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Key Points:

- All groundwater samples at soil depths between 3 and 20 m showed $p\text{CO}_2$ oversaturation relative to the atmosphere
- Along the soil depth profile, $p\text{CO}_2$ in groundwater was negatively related to both $\delta^{13}\text{C}\text{-DIC}$ and pH
- The positive $\delta^{13}\text{C}\text{-DIC}$ -depth relationship was likely due to diffusion-related fractionation and isotopic discrimination thru soil respiration

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Groundwater Carbon Within a Boreal Catchment: Spatiotemporal Variability of a Hidden Aquatic Carbon Pool

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Abstract Groundwater is an essential resource providing water for societies and sustaining surface waters. Although groundwater at intermediate depth could be highly influential at regulating lake and river surface water chemistry, studies quantifying organic and inorganic carbon (C) species in intermediate depth groundwater are still rare. Here, we quantified dissolved and gaseous C species in the groundwater of a boreal catchment at 3- to 20-m depth. We found that the partial pressure of carbon dioxide ($p\text{CO}_2$), the stable carbon isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}\text{-DIC}$), and pH showed a dependency with depth. Along the depth profile, a negative relationship was observed between $p\text{CO}_2$ and $\delta^{13}\text{C}\text{-DIC}$ and between $p\text{CO}_2$ and pH. We attribute the negative $p\text{CO}_2$ -pH relationship along the depth gradient to increased silicate weathering and decreased soil respiration. Silicate weathering consumes carbon dioxide (CO_2) and release base cations, leading to increased pH and decreased $p\text{CO}_2$. We observed a positive relationship between $\delta^{13}\text{C}\text{-DIC}$ and depth, potentially due to diffusion-related fractionation in addition to isotopic discrimination during soil respiration. Soil CO_2 may diffuse downward, resulting in a fractionation of the $\delta^{13}\text{C}\text{-DIC}$. Additionally, the dissolved organic carbon at greater depth may be recalcitrant consisting of old degraded material with a greater fraction of the heavier C isotope. Our study provides increased knowledge about the C biogeochemistry of groundwater at intermediate depth, which is important since these waters likely contribute to the widespread CO_2 oversaturation in boreal surface waters.

Plain Language Summary Groundwater is the second largest reservoir of freshwater on Earth, sustaining rivers and lakes and providing water for humans. Groundwater can have high concentrations of carbon and be a source of carbon dioxide, both to surface waters and to the atmosphere. We performed our study to get a better understanding of how much carbon and carbon dioxide there is in groundwater at intermediate depths, between 3 and 20 m, as this water will eventually reach downstream rivers and lakes. Our results show that the groundwater in the studied catchment contained much higher levels of carbon dioxide than the atmosphere. We also observed large variation in the concentrations of carbon dioxide at different depths and at different locations across the catchment. Several factors are responsible for the observed carbon dioxide variations, with soil respiration and weathering of silicate minerals being the most important ones. Our study provides a better understanding of the distribution and dynamics of carbon at intermediate depth groundwater, which is important since it is an essential regulator of surface water chemistry in lakes and rivers, and indirectly being a source of carbon dioxide to the atmosphere.

1. Introduction

Groundwater is the second largest freshwater reservoir making up to 30% of all freshwater globally, to be compared with the surface water reservoir of approximately 0.3% (Shiklomanov, 2000). Groundwater is an integral part of a complex hydrologic cycle and plays a crucial role in sustaining surface water systems (streams, lakes, and wetlands) with water (Alley, 2009). Despite the groundwater-surface water connectivity, the chemical composition of groundwater and the biogeochemical processes leading to changes in the chemical composition of groundwater have received relatively little attention in surface water studies (LaBaugh, 2009).

Small headwater streams are generally fed by shallow groundwater; hence, the water chemistry in these systems closely reflects terrestrial processes such as those occurring in the riparian zone (Grabs et al., 2012;

Ledesma et al., 2015). Consequently, the importance of catchment processes generally becomes prominent in small headwater streams; however, at larger scales stream water chemistry becomes regulated by factors other than shallow flow paths alone (Tiwari et al., 2014). As a consequence, as the catchment scales up from headwater to mesoscale and macroscale systems, there are increasing contributions from deeper groundwater with longer hydrological pathways, particularly during baseflow (Hood et al., 2005; Peralta-Tapia et al., 2015). Larger streams further down in a catchment are fed by both shallow and deep groundwater as well as by surface water from upstream. The combination of these sources, in addition to in-stream processes, regulates the downstream water chemistry (Hagedorn et al., 2000; Klaminder et al., 2011). However, groundwater input in relation to total stream water volume decreases along a stream-river continuum (Hotchkiss et al., 2015).

Groundwater usually contains high concentrations of dissolved inorganic carbon (DIC; Boerner & Gates, 2015; Macpherson, 2009) and has been recognized as an important source of carbon dioxide (CO_2) in riverine systems, particularly in small headwater streams (Hotchkiss et al., 2015; Winterdahl et al., 2016). Direct inputs of CO_2 produced in catchment soils and delivered via subsurface and shallow groundwater flow to surface waters can result in high fluvial and in-lake CO_2 concentrations (Leith et al., 2015; Maberly et al., 2013; Weyhenmeyer et al., 2015). Despite this, groundwater has yet not sufficiently been considered in the global carbon (C) cycle, mainly due to the lack of empirical data.

