Natural vs. anthropogenic effects in the composition of dissolved inorganic carbon in a boreal river with a seasonal base flow component

Paula I. A. Niinikoski and Juha A. Karhu

ABSTRACT

Studying the carbon balance in surface waters gives information on the annual cycles of photosynthesis and respiration. It also provides insight on the water body's capability to serve as a source or sink for atmospheric CO_2, which may be essential in evaluating the effects of climate change. The target of this study was the Vantaanjoki River known to have a significant base flow component, located in a densely populated area in southern Finland. The aims of this study were firstly to study if human induced changes are evident in the inorganic carbon quality of the river, and secondly to determine whether the river releases carbon to the atmosphere. These aims were achieved by studying the isotopic composition and contents of dissolved inorganic carbon (DIC) in relation to river discharge. It was evident from the results that the human activities only have mild local and temporal effects on the quality of the DIC in the river. The most important contributors to the changes in the carbon balance are the annual changes in the proportion of the base flow and surface flow components and the escape of CO_2 to the atmosphere.

Key words | C-13/C-12, carbon cycle, catchment hydrology, DIC, groundwater–surface water interaction

Paula I. A. Niinikoski (corresponding author)
Juha A. Karhu
Department of Geosciences and Geography,
University of Helsinki,
P.O. Box 64,
Helsinki 00014,
Finland
E-mail: paula.niinikoski@helsinki.fi

INTRODUCTION

Understanding the carbon budget of surface water systems gives information on the carbon balance of the whole atmosphere. Whether surface waters serve as a source or a sink of carbon can have an effect on atmospheric change in a global scale (Toggweiler 1995; Telmer & Veizer 1999). It has been shown that most rivers have carbon dioxide contents larger than those expected for equilibrium with the atmosphere (Schulte et al. 2011). This implies that they do not serve as a sink of CO_2 but rather release it into the atmosphere, which may have an effect on the global climate (Telmer & Veizer 1999). Understanding the carbon cycle in rivers is therefore an important part of preparing for changes brought on by an increase in the CO_2 contents of the atmosphere, but it is also essential for understanding the carbon balance in individual rivers as part of estimating the vulnerability of catchments.

The contents of dissolved inorganic carbon (DIC), as well as the partial pressure of carbon dioxide (pCO_2), and the isotopic composition of DIC are influenced by the natural annual cycles of photosynthesis and decomposition in the river water as well as soil respiration and carbonate weathering (Barth & Veizer 1999; Telmer & Veizer 1999). In base flow dominated rivers, the carbon contents of the local groundwater can affect the carbon quality of the river water (Aravena & Suzuki 1990; Atekwana & Krishnamurthy 1998). However, the base flow component in river systems is not constant (Barth & Veizer 1999; Niinikoski et al. 2016), which leads to complications in differentiating between the base flow signal and the signal brought on by other sources of DIC. Catchments with groundwater–surface water interaction are common (Aravena & Suzuki 1990; Atekwana & Krishnamurthy 1998; Korkka-Niemi et al. 2012; Rautio et al.

2015; Niinikoski *et al.* 2016), and especially vulnerable to changes in water quality, as they may affect human populations using groundwater as a source of drinking water (Korkka-Niemi *et al.* 2012; Rautio *et al.* 2015). Therefore, it is essential to differentiate, if possible, between biological processes and groundwater influence, as reasons for changes seen in the carbon quality of a river. Interaction between groundwater and surface water increases the fragility of catchments, since possible contaminants can spread from the river channel into groundwater or vice versa (Korkka-Niemi *et al.* 2012; Rautio *et al.* 2015). For example, high contents of organic carbon in water can lead to unwanted microbial growth, which can render the water unsuitable for human consumption (Kortelainen & Karhu 2006). Understanding the carbon cycle in rivers and streams helps in predicting the behaviour of the river system in case of contamination, and in assessing the possible contaminating effect of the river water on groundwater.

In water bodies in contact with the atmosphere for long periods of time, the isotopic composition of DIC and its concentration are in equilibrium with the atmosphere, if there are no other sources contributing to the DIC pool (Keeling *et al.* 2005). However, this is very rarely the case (Aravena & Suzuki 1990; Toggweiler 1995; Atekwana & Krishnamurthy 1998; Telmer & Veizer 1999). If the partial pressure of CO_2 in the water is higher than atmospheric, there can be significant CO_2 degassing (Doctor *et al.* 2008; Butman & Raymond 2011; Wallin *et al.* 2012). CO_2 degassing prefers the lighter carbon isotope, which leads to the remaining DIC becoming enriched in the heavier isotope (Doctor *et al.* 2008; van Geldern *et al.* 2015).

