency was not consistent in time and between variables. For most records of DIC, however, corresponding measurements for the other variables existed. In sections 2.2.1 – 2.2.6, sampling and analysis details for each variable are outlined.

The additional variables were chosen for their established or proposed impact on DIC: DOC to examine if the suggested spatial relationship with DIC (Lapierre et al. 2013; Sobek et al. 2003) holds true across time in the Krycklan data; pH because it affects the DIC speciation (Butler 2019), and subsequently how much CO_2 can dissipate from the

[2] Strahler order starts at 1 for headwater streams, and increases by one when two streams of the same order join. If two streams of different order join, the largest of the two orders is kept.

[3] `https://www.slu.se/en/departments/field-based-forest-research/experimental-forests/vindeln-experimental-forests/krycklan/`

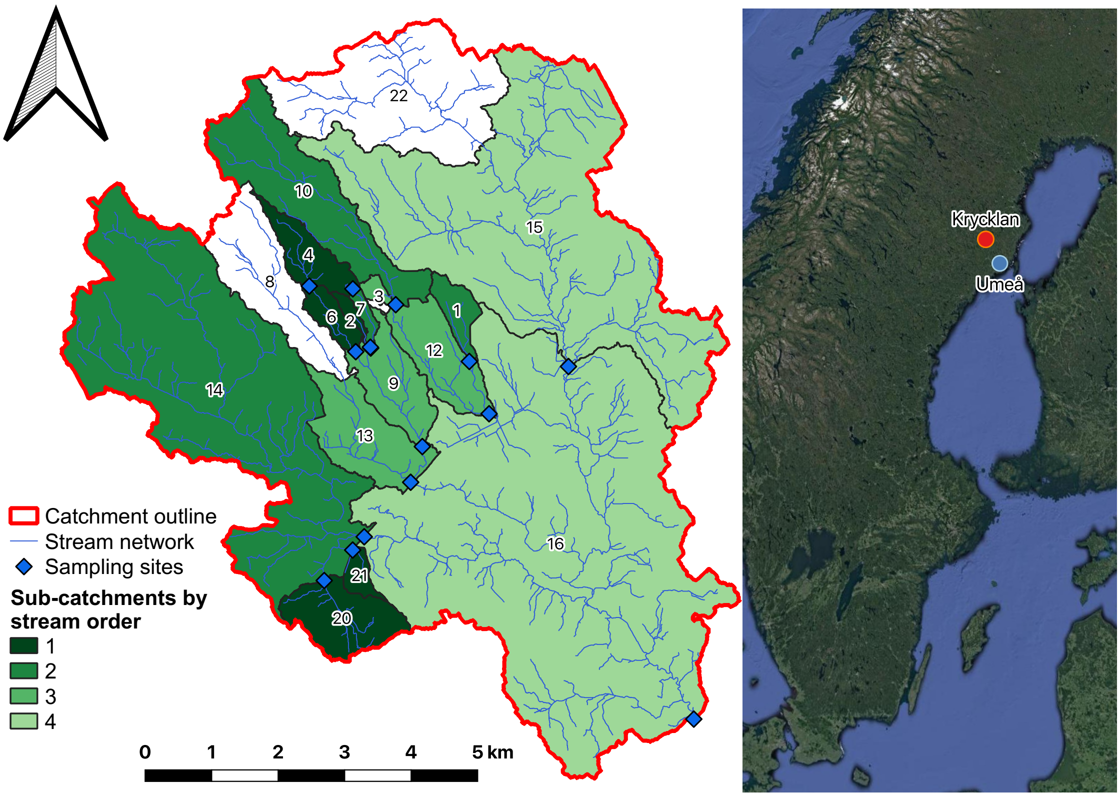

Figure 2: The Krycklan catchment and its sub-catchments grouped by stream order, along with stream network and sampling sites (left), and the catchment's position relative to Umeå in Sweden (right). Note that sites 3, 8 and 22 were not included in the study. Background map is satellite imagery for GIS from Google Maps (2020) Krycklan catchment map and characteristics from the open GIS files at the Krycklan Catchment Study web site.

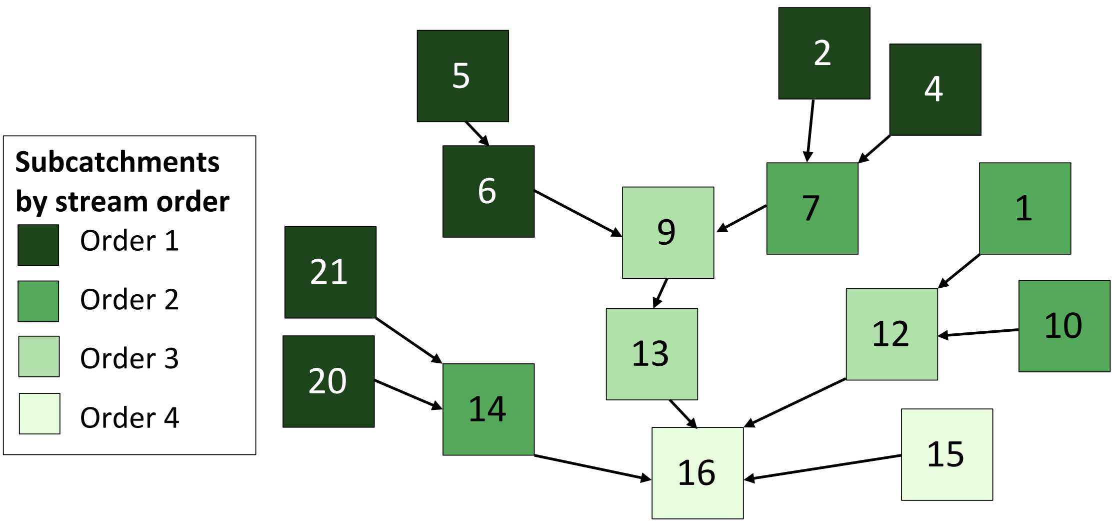

Figure 3: Schematic overview of how the sub-catchments within Krycklan are connected.

Figure 4: Catchment outlet and monitoring site for sub-catchment 1, instrumented with a v-notch weir (Lukas Rehn, 2020-10-21).

Table 1: Characteristics for the Krycklan sub-catchments relevant to this study. Area and land use data from Laudon et al. (2013) and stream order for sub-catchments 1–16 from Ågren et al. (2007).

Sub-catchment	Stream order at outlet	Area (ha)	Lakes (%)	Forest (%)	Mire (%)	Arable and open land (%)
1	2	48	0.0	98.0	2.0	0.0
2	1	12	0.0	99.9	0.0	0.0
4	1	18	0.0	55.9	41.1	0.0
5	1	65	6.4	54.0	39.5	0.0
6	1	110	3.8	71.4	24.8	0.0
7	2	47	0.0	82.0	18.0	0.0
9	3	288	1.5	84.4	14.1	0.0
10	2	336	0.0	73.8	26.1	0.0
12	3	544	0.0	82.6	17.3	0.0
13	3	700	0.7	88.2	10.3	0.8
14	2	1410	0.7	90.1	5.4	3.8
15	4	1913	2.4	81.6	14.5	1.5
16	4	6709	1.0	87.2	8.7	3.0
20	1	145	0.0	87.7	9.6	2.6
21	1	26	0.0	98.9	1.0	0.0

Table 2: Number of observations available for each variable in each site (2006–2019). Air temperature data was available in one climate station, separate from the sites.

Site	DIC	DOC	pH	Air temperature	Discharge	Water temperature
S 1	303	289	294		660	615
S 2	319	305	310		4065	1067
S 4	333	319	325		3897	
S 5	325	312	316		1747	1400
S 6	325	313	315		1548	
S 7	327	315	319	6153	4700	4360
S 9	328	315	320		3615	3114
S 10	309	296	300			
S 12	293	282	285		3852	2595
S 13	316	306	308		3218	1664
S 14	300	288	291		3490	2225
S 15	299	287	290			3240
S 16	319	307	310		4224	2874
S 20	285	272	275		3733	
S 21	222	211	214			

streams; discharge to represent the hydrological conditions in the stream, and to examine if DIC was diluted following high flows, such as has been suggested (Dinsmore & Billett 2008; Lynch et al. 2010); air- and water temperature data to accommodate the expected behavior of DIC to increase during the growing season (Öquist et al. 2009).

2.2.1 Dissolved Inorganic Carbon

For all sites, DIC data were available for the entire study period 2006-2019. DIC sampling was done using a headspace method where bubble-free water (2 ml in 2006, for the remaining years 5 ml) was injected in a 22.5 ml glass vial which was sealed with a bromobutyl rubber septa (Wallin et al. 2010). The vials were prepared with N_2 headspace and, between 2006 and 2011, 0.5 ml 0.6% HCL to acidify the samples, while from 2011 onward, HCL was replaced with 0.1 ml 85% H_3PO_4 (Leach et al. 2016). Samples were stored for up to a week in 4 °C before being analyzed using a gas chromatograph with methanizer and flame ionization detector equipped (GC–FID) (Leach et al. 2016). Between 2006 and 2011, the GC–FID used was a PerkinElmer Clarus 500, while from 2011 forward, a PerkinElmer Clarus 580 connected to a Turbo Matrix 110 autosampler replaced the previous GC–FID (Leach et al. 2016). This acidified headspace method was compared to the more common direct headspace method by Åberg & Wallin (2014), who found that differences between the methods were minor.

2.2.2 Dissolved Organic Carbon

For all sites, DOC data were available for the entire study period 2006-2019. Samples of DOC were collected and filtered in the lab using a 0.45 µm MCE membrane, Millipore, after which they were stored and refrigerated for up to 10 days (Fork, Sponseller, & Laudon 2020). The samples were analyzed on a Shimadzu TOC analyzer (Shimadzu, Duisburg, Germany) (Fork, Sponseller, & Laudon 2020).

2.2.3 pH

Like DIC and DOC, pH data were available for all sites for the entire study period 2006-2019. Samples of pH were collected in polyethylene bottles without headspace, stored dark and cold, and analyzed in a lab within 24 hours of sampling (Wallin et al. 2010). For the period 2006–2010, analysis was done using an Orion 9272 pH meter with a Ross 8102 low-conductivity combination electrode equipped, at 20 °C (Wallin et al. 2010). From 2011, the analysis was conducted using an automated titrator with a temperature-controlled flow-through cell at 20 °C (Neubauer et al. 2013).

2.2.4 Discharge

Daily discharge data were only available for some of the sites and for different time periods, with many data ranges being much shorter than the study period. Site 7 had the longest series of data, 2006-2018. To be able to compare DIC with discharge for all sites, it was assumed that the hydrological conditions in Krycklan were homogeneous enough to use discharge data from site 7 to approximate discharge in other sites. Specific discharge (discharge per area unit), was calculated from site 7 according to equation 2, where q_s is specific discharge (mm/day), Q is discharge (L/s) and A is sub-catchment area (m^2). Thereafter, the specific discharge was multiplied with the area of each sub-catchment to find the approximated discharge for that site.

$$q_s = 24 * 3600 * \frac{Q}{A} \tag{2}$$

The approximated data were validated by checking the relative difference between calculated and measured data for the other sites where data was available (Appendix A). Doing this, some records produced large errors, particularly for low discharge values, but the vast majority of records had errors very close to 0. Sites 2 and 20 had the largest and most frequent relative errors. Discharge data were collected as high-resolution logger data (Laudon et al. 2013).

2.2.5 Water Temperature

Water temperature data, like discharge, were only available for some of the sites and for incomplete time series. Site 7 was the only site with a complete record of water temperature data for the period 2006–2019. Again, like for discharge, it was assumed that site 7 was approximately representative of the other sites in terms of water temperature. The water temperature for site 7 was therefore used for all sites. This approximated water temperature was then validated by checking the relative errors between the data for site 7 and the other respective sites (Appendix A). A few records produced very large relative errors but the vast majority of records had values relative errors very close to 0. Water temperature data were collected as high-resolution logger data (Laudon et al. 2013).

2.2.6 Air Temperature

For air temperature measurements, the main measuring site in Krycklan, called Hygget, was chosen. Hygget is located at 225 meters a.s.l. in the southwestern part of the Krycklan catchment (64°14′N, 19°46′E). Since it is a single measuring site, the measured temperature is likely to differ from actual temperature at the different sites, like water temperature differs. This affects the accuracy of the analyses, but like water temperature, it is expected that this difference is relatively small for most records. According to the Reference Climate Monitoring Program at SLU experimental forests and SITES Svartberget, daily mean air temperature data were based on minute measurements using a thermistor (Campbell Sci. model T107) in a ventilated radiation shield, 1.7 m above the ground (SITES 2020).

2.3 ANALYSIS METHODS AND STATISTICAL SIGNIFICANCE

All statistical tests were conducted on each of the 15 sites, corresponding to the 15 sub-catchments. Thus, for every test, results for all 15 sites were displayed. For most graphical analyses, the results from four sites, one of each stream order, were displayed, with the remaining plots in each test's respective appendix. The four chosen sites were 4, 7, 13 and 16. These sub-catchments are also connected, with sub-catchment 4 flowing into 7, sub-catchment 7 flowing into 13 (via 9), and sub-catchment 13 flowing into 16, where the site corresponds to the outlet for the Krycklan catchment (Figure 3).

For the analyses, the significance level 5% was chosen ($p \leq 0.05$), meaning that the for each analysis, it is 95% confident that the confidence interval contains the true value. To that is added the estimate of the true value given by the analysis. In essence, the estimated values of each analysis are considered significant if the p-value is less than or equal to 0.05. Additionally, 10% significance levels were also noted ($p \leq 0.1$) to catch any trends that had p-values just outside the predetermined 95% confidence range. This was done to see if many of the trends would have been significant if a less strict significance level was chosen for the estimate.

2.4 EXPLORATORY DATA ANALYSIS

In order to determine if all the data were usable and which statistical methods to choose for the analyses, the data were first visualized and examined. The extent of the time series for all sites and variables were checked so that any gaps or inconsistencies in the data were known. The DIC data for each site were then visualized as time series, histograms and boxplots using the ggplot2 package in RStudio. To find if the DIC data were normally distributed, the data were examined using quantile quantile plots (QQ-plots) and the Shapiro-Wilk test of normality. A QQ-plot plots the data distribution as a function of the normal distribution (Davies 2016). If the data follows the normal distribution, the resulting data points will all lie on a straight line, but if any part of the data is non-normally distributed, that part of the data will deviate (Wilk & Gnanadesikan 1968). The Shapiro-Wilk test is a statistical test to find if the data set significantly deviates from the normal distribution (Davies 2016).

Based on the results from the exploratory data analysis (Section 3.1), it was decided that non-parametric analysis methods were to be used.

2.5 SPATIAL PATTERNS IN THE DIC CONCENTRATION DATA

The DIC distributions and time series were first examined qualitatively for each site to display any spatial patterns in the data. Differences in DIC levels between the sites were noted by looking at the time series and boxplots in relation to each other. The distributions of DIC data were compared between sites by ordering the sites by total sub-catchment area, land use (percentage mire of total sub-catchment area) and stream order. Stream order was seen as a way to group the sites by their relative placements in the catchment, with lower stream order corresponding to places higher up in the catchment and higher stream orders corresponding to places where many streams have already joined.

2.6 TEMPORAL TRENDS IN THE DIC CONCENTRATION DATA

To analyze temporal trends in the DIC data, Mann-Kendall (MK) trend tests and their associated Theil-Sen slope estimates were chosen as the method of analysis. This was deemed suitable for the data at hand, since MK tests do not require the data to follow any specific distribution, and since MK tests have historically been favoured when working with hydrological and environmental data (Hipel & McLeod 1994).

2.6.1 Mann-Kendall Tests and Theil-Sen Slopes

The MK test is a non-parametric test designed to find significant trends in data series (Hipel & McLeod 1994). Being non-parametric, the test is independent of distribution, which means that it is suitable to use on non-normally distributed data where parametric methods, like linear regression, can be less reliable or more difficult to apply (Hipel & McLeod 1994). The null hypothesis for the MK test is that the data comes from a population of random, independent and identically distributed variables (Hipel & McLeod 1994). Following that, the alternative hypothesis is that the data follows a monotonic trend[4] (Hipel & McLeod 1994). For a data set of n random observations from a population, x_1, x_2, ..., x_n, the test statistic S is calculated according to equation 3. This equates to comparing each data point to all previous points in the data set and finding whether the latter point has a higher, equal or lower value than the former, assigning that pair +1, 0 or -1 respectively, before summing up the results to give S.

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} sgn(x_j - x_k),\ sgn(x) = \begin{Bmatrix} +1 & x > 0 \\ 0 & x = 0 \\ -1 & x < 0 \end{Bmatrix} \tag{3}$$

A positive S value indicates that there are more points later in the data with a higher value, than there are earlier in the data, while a negative S indicates the opposite (Hipel & McLeod 1994). As the number of observations increases, the distribution of the statistic S approaches the normal distribution (Hipel & McLeod 1994). The variance in S is then used to calculate standard normal variance, which is compared to the desired significance level (Hipel & McLeod 1994). If S is found to be significantly positive, the data set exhibits a monotonic positive trend, and conversely, if S is found to be significantly negative, the data set exhibits a monotonic negative trend (Hipel & McLeod 1994).

The Theil-Sen slope estimator[5] is used as an indicator of the degree of change in the data set per unit time. In order to determine the slope, first the slopes of each individual pair of points are calculated by taking $\Delta y/\Delta x$, where Δy is the difference in value between the data points and Δx is the distance between the data points (Helsel & Hirsch 2002). The different slopes are then ranked by size and the median slope is selected, yielding

[4] A monotonic trend is either never-decreasing, i.e. positive and/or flat everywhere, or never-increasing, i.e. negative and/or flat everywhere.

[5] The Theil-Sen slope estimator is sometimes called Kendall-Theil robust line, or a number of different similar terms.

a result that is highly resistant to outliers (Helsel & Hirsch 2002). Thus, the Theil-Sen slope does not give an estimate of actual rate of change throughout the data set, but rather gives a median rate of change for the data. This gives some indication about the size of the change, but does not give an exact estimation.

2.6.2 Trend Tests for the Full Time Period Data Sets

To compute MK tests in RStudio, the package *rkt* (Marchetto 2017) was used. This package was chosen for its ability to easily compute different kinds of MK tests, for its ability to calculate the Theil-Sen slope and because it has been used in a previous studies of water chemistry, including DOC, in Krycklan (Fork, Sponseller, & Laudon 2020; Laudon, Sponseller, & Bishop 2020). The *rkt* package requires dates expressed as years or fractions of years, so whenever more than one data point was used for a year, the dates were expressed as the current year with the day of month as a decimal (for example, the date 2009–02–10 corresponds to 2009.11). This means that Theil-Sen slope estimators for DIC are expressed in the unit mg/L/year.

The MK tests were computed for the monthly median values of the complete 2006–2019 data set. Monthly medians were used instead of all values because different parts of the year had a different number of records (with many more records during the spring months than the rest of the year, and very few records during winter). This uneven distribution meant that if all data were considered, the spring months would contribute more records to the overall trend, and thus the overall trend would be unevenly weighted and misleading.

2.6.3 Trend Tests for Individual Months

MK tests were computed on each month of each site separately. This was to find if the trends in all months were similar or not. For this test, all data for each month was used instead of only monthly median data. Data within each month were evenly distributed, so it was assumed that the collected data records in each month were representative of the DIC concentrations in that site during that month. The issue of uneven weighting for different months outlined for the full time period MK tests was not a problem here, because the MK tests for different months were conducted separately. Thus, the statistical strength of the MK tests differed between months[6]. The benefit of using all data instead of monthly median data was that all tests would be more accurate, even if they would not be equally accurate.

In order to calculate a MK test, at least 4 data records are required (Marchetto 2017). Though the total data sets were all well above 4 records each, the total number of records available for each month was examined to make sure that MK tests could be carried out for each month individually, as well as any desired groupings of months. For most sites, there were about 8–70 records per month across the full time period, with fewer records during the winter months and more records during April and May. Only one month for one site, February for site 21, had fewer than 4 records across all the years. Thus, MK tests were computed for all months and sites except February for site 21.