Heterotrophic respiration of organic matter in soils and root respiration (i.e., soil respiration) are key sources of CO_2 in groundwater. Both processes occur with negligible isotopic discrimination between the organic matter substrate and the CO_2 produced (Lin & Ehleringer, 1997). Therefore, the stable C isotopic composition ($\delta^{13}\text{C}$) of CO_2 produced by respiration is approximately equivalent to the $\delta^{13}\text{C}$ of the predominant organic matter (Doctor et al., 2008). Dissolution of soil CO_2 and mineral weathering are key sources of DIC in groundwater, making the $\delta^{13}\text{C}$ of DIC a useful tool for deciphering the DIC sources (Campeau et al., 2018; Craft et al., 2002; Deirmendjian & Abril, 2018). Carbonate containing rocks and minerals have a $\delta^{13}\text{C}$ of approximately 0‰, resulting in a less negative $\delta^{13}\text{C}$ -DIC if carbonate weathering occurs (Clark & Fritz, 1997). Silicate weathering, on the other hand, results in a $\delta^{13}\text{C}$ -DIC similar to soil respiration (Telmer & Veizer, 1999). The $\delta^{13}\text{C}$ -DIC of soil respiration is close to that of the dominating plants in the catchments and ranges between -22 and -34 ‰ for C_3 plants (Vogel, 1993). Mineral weathering can also lead to increased acid neutralizing capacity and enhanced pH through the release of base cations, which could subsequently lead to a shift in the carbonate equilibrium toward a lower proportion CO_2 in comparison to other inorganic C species. Consequently, pH often increases with depth (Klaminder et al., 2011), which subsequently decrease the CO_2 proportion of the DIC pool. Although silicate weathering could lead to a shift in the carbonate system due to a change in pH, this would not influence the $\delta^{13}\text{C}$ -DIC signature. Additionally, the isotopic composition of soil CO_2 can become enriched in ^{13}C by up to 5‰ relative to soil organic matter since the different isotopes diffuse against their own gradients through the soil pores (Amundson et al., 1998). Another important process that could lead to a change in isotopic composition of CO_2 is isotopic discrimination during microbial decomposition (Formanek & Ambus, 2004).

A number of studies have shown groundwater to be supersaturated with methane (CH_4) relative to the atmosphere (Deirmendjian et al., 2019; Jurado et al., 2018; Molofsky et al., 2016). Groundwater could act as a significant pathway for the indirect emission of both CO_2 and CH_4 (Minamikawa et al., 2010). In groundwater systems less than 400-m deep, CH_4 is produced solely through biogenic pathways (i.e., microbial mineralization; Coleman et al., 1977). Biogenic CH_4 can be produced via CO_2 reduction or fermentation of acetate; however, in shallow groundwater acetate fermentation has primarily been assumed to be the dominating process (Chapelle, 2001). However, a recent study of shallow groundwater in peat-rich areas demonstrated that CO_2 reduction was the dominating pathway for CH_4 production (Campeau et al., 2018). Confined conditions where water circulation is absent or infrequent have been suggested to have highest reductive potential for CH_4 in groundwater due to the prevalence of anoxia (Goddy & Darling, 2005).

Although groundwater may be a minor volumetric source of water to many lakes, the high concentrations of dissolved species could make groundwater a major driver of surface water chemistry (Einarsdottir et al., 2017; Schmidt et al., 2009; Shaw et al., 2013). Furthermore, deeper groundwater input could be highly

influential regulating downstream river chemistry, specifically during base flow conditions (Tiwari et al., 2017). Despite the importance of groundwater to surface water chemistry (Cook et al., 2003; Hotchkiss et al., 2015; Su et al., 2015), little is known about the groundwater chemical composition at intermediate depths (down to 20 m) and its influence on surface water chemistry. As groundwater at intermediate depth could potentially be a significant source to downstream surface waters in larger catchments (Sterte et al., 2018) it could also be an important source of various C species.

Here our goal was to overcome previous lack of empirical data and improve our understanding of the C biogeochemistry of groundwater at intermediate depths of the boreal landscape, thereby providing better knowledge about its role in C dynamics of inland waters. To meet this goal, we quantified dissolved and gaseous C species in the groundwater across a mesoscale boreal catchment at depths between 3 and 20 m. By sampling at different depths, locations, and seasons we assessed the spatial and temporal variability in groundwater C.

2. Materials and Methods

2.1. Study Area

The study was carried out within the 68-km² large Krycklan Catchment area (64°14'N, 19°46'E) located in the boreal region of northern Sweden (Figure 1; for further details, see Laudon et al., 2013). The catchment is composed of 15 monitored subcatchments 0.03 to 21.7 km² and has been intensively monitored for multidisciplinary research projects within the Krycklan Catchment Study (KCS) since 2002. The KCS also includes the Svartberget catchment where monitoring began already in 1981. Mean annual air temperature in the catchment is 1.8°C, and the annual precipitation is about 600 mm of which approximately 50% becomes runoff (Laudon et al., 2013). The average period of snow cover is 167 days, from late October to early May (Laudon & Löfvenius, 2016).

Forest covers most of the catchment (54–98%, of the subcatchments), with lower proportions of peatlands (0–44%) and agricultural land (0–3%). Surface waters (sum of lake and stream area) cover 0.1–4.7% of the subcatchments. The dominant tree type, particularly in the dry upslope areas, is Scots pine (*Pinus sylvestris*; 63%), followed by Norway spruce (*Picea abies*; 26%), which is found mostly in the wetter, lowland areas. The understory is dominated by ericaceous shrubs, mostly European blueberry (*Vaccinium myrtillus*) and lingonberry (*Vaccinium vitis-idaea*) on moss mats of *Hylocomium splendens* and *Pleurozium schreberi*. Deciduous shrubs and trees, primarily birch (*Betula* spp.) but also alder (*Alnus incana*) and willow (*Salix* spp.), are found in the riparian forest along larger streams (Andersson & Nilsson, 2002). Peatlands are dominated by *Sphagnum* species and can be categorized as acid, oligotrophic, and minerogenic mires.