Photosynthesis removes the lighter carbon from the water increasing the $^{13}C/^{12}C$ ratio in DIC, and decreasing the overall contents of DIC (Barth & Veizer 1999; Telmer & Veizer 1999). Atmospheric carbon can replace the missing carbon, which also serves to make the isotopic composition of the DIC heavier (Barth & Veizer 1999). Bacterial respiration adds light carbon favoured by photosynthesis into the DIC pool, decreasing the $^{13}C/^{12}C$ ratio and increasing the overall contents of DIC (Barth & Veizer 1999). Dissolution of carbonate minerals, where available, changes the isotopic composition, and overall contents of DIC depending on the source of the carbonate.

The Vantaanjoki River, in southern Finland, has a considerable base flow component (Korkka-Niemi *et al.* 2012; Niinikoski *et al.* 2016). Groundwater–surface water interaction

makes the catchment particularly vulnerable to contaminants. Since it is located in the most densely populated area in Finland and also has a considerable amount of agriculture, the risk of such contamination is also elevated (Vahtera *et al.* 2010; Niinikoski *et al.* 2016). Groundwater in the area is used as drinking water, and a managed aquifer recharge facility is in operation in the area. For all these reasons, the Vantaanjoki River is an ideal example of a vulnerable river system characterized by a significant base flow component.

In this study the carbon quality in the river was examined by analyzing the isotopic composition of DIC, along with the concentration of DIC in the river water. The aims were firstly to determine if and how human induced changes can be seen in the inorganic carbon contents of the river water along with its concentration. Similar studies have been conducted in Sweden (Jonsson *et al.* 2001; Wallin *et al.* 2010; Wallin *et al.* 2012), but this time we are attempting to take into account anthropogenic effects.

STUDY AREA

More than one million people live within the catchment area of the Vantaanjoki River (Vahtera *et al.* 2010). The main channel is approximately 100 km in length and discharges into the Gulf of Finland (Korkka-Niemi *et al.* 2012). The catchment covers 1,700 km². Lakes cover only 3% or the catchment area, most of it being forests (41%) and agricultural areas (36%), while urban housing and leisure areas, industry and transportation make up approximately 20% of the catchment (Figure 1). There are seven wastewater purification facilities, a sawmill and a landfill, located in the catchment, which could have an effect on the water quality in the river (Vahtera *et al.* 2010). The discharge of the Vantaanjoki River is subject to significant changes (SYKE 2012). In the winter, it can decrease to 1–2 m³/s, and during the snowmelt season in the spring it rises up to 200 m³/s (Korhonen & Kuusisto 2010). The mean annual discharge is 16 m³/s (SYKE 2012). In the catchment, Precambrian bedrock is overlain by Quaternary sedimentary deposits (Saarnisto & Salonen 1995). The lowermost part of the sediment is till, and aquifers are located in overlying glaciofluvial sand and gravel deposits, with negligible carbonate minerals (Tikkanen 1989; Saarnisto & Salonen 1995).
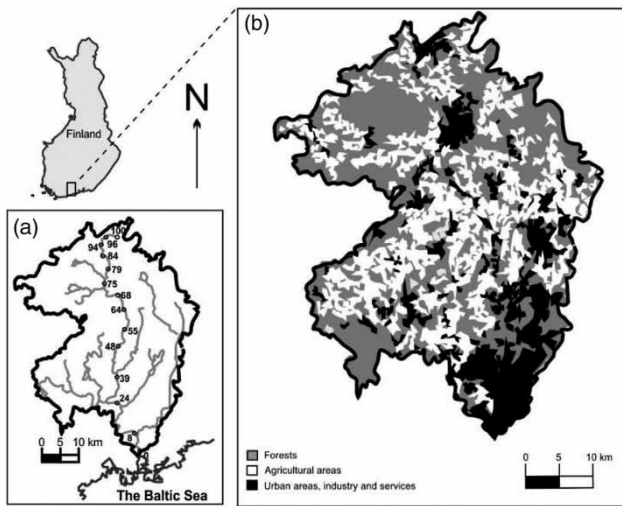
Figure 1 | A map of the catchment of the Vantaanjoki River, showing different land uses and the sampling points (modified after SYKE 2012).

Interaction between the Vantaanjoki River water and groundwater has been investigated using thermal imaging, which showed several points of groundwater discharge into the river channel along the flow path (Korkka-Niemi et al. 2012). It was inferred that a significant component of the river water is sourced from groundwater. In a later study by Niinikoski et al. (2016), the proportion of base flow and the seasonal changes in it were investigated. It was concluded, that the base flow component is the largest during the low flow seasons, especially in the winter when most of the river channel is mostly covered by ice. During this time, the proportion of base flow was estimated by using the isotopic composition of oxygen in the water to be more than 60% of the discharge (Niinikoski et al. 2016). During high flow seasons, in the autumn with increased precipitation and especially in the spring during snow melt, the proportion of base flow was found to be significantly lower. The base flow minimum was reached during spring flooding, when virtually all of the river water constitutes of surface flow generated by snowmelt (Niinikoski et al. 2016).