[6]For example, even if May and June would exhibit equivalent MK trends for a site, the p-value would likely be smaller for May because of the difference in available data

2.6.4 Trend Tests for Grouped Data

In addition to running MK tests for each month, the data was further grouped into different seasons depending on expected similarities in the data. To determine appropriate groupings, the MK tests for individual months were checked to find which months had similar trends for any given site. Seasonal patterns in the boreal hydrological regime were also considered. Many different groupings were tested by alternating the number of seasons and shifting the months between the seasons, based on the appearance of the MK tests for the individual months. The seasonal division that seemed to capture the most of the patterns within the months MK test was ultimately chosen. This division used four seasons, roughly corresponding to winter, the spring flood, summer and autumn. The four seasons division was obtained by classifying the individual months' Theil-Sen slopes as either positive (above 0.02 mg/L/year), neutral (between –0.02 and 0.02 mg/L/year) or negative (below 0.02 mg/L/year), regardless of significance. This was done to see if the different months followed similar trends, and where the trends shifted in the data. Based on these trends, it was decided to divide the data into winter (December–March), spring flood (April–May), summer (June–August) and autumn (September–November).

As with the MK tests for individual months, all available data for any given season were used. It was assumed that the data were roughly evenly distributed within each season and that they were representative of the DIC concentrations in that site for that season. Though the exact number of data points for each month within any given season did not match completely, the seasons were constructed so that all months within each season had a similar number of records. As with the months, the four seasons contained different amounts of data, with about 20-50 records per site for winter across the 14-year period, 80–140 records per site for spring, 60–80 records per site for summer and 60–70 records per site for autumn. Thus, different statistical accuracies were expected for the different seasons.

2.7 TEMPORAL TRENDS IN EXPLANATORY VARIABLES

In order to understand how the other variables related to DIC, their individual data ranges were first examined using MK tests in the same way as for DIC. For the full time period MK tests, monthly median data were used for all variables. For the individual months MK tests, all available data for each month were used for each variable. For the seasonally grouped MK tests, all available data for each season were used for the variables DOC and pH. The amounts of data available for discharge, air temperature and water temperature, however, were too large to compute MK tests on the complete data sets using the available computer. To circumvent this technical issue, weekly mean values were calculated for those variables and MK tests for the seasonally grouped discharge, air temperature and water temperature data computed for weekly mean data instead.

2.8 CORRELATION ANALYSIS WITH KENDALL'S τ

There are several alternatives when determining the correlation between data sets, each with different calculation methods. For non-normally distributed data, Kendall's rank correlation test and its associated coefficient τ, and Spearman's rank correlation test and its associated coefficient ρ, are among the most common tests. Kendall's τ is a measurement of the strength of monotonic relationship in a data set (Helsel & Hirsch 2002). In fact, the MK test is a special case of the Kendall correlation test. Kendall's τ can be determined by calculating the MK test statistic S, and dividing it by the maximum theoretical value of S (which occurs when $x_1 < x_2 < ... < x_n$) (Hipel & McLeod 1994). In other words, the Kendall rank correlation test is a test of how closely a given data set follows a perfect positive monotonic trend. Kendall's τ can assume values between –1 and 1. Though both Kendall's τ and Spearman's ρ are frequently used, some authors have proposed that Kendall's τ is preferable, in part because the coefficient is easier to interpret than Spearman's ρ (Kruskal 1958; Newson 2002). Another case for Kendall's τ is that it is more resistant to outliers and thus useful for heavily skewed data (Helsel & Hirsch 2002). In studies of the performance of both correlation coefficients, however, they have performed similarly, though Spearman's ρ has a tendency to yield slightly higher values than Kendall's τ (Helsel & Hirsch 2002; Winner 2006).

Kendall's τ was chosen as the correlation coefficient for this study, partly because it is more applicable to skewed data with extreme outliers, partly because it is easier to interpret directly and in relation to the MK tests. Kendall's τ and the p-values for Kendall's τ were calculated for all sites, for the correlation between DIC and DOC, pH, mean air temperature, discharge and water temperature, respectively.

2.8.1 Plots of DIC as a Function of the Explanatory Variables

As a complement to the correlation analysis, DIC was plotted as a function of DOC, pH, air temperature, discharge and water temperature. This was done to check the relationships between DIC and the explanatory variables for linearity or any other patterns. The plots for four sites were chosen to be displayed in Results, one of each stream order.

Table 3: Summary of included data for each statistical test.

Analysis	Data used
For DIC	
Graphical spatial analysis	All data
Full time period MK test	Monthly median values
Individual months MK test	All data for that month
Individual seasons MK test	All data for that season
For DOC and pH	
Full time period MK test	Monthly median values
Individual months MK test	All data for that month
Individual seasons MK test	All data for that season
For discharge, air temp and water temp	
Full time period MK test	Monthly median values
Individual months MK test	All data for that month
Individual seasons MK test	Weekly mean data for that season
For all variables	
Correlation analysis	All data

3 RESULTS

3.1 EXPLORATORY DATA ANALYSIS

Upon visual examination of the histograms and boxplots for DIC concentration in the different sites, data in all sites exhibited positive skew, and all sites included several high-value outliers (Appendix B). Furthermore, QQ-plots and Shapiro-Wilk tests for all sites indicated that the DIC data for all sites were significantly non-normally distributed. The site-specific DIC time series (Figure 5 and Appendix B), showed similar disparate, slightly cyclical patterns for all sites. There were no large gaps in the DIC data.

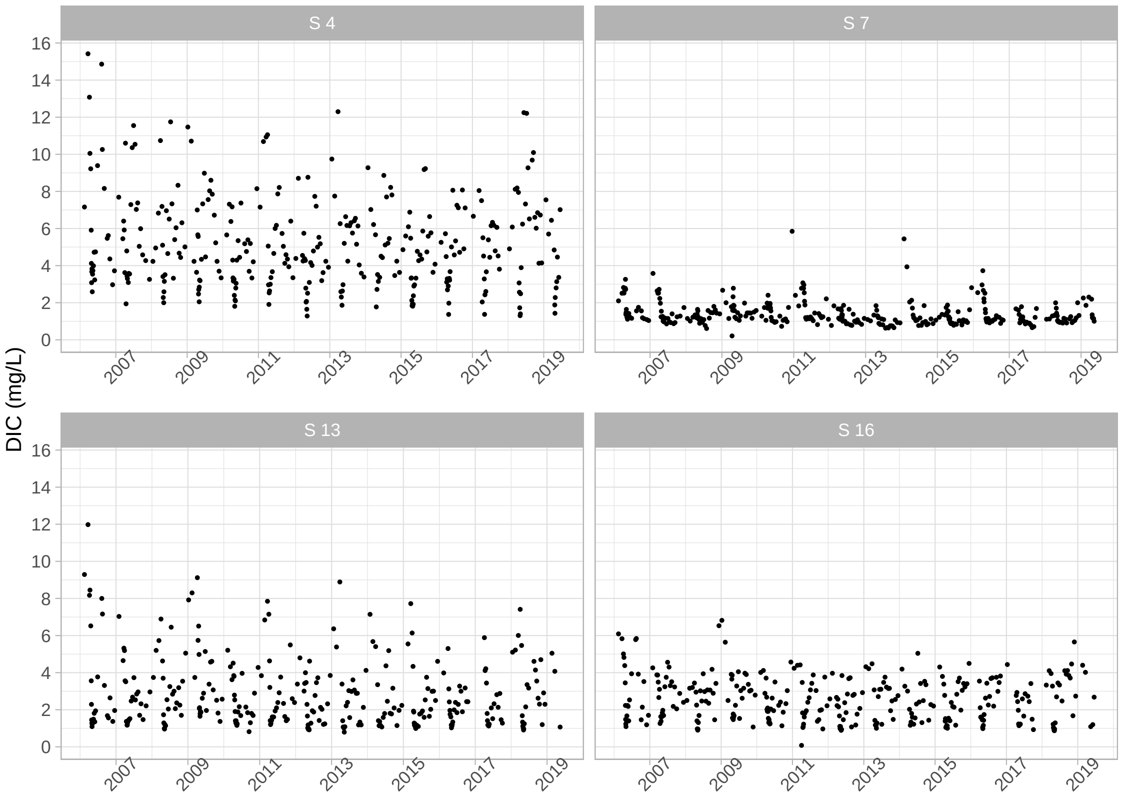

Figure 5: Example time series for DIC data in one site for each stream order – sites 4 (order 1), 7 (order 2), 13 (order 3) and 16 (order 4). Includes all available data for 2006–2019 for the sites.

3.2 SPATIAL PATTERNS IN THE DIC CONCENTRATION DATA

The DIC range of variation between some sites varied considerably, even between sites with the same stream order (Figure 6). Both the medians and overall ranges in DIC concentrations were highly variable between the different sites. The median DIC concentrations for the sites with first order streams (sites 2, 4, 5, 6, 20 and 21) were between 1.36 and 4.72 mg/L, with interquartile ranges (IQR)[7] between 1.05 and 3.28 mg/L. Sites 4 and 20 stood out with considerably higher median values than the rest, and site 4 also had a much wider range of values than the other sites. The sites with second order streams (sites 1, 7, 10 and 14) had median DIC concentrations between 0.91 and 2.23 mg/L, with

[7] IQR is the distance between the 1st and 3rd quadrants; essentially the length of the box.

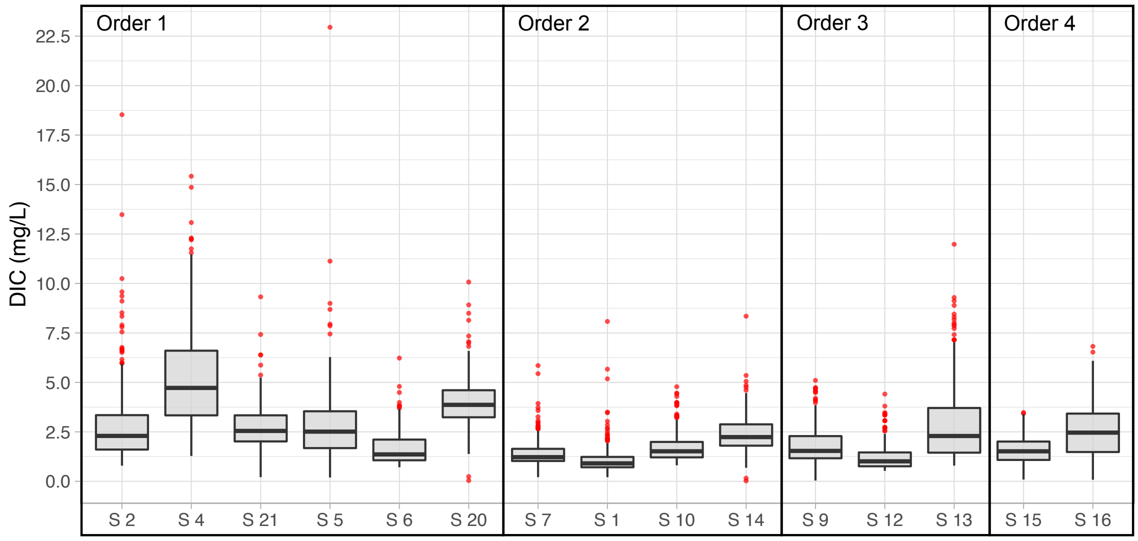

Figure 6: Boxplots with DIC data (2006–2019) for all sites, grouped by stream order, with median marked as a horizontal line inside each box, whiskers of up to 1.5 times the interquartile range, and outliers marked as red dots.

IQR between 0.53 and 1.08 mg/L. The sites with third order streams (sites 9, 12 and 13) had median DIC concentrations between 1.01 and 2.29 mg/L, with IQR between 0.70 and 2.27 mg/L. While sites 9 and 12 were similar, site 13 stood out with the highest median and IQR. Sites 15 and 16, with stream order 4, had median values of 1.52 and 2.46 mg/L, with IQR of 0.94 and 1.94 mg/L, respectively. The upper limits of DIC concentrations varied considerably between the sites, but the lower limits were relatively consistent, with values between 0 and 1.25 mg/L for all sites.

Grouping the sites' DIC concentration data by stream order (Figure 6), ordering them by sub-catchment area, or ordering them by mire percentage of area (Appendix C) did not produce any clear patterns.

3.3 TEMPORAL TRENDS IN THE DIC CONCENTRATION DATA

The MK tests on the monthly medians of the DIC data showed only two significant trends at 95% confidence, for sites 7 and 21, and one at 90% confidence, for site 14, all three negative (Table 4). All but two of the sites had negative Theil-Sen slopes, though apart from the three mentioned above, none of the sites had significant trends.

The MK tests on DIC data divided into individual months showed vastly different results for the different months (Figure 7 and Appendix D). The MK tests for December–March yielded disparate and largely non-significant results (the only exception being March for site 6, which had a significant negative trend at 90% confidence). April and May had significant negative trends in almost all sites (14 and 12 sites, with 11 and 10 at 95% confidence, respectively). June and July had a appeared similar in Theil-Sen slope results to April and May, but fewer of the sites exhibited significant negative trends (7 and 6 sites, with 2 and 3 at 95% confidence, respectively). Of note was that site 5 exhibited a significant positive trend (90% confidence), contrary to the other significant trends. August also followed a similar distribution in Theil-Sen slopes, but had only two significant

Table 4: Theil-Sen slopes (mg/L/year) and p-values for Mann-Kendall tests for the monthly median DIC concentration data (2006–2019) for all sites. Significant trends are marked in black font (90% confidence) and bold black font (95% confidence).

Site	Theil-Sen slope	p-value
S 1	– 0.012	11%
S 2	– 0.033	23%
S 4	– 0.034	45%
S 5	+ 0.006	78%
S 6	– 0.015	35%
S 7	**– 0.019**	1.5%
S 9	– 0.008	61%
S 10	– 0.002	82%
S 12	– 0.010	35%
S 13	– 0.042	21%
S 14	– 0.028	6.8%
S 15	– 0.019	18%
S 16	– 0.028	30%
S 20	+ 0.005	86%
S 21	**– 0.053**	4.6%

trends, one positive in site 5, one negative in site 7 (both at 90% significance. September–November largely reversed the distribution in Theil-Sen slopes, with most of the signs being positive. There were, however, very few significant trends in these months, with only two in September (both negative, site 7 at 95% and site 21 at 90% confidence) and three in October (site 7 negative at 95% confidence, site 12 positive at 90% confidence and site 16 positive at 95% confidence).

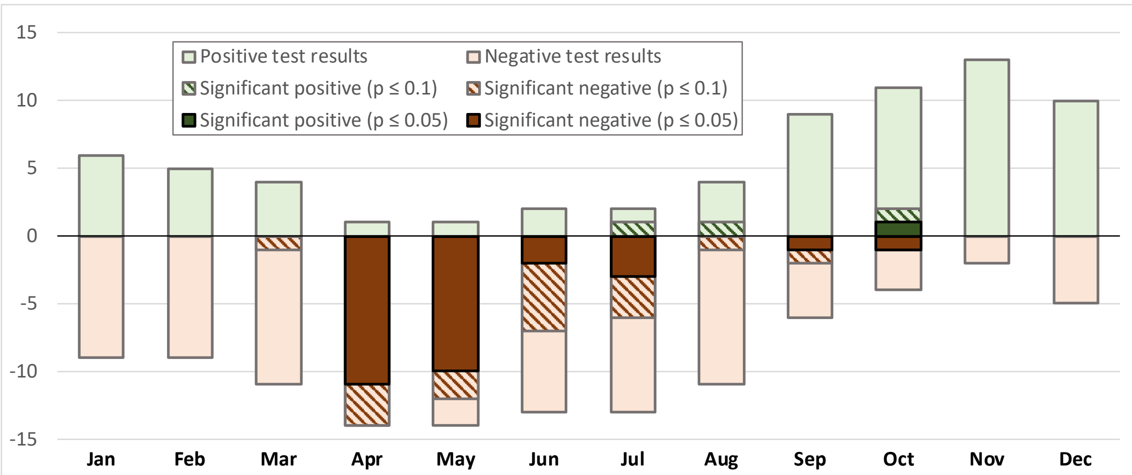

Figure 7: Number of sites exhibiting positive and negative Mann-Kendall test results for DIC concentration data (2006–2019), non-significant and significant with both 90% and 95% confidence, for each month.

When the DIC data were grouped according to season, distinct differences between the seasons emerged (Table 5 and Figure 8). The winter (December–March) data showed

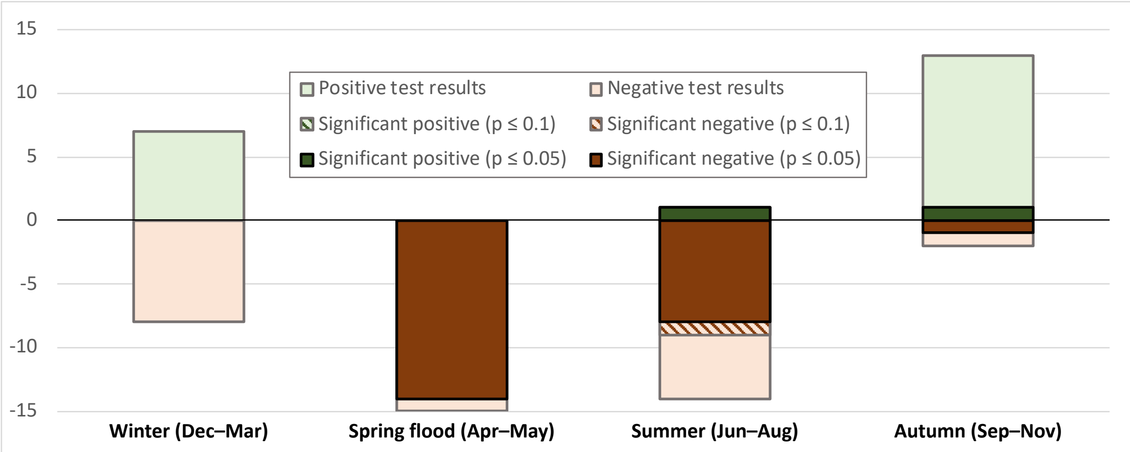

Figure 8: Number of sites exhibiting positive and negative Mann-Kendall test results for DIC concentration data (2006–2019), non-significant and significant with both 90% and 95% confidence, for each season.

no significant trends over time. The spring flood (April–May) data, on the other hand, showed a clear pattern with significant negative trends for all sites except for one (site 20). The summer (June–August) data largely resembled the spring flood data in that most Theil-Sen slopes were negative, but only about little more than half the sites exhibited significant negative trends. Site 5 exhibited a significant positive trend. The autumn data showed a different tendency, with one significant negative (site 7), and one positive (site 16), trend. Most sites had positive Theil-Sen slopes during that season.

3.4 TEMPORAL TRENDS IN EXPLANATORY VARIABLES

The MK tests for the monthly median values of the explanatory variables produced few significant trends (Appendix E). All the significant trends were for either DOC (sites 1, 2 and 5) or pH (sites 5 and 14), with most significant trends being positive. Breaking the positive pattern was DOC for site 5 and pH for site 14, which had significant negative trends (95% confidence and 90% confidence, respectively).

The seasonally divided data showed differences between seasons for all variables (Appendix E). In the winter data sets, only a few trends were significant. All significant DOC trends were positive except site 5. Two pH trends were significantly positive, as was the water temperature trend. In the spring flood data, most trends were significant for DOC pH and water temperature. DOC and water temperature trends were generally positive while significant pH trends were all negative. The summer data largely resembled the spring flood data, but with fewer significant trends for all variables. The autumn data brought significant trends for most sites for DOC and pH, though the trends were opposed to the trends in the other seasons with pH being positive and the other negative. Discharge and air temperature had no significant trends in any of the seasons, though it was noted that in the individual months, air temperature had one significant positive trend, May, and one negative, August, and discharge had significant positive trends for April, June and July, and negative trends for several months from August to February.