The gneissic bedrocks consist of Svecofennian rocks with 94% metasediments/metagraywacke, 4% acid and intermediate metavolcanic, and 3% basic metavolcanic rock (Ågren et al., 2007). Altitude ranges from 127 m above sea level (asl) at the outlet to 372 m asl at the highest elevation of the catchment. The region was glaciated and is undergoing isostatic rebound following the last deglaciation. The highest postglacial coastline traverses the catchment at approximately 255–260 m asl dividing the catchment into two distinctly different parts. The upper part of the watershed is covered by quaternary deposits that are dominated by glacial till varying in thickness from zero to up to tens of meters. The lower part of the catchment is dominated by postglacial sediments largely composed of silt and fine sand that were deposited in the distal of a postglacial delta. The total sediment depth in the area varies between 5 and 40 m (Laudon et al., 2013). The sediment deposits form a thick layer through which the larger traversing streams have deeply incised channels, in some cases forming ravines and bluffs of up to 30-m height (Buffam et al., 2008). In the till soils, well-developed iron podzols dominate the forest floor soils, but near the stream channels, the organic content increases, forming a riparian peat zone along the streams. The mineralogy of the soils in the catchment is spatially relatively homogeneous and dominated by silicate containing minerals and with no known carbonate containing minerals (Ledesma et al., 2013). Soil water pH usually ranges from 5.8- at 0.50-m depth to 7.0- at 4.3-m depth (Klaminder et al., 2011). Groundwater levels in the Krycklan catchment vary from 3.1 (± 0.4 SE) m below the surface at base flow to 0.43 (± 0.1 SE) m below the surface during high flow (based on long-term monitoring data).

Figure 1. Map of the Krycklan catchment showing the sampled groundwater wells and the subcatchments included in the study.

2.2. Groundwater Sampling

Sampling was performed in the main Krycklan catchment (C16) and five subcatchments (C2, C7, C8, C9, and C13), in which a number of groundwater wells were installed in 2012 (Table 1 and Figure 1). The wells were installed to cover the entire catchment to allow for investigations of regional groundwater flow as well as to study local water pathways. Groundwater was collected from 16 wells, at depths ranging from 3.4 to 19.5 m. The diameter of each groundwater well is 8.7 cm. Sampling was performed at three different

Table 1
Catchment Characteristics of the Main Catchment (C16) and the Five Subcatchments Sampled in This Study

Catchment	Name	Area (km ²)	Forest (%)	Wetland (%)	Till (%)	Thin soils (%)	Peat (%)	Postglacial sediments ^a (%)
C2	Västrabäcken	0.12	100	0	84	16	0	0
C7	Kallkällsbäcken	0.47	81	19	65	15	18	0
C8	Fulbäcken	2.30	81	17	63	19	12	2
C9	Nyängsbäcken	2.88	80	15	69	7	14	2
C13	Långbäcken	7.00	86	12	61	9	10	16
C16	Krycklan	68.91	88	9	51	7	9	30

^aDominated by silt.

occasions (summer, autumn, and spring) to allow for comparisons across seasons. Summer sampling took place on the 12th to 16th of June 2017, autumn sampling on the 11th to 15th of September 2017, and spring sampling on the 7th to 11th of May 2018. Spring sampling was performed directly after peak spring flood. The water level in each well was measured before sampling to allow calculation of the total volume of water in the well. Prior to sampling at least 3 times, the volume of the well of water was removed using a submersible centrifugal pump (Supernova70®, Proactive Environmental Products) such that only the new infiltrating water was used for analysis. Groundwater was collected from approximately 10 cm above the bottom of the well.

For the partial pressure of CO₂ ($p\text{CO}_2$), triplicate samples of 30 ml were taken with a 60-ml syringe equipped with a three-way stopcock directly from the pump-connected tube to minimize degassing of CO₂. Directly after sampling, 30 ml of ambient air was added to the syringe creating a headspace. For DIC and CH₄ determination, a 5-ml sample of bubble-free water was taken directly from the pump-connected tube using a sterile syringe, which was flushed with groundwater before sampling. The sample was injected into a 22.5-ml glass vial sealed with a bromobutyl septa. The vial was prefilled with 0.1 ml of 85% phosphoric acid (H₃PO₄) and nitrogen gas (N₂) at atmospheric pressure. For $\delta^{13}\text{C}$ -DIC determination, a 2-ml water sample was injected into a helium flushed 12-ml bromobutyl septa capped Exetainer glass vial, which was prefilled with 200- μl phosphoric acid (H₃PO₄) and 20- μl zinc chloride (ZnCl₂; Campeau et al., 2017). Samples for dissolved organic carbon (DOC) and total nitrogen (N) were collected without headspace in 250-ml acid washed high-density polyethylene bottles. Samples for pH and conductivity analysis were collected without headspace in 50-ml acid washed high-density polyethylene bottles sealed with a gas tight septa. All samples, except for $p\text{CO}_2$, which were analyzed directly in the field, were stored in the dark at 4°C for a maximum of 7 days until analysis.

2.3. Chemical Analyses

Analysis of $p\text{CO}_2$ was conducted in the field using the headspace equilibrium method as modified and described by Kokic et al. (2015). Equilibrated gas samples were analyzed on a portable infrared gas analyzer (IRGA, EGM-4) within 5 min from sampling. The $p\text{CO}_2$ was calculated using the appropriate Henry's constant Weiss (1974) and after correcting for temperature, atmospheric pressure, and the amount of CO₂ in the added ambient air.

Headspace CO₂ and CH₄ concentrations were analyzed by a GC-FID (Clarus 580, Perkin Elmer Autosystem Gas chromatograph) connected to an autosampler (TurboMatrix 110, PerkinElmer). Concentrations of DIC and CH₄ were then calculated from the GC determined headspace of $p\text{CO}_2$ and partial pressure of CH₄ ($p\text{CH}_4$) using temperature-dependent equations for the carbonate equilibrium (Gelbrecht et al., 1998) and Henry's Law (Weiss, 1974; Wiesenburg & Guinasso, 1979), following methods outlined in Wallin et al. (2010, 2014) and Åberg and Wallin (2014) with the difference that we calculated the dissolved and hydrated CO₂ (H₂CO₃*) as a product of the headspace determined CO₂ and Henry's constant. The detection limit of the instrument was 50 ppm for CO₂ and 1 ppm for CH₄ in the headspace gas corresponding to a field DIC and $p\text{CH}_4$ of 0.11 mg/L and 75 μatm , respectively. Due to the detection limit, CH₄ was not detected in all wells.

For $\delta^{13}\text{C}$ -DIC, samples of 100- μl headspace gas were analyzed using an isotope ratio mass spectrometer (DeltaV Plus, Thermo Fisher Scientific, Bremen, Germany) Gasbench II (Thermo Fisher Scientific, Bremen, Germany) measuring the CO₂ in the headspace. Each sample was analyzed seven times, and the first two injections for each sample were discarded to avoid memory effects, and the other five were averaged to give the final result. The $\delta^{13}\text{C}$ values are expressed in terms of deviation from the standard Vienna Pee Dee Belemnite in per mille. The $\delta^{13}\text{C}$ -DIC was calibrated against laboratory standards (NaHCO₃ and K₂CO₃); these standards had been calibrated against certified standards (IAEA-600, USGS 40, IAEA-CH-6, NBS 19). The accuracy of the readings was $\pm 0.15\text{‰}$.

The DOC was measured as total organic C (TOC) on a Shimadzu TOC-VCPH using catalytic combustion, after acidification with 2M HCl to remove inorganic C. The DOC concentrations can be assumed equal to the TOC concentrations as the particulate fraction of organic C in freshwaters in Krycklan generally is less than 1% (Laudon et al., 2011). Total N was measured by wet chemical oxidation on a Shimadzu TNM1. The pH and conductivity were analyzed using a closed pH cell to avoid any outgassing of CO₂ and measured with

a Mettler Toledo Digi117-water combined pH meter equipped with a glass electrode with sensor chip stirring gently at ambient temperature (22°C), using a two-point calibration at pH 4.01 and 7.0.

2.4. Statistical Analyses

We used one-way analyses of variances to test for differences of chemical variables between seasons. To test for relationships between $p\text{CO}_2$ and DOC, DIC, $\delta^{13}\text{C}$ -DIC, $p\text{CH}_4$ and pH, we performed linear regressions on the mean of the values measured at the different seasons. Data were tested for normality using the Shapiro-Wilk test and for homogeneity of variance using Bartlett's test. Only DOC showed a nonnormal distribution, and these data were log transformed to achieve normal distribution. Statistical analyses were performed in the software package JMP version 13.0.0 (SAS Institute Inc. 2016). Significance was set at $p < 0.05$ for all tests.

3. Results

The groundwater in the Krycklan catchment was generally highly oversaturated in $p\text{CO}_2$ relative to the atmosphere, with values ranging from 716 up to 12584 μatm (Table 2). Highest $p\text{CO}_2$ was observed at C13, where the well penetrates down to 5.6 m. Lowest $p\text{CO}_2$ was found in the deepest well (18.0 m) at C2. Highest DOC was also found at C13, whereas lowest DOC was observed in the 5.0-m-deep well at C9. We also found highest DIC at C13, while lowest DIC was found in the 6.8-m-deep well at C2. Highest $\delta^{13}\text{C}$ -DIC, of -18.1‰ , was found in the deepest well sampled (19.5 m) located at C7. Lowest $\delta^{13}\text{C}$ -DIC, of -25.2‰ , was observed in the 4.9-m-deep well at C7. As with the other C species, $p\text{CH}_4$ was highest at C13. In three of the wells at C2 and in three of the wells at C7, $p\text{CH}_4$ were below the detection limit (i.e., below 75 μatm in headspace). The pH ranged between 5.5 and 7.3 across all groundwater wells with lowest pH at C13 and highest in the 18.0-m-deep well at C7 (Table 2). The CO_2 was on average 58% (± 20 standard deviation) of the total DIC in the groundwater of the wells.

Although $p\text{CO}_2$ showed commonly lower values with less than 6,500 μatm in wells located at greater depths (> 7 m; Table 3), we found a high variation in $p\text{CO}_2$ in wells at 3- to 7-m depths, where values ranged between 1,819 and 12,584 μatm (Figure 2a). Nevertheless, $p\text{CO}_2$ showed a significant decrease with depth of the well (Table 3). Conversely, $\delta^{13}\text{C}$ -DIC increased significantly with increasing depth of the wells (Table 3), although they were still rather variable at 3- to 7-m depths (Figure 2d). Also, pH increased significantly with depth of the wells (Table 3), while we did not observe any significant depth relationship for DOC, DIC, and $p\text{CH}_4$ (Figure 2).