Table 5: Theil-Sen slopes (mg/L/year) and p-values for Mann-Kendall tests on the four seasonal groupings of DIC concentration data. Significant trends are marked in black font (90% confidence) and bold black font (95% confidence).

	Winter (Dec–Mar)		**Spring flood (Apr–May)**	
Site	Theil-Sen slope	p-value	Theil-Sen slope	p-value
S 1	+ 0.002	92%	**– 0.020**	**0.0094%**
S 2	– 0.006	94%	**– 0.052**	**0.0060%**
S 4	– 0.007	93%	**– 0.092**	**0.075%**
S 5	+ 0.017	57%	**– 0.076**	**0.043%**
S 6	– 0.047	24%	**– 0.033**	**0.0053%**
S 7	– 0.010	78%	**– 0.033**	**0.025%**
S 9	+ 0.029	44%	**– 0.028**	**0.083%**
S 10	+ 0.005	97%	**– 0.023**	**0.025%**
S 12	+ 3.1E-05	99%	**– 0.023**	**0.0076%**
S 13	– 0.036	67%	**– 0.034**	**0.37%**
S 14	– 0.003	84%	**– 0.034**	**0.76%**
S 15	– 0.011	72%	**– 0.031**	**0.021%**
S 16	– 0.005	95%	**– 0.046**	**0.051%**
S 20	+ 0.043	43%	– 0.008	77%
S 21	+ 0.037	74%	**– 0.067**	**0.37%**

	Summer (Jun–Aug)		**Autumn (Sep–Nov)**	
Site	Theil-Sen slope	p-value	Theil-Sen slope	p-value
S 1	**– 0.027**	**0.36%**	– 0.001	87%
S 2	– 0.082	9.1%	+ 0.005	87%
S 4	– 0.104	11%	+ 0.076	23%
S 5	**+ 0.051**	**1.0%**	+ 0.014	46%
S 6	– 0.013	59%	+ 0.008	65%
S 7	**– 0.017**	**3.3%**	**– 0.030**	**0.31%**
S 9	– 0.021	24%	+ 0.030	27%
S 10	– 0.023	7.6%	+ 0.010	52%
S 12	**– 0.035**	**0.66%**	+ 0.020	19%
S 13	– 0.045	12%	+ 0.035	38%
S 14	**– 0.045**	**1.1%**	+ 0.018	53%
S 15	**– 0.041**	**1.1%**	+ 0.025	25%
S 16	**– 0.064**	**2.6%**	**+ 0.072**	**3.9%**
S 20	– 0.032	16%	+ 0.026	41%
S 21	**– 0.078**	**4.1%**	– 0.059	18%

3.5 CORRELATION ANALYSIS WITH KENDALL'S τ

The results showed that DIC is correlated with all of the explanatory variables for at least some of the sites (Table 6). Generally, DIC correlated negatively with DOC, air temperature, discharge and water temperature, and positively with pH (with a few sites as exceptions). Water temperature had significant correlations for seven sites, five of which were negative, with correlation strengths varying between 0.083 and 0.43. Air temperature had significant correlations for ten sites, all negative and between 0.087 and 0.27 in strength. For DOC, all but one site (site 20) had significant correlations (13 sites at 95% confidence, one at 90%). Sites 4 and 5 had positive correlations, while the other sites correlated negatively. The correlation strengths varied between 0.066 and 0.56. For pH, all but one site (site 7) had significant (95% confidence) correlations, all positive except one (site 5), with correlation strengths between 0.22 and 0.68. Discharge correlated well with DIC for all but one site (site 5), with significant negative correlations for 13 sites, and a significant positive correlation for site 7 (all at 95% confidence), and correlation strengths between 0.15 and 0.73. Among the explanatory variables, pH and discharge had the strongest correlations and the highest number of them, with eight and seven correlation strengths above 0.5, respectively.

Table 6: Kendall's τ correlation coefficients for DIC–DOC, DIC–pH, DIC–air temperature, DIC–discharge and DIC–water temperature. Significant correlations are marked in black font (90% confidence) and bold black font (95% confidence). Correlations of strength 0.5 or greater are also marked with a *.

Site	DOC	pH	Air temp	Discharge	Water temp
S 1	**– 0.34**	**+ 0.34**	**– 0.22**	**– 0.26**	**– 0.29**
S 2	**– 0.14**	**+ 0.54***	– 0.023	**– 0.58***	+ 0.033
S 4	**+ 0.34**	**+ 0.29**	+ 0.056	**– 0.68***	**+ 0.22**
S 5	**+ 0.20**	**– 0.22**	**– 0.22**	+ 0.036	**– 0.35**
S 6	**– 0.30**	**+ 0.59***	**– 0.12**	**– 0.51***	– 0.056
S 7	– 0.066	– 5.9E-05	**– 0.27**	**+ 0.15**	**– 0.43**
S 9	**– 0.33**	**+ 0.53***	**– 0.15**	**– 0.48**	**– 0.083**
S 10	**– 0.10**	**+ 0.44**	– 0.056	**– 0.37**	– 0.051
S 12	**– 0.27**	**+ 0.53***	**– 0.15**	**– 0.42**	**– 0.14**
S 13	**– 0.18**	**+ 0.55***	**– 0.15**	**– 0.57***	– 0.040
S 14	**– 0.30**	**+ 0.58***	– 0.040	**– 0.54***	+ 0.060
S 15	**– 0.41**	**+ 0.61***	**– 0.11**	**– 0.60***	– 0.014
S 16	**– 0.56***	**+ 0.68***	**– 0.087**	**– 0.73***	+ 0.056
S 20	+ 0.015	**+ 0.28**	**– 0.087**	**– 0.32**	+ 0.0072
S 21	**– 0.21**	**+ 0.27**	+ 0.071	**– 0.39**	**+ 0.13**

3.5.1 Plots of DIC as a Function of the Explanatory Variables

The relationships visible in the plots differed considerably between explanatory variables, but were generally similar for all sites for any single variable (Figures 9 – 12 and Appendix F). For DOC, most sites displayed a disparate, slightly negative relationship corresponding to the negative correlations. Site 4 and 5 differed, with site 4 displaying a positive relationship and site 5 displaying a very slight positive tendency. For pH, all sites except one (site 5) showed a positive relationship. Site 5 displayed a slight negative tendency for most of the data, with a few data points with higher DOC values instead indicating a positive relationship. For air temperature, most sites displayed a very weak negative relationship, while others (e.g. site 4) displayed disparate, almost random distributions of data. For discharge, a distinct non-linear negative relationship was present in all sites except two (sites 5 and 7). Lower discharge values corresponded to highly variable DIC values, but as discharge increased, DIC generally converged towards a low value. Sites 5 and 7 showed no or very weak tendencies, but also displayed higher variability among data points with low discharge. Due to the distinct pattern in the DIC–discharge relationship, DIC was also plotted as a function of log(discharge), which produced near-linear negative relationships for most sites. For water temperature, most plots followed a distinct pattern with two different regimes; water temperature values near 0 °C displayed highly variable DIC values similar to discharge, but higher water temperatures generally displayed a disparate, positive relationship.

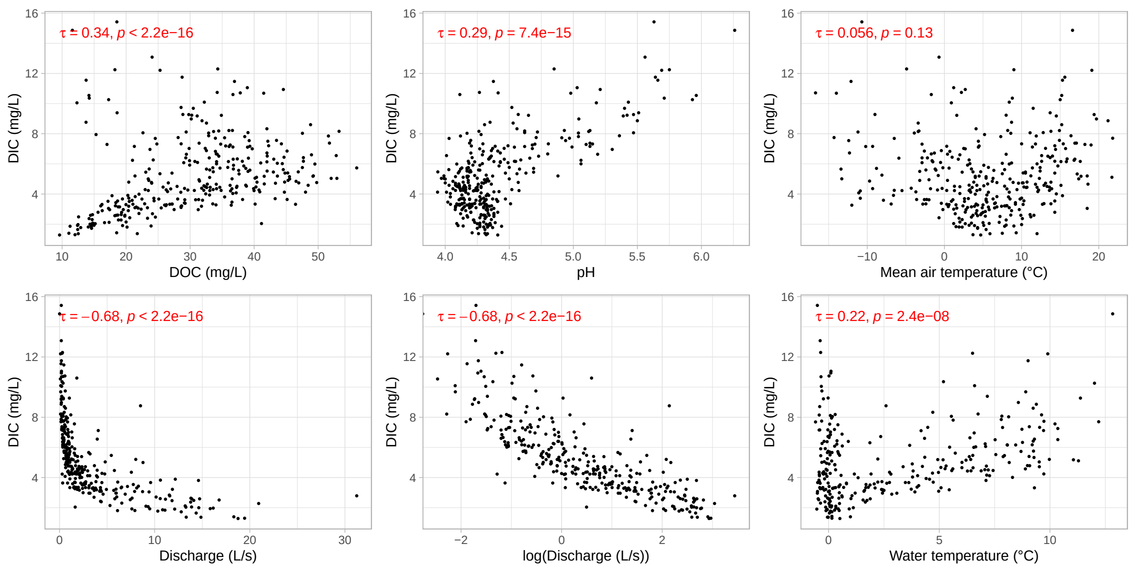

Figure 9: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 4. Kendall's τ with corresponding p-value is also shown.

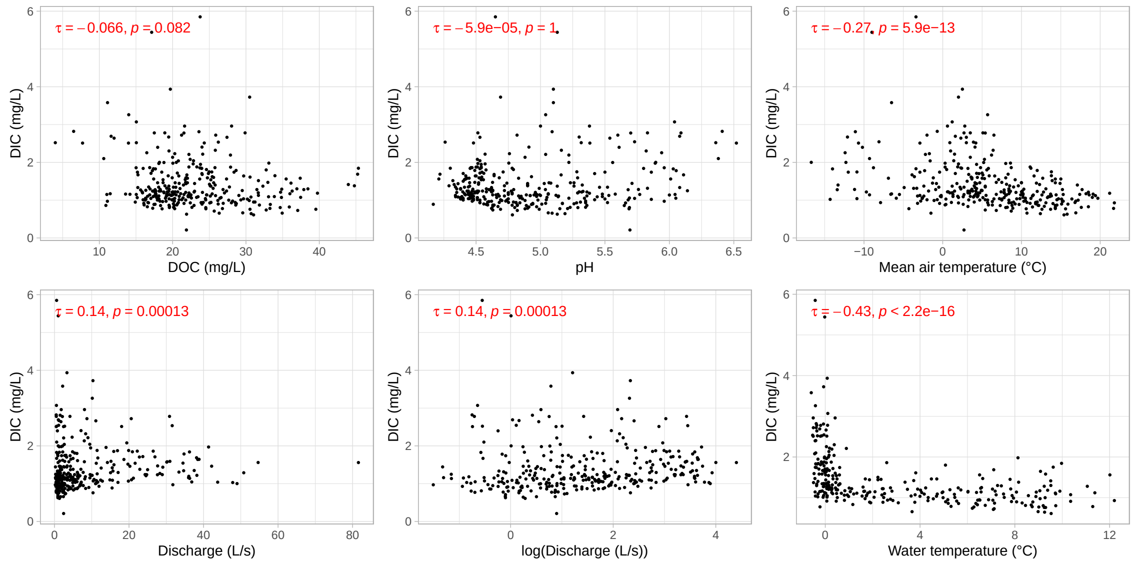

Figure 10: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 7. Kendall's τ with corresponding p-value is also shown.

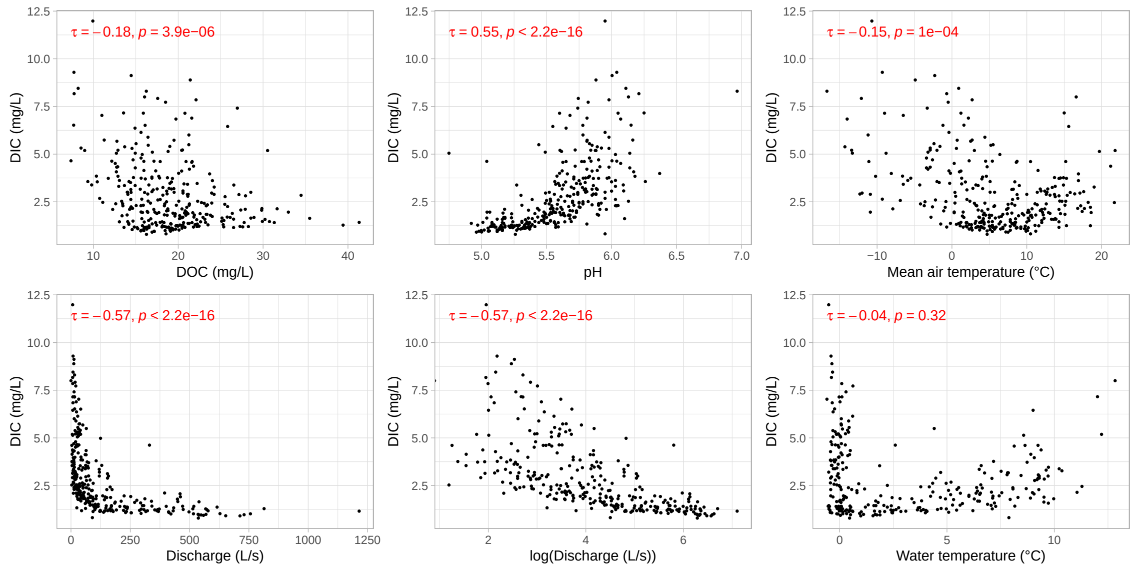

Figure 11: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 13. Kendall's τ with corresponding p-value is also shown.

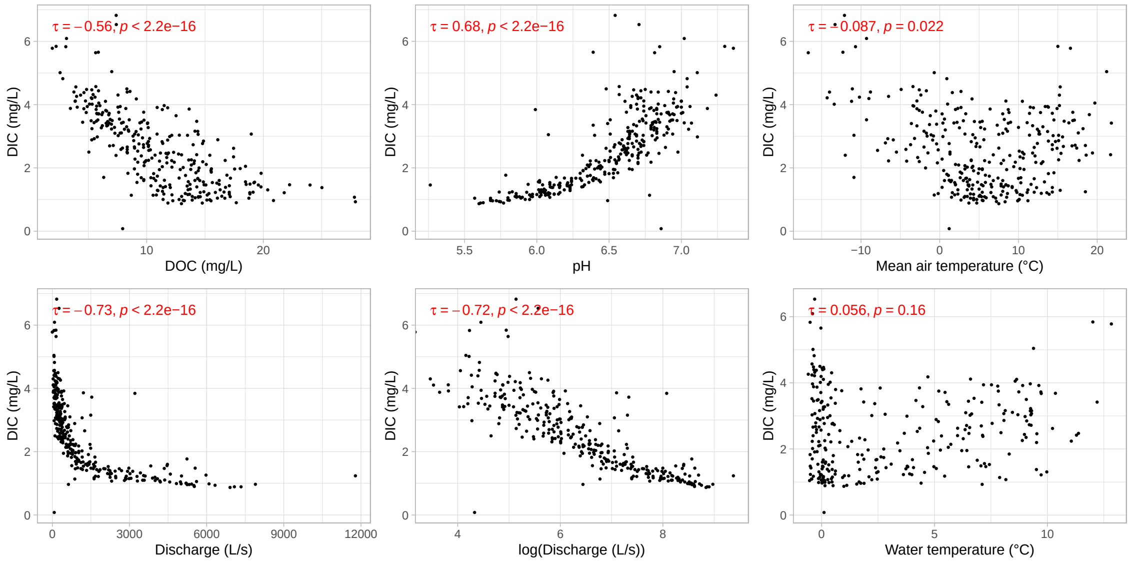

Figure 12: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 16. Kendall's τ with corresponding p-value is also shown.

4 DISCUSSION

4.1 SPATIAL PATTERNS IN DIC DATA

The DIC concentrations in Krycklan varied greatly between sites (Figure 6). The median concentrations for the full time period for all sites ranged from 0.91 to 4.72 mg/L. The site-specific ranges in DIC concentration among the sites were high as well, with IQR ranging from 0.53 to 3.28 mg/L and several outliers for all sites. These DIC concentration ranges were largely consistent with previous literature on boreal streams, with Krycklan exhibiting similar values to boreal areas in Finland (Huotari et al. 2013; Rantakari et al. 2010), Quebec, Canada (Hutchins, Prairie, & Giorgio 2019), and in the Degerö mire in the immediate vicinity of Krycklan (Leach et al. 2016). The lower median values were close to concentrations found by Einarsdottir, Wallin, & Sobek (2017) for the inlet to a Swedish lake. The spatial variability seen in the results from for example Hutchins, Prairie, & Giorgio (2019) was found to be considerable in the Krycklan DIC concentrations as well, with differences both within and between sites. As the climate conditions were expected to be the same across the entire Krycklan catchment, any major differences in DIC concentrations between sites are attributed to differences in catchment characteristics.

The examined catchment characteristics did not explain spatial DIC variability well, but some general patterns were still discernible. Sites of first stream order, for example, displayed higher median DIC concentrations and a greater variability than most of the higher order sites. Similarly, the three sites with highest maximum observed concentrations were all of first stream order (sites 2, 4 and 5). This greater variability among low order streams is expected, as headwater streams are more directly affected by changes in the catchment soils. It has also been estimated that most of the CO_2 in headwater streams emits to the atmosphere within the first few hundred meters (Öquist et al. 2009). This would explain the generally higher concentrations observed in first order streams, but also the greater variability since the CO_2 concentration should stabilize somewhat further downstream. This behavior was visible in the first order sites when compared to the higher order sites, but differences between second, third and fourth order streams were not detectable. Among the higher order sites, two (sites 13 and 16) displayed considerably higher median DIC concentrations as well as greater variability, more like the first order sites than the other third and fourth order sites. This was surprising, as the related sub-catchments did not deviate substantially in any other characteristics.

Wallin et al. (2010) have previously reported that both DIC and CO_2 were positively correlated with peatland cover in Krycklan. In contrast, no such significant pattern was observed in this study (Figure C2 in Appendix C). Still, site 4, the sub-catchment with the highest peatland percentage (ca 40%) of the area stood out as having the highest median DIC concentration, as well as the highest IQR. Whether a general positive spatial correlation between peatlands and DIC exists has been discussed. Positive spatial relationships have been identified in previous literature (e.g. Rantakari et al. 2010), so the higher DIC concentrations found in site 4 could likely be related to the greater peatland cover. Site 5 also corresponds to a sub-catchment with a high percentage of peatland (ca 40%), but here the observed DIC concentrations were closer to some of the other sites. Site 5 is, however, situated downstream a small lake, which largely controls the DIC output from the sub-catchment. The longer retention time for the water in a lake compared to streams means that CO_2 in the surface water has more time to degas to the atmosphere and at the same time more time for in-situ production and and consumption of CO_2 due to metabolic and photochemical processes (Algesten et al. 2004; Humborg et al. 2010; Jonsson, Karlsson, & Jansson 2003; Sobek et al. 2003). The direct response of DIC to changes in discharge is also dampened, as groundwater mixes with the lake water. The combined effect results in different DIC levels and dynamics compared to streams without lake influence (Einarsdottir, Wallin, & Sobek 2017; Weyhenmeyer et al. 2015). By examining only the peatland cover, sites 4 and 5 may be expected to exhibit similar concentrations in DIC, but that was not the case. Though the lake is small, it has an important impact on the DIC concentration in the outlet stream. This was further revealed by the time series plots, where a yearly cyclical behavior of the data was seen more clearly compared to other sites (Figure B1 in Appendix B). Though the exact impacts of the lake on DIC are not known, the complex dynamics of the lake appear to dampen the direct signal of DIC from the sub-catchment by mixing incoming groundwater with lake water largely affected by in-situ processes.

Grouping the DIC data by sub-catchment size did not yield any particularly interesting results. Grouping by peatland cover or stream order gave some information about the spatial control on stream DIC, but did not sufficiently explain the variability either. This analysis was far from exhaustive though, because the stream network is affected by a multitude of interacting factors. Soil type can be important by providing CO_3^{2-} ions through weathering (Riebeek 2011), and by affecting the hydrological conditions; for example groundwater flow patterns, infiltration capacity and water retention in the soil (Novák & Hlaváčiková 2019). Krycklan bedrock and soils do not contain any substantial amounts of calcareous rock (Laudon et al. 2013), so the importance of carbonate weathering is likely minimal, but the effect of soil characteristics on hydrology could have considerable impact on the variability of DIC within and between sub-catchments. Because of the mineral composition and acidic environment, silicate weathering is likely a source of HCO_3^-, but since silicate weathering consumes CO_2 this does not necessarily increase the total DIC concentration measured in the stream (Stumm & Morgan 2012). Other influential factors may be altitude and topography, again by affecting the flow patterns of groundwater and surface flow, as well as the accumulation of organic matter in riparian soils, as has been suggested by Leith et al. (2015). The slope of the watercourse could also be noteworthy by affecting the turbulence in the water, subsequently increasing the potential for CO_2 to emit to the atmosphere as has been shown by (Wallin et al. 2011). Ultimately, the selected parameters were not sufficient in explaining the spatial variability of DIC concentrations in Krycklan. It is possible that including other variables, such as slope gradients and soil types, could have improved the prediction of DIC patterns.

4.2 TEMPORAL TRENDS IN DIC DATA

Only two sites in the full time period MK analysis displayed significant trends in DIC concentrations over the 14-year period, both with negative trends (Table 4). Most of the other sites had p-values very far from 0.05, meaning that even with less strict confidence levels, most would not yield significant results. Given these results, it was not possible to conclusively say whether DIC concentrations in Krycklan increased or decreased in general over the period.

When the data were divided into months and seasons, a clear seasonal pattern emerged

(Figures 7 and 8), with overwhelmingly negative trends during the spring flood season (April–May); a majority of sites exhibiting negative trends during summer (June–August); few significant trends, but a majority of positive Theil-Sen slopes during autumn (September–November); and disparate, inconclusive results during winter (December–March). The seasonal differences in trends indicated that DIC concentrations in Krycklan were subject to considerably different regimes depending on the season during the period. Since few sites exhibited positive trends in any of the seasons but almost all exhibited negative trends in spring, and most in summer, it would be reasonable for the trends in those seasons to be visible in the the analysis of the full time period. This did not happen for most sites, as only sites 7 and 21 exhibited significant negative trends. The reason for this could be related to the selection of data. For the full time period data, monthly median values were used to remove the uneven weighting caused by different amounts of available data for different months. Since the data for each individual month was relatively evenly spread, it was assumed that the data were representative of each month; therefore, all data were used in the MK tests on individual months. Since the seasons were constructed to contain months with similar trends, it was further assumed that the seasonally grouped data were representative for each season. Thus, all available data were used for MK tests on seasonally grouped data as well. The purpose of this change in method was to improve the statistical accuracy of the tests. There is a risk of slightly uneven weighting for the seasonally grouped data specifically, but the distribution of data within each season was generally evenly split between the months so this risk was considered minor. A consequence of using all data instead of monthly median data is that the statistical strength of the tests, which depends on the amount of data used, is different for the different months and seasons. Trends in spring flood data, therefore, were more likely to be displayed than trends in the other seasons. It is possible, therefore, that including more data would increase the number of trends visible in the data for other seasons. The tendency towards negative MK test results in summer and positive test results in autumn, even when non-significant, is an indication of this. If more data were indeed available for the other seasons as well, it is possible that the individual seasons as well as in the full time period would exhibit significant trends for more sites. Given the available data, using monthly median values for establishing the seasonal trends would circumvent the outlined issue, but the result would be that visible trends in spring and summer data would likely be weaker. It should be noted that though the amount of winter and spring flood data deviated considerably from the other seasons, both the summer and autumn periods contained about the same number of data points, evenly distributed across the months. Thus, the statistical accuracy for both of the seasons should be the same, and if the actual trends were of similar strength the same number of sites should exhibit significant trends for both seasons. This was evidently not the case. The difference in MK results between summer and autumn could either mean that there were no actual trends for DIC concentrations during autumn, or that any actual trends were too weak to be found with the limited available data. Either way, DIC concentrations could only be conclusively said to have decreased for most sites during spring and summer.

The complete lack of significant trends in winter data could possibly be attributed to the smaller amount of available data. It could also have been influenced by snow and ice obstructing the streams. During the winter months, air temperatures in Krycklan were regularly below 0 °C, as would be expected for a boreal catchment. Ice conditions were not included as a parameter in this analysis, but could have been a factor impacting the stream surfaces as well as the flow of water through the soils. Most of the influx of DIC during winter is expected to be from the deeper groundwater flow as precipitation falls mainly as snow and ice. In an Alaskan stream network, base flow DIC was concluded to be a combination of new and old carbon, compared to the mostly newer DIC found at higher discharge conditions (Smits et al. 2017). Should Krycklan base flow follow similar DIC compositions, this could provide one explanation of why no temporal trends were detected for winter data. If the origin is generally older for base flow carbon, the impact of trends today could possibly be lessened compared to the other seasons.

The actual trends in relation to the measured DIC concentrations, were considerable (Tables 4 and 5). Among the full time period results, the two significant trends for sites 7 and 21 had Theil-Sen slopes of –0.019 and –0.053 mg/L/year, respectively. This median yearly rate of change is considerable when compared to the median DIC concentrations of 1.2 and 2.5 mg/L in the two sites, respectively. The significant negative trends in seasonally grouped DIC data had Theil-Sen slopes between –0.017 and –0.092 mg/L/year; all relatively close to the two significant results for the full time period. The two positive trends (summer for site 5 and autumn for site 16) had Theil-Sen slopes of 0.051 and 0.072 mg/L/year, again reasonably close in strength to the other trends. Due to the non-linear nature of the data, the decrease represented by the Theil-Sen slope cannot be viewed as a strict linear decrease, so exact decreases in the output of DIC, either in terms of concentration or total amount of DIC, cannot be calculated from the trends. The rates of change give an indication, however of the magnitude of the decrease or increase represented by the found trends, and as such illustrates the scope of the changes. The rates of change exhibited during the spring flood and summer periods are not inconsiderable, and could lead to substantially altered spring and summer DIC concentrations after a few years.

4.3 DIC AND EXPLANATORY VARIABLES

The considerable differences in DIC concentrations between seasons as well as the seasonal variations in DIC trends indicated the importance of seasonal hydrometeorological conditions in controlling DIC. Through the correlation analyses, DIC was found to be correlated to most of the selected explanatory variables (Table 6). Similar to DIC, the MK trend tests for the explanatory variables during the full time period revealed few significant trends (Table E1 in Appendix E), but the seasonally grouped data contained some interesting results discussed in sections 4.3.1–4.3.3.

4.3.1 DOC and pH

DIC was found to be generally positively correlated with pH and negatively correlated with DOC. The MK trend tests for seasonally grouped data revealed that for spring and summer, trends in DOC were largely opposed to trends in DIC, while both pH and DIC displayed negative trends (Table E3 in Appendix E). The winter season MK tests displayed very few significant trends for DOC and pH, but autumn trends diverged considerably from the trends in DIC by exhibiting significant negative trends for DOC, and significant positive trends for pH, in most sites (ten sites each).

The positive relationship between DIC and pH was not unexpected. Higher pH shifts the DIC equilibrium towards the ionic forms of DIC and away from CO_2 (Stumm & Morgan 2012), meaning that less DIC can degas across the stream surface. As most of the CO_2

leaves the stream within the first few hundred meters (Öquist et al. 2009), a higher pH making more of the DIC involatile could drastically increase the amount of DIC that is measured in the outlet for a sub-catchment. In the Krycklan data, pH values were relatively low (median values ranged from 4.3 to 6.6 for the different sub-catchments), meaning that CO_2 was likely the dominating DIC fraction for most of the period. Small shifts in pH, especially in the sites where the pH values are a little higher, could significantly alter the DIC equilibrium, thus altering the amount of DIC being degassed. The positive relationship between DIC and pH exhibited for most sites seemed to confirm this. Two sites differed from this general positive relationship; site 5 exhibiting a negative relationship and site 7 displaying no significant relationship at all. Site 5 was also the only site to exhibit a significant (positive) trend in pH over the full time period. The previously mentioned lake was probably an important contributing factor to the differences in behavior for pH here, compared to the other sites. The increase in pH could correspond to the lake recovering from many decades of acidification seen in inland waters across the Nordic countries (Arvola et al. 2010). The complexity of interacting carbon cycling processes in boreal lakes (Tranvik et al. 2009) makes predicting the direct impact of the lake on the DIC-pH relationship difficult. Subsequently, the cause for the different relationship exhibited in site 5 could not be determined. The deviation of site 7 from the general pattern was likewise hard to explain. The sub-catchment receives water from sites 2 and 4; two sub-catchments with very different land use compositions and different DIC distributions. In terms of the catchment characteristics detailed by Laudon et al. (2013), sub-catchment 7 appeared similar to sub-catchment 12, which displayed a positive relationship between DIC and pH. There were no distinguishing features in the characteristics likely to cause an altered relationship between DIC and pH, so the lack of a DIC–pH relationship could not be explained by the factors examined in this study.

Previous findings by for example Lapierre et al. (2013) have indicated a positive spatial correlation between DIC and DOC, suggesting that a substantial part of DIC in streams is generated from the mineralization of DOC in streams. The negative correlations between the two variables found in this study, however, showed that the positive relationship did not hold true over time for the Krycklan data. This was further emphasized by the MK trends present in the seasonally grouped DOC data, where the results largely opposed the MK trends for DIC. This could indicate different hydrological pathways for DIC and DOC in the catchment, as has been suggested to be the case for the nearby Degerö mire (Leach et al. 2016). Humborg et al. (2010) similarly proposed that organic carbon compounds and weathering-induced carbon species in Swedish inland waters followed different hydrological pathways, possibly indicating a mechanistic decoupling of DIC and DOC. Studying the sources of DOC in Krycklan, Laudon et al. (2011) found that during low-flow conditions, peatlands were the dominant source of DOC, whereas forest soils dominated during higher flows. The pathways for DIC are not as well known, but a predominant groundwater flow has been suggested (Leith et al. 2015; Öquist et al. 2009). The general relationship was opposed by sites 4 and 5, both of which exhibited significant positive, albeit weak, correlations between DIC and DOC. The different relationships observed in these sites could be caused by the prevalence of mire, and the positive correlations may suggest that DIC and DOC are hydrologically linked. Interestingly, this diverges from the findings of Leach et al. (2016) indicating different pathways for DIC and DOC in a mire. The relationship is slightly stronger in site 4 than 5, possibly because of the lake delaying and mixing incoming DIC and DOC in sub-catchment 5.

In a previous study of DOC in some of the sites (sites 1–16 in this study), DOC was found to significantly ($p < 0.05$) increase across all sites except for site 4 during the period 2003–2017 (Fork, Sponseller, & Laudon 2020). That study used the seasonal Mann-Kendall (SMK) test, which calculates MK test statistics for individual seasons (in this case seasons were defined as months) and sums them up to yield a metric more or less comparable to the MK test statistic for the full data set. Fork, Sponseller, & Laudon (2020) used monthly median values to calculate trends. The results in their study differed from the results observed in the current study, but the different study period and method could be the reason for the disparity. Using the SMK test yields more reliable results for data displaying seasonality, such as is typical for hydrological data (Helsel & Hirsch 2002). It is only applicable, however, if the individual seasons display similar monotonic trends, and should otherwise be eschewed in favor of the MK test (Hipel & McLeod 1994). Since the current study primarily focused on the DIC trends and the DIC trends differed considerably between seasons, the MK test was deemed more reliable. Finding the individual trends in each month and calculating the overall trends from those could better reveal trends if that method was applicable to the data. In the interest of consistency with the other analyses, a different method was chosen for the current study, possibly leading to the trends in DOC being weaker than those found by Fork, Sponseller, & Laudon (2020).

In the MK trend tests for DOC and pH, the autumn results were particularly interesting. Whereas DIC exhibited very few trends in the autumn period across the sites, DOC and pH displayed ten significant trends each. The amount of data was roughly the same for all three variables so the statistical accuracy of the test should also be equivalent. The fact that trends appear in the DOC and pH data but not in the DIC data suggests that there were no actual trends in the DIC data during the autumn. This contradicts the point made earlier; that the lack of trends could be caused by insufficient amounts of data for the season. The difference in results could be because of a difference in the strength of the trends. As previously noted when comparing the DIC trends for the summer and autumn data, a difference in statistical strength could cause trends to be displayed only where they are stronger. The most reasonable assumption given the differing results between DIC, DOC and pH, however, was that the lack of trends in autumn DIC data was accurate.

4.3.2 Discharge

All sites except two (sites 5 and 7) exhibited a negative relationship between discharge and DIC. This indicates a general dilution effect on DIC with increasing discharge, such as has been proposed previously for Krycklan (Wallin et al. 2010) and elsewhere (Teodoru et al. 2009). The strength of the correlations further indicate that, for most sites, an increase in discharge has a profound effect on DIC, more so than the other examined variables (e.g. DOC). However, discharge did not display any significant trends for either the full time period or during any of the individual seasons. Significant trends in some of the individual months were noted, but these monthly trends did not carry through to the seasonal grouping of data or the full time period. Thus, the negative trends in DIC during the spring flood and summer seasons could not be attributed to changes in discharge over time. Instead, the negative trends may have accounted for shifts in hydrology, despite relatively consistent amounts of runoff. Because the variables were measured at the discrete points, the sub-catchment outlets, flow dynamics through each sub-catchment were not captured. Changes in the hydrological pathways, therefore, could potentially alter the mobilization of DIC from catchment soils without discharge having to exhibit trends over time. The hydrology has been shown to greatly affect how DIC accumulates and flows through soils. Leith et al. (2015) and Öquist et al. (2009) each identified intermediate soil horizons of depths around 30–60 cm as hotspots where DIC concentrations were higher than in both surface and deep soils horizons. Laudon & Sponseller (2018) acknowledged the importance of periodically activated pathways within soil layers, as well as groundwater input zones, where groundwater is concentrated in topographical sinks before entering the stream. Discharge is assumed to be one of the important drivers of DIC in streams, so changes in the hydrological pathways during specific seasons could be one of the causes for the different trends in DIC.

As with pH, the deviating sites for DIC–discharge correlations were sites 5 and 7. The lake in site 5 could be expected to alter the discharge–DIC relationship substantially because of the delaying of incoming water and mixing with lake water. Thus, seeing no significant correlation between DIC and discharge for site 5 was not unexpected. The very weak positive relationship exhibited for site 7 was, however, surprising. The DIC–discharge plot for site 7 visualized the slightly positive relationship, very different from the other sites (Figure 10). The DIC–log(discharge) plot showed more clearly that DIC increased somewhat with higher discharge. Since the site did not particularly differ in characteristics from the rest of Krycklan, and since the individual sub-catchments supplying site 7 with water (sub-catchments 2 and 4) did not exhibit positive relationships between DIC and discharge, the cause for the positive correlation could not be established.

It was noteworthy that trends in DIC were found primarily for the spring flood period, and to a lesser extent the months following the spring flood. An integral part of the hydrological regime of the boreal region is the snowmelt during spring. The importance of this event on the hydrological pathways in Krycklan has been emphasized (Leith et al. 2015). Though no temporal trends in discharge could be determined, the DIC changes during spring and summer, coupled with the significant negative correlations with discharge, indicate either a shift in the hydrology around the time of the snowmelt, or a shift in hydrology during winter, causing a decrease in the available DIC pool once snowmelt begins.

In addition to considerably affecting DIC, discharge impacts other chemical and physical properties across the stream network. This complicates the relationships and causalities considerably, so that it is hard to say exactly how much discharge impacts DIC compared to, for example, DOC. This needs to be kept in mind when discussing the interactions between all variables and DIC.

4.3.3 Temperature and Future Climate Conditions

Air and water temperature data were significantly correlated with DIC for some of the sites (10 and 7 sites, respectively), but most of the correlations were very weak. The correlation with air temperature was consistently negative, whereas the correlation with water temperature was negative for most sites, but positive for two (sites 4 and 21). The negative relationship was unexpected, as temperature variables were chosen to be proxy variables for the growing season conditions. Öquist et al. (2009) noted that DIC concentrations tend to be higher during the growing season. Since the correlations were quite weak and negative when a positive relationship was expected, it is possible that the temperature variables were not suitable proxy variables for the growing season. It is also possible that the effect of the growing season is not as strong as expected over time. To determine the relationship between DIC and temperature, alternative methods could be to used, such as using a threshold temperature to examine data above or below that temperature separately, or by seasonally grouping the data by growing and non-growing seasons based on temperature. A likely issue with the data is that temperatures near or below 0 °C occur when there is a risk of snow and ice in the streams, obstructing the diffusion of CO_2. Additionally, freezing temperatures in the soil could, as previously mentioned, alter the hydrological pathways and minimize the flow of water to streams. These effects combine to create different DIC behaviors for near-freezing compared to higher temperatures, as can clearly be seen in most of the DIC–water temperature plots (e.g. Figure 11). The plots show that the DIC concentrations for temperatures near 0 °C follow a different pattern compared to higher temperatures. Indeed, some of the sites appear to have a positive relationship between DIC and higher water temperatures once the near-freezing temperatures are excluded.

The projected future changes in climate are expected to substantially impact temperatures; subsequently altering the hydrology and chemistry of boreal stream networks and affecting DIC exports. In a series of reports by the Swedish Meteorological and Hydrological Institute, SMHI, the climate scenarios presented in the IPCC's Fifth Assessment Report (IPCC 2014) were used to predict future changes in climate and its subsequent effects on the different Swedish counties, specifically focusing on the state of the environment at the turn of the next century (Berglöv et al. n.d.). The reports work with two different scenarios; one where current trends in environmental progress are accelerated and political and societal efforts push towards limiting global warming and other environmental threats, and one where environmental progress is stymied by lacking political will and technical progress (Berglöv et al. n.d.). In the report for Västerbotten County where Krycklan is situated, predictions include increasing temperatures, with the greatest increase during winter, increased precipitation and runoff, and an increased likelihood of extreme weather events (Berglöv et al. n.d.). Higher temperatures are also predicted to increase the growing period by some 30–50 days (Berglöv et al. n.d.). The seasonal patterns present in all climatological and hydrological data are expected to remain, with continuing high spring and autumn flows while summer and winter flows remain smaller, but the flows are expected to increase the most during winter and autumn (Berglöv et al. n.d.). The negative relationship between DIC and discharge suggests that the predicted increases in runoff will lead to a dilution of DIC concentrations in the future. This would likely continue the trends found in the spring flood and summer seasons in this study. The result of increasing temperatures and a lengthening growing season is likely to be an increase in DIC (Öquist et al. 2009). The results in this study do not directly indicate such a change, but discounting the near-freezing temperatures, the relationship between DIC and water temperature may support that conclusion. Increased discharge and increased temperatures seem to contradict each other here, so it is difficult to say what the resulting effect of a changing climate on DIC would be. It depends on the magnitude of the effects from the different variables. Judging by the correlations and corresponding relationship plots in this study, discharge appears more closely related to DIC than temperature. To the point of discussing the effects of temperature on DIC, it has been suggested that rising temperatures could contribute to increased future carbon losses, particularly in areas with large carbon stocks like the boreal region (Crowther et al. 2016). Though the scale of losses is highly uncertain, the trends indicate that warming-induced carbon losses could become an important driver of climate change (Crowther et al. 2016). Whether this will affect DIC concentrations is not detailed in the study, but the concept adds to the the uncertain future of DIC.