The chemical composition of the groundwater was stable across all seasons, with no significant differences between seasons for any of the measured variables (Figure 3 and Table 4).

Although $p\text{CO}_2$ is a component of DIC, there was only a weak relationship between $p\text{CO}_2$ and DIC (Table 3 and Figure 4). A strong negative relationship was however observed between $\delta^{13}\text{C}$ -DIC and $p\text{CO}_2$ and, although not as strong, there was also a significant negative relationship between $p\text{CH}_4$ and $p\text{CO}_2$ (Figure 4). As expected we observed increasing $p\text{CO}_2$ with decreasing pH, whereas we found no relationship between DOC and $p\text{CO}_2$ (Figure 4).

4. Discussion

4.1. Groundwater $p\text{CO}_2$, DOC, and $p\text{CH}_4$

The groundwater in the Krycklan catchment was oversaturated with CO_2 relative to the atmosphere across all investigated wells. The degree of oversaturation was however highly variable across well depth and across the catchment (Figure 2a). We did observe a weak, but significant, decreasing trend of $p\text{CO}_2$ with depth. There was a large variation in $p\text{CO}_2$, ranging between 1,819 and 12,584 μatm , in the 11 wells that were between 3- and 7-m deep, which are distributed all across the entire study catchment. High spatial variation in groundwater $p\text{CO}_2$ across a catchment has previously been demonstrated (Worrall & Lancaster, 2005). Soil respiration as well as CO_2 diffusion and dissolution are important processes that regulate groundwater $p\text{CO}_2$ (Kessler & Harvey, 2001). Our observed variation in $p\text{CO}_2$ across the catchment demonstrates that these processes are spatially heterogeneous. Soil respiration could be spatially variable even at local scales, which would affect groundwater $p\text{CO}_2$ and could potentially explain the observed patterns in $p\text{CO}_2$ (Vincent et al., 2006). The observed variations in groundwater $p\text{CO}_2$ may also be due to differences in soil porosity,

Table 2

Range of Measured Groundwater Chemistry Variables in the 16 Groundwater Wells Sampled at Three Occasions Covering Three Different Seasons (Summer, Autumn, and Spring)

Catchment	Well	Elevation (m. asl)	Soil type	Depth (m)	Water temperature (°C)	pCO ₂ (μatm)	DOC (mg L ⁻¹)	DIC (mg L ⁻¹)	δ ¹³ C-DIC (‰)	pCH ₄ (μatm)	pH	Conductivity (μS/cm)
C2	201	259	Till	4.2	2.1–6.7	8,001–11,526	1.1–1.9	8.7–11.6	–22.4 to –22.3	64.9–75.5	5.9–6.3	39.4–53.4
C2	301	252	Till	5.0	1.7–7.1	5,698–6,005	1.0–1.4	5.8–15.9	–22.1 to –21.1	-	5.8–5.9	32.4–38.6
C2	302	252	Till	3.4	2.0–6.8	4,000–6,578	1.1–1.3	4.2–5.2	–21.7 to –21.4	64.0–64.8	5.8–6.1	20.5–25.2
C2	303	252	Till	6.0	3.2–5.9	1,717–1,846	0.9–2.0	5.4–6.7	–20.7 to –20.4	-	6.1–6.7	77.1–79.1
C2	304	252	Till	11.7	1.7–4.6	2,638–3,199	2.0–2.3	4.4–6.8	–20.9 to –19.9	-	6.4–6.8	37.2–91.2
C7	211	252	Till	6.8	4.0–6.8	2,360–2,570	0.7–1.4	3.7–4.1	–18.9 to –18.3	-	6.3–6.5	29.9–32.3
C7	212	252	Till	19.5	5.3 ^a	1741 ^a	3.9 ^a	6.8 ^a	–18.1 ^a	-	6.7 ^a	139.6 ^a
C7	401	240	Till	4.8	2.7–4.9	7,643–8,497	3.8–8.0	9.3–12.0	–25.0 to –22.9	-	5.9–7.2	57.3–63.4
C7	403	240	Till	4.9	1.8–5.1	9,605–11,395	4.6–6.9	13.7–14.7	–25.6 to –25.0	91.1–181	6.0–6.4	56.3–65.7
C7	404	240	Till	10.8	3.2–4.7	1,676–1,896	1.4–2.6	8.9–9.7	–19.8 to –19.4	211–281	6.4–6.8	95.0–97.2
C7	411	239	Till	15.0	3.5–4.8	4,548–4,781	4.8–5.8	9.0–12.2	–23.5 to –22.7	178–251	6.5–7.0	88.3–94.1
C7	412	239	Bedrock	18.0	3.2–5.2	716–1,196	2.0–4.1	11.7–12.5	–19.5 to –18.7	199–266	6.8–7.3	126.1–128.1
C8	511	235	Till	5.0	2.5–6.3	8,363–1,1709	1.3–4.6	11.7–21.5	–21.4 to –21.3	377 ^a	6.0–6.7	70.0–129.1
C9	501	182	Till	5.0	2.9–4.3	1,309–1,398	0.9 ^a	18.4–11.7	–20.0 to –19.8	63.8–67.1	6.8–7.3	99.7 ^a
C13	601	173	Sand	7.0	3.2–4.5	9,739–12,584	1.6–9.3	18.0–24.0	–24.2 to –21.6	4,824–22,985	5.5–6.2	64.2–87.3
C16	701	128	Sand	5.6	2.6–4.	8,498–9,578	2.2–2.5	14.6–15.5	–22.4 to –23.2	118–160	6.1–6.5	103.1–108.1