4.4 ASSUMPTIONS AND UNCERTAINTIES

One important note to make is that the analyses in this study were conducted on data collected at the outlet from each sub-catchment. As such, the data reflected the resulting variables from the sub-catchment, but not the complete processes and dynamics within the catchment. This is especially important with regards to DIC, since the two-dimensional nature of the transport causes some of the DIC to degas before the catchment outlet. This is further complicated by the nested nature of the sub-catchments, where downstream sites are dependent on conditions at sites upstream. When analyzing the trends in the different sites, this needs to be remembered.

The DIC data were collected and analyzed using established methods which had been validated by Åberg & Wallin (2014). Discharge, DOC, pH and water and air temperature data were similarly collected and analyzed using conventional methods. The uncertainty in discharge and temperature data was higher because the variables were collected at only one site each (the climate station Hygget for air temperature, site 7 for discharge and water temperature) and assumed to be accurate for all sites. The specific discharge in Krycklan has been found to vary greatly both spatially and temporally, especially for the smaller sub-catchments (Lyon et al. 2012). Therefore, the assumption of a uniform specific discharge across the entire Krycklan catchment is associated with an uncertainty. The estimated discharge and water temperature were however validated against the scarce existing data in other sites by comparing the relative difference between the estimated and actual data. Comparatively few data points produced large errors for both discharge and water temperature, particularly data points with calculated values close to 0. Those few points sometimes had several tens or hundreds of times the actual value. However, the chosen methods, both the MK test and Kendall's τ for correlation, are highly resistant to outliers in the data, and since the vast majority of data points had relative errors very close to 0, the actual impact of these errors was expected to be small. The air temperature data could not be validated, but was expected to follow similar tendencies as discharge and water temperature data. The expected errors arising from using these variables were deemed acceptable to the general analysis.

The MK test was chosen as method specifically because it is applicable to non-linear data and is resistant to outliers. The test lacks the modeling and extrapolating capabilities of linear regression, but gains immensely in its ability to work with heavily skewed and unevenly distributed data. For that reason, the tests produce less specific statistics, but the results can still be used to give broad indication of the present trends, and the results are more reliable than they would be using linear regression or something equivalent. Kendall's τ is similar and was chosen because of its relation to the MK test and because of its resistance to outliers.

4.5 PRACTICAL IMPLICATIONS AND FURTHER STUDIES

The aim of this study was to explore the trends in DIC over an extended period of time to gain a better understanding of DIC in the boreal region. The analyses did not produce clear results for the entire data set, but yielded important insights into seasonal trends in DIC concentrations and the causes for these trends. Even for a relatively small catchment like Krycklan, the spatial heterogeneity in DIC was considerable, and the resulting trends differed between sub-catchments with different characteristics. The results indicated that understanding local processes and interactions in both the soil and the stream is integral to describe DIC dynamics in the region. Temporally, the seasonal patterns showed that the variations in hydrology causes different trends in DIC concentrations for different seasons, thus affecting the environment differently depending on the season. More research is needed to extrapolate these trends to greater areas and to longer time scales, but these analyses give a first indication of how the DIC concentrations are changing in the boreal region.

There are many potential future research possibilities that could continue to improve the understanding of these boreal systems. The analyses of particularly discharge and water temperature would be interesting to expand. Accounting for the effect of variations in discharge on concentrations could potentially be done using flow-adjusted concentrations, as described by Hirsch, Slack, & Smith (1982). The relationship with water temperature could be examined further by accounting for the effects near freezing temperatures, possibly by excluding those records. The spatial analysis could also be deepened by either including other parameters, like hillside slope gradient, stream slope gradient and soil composition, or by analyzing the effects of several parameters at once through multivariate analysis. By analyzing the seasonal and annual trends in Krycklan further, it may also be possible to extrapolate the trends in time to create scenarios of how DIC in the catchment could continue to change in the future, given the expected changes in meteorology. Expanding the perspective, examining DIC trends elsewhere within the boreal region, both in catchments resembling Krycklan and catchments with different characteristics, could lead to an increased understanding of the spatial and temporal variabilities across the greater boreal region.

5 CONCLUSIONS

The trend and correlation analyses provided some interesting insights into the DIC concentrations in Krycklan over the period 2006–2019. Only two sites exhibited significant ($p \leq 0.05$) trends over the 14-year period, both being negative. When the data were grouped by season, distinct patterns emerged. No significant trends were found for the winter (December–March) data, and few significant trends were found for the autumn (September–November) data. The spring flood period (April–May) and to a lesser extent summer (June–August), however, exhibited significant negative trends across most sites (14 and 8 sites, respectively). This pattern suggested that DIC concentrations were subject to different regimes of change depending on the time of year.

For most sites in Krycklan, DIC concentrations were positively correlated with pH, showing the expected relationship between the two variables. Conversely, DIC was negatively correlated with DOC and discharge for most sites. Though a positive spatial relationship between DIC and DOC has been suggested in previous literature, it appears that this relationship does not hold for the Krycklan data. This could possibly indicate that DIC and DOC in Krycklan originate from different processes affected differently by external parameters. Increased discharge has previously been linked to dilution of DIC, and the observed negative correlations suggested that such was the case in Krycklan.

Finally, the spatial and temporal variability in DIC concentrations, as well as the appearance of differing trends in different sites, emphasized the need to understand local-scale processes to sufficiently describe DIC dynamics. This was exemplified by two sites in particular (sites 4 and 5), where the interactions of forest, peatland, and for one of the sites, a small lake, caused significant deviations from the general patterns in DIC.

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APPENDIX

A. DISCHARGE AND WATER TEMPERATURE VALIDATION

Relative error (estimated value – measured value)/estimated value) for discharge and water temperature data for all available sites (Figures A1 and A2). Time periods vary between 2006 and 2019 depending on site.

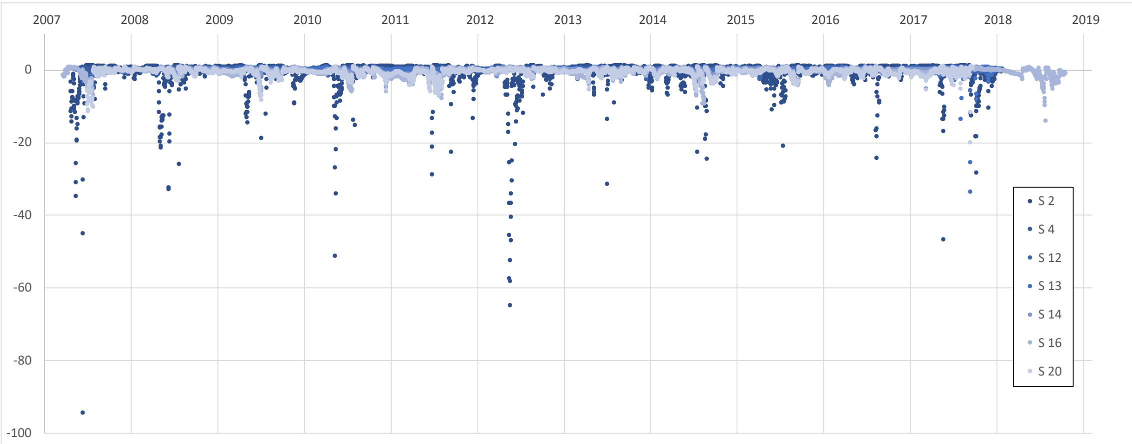

Figure A1: Relative error for discharge data. Estimated data is from site 7, and measured data existed for sites 2, 4, 12, 13, 14, 16 and 20.

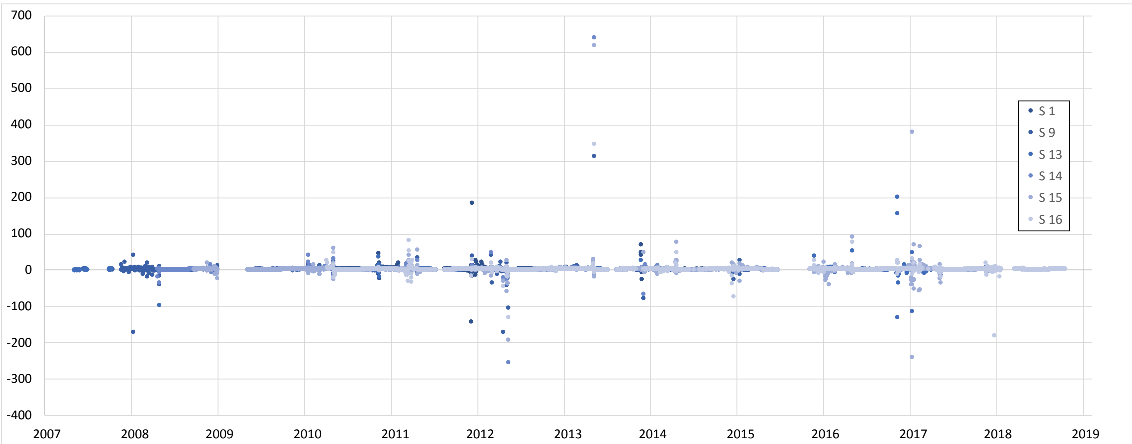

Figure A2: Relative error for water temperature data. Estimated data is from site 7, and measured data existed for sites 1, 9, 13, 14, 15 and 16.

B. EXPLORATORY ANALYSIS PLOTS AND TESTS

Time series (Figures B1 – B4), histograms (Figures B5 – B8), QQ-plots (Figures B9 – B12) and Shapiro-Wilk tests of normality (Table B1) for all sites.

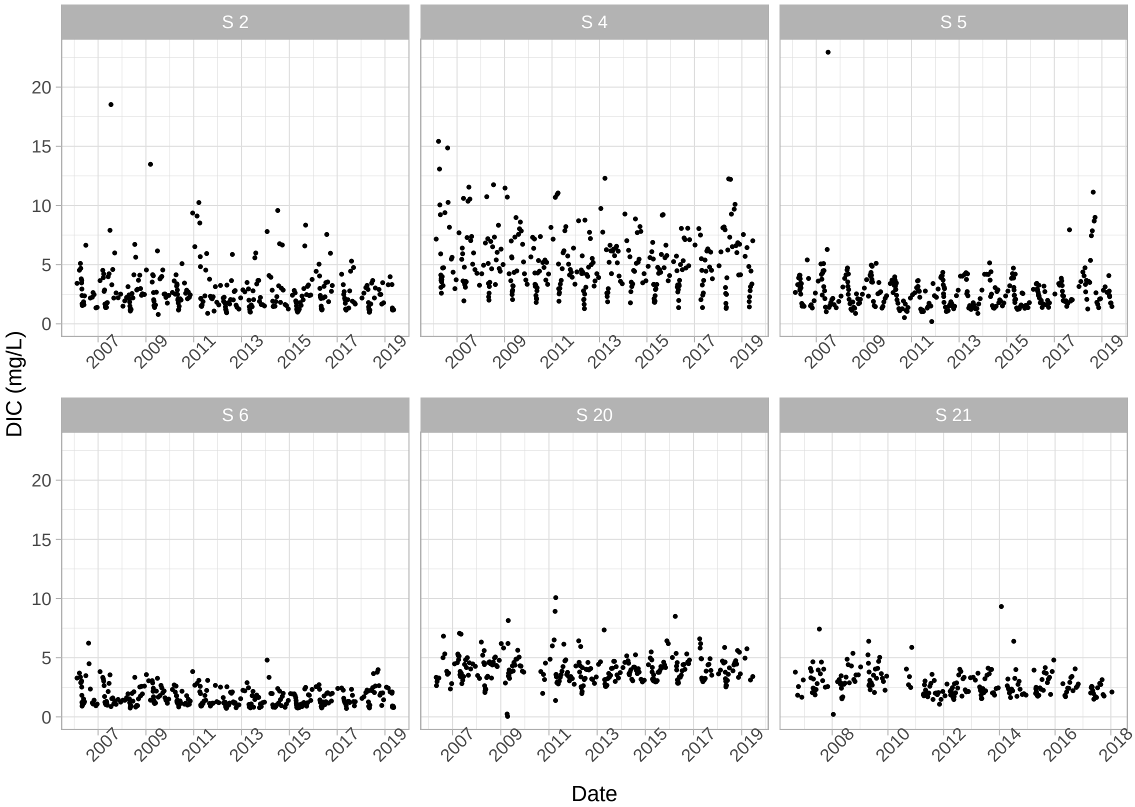

Figure B1: Time series for DIC data in sites with stream order 1.

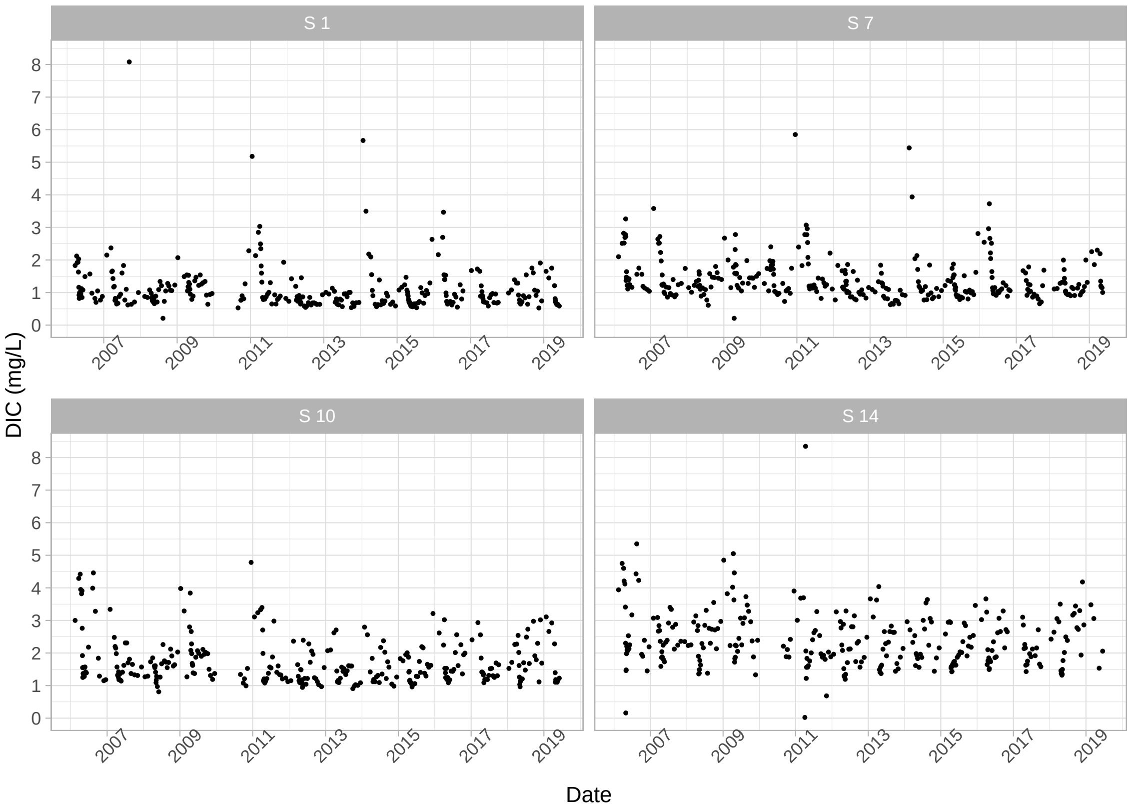

Figure B2: Time series for DIC data in sites with stream order 2.

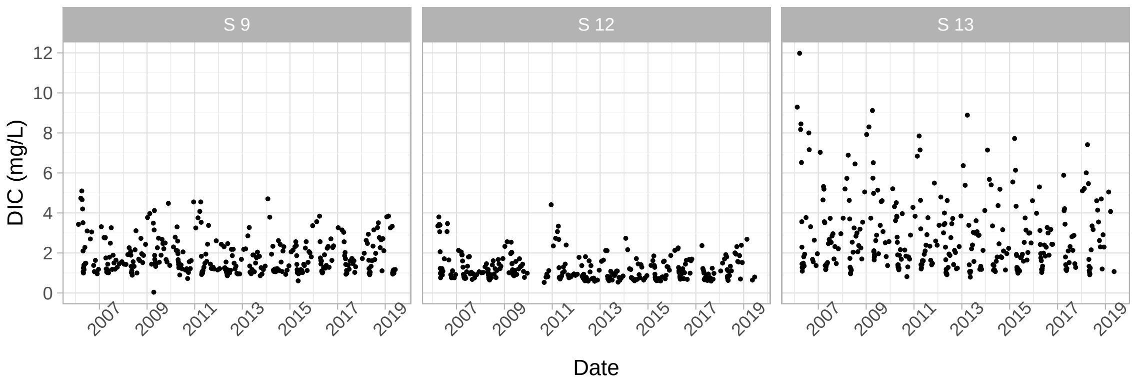

Figure B3: Time series for DIC data in sites with stream order 3.

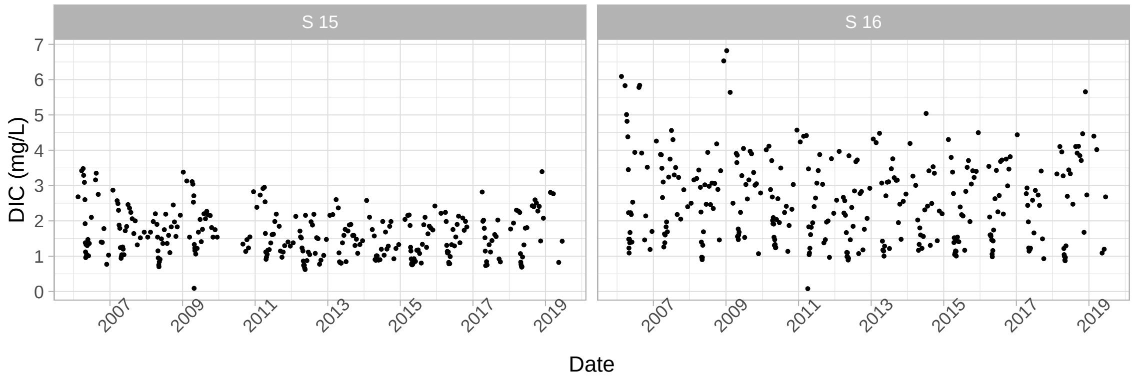

Figure B4: Time series for DIC data in sites with stream order 4.

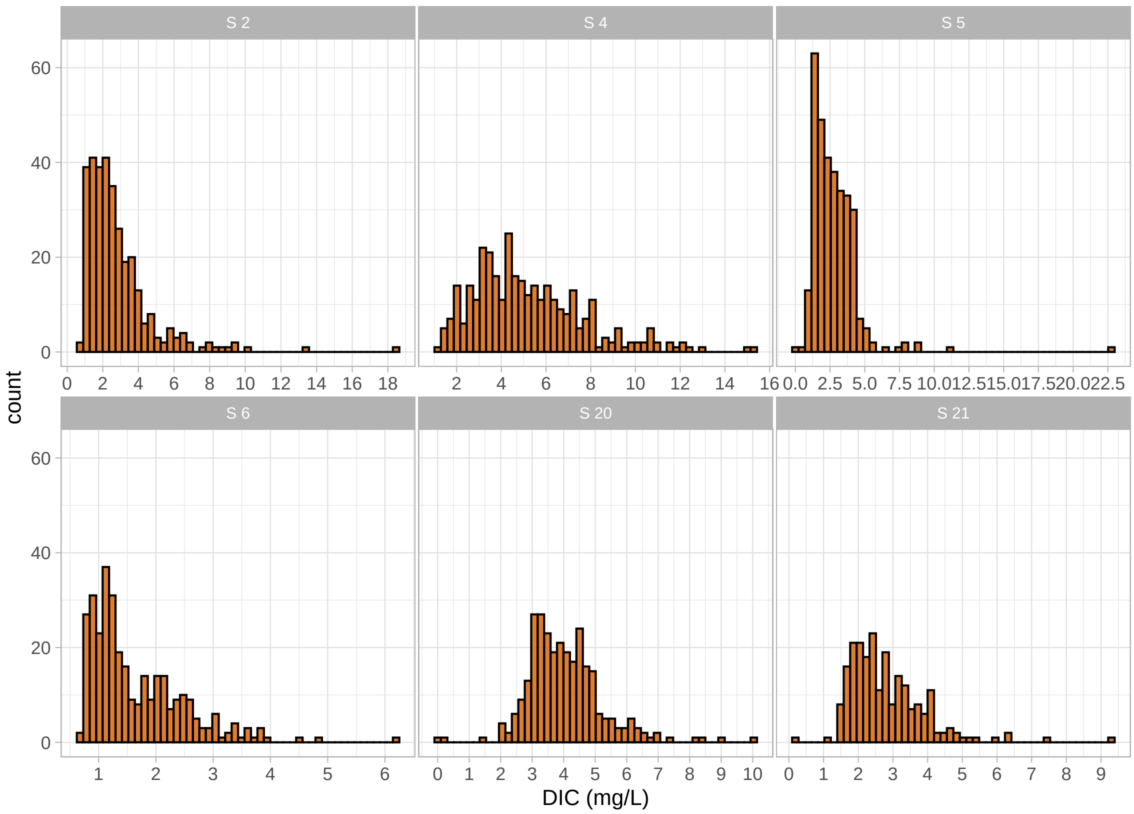

Figure B5: Histograms for DIC data in sites with stream order 1 (2006–2019).