^aSampled only at one occasion.

the degree of soil saturation, and permeability (i.e., the hydraulic conductivity) as this would affect both CO₂ diffusion and dissolution, and which in turn could also affect the soil respiration rates (Hu et al., 2018; Moldrup et al., 2000). Differences in local and regional topography (i.e., hydraulic gradient) could also be important as both hydraulic conductivity and gradient affects the subsurface hydrological pathways, and thus regulate the movement of groundwater (LaBaugh, 2009; Wu & Selvadurai, 2016). Variations in

Table 3

Summary of Results From Linear Relationships Presented in Figures 2 and 4, Showing the Adjusted R² Values, Number of Observations (n), and p-Values for the Regression Models

Chemical Variable	Equation	R ² _{adj}	n	p
<i>Linear regression with depth (Figure 2)</i>				
pCO ₂	log (pCO ₂) = 9.11–0.10*depth	0.27	16	0.022
δ ¹³ C-DIC	exp(δ ¹³ C-DIC) = –1.62e ^{–9} + 4.72e ^{–10} *depth	0.39	16	0.006
pH	exp (pH) = 412 + 29*depth	0.32	16	0.013
<i>Linear regression with pCO₂ (Figure 4)</i>				
DIC	pCO ₂ = –349 + 546*DIC	0.42	16	0.004
δ ¹³ C-DIC	pCO ₂ = –26,983–1,520* δ ¹³ C-DIC	0.65	16	0.0002
pCH ₄	pCO ₂ = 9,995–26*pCH ₄	0.41	9	0.038
pH	pCO ₂ = 51,847–7,232*pH	0.49	16	0.002

Figure 2. (a) $p\text{CO}_2$, (b) dissolved organic carbon (DOC), (c) DIC, (d) $\delta^{13}\text{C}$ -dissolved inorganic carbon (DIC), (e) $p\text{CH}_4$, and (f) pH in groundwater wells at different depths. For all variables, data are presented as mean values $\pm$ standard error ($n=3$, SE). A linear regression line is shown for variables with a significant relationship to well depth. For statistical details see Table 3.

hydraulic properties (i.e., hydraulic conductivity and gradient) have been shown to be of importance for surface and groundwater interactions at both subcatchment and full catchment scale in the Krycklan catchment (Sterte et al., 2018).

The observed spatial variation in $p\text{CO}_2$ may also be due to local differences in silicate weathering and/or accumulation of base cations as these would affect the pH and consequently $p\text{CO}_2$ (Buffam et al., 2008; Stets et al., 2017; Warfvinge et al., 1993). In the upper, more organic horizons of the soil, higher soil respiration was expected compared to deeper soil horizons. This would lead to higher $p\text{CO}_2$ and lower pH in soil water near the surface compared to the deeper soil layers, where lower organic content and increased mineral weathering will lead to an enhanced pH through the release of base cations and increased acid neutralizing capacity (Klaminder et al., 2011). Additionally, weathering of silicate minerals consumes CO_2 and produces HCO_3^- , which subsequently increases pH (Brady, 1991). It has previously been shown that concentrations of base cations and pH in groundwater between 0.5- to 4.3-m depth in the Krycklan catchment increased along a 70-m-long hillslope (Klaminder et al., 2011). Shallow groundwater (at 0.5-m depth) had a pH of 5.8, whereas deeper groundwater, at 2.9- to 4.3-m depth, had a pH of 6.9 to 7.2, respectively. This could be attributed to increased influence of silicate weathering because of long residence time of water (Klaminder et al., 2011). Weathering processes are slow; however, groundwater age generally increases with depth (Kim et al., 2008); hence, it is possible that there has been enough time for significant silicate weathering to occur resulting in enhanced pH in the groundwater of our deep wells. The change in pH could also explain the observed negative relationship between $p\text{CO}_2$ and depth. There was a strong negative relationship between pH and $p\text{CO}_2$ (Figure 4e), suggesting that the pH-driven carbonate buffering system plays an important role for C dynamics in groundwater at intermediate depths. Concurrently, the change in pH with depth could also be due to decreased soil respiration with depth as this may have caused $p\text{CO}_2$ to

Figure 3. Normal quantile boxplots for (a) $p\text{CO}_2$, (b) dissolved organic carbon (DOC), (c) dissolved inorganic carbon (DIC), (d) $\delta^{13}\text{C-DIC}$, (e) $p\text{CH}_4$, and (f) pH during autumn, spring, and summer. For statistical details see Table 4.

decrease, subsequently increasing the pH. It is difficult to elucidate whether pH is driving $p\text{CO}_2$ or vice versa in the study catchment, but it is likely that both increased silicate weathering and decreased soil respiration with depth are important factors. As there are no carbonate minerals in the Krycklan catchment carbonate weathering could not explain the observed trends in $p\text{CO}_2$ or pH.

In shallow soil water, DOC concentrations have generally been found to decrease with increasing soil depth (Grabs et al., 2012; Kaiser & Kalbitz, 2012; Lyon et al., 2011). In contrast, we did not observe any relationship between DOC and sampling depth across the 3- to 20-m range included in our study (Figure 2b). Instead, DOC concentrations were variable ranging between 1 and 6 mg/L. This lack of DOC depth dependency could be due to the overall low DOC concentrations, which in turn are controlled by biodegradation rates, adsorption, and coprecipitation (Graham et al., 2015). A lack of DOC mobilization could perhaps also

explain the lack of relationship between DOC and sampling depth. In the upper soil profile, DOC may be immobilized by iron oxide (Kindler et al., 2011). Reducing conditions favoring the dissolution of iron oxides, and thus leaching of DOC, are created when the groundwater reaches superficial organic horizons (Stemmler et al., 2004). When the groundwater is below superficial organic horizons, DOC mobilization is limited resulting in a lack of relationship between DOC and depth.

As with DOC, there was no relationship between $p\text{CH}_4$ and depth of the sampling well. There were a number of wells where $p\text{CH}_4$ was below detection limit of the analytical method and all these wells are located in the upper part of the catchment (i.e., C2 and C7). However, in the three deeper wells at C7, which are between 10- and 18-m deep, $p\text{CH}_4$ was between 209 and 254 μatm . One

Table 4

F-Statistics and p-Values From One-Way Analyses of Variances (ANOVA) for Differences in the Chemical Variables $p\text{CO}_2$, DOC, DIC, $\delta^{13}\text{C-DIC}$, $p\text{CH}_4$, and pH Between Three Seasons (Summer, Autumn, and Spring)

Chemical Variable	F	p
$p\text{CO}_2$ (μatm)	0.575	0.567
log DOC (mg/L)	3.099	0.056
DIC (mg/L)	0.251	0.779
$\delta^{13}\text{C-DIC}$ (‰)	0.623	0.541
$p\text{CH}_4$	0.435	0.652
pH	2.604	0.086

Abbreviations: DIC: dissolved inorganic carbon; DOC: dissolved organic carbon.

Figure 4. Relationships between (a) dissolved organic carbon (DOC), (b) dissolved inorganic carbon (DIC), (c) $\delta^{13}\text{C}$ -DIC, (d) $p\text{CH}_4$, and (e) pH and $p\text{CO}_2$ and in the groundwater of the Krycklan catchment. The symbols are color coded according to the depth of the sampled well. For all variables, data are presented as mean values $\pm$ standard error ($n=3$, SE).

important factor for CH_4 production is whether the environment is anoxic or not. We found a negative relationship between $p\text{CO}_2$ and $p\text{CH}_4$ (Figure 4d), which suggests that the oxygen (O_2) supply exerts a control on the metabolic process responsible for the decomposition of organic C. Hence, the negative relationship between $p\text{CO}_2$ and $p\text{CH}_4$ could also be due to higher aerobic soil respiration at more shallow depth and increased methanogenesis toward deeper soil layers. There are a few environmental factors, other than organic C substrates and O_2 concentrations, that also influence CH_4 metabolism, such as soil temperature and redox potential (Song et al., 2006; Wang et al., 2017). Such environmental factors could vary between and within catchments but were not measured in this study, but should be considered in future work.

In the well at C13, which is 5.6-m deep, we observed the highest $p\text{CO}_2$, DOC, $p\text{CH}_4$, and DIC. A mire is situated just upslope of C13, and it is possible that water from the mire infiltrates the soil profile and reaches the groundwater well. Hence, it is possible that the mire is a major source of the high C concentrations also observed in the groundwater at C13. Lowest $p\text{CO}_2$ was observed in the deepest well at C7, which is 18-m deep. This was not surprising as this well is the only one that was drilled into bedrock; hence, influence of soil respiration would be limited. Although the well reaches down into bedrock, $p\text{CO}_2$ was still oversaturated relative to the atmosphere. This is likely due to downward diffusion of soil CO_2 produced in the above soil horizon. Another possible explanation for the observed $p\text{CO}_2$ concentration in the bedrock could be infiltration of groundwater enriched in dissolved CO_2 into bedrock cracks, pores, and hollows (Rodhe & Bockgrd, 2006).

4.2. Groundwater DIC and $\delta^{13}\text{C}$ -DIC

Similar to $p\text{CO}_2$, DIC concentrations were found to be variable around 3- to 7-m depth ranging between 4.7 and 21.9 mg/L with highest concentration in the well at C13. However DIC did not show a dependency with well depth (Figure 2c). On the contrary, we found a positive relationship between the $\delta^{13}\text{C}$ -DIC and sampling depth (Figure 2d), with less negative $\delta^{13}\text{C}$ -DIC at greater depths. The vegetation in the Krycklan catchment consists only of C_3 plants, which have a $\delta^{13}\text{C}$ between -22 and -34‰ (Vogel, 1993). We observed slightly less negative $\delta^{13}\text{C}$ -DIC values in the groundwater, between -18.1 and -25.2 (mean $-21.3 \pm 2.0\text{‰}$). Closer to the surface, we observed more negative $\delta^{13}\text{C}$ -DIC, which are in the range of $\delta^{13}\text{C}$ for C_3 plants; however, further down the soil profiles, the $\delta^{13}\text{C}$ -DIC increased. This change in $\delta^{13}\text{C}$ -DIC could be due to diffusion-related fractionation as CO_2 diffusion has the potential to increase the $\delta^{13}\text{C}$ of up to 5‰ (Amundson et al., 1998). While Amundson et al., (1998) found a negative relationship between $\delta^{13}\text{C}$ - CO_2 and depth, we observed a positive relationship between $\delta^{13}\text{C}$ -DIC and depth. This discrepancy could be due to differences in the study design. The study by Amundson et al. (1998) was confined to the upper 4 m of the soil layer, whereas our study focused on groundwater below 4 m. At shallow depth, the diffusion of soil CO_2 to groundwater is facilitated by the proximity of the upper soil layers and thus have a higher $\delta^{13}\text{C}$ -DIC than the biogenic source due to diffusion-related fractionation. At greater depth (10–20 m), soil respiration is likely low and CO_2 may diffuse downward resulting in a fractionation in the $\delta^{13}\text{C}$ -DIC toward more positive values.