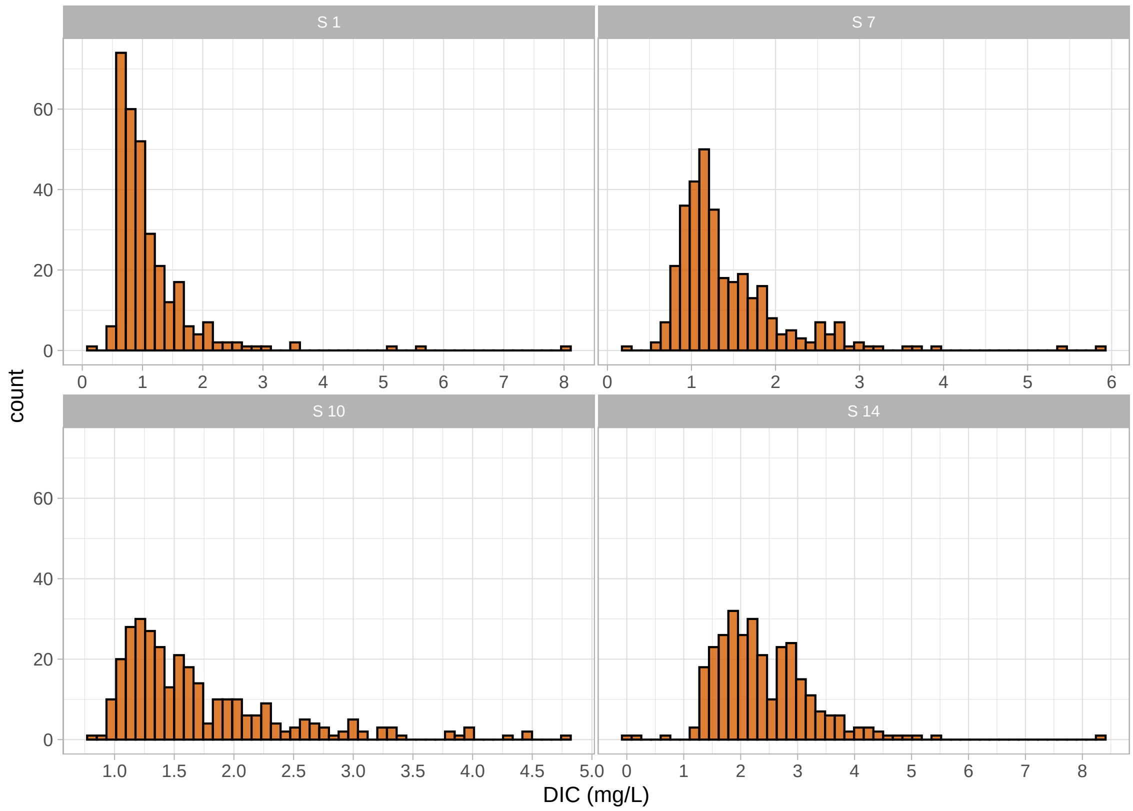

Figure B6: Histograms for DIC data in sites with stream order 2 (2006–2019).

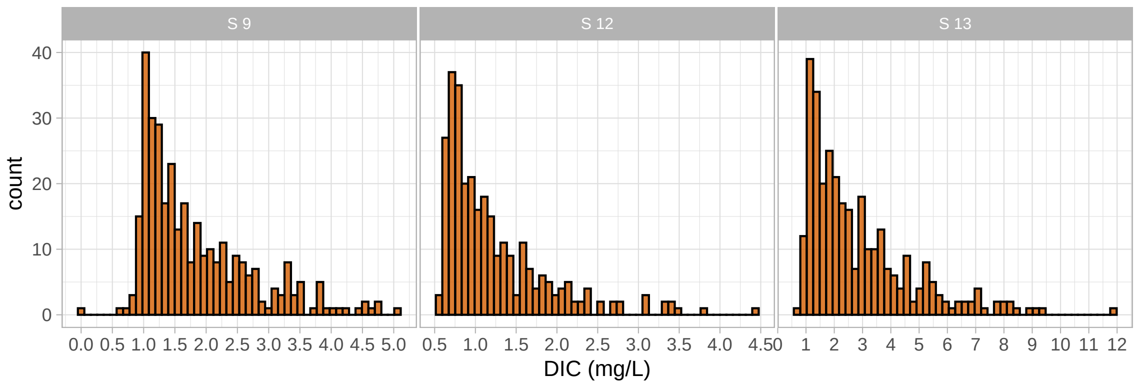

Figure B7: Histograms for DIC data in sites with stream order 3 (2006–2019).

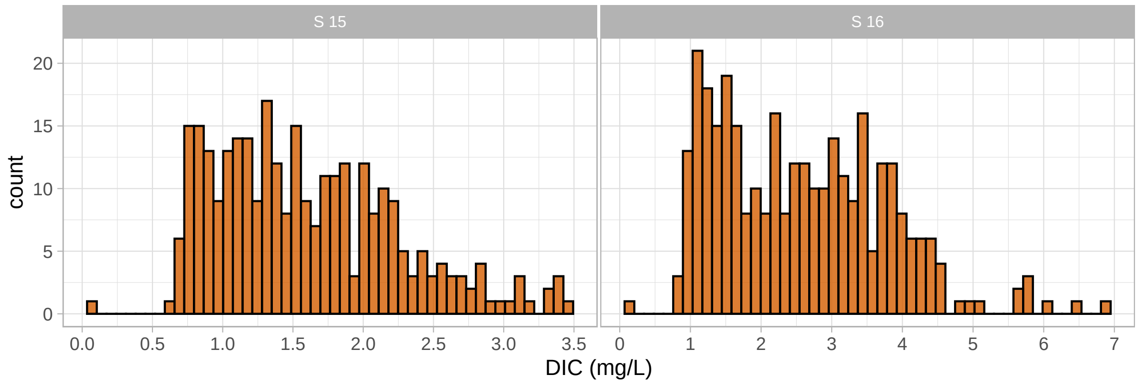

Figure B8: Histograms for DIC data in sites with stream order 4 (2006–2019).

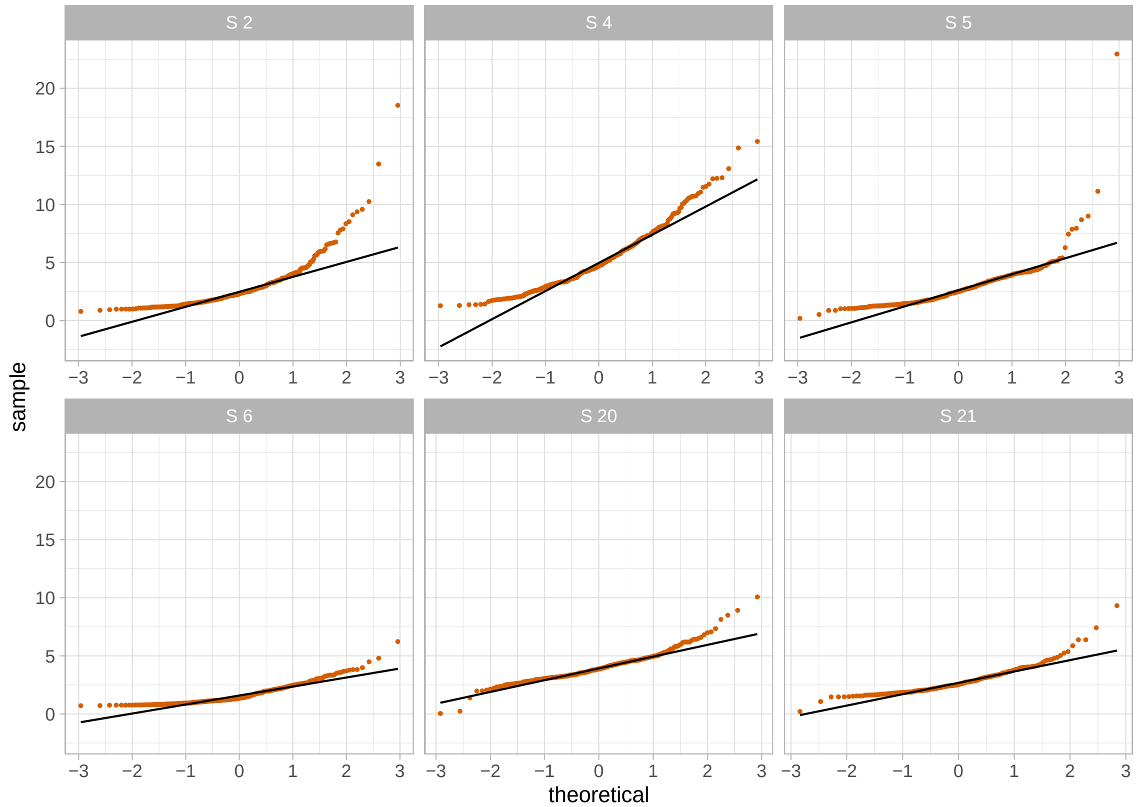

Figure B9: QQ-plots for DIC data in sites with stream order 1 (2006–2019).

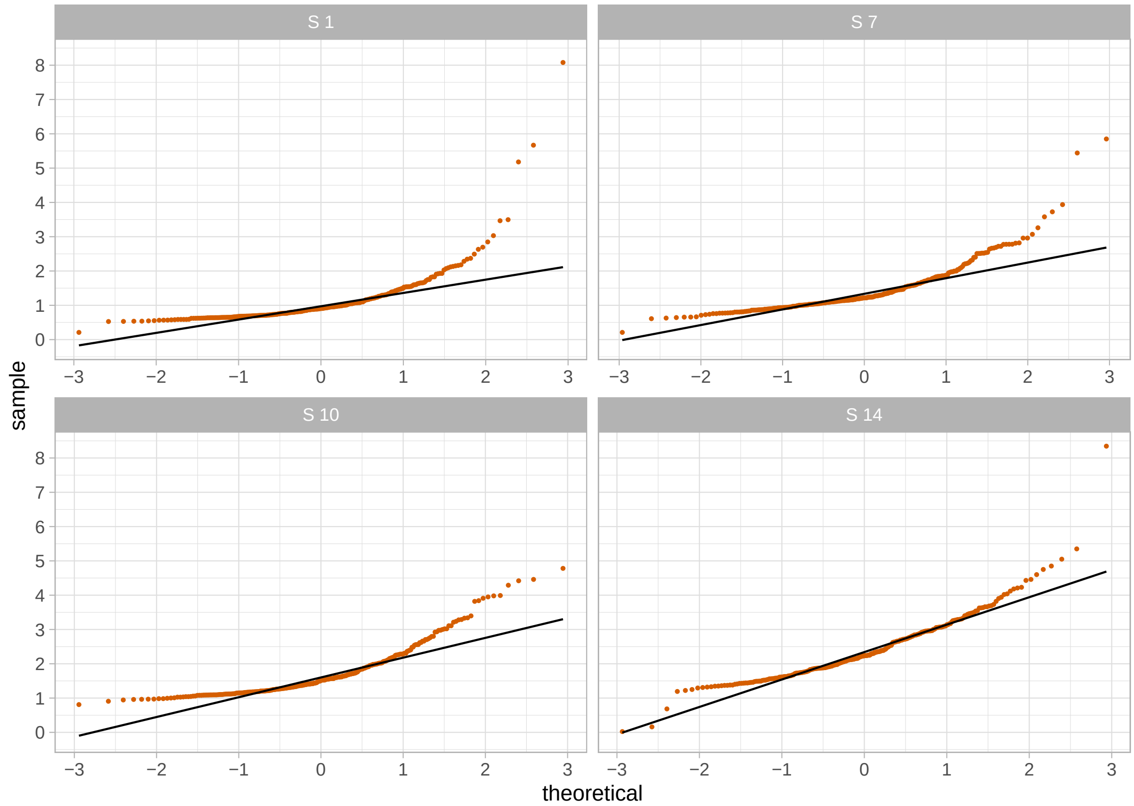

Figure B10: QQ-plots for DIC data in sites with stream order 2 (2006–2019).

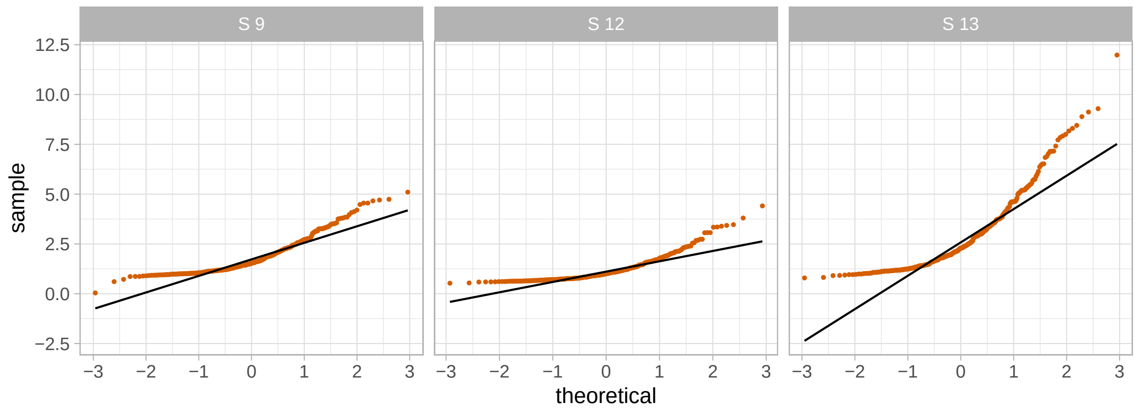

Figure B11: QQ-plots for DIC data in sites with stream order 3 (2006–2019).

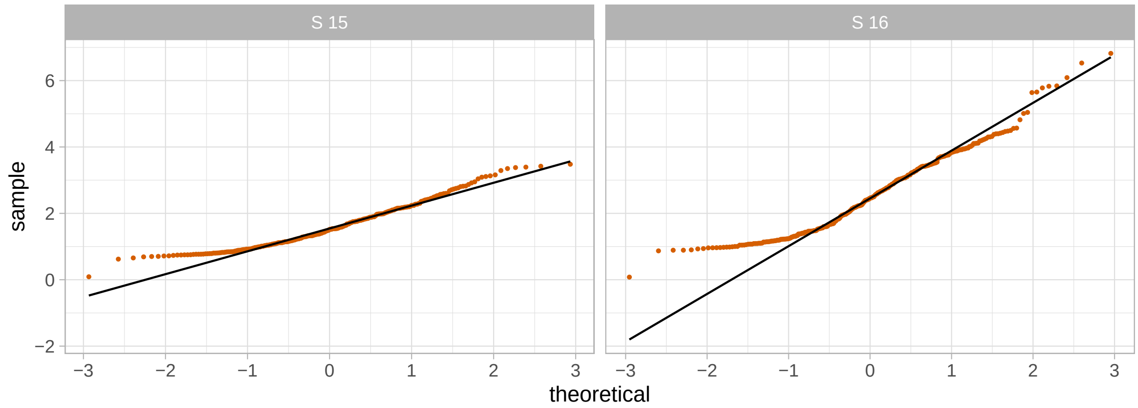

Figure B12: QQ-plots for DIC data in sites with stream order 4 (2006–2019).

Table B1: Shapiro-Wilk tests of normality for DIC data for all sites (2006–2019). Significant test results are marked in bold black font (95% confidence).

Site	Shapiro-Wilk score	p-value
S 1	**0.60**	**5.1E-26**
S 2	**0.73**	**2.1E-22**
S 4	**0.94**	**1.1E-10**
S 5	**0.66**	**6.5E-25**
S 6	**0.87**	**4.6E-16**
S 7	**0.79**	**4.0E-20**
S 9	**0.88**	**1.3E-15**
S 10	**0.83**	**8.6E-18**
S 12	**0.81**	**3.2E-18**
S 13	**0.85**	**4.7E-17**
S 14	**0.91**	**1.1E-12**
S 15	**0.96**	**6.3E-08**
S 16	**0.95**	**1.1E-08**
S 20	**0.93**	**3.8E-10**
S 21	**0.88**	**1.7E-12**

C. SPATIAL ANALYSIS BOXPLOTS

Boxplots over DIC concentrations in all sites, with data ranked by sub-catchment area (Figure C1) and percent of sub-catchment area covered by mire (Figure C2).

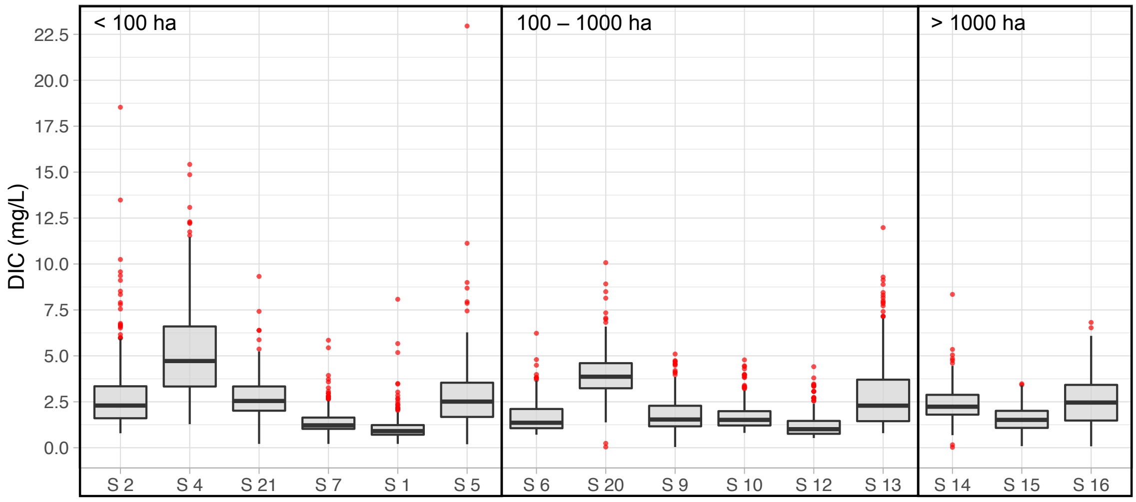

Figure C1: Boxplot with DIC data (2006–2019) for all sites ordered by sub-catchment area, from smallest (left) to largest (right), with median marked as a horizontal line inside each box, whiskers of up to 1.5 times the interquartile range, and outliers marked as red dots.