As there are no carbonate containing minerals in the soils of the Krycklan catchment (Klaminder et al., 2011), less negative $\delta^{13}\text{C}$ -DIC values cannot be explained by carbonate weathering. Since silicate weathering does not yield any additional C, it only fixes soil CO_2 , the DIC must have a pure biogenic origin. The $\delta^{13}\text{C}$ -DIC of silicate weathering and soil respiration are similar; hence, silicate weathering is supposed to have only a minor direct effect on the groundwater $\delta^{13}\text{C}$ -DIC (Telmer & Veizer, 1999). Another potential explanation for the observed positive relationship between $\delta^{13}\text{C}$ -DIC and depth could be a change in the quality of the soil C with depth. Earlier studies have shown that there is an increase in $\delta^{13}\text{C}$ of soil organic matter with depth, and it was argued that this was due to the accumulated influence of isotopic discrimination during microbial decomposition (Buchmann et al., 1997; Formanek & Ambus, 2004; Nadelhoffer & Fry, 1988). As a result, the heavier isotope in the oldest and most degraded material is left behind in the deeper soil layers (Formanek & Ambus, 2004). This vertical enrichment in $\delta^{13}\text{C}$ was also reflected in the soil- CO_2 evolved from respiration (Formanek & Ambus, 2004). It is possible that the enriched $\delta^{13}\text{C}$ -DIC at greater depth in our study catchment is a result of soil respiration utilizing older C with higher $\delta^{13}\text{C}$. Likewise, the variation in $\delta^{13}\text{C}$ -DIC in groundwater at 3- to 7-m depth across the catchment could also be due to local differences in C quality resulting in isotopic discrimination during soil respiration.

It is likely that the observed positive relationship between $\delta^{13}\text{C}$ -DIC and depth is due to both diffusion-related fractionation and isotopic discrimination during soil respiration. At more shallow depth we expected the $\delta^{13}\text{C}$ -DIC to be close to the $\delta^{13}\text{C}$ -DIC from respiration of organic matter from C_3 plants; however, we observed less negative $\delta^{13}\text{C}$ -DIC values. This less negative $\delta^{13}\text{C}$ -DIC could be explained by diffusion-related fractionation since there is likely selective molecular diffusion of CO_2 through the soil pores at more shallow depths (Amundson et al., 1998). At greater depth, the $\delta^{13}\text{C}$ -DIC values are more negative than at shallower depth. Since deeper soil layers would be more humid than the upper soil layers and diffusion-related fractionation is related to humidity with higher fractionation in drier soils (Wang et al., 2015), diffusion-related fractionation may be a less important process at greater depth. Instead, isotopic discrimination during soil respiration could be the more important process explaining the observed positive $\delta^{13}\text{C}$ -DIC-depth relationship as the organic matter at greater depth would be much older and thus likely have a higher $\delta^{13}\text{C}$.

Another process that could affect the enhanced $\delta^{13}\text{C}$ -DIC is methanogenesis. This process was previously found to result in a fractionation of up to 10‰ of the $\delta^{13}\text{C}$ -DIC (Wimmer et al., 2013). Anaerobic conditions in groundwater are likely to be common at the depths investigated in this study, and CH_4 was higher in the deeper wells. Although methanogenesis-related fractionation of $\delta^{13}\text{C}$ -DIC could contribute to the observed positive relationship with depth, the CH_4 production is likely too low due to low organic C content to have any major influence on the $\delta^{13}\text{C}$ -DIC.

4.3. Groundwater-Surface Water Connectivity

As small headwater streams transition into larger streams and further into rivers, the hydrological flowpaths that deliver water and solutes may shift from being dominated by shallow groundwater in the headwaters to increased influence from deep groundwater further downstream (Carroll et al., 2018; Creed et al., 2015). The combination of shallow and deep groundwater contribution to downstream chemistry vary not only with catchment size but also with season and runoff conditions (Sophocleous, 2002; Winter, 1999). For instance, during baseflow, the contribution of deep groundwater to stream surface water could be up to 80% for boreal catchments larger than 10 km² (Peralta-Tapia et al., 2015). Due to the large spatial variation in C concentrations across the Krycklan catchment, it is however difficult to assess what proportion of surface water C originates from deep groundwater, particularly as adjacent subcatchments may function very differently despite seemingly similar characteristics (Karlsen et al., 2016; Sterte et al., 2018). Our study shows that the groundwater chemistry of a small catchment can vary substantially both within and between subcatchments. To fully understand the contribution of deep groundwater to surface water C concentrations, we need a better understanding of the catchment hydrology as well as combined measurements of surface water and groundwater chemistry.

5. Conclusions

In conclusion, our study shows that there is large spatial variation in groundwater chemistry across a boreal catchment and that local differences in both soil respiration and weathering processes most probably play a major role in controlling C dynamics of groundwater at intermediate depths. Deep groundwater will eventually connect with surface water, although it could take decades to centuries (Alley, 2009). Considering that about one third of the global total volume of freshwater is groundwater (Shiklomanov, 2000), deep groundwater might play a more vital role in the global C cycle than commonly believed. We suggest that due to the great variation in C concentrations over depth and across the catchment, it is essential to have multiple sampling locations when aiming to upscale C concentrations of intermediate groundwater to regional or global scale. Our study provides a step toward a better understanding of the C content and dynamics of intermediate and deep groundwater, which is of great importance as these waters could be an indirect source of CO₂ to the atmosphere.

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