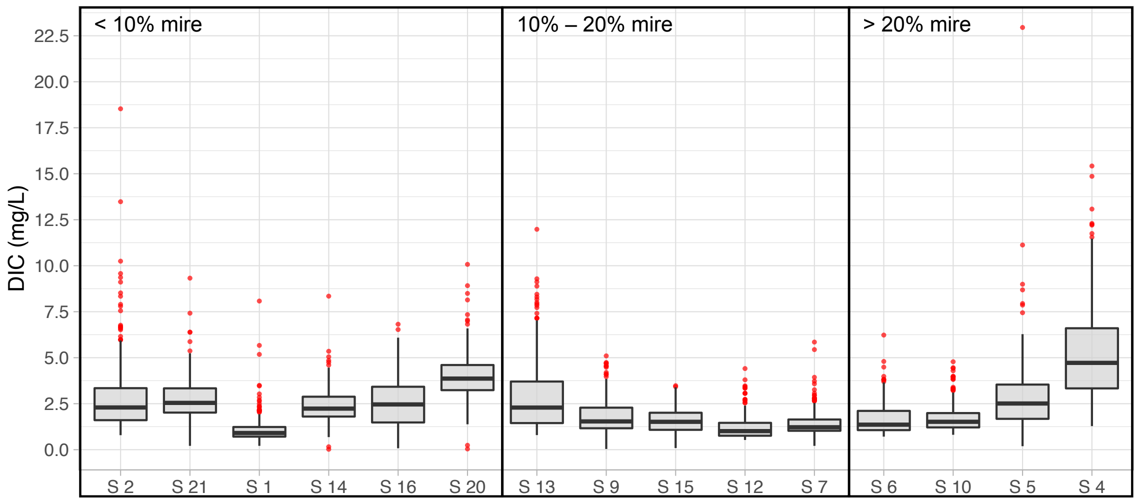

Figure C2: Boxplot with DIC data (2006–2019) for all sites ordered by percent of sub-catchment area covered by mire, from least mire (left), to most mire (right), with median marked as a horizontal line inside each box, whiskers of up to 1.5 times the interquartile range, and outliers marked as red dots.

D. TREND TESTS FOR MONTHLY GROUPED DATA

Mann-Kendall test results expressed as positive or negative signs for the test statistics for DIC concentration data grouped by month for all sites (Table D1).

Table D1: Mann-Kendall test results (positive or negative) for the monthly grouped DIC concentration data (2006–2019). Significant trends are marked in bold black font (90% confidence) and bold black font within brackets ”()” (95% confidence).

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
S 1	−	+	−	**−**	**(−)**	**(−)**	**−**	−	−	−	+	−
S 2	+	−	−	**(−)**	**(−)**	**−**	−	+	+	−	+	−
S 4	−	+	−	**(−)**	−	−	−	−	+	+	+	+
S 5	+	+	−	**(−)**	**(−)**	+	**+**	**+**	+	+	+	−
S 6	−	−	**−**	**(−)**	**(−)**	−	−	+	+	+	−	+
S 7	−	+	−	**(−)**	**(−)**	**(−)**	+	**−**	**(−)**	**(−)**	+	−
S 9	+	−	+	**(−)**	**(−)**	**−**	−	+	+	+	+	+
S 10	−	−	+	**(−)**	**(−)**	−	−	−	−	+	+	+
S 12	+	+	−	**(−)**	**(−)**	**−**	**−**	−	+	**+**	+	+
S 13	−	−	−	**(−)**	**−**	−	−	−	+	+	+	+
S 14	−	−	+	**−**	**−**	**−**	**(−)**	−	−	+	+	+
S 15	−	−	−	**(−)**	**(−)**	−	**(−)**	−	+	+	+	+
S 16	+	−	−	**(−)**	**−**	**−**	−	−	+	**(+)**	+	+
S 20	−	−	+	+	+	+	**−**	−	−	+	+	+
S 21	+		−	**−**	−	−	**(−)**	−	**−**	−	−	−

E. TREND TESTS FOR EXPLANATORY VARIABLES

Mann-Kendall test results expressed as positive or negative signs for the test statistics for monthly median data for the explanatory variables for all sites (Table E1), seasonally grouped discharge, air temperature and water temperature for site 7 and the weather station (Table E2) and seasonally grouped DOC and pH for all sites (Table E3).

Table E1: Mann-Kendall test results (positive or negative) for the monthly median DOC concentration, pH, discharge, air temperature and water temperature data (2006–2019). Significant trends are marked in bold black font (90% confidence) and bold black font within brackets ”()” (95% confidence).

Site	DOC	pH	Discharge	Air temp	Water temp
S 1	**(+)**	+			
S 2	**(+)**	+			
S 4	+	+			
S 5	**(–)**	**(+)**			
S 6	+	+			
S 7	+	+	–	+	+
S 9	+	–			
S 10	+	+			
S 12	+	+			
S 13	+	–			
S 14	+	**–**			
S 15	–	–			
S 16	+	–			
S 20	+	–			
S 21	+	+			

Table E2: Mann-Kendall test results (positive or negative) for the seasonally grouped discharge, air temperature and water temperature data (2006–2019). Significant trends are marked in bold black font (90% confidence) and bold black font within brackets ”()” (95% confidence). Note that discharge and water temperature were only available in site 7, and air temperature in a separate weather station.

Season	Discharge	Air temp	Water temp
Winter (Dec–Mar)	**–**	+	**(+)**
Spring flood (Apr–May)	–	+	**(+)**
Summer (Jun–Aug)	+	+	**(+)**
Autumn (Sep–Nov)	–	–	+

Table E3: Mann-Kendall test results (positive or negative) for the seasonally grouped DOC concentration and pH data (2006–2019). Significant trends are marked in bold black font (90% confidence) and bold black font within brackets ”()” (95% confidence).

	Winter (Dec–Mar)		Spring flood (Apr–May)	
Site	DOC	pH	DOC	pH
S 1	**+**	**(+)**	**(+)**	**(–)**
S 2	+	+	**(+)**	**(–)**
S 4	+	+	**(–)**	–
S 5	**(–)**	**(+)**	+	**(–)**
S 6	+	+	**(+)**	**(–)**
S 7	**+**	+	+	**(–)**
S 9	+	0	**(+)**	**(–)**
S 10	+	+	+	**(–)**
S 12	**+**	+	+	**(–)**
S 13	+	+	**(+)**	**(–)**
S 14	+	–	**+**	**(–)**
S 15	+	–	**(+)**	**(–)**
S 16	**+**	–	+	**(–)**
S 20	**+**	–	+	**(–)**
S 21	**–**	+	–	+

	Summer (Jun–Aug)		Autumn (Sep–Nov)	
Site	DOC	pH	DOC	pH
S 1	**(+)**	**–**	–	**(+)**
S 2	**(+)**	+	+	**(+)**
S 4	+	–	**–**	**(+)**
S 5	**(–)**	**(+)**	**(–)**	**(+)**
S 6	+	–	**(–)**	**(+)**
S 7	**(+)**	–	**(–)**	**(+)**
S 9	**+**	–	**(–)**	**(+)**
S 10	+	–	**(–)**	**(+)**
S 12	+	–	**–**	**(+)**
S 13	**(+)**	**–**	**(–)**	**(+)**
S 14	+	**(–)**	**(–)**	+
S 15	+	**(–)**	**(–)**	+
S 16	+	**(–)**	**(–)**	+
S 20	+	**(–)**	**(–)**	0
S 21	+	–	–	+

F. DIC–EXPLORATORY VARIABLE PLOTS

Plots of DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for each site, along with calculated Kendall's τ and corresponding p-value for each variable (Figures F1 – F15).

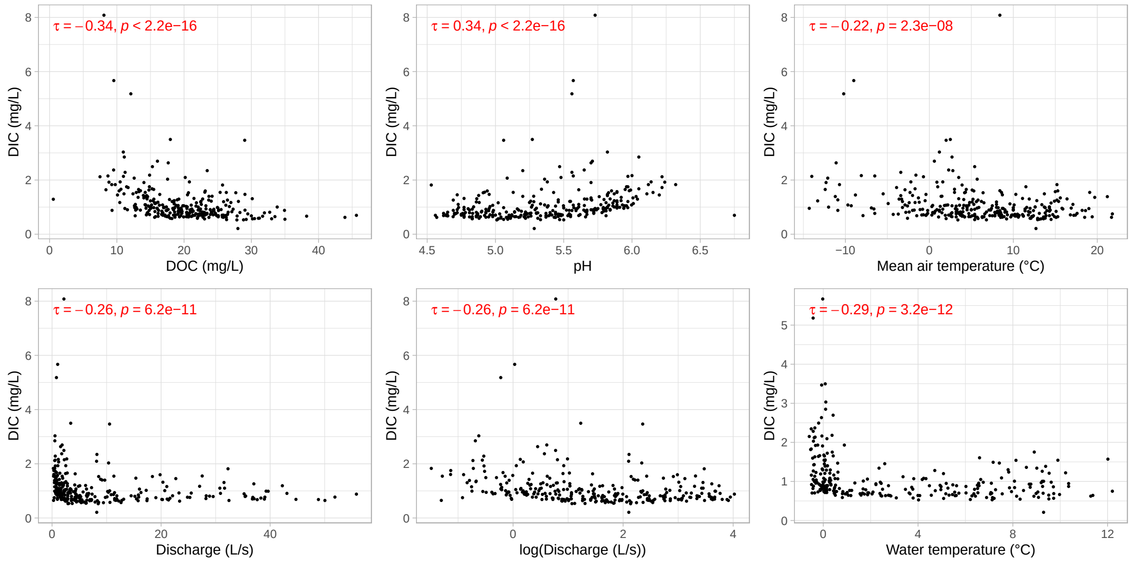

Figure F1: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 1. Kendall's τ with corresponding p-value is also shown.

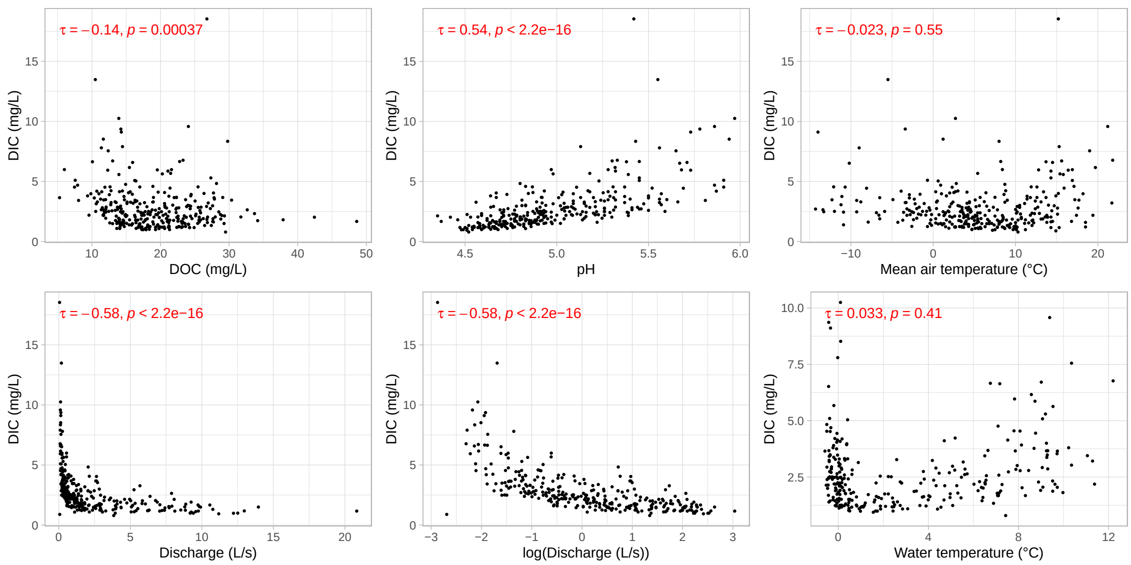

Figure F2: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 2. Kendall's τ with corresponding p-value is also shown.

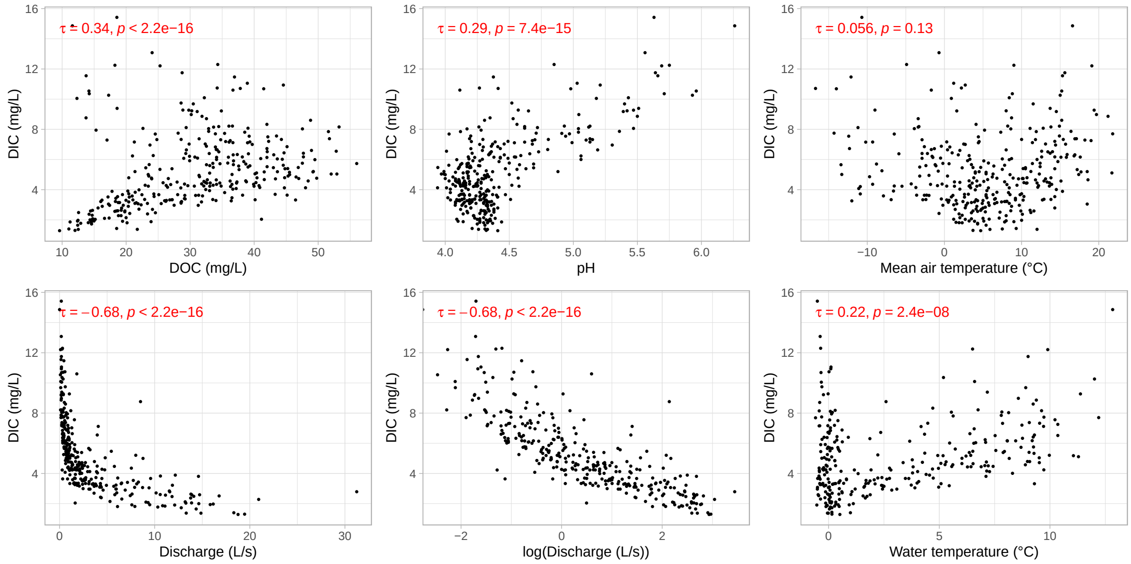

Figure F3: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 4. Kendall's τ with corresponding p-value is also shown.

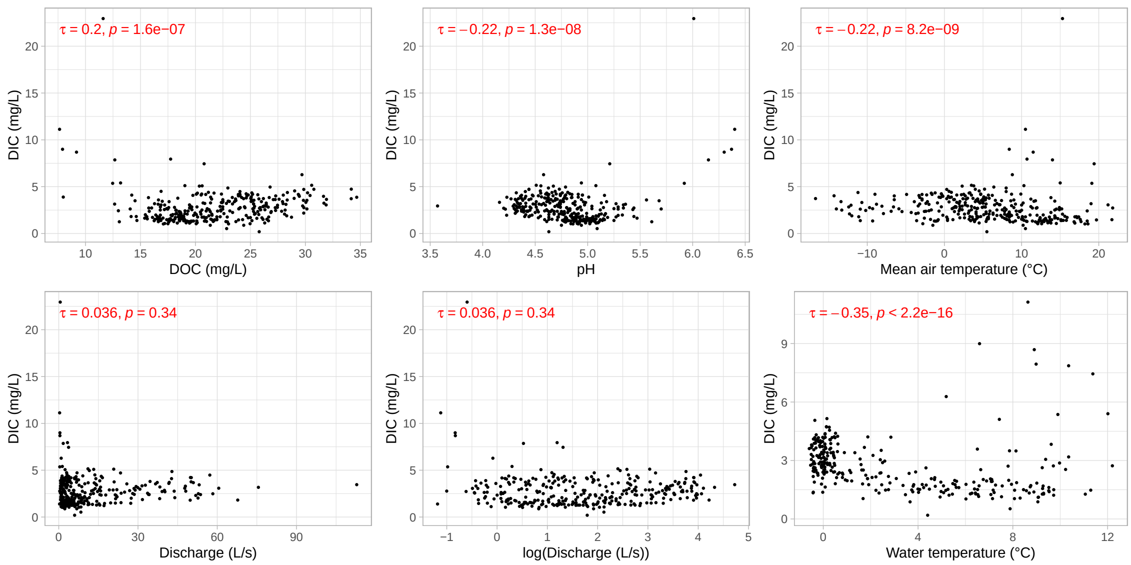

Figure F4: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 5. Kendall's τ with corresponding p-value is also shown.

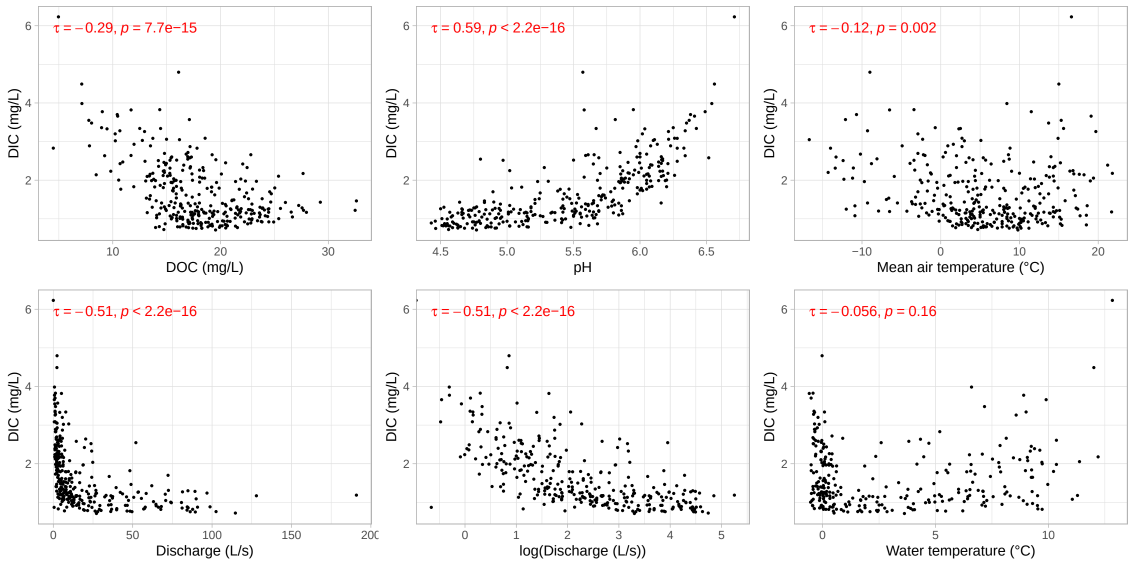

Figure F5: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 6. Kendall's τ with corresponding p-value is also shown.

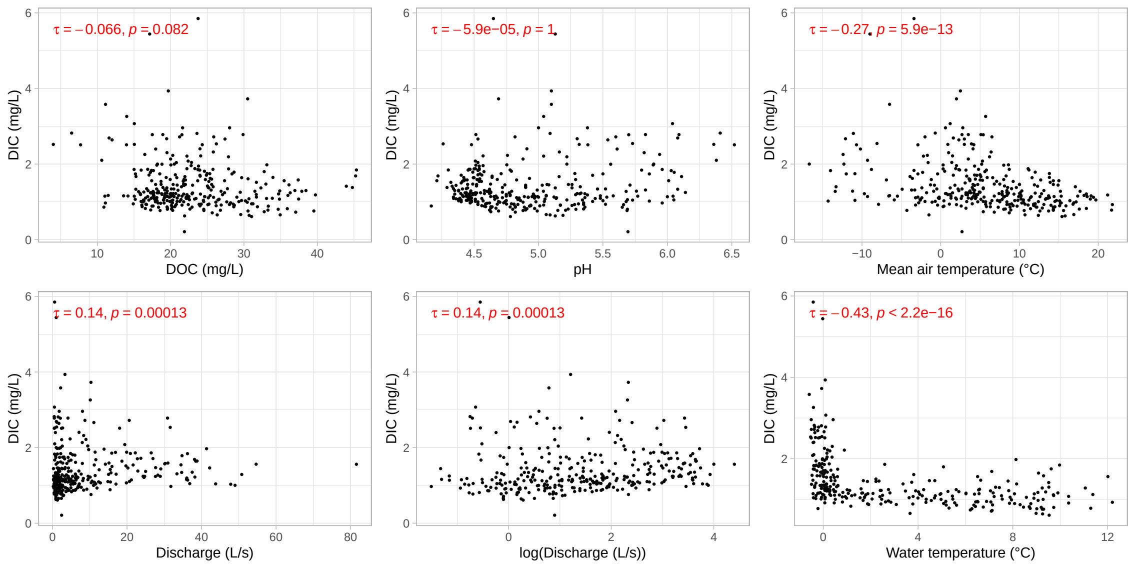

Figure F6: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 7. Kendall's τ with corresponding p-value is also shown.

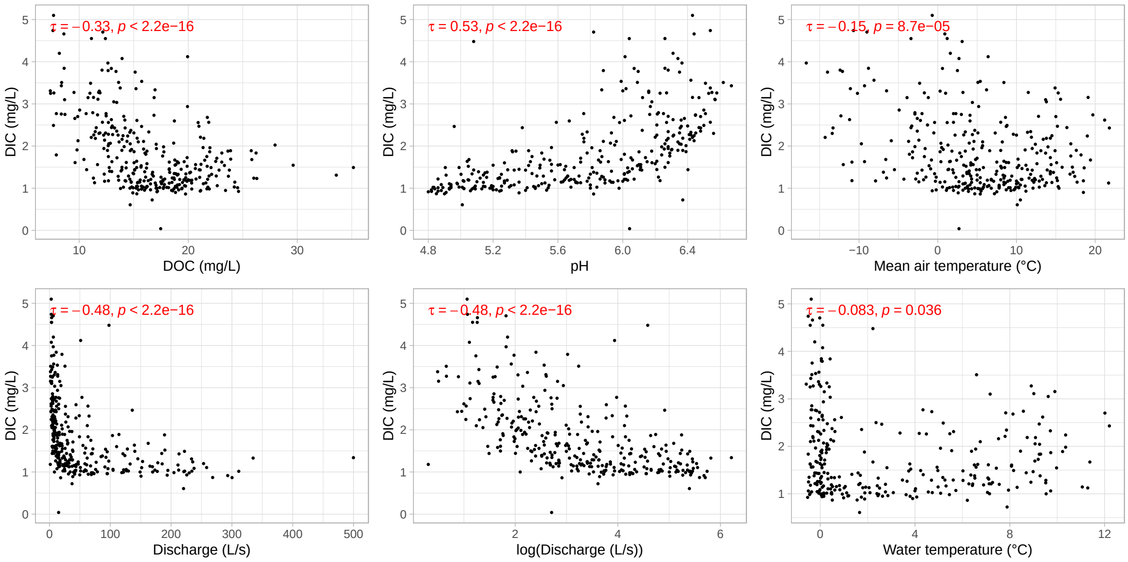

Figure F7: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 9. Kendall's τ with corresponding p-value is also shown.

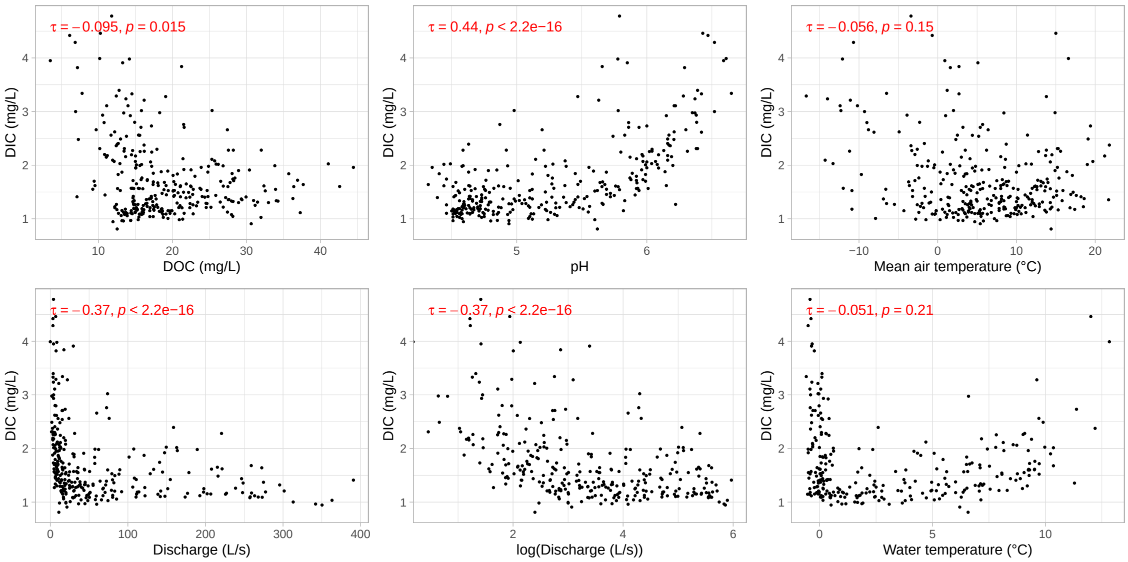

Figure F8: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 10. Kendall's τ with corresponding p-value is also shown.

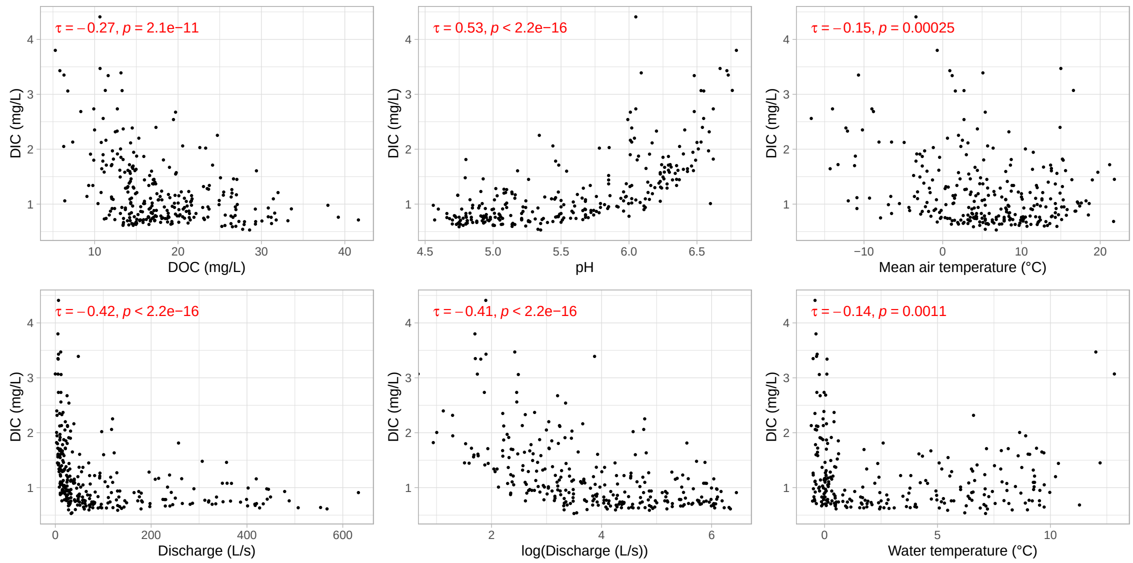

Figure F9: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 12. Kendall's τ with corresponding p-value is also shown.

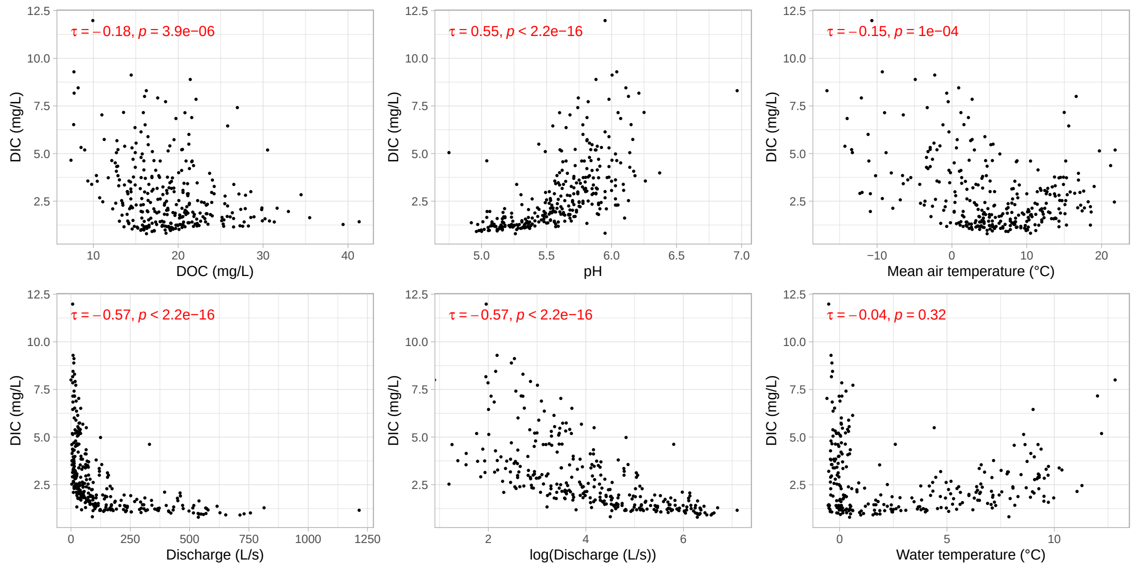

Figure F10: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 13. Kendall's τ with corresponding p-value is also shown.

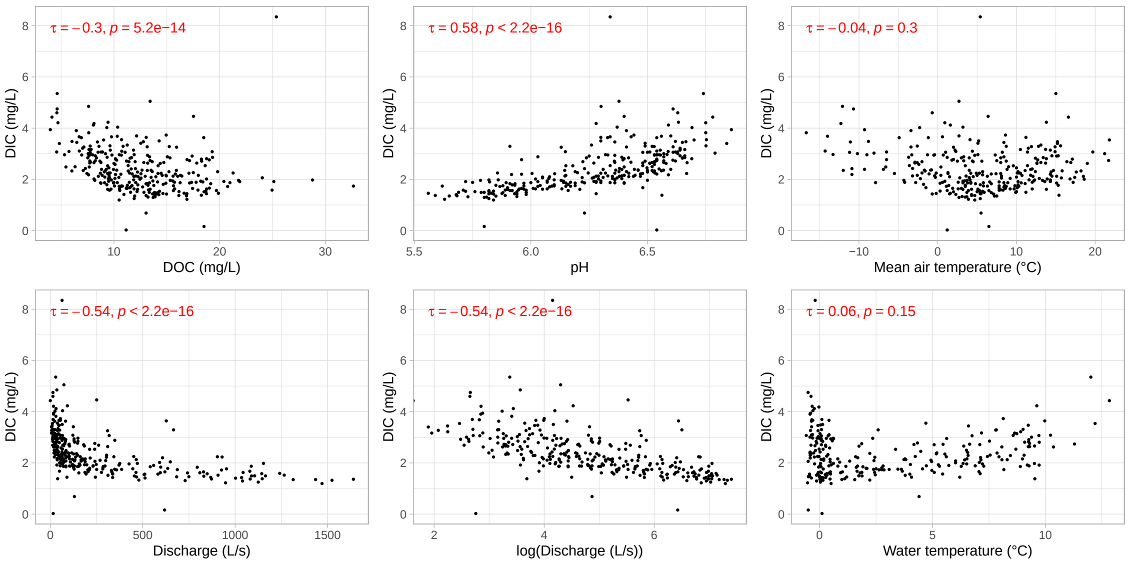

Figure F11: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 14. Kendall's τ with corresponding p-value is also shown.

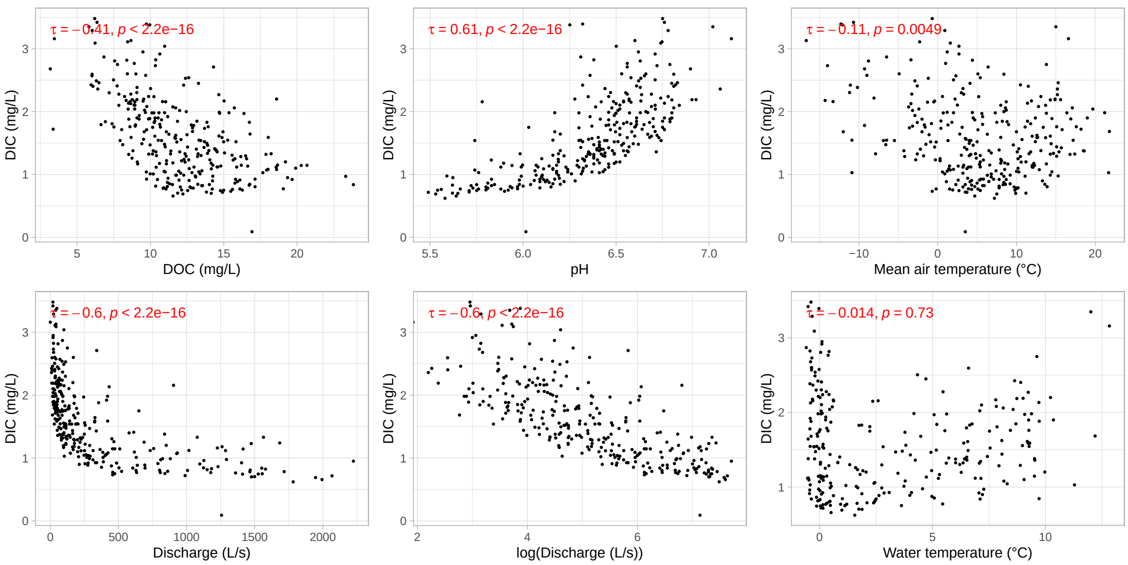

Figure F12: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 15. Kendall's τ with corresponding p-value is also shown.

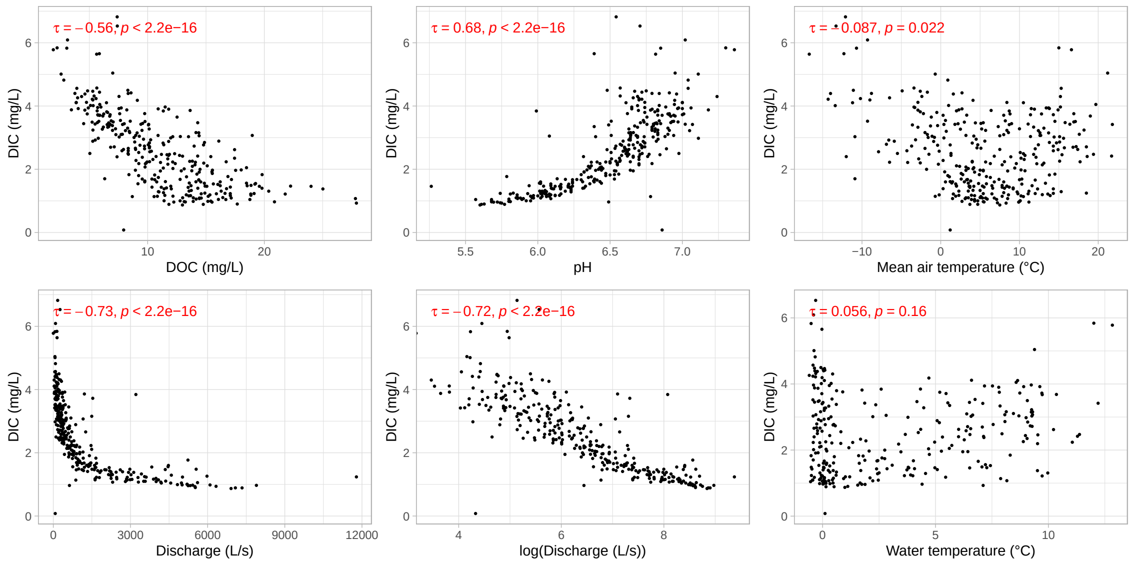

Figure F13: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 16. Kendall's τ with corresponding p-value is also shown.

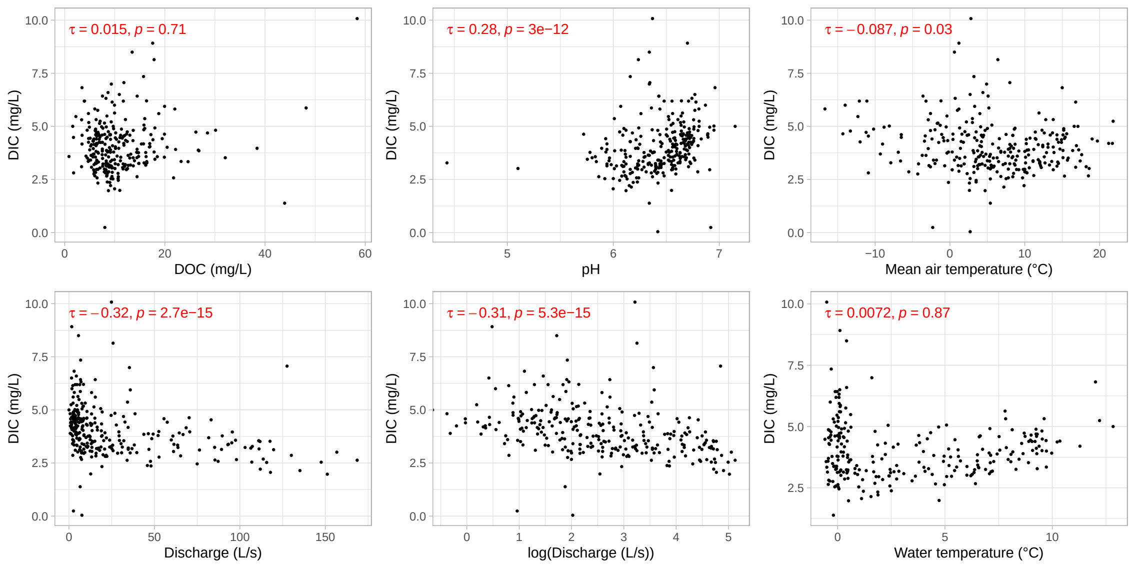

Figure F14: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 20. Kendall's τ with corresponding p-value is also shown.

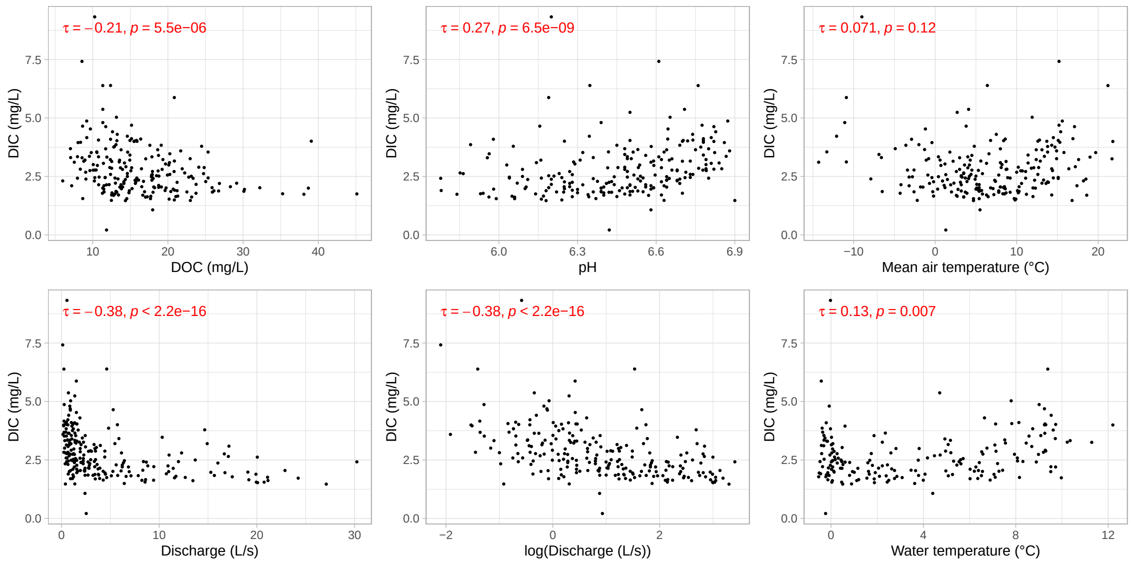

Figure F15: DIC as a function of DOC, pH, mean air temperature, discharge, log(discharge) and water temperature for site 21. Kendall's τ with corresponding p-value is also shown.