MATERIALS AND METHODS

The sampling took place between February 2010 and October 2011. Samples for the DIC isotope analysis, alkalinity and pH were collected monthly from the mouth of the river (Figure 1). During the spring flood of the year 2011, the sampling was executed daily. Also the whole river channel was sampled four times in 2011 (Figure 1). During each sampling campaign, 14 samples were collected along the flow path from a pond at the headwater of the river to the mouth of the river where it discharges to the Baltic Sea. Some of the smaller tributaries discharging into the Vantaanjoki River were also sampled four times in 2011.

The samples were collected from bridges. This was preferable, as bridges are most often built where the river is narrow, which also makes the water in the stream better mixed (Telmer & Veizer 1999). The samples were collected by lowering a Limnos surface water sample collector (GWM Engineering) into the river in the middle of the stream. First the depth of the channel was measured and then the sample collected so that it was both vertically and horizontally in the middle of the river. The Limnos sample collector allows the sample to be collected at the desired depth. It is open in both ends, hence the water flows through, until it is closed which can be done at the desired depth capturing the sample inside. The sampling volume was 2 litres, which was sufficient for all desired analyses.

Alkalinity and pH were analyzed from all samples by automatic titration with Schott TitroLine alpha. The accuracy of the analysis was ±0.003 mmol/L. In addition, the isotopic composition of DIC was analysed. The mean volume of discharge of the Vantaanjoki River was taken from the HERTTA database (SYKE 2012), which includes environmental data collected, and analysed by the Finnish Environment Institute. The isotopic composition of water is shown as δ values which are calculated from isotope ratios (the heavier isotope against the lighter one):

$$\delta_{sample} = \frac{R_{sample}}{R_{std}} - 1 \qquad (1)$$

In Equation (1), R_{sample} is the isotope ratio of the sample and R_{std} that of the standard (Coplen 2011). For carbon, the standard is Vienna PeeDee Belemnite (VPDB).

All samples were analysed in the Department of Geosciences and Geography at the University of Helsinki. For the DIC isotope analysis, 5 ml of water was injected through a 0.8/0.2 μm Supor membrane syringe filter into a helium-filled Exetainer tube that contained eight drops of 85% phosphoric acid. The samples were then analysed

by Isotope-ratio mass spectrometry, using a Thermo Finnigan Delta Advantage mass spectrometer equipped with Gasbench, together with laboratory standards, which had been calibrated against an international standard (NBS19). The precision for the analysis was 0.1‰. The standards were prepared using an identical procedure as that utilized for the samples. Before analysis, the tubes were allowed to stand 24 hours at room temperature. The DIC content and the partial pressure of carbon dioxide (pCO_2) were calculated from the alkalinity and pH using the geochemical modelling program PHREEQC (Parkhurst & Appelo 2013).

RESULTS AND DISCUSSION

The amount of carbon in the river

The results of the carbon isotope, alkalinity and pH analysis, and the calculated DIC contents and pCO_2 are given in Tables 1

Table 1 | Carbon isotope, pH and alkalinity analyses, and the calculated contents of DIC and pCO_2 along the flow path of the Vantaanjoki River

	Alkalinity mmol/L	pH	$\delta^{13}C_{DIC}$ ‰ VPDB	DIC mmol/L	$p(CO_2)$ mbar		Alkalinity mmol/L	pH	$\delta^{13}C_{DIC}$ ‰ VPDB	DIC mmol/L	$p(CO_2)$ mbar
8.3.2011						**14.6.2011**					
V0	1.0	7.5	−15.6	1.1	2.0	V0	1.1	7.5	−12.0	1.2	2.2
V8	0.9	7.4	−14.6	1.0	2.6	V8	1.1	7.5	−12.6	1.2	2.2
V24	0.8	7.4	−14.3	0.9	2.1	V24	1.1	7.5	−13.0	1.2	2.3
V39	0.7	7.4	−14.1	0.8	2.0	V39	1.0	7.6	−12.3	1.1	1.6
V48	0.7	7.3	−14.5	0.8	2.3	V48	0.9	7.5	−13.1	1.0	1.9
V55	0.7	7.4	−14.1	0.8	1.8	V55	0.9	7.7	−12.8	0.9	1.1
V64	0.6	7.2	−14.7	0.7	2.6	V64	0.8	7.4	−12.1	1.0	2.4
V68	0.6	7.3	−14.7	0.7	2.2	V68	0.9	7.4	−12.3	1.0	2.5
V75	1.0	7.4	−15.8	1.1	2.5	V75	1.4	7.6	−13.2	1.6	2.6
V79	0.9	7.3	−16.1	1.1	3.0	V79	1.6	7.5	−13.8	1.7	2.9
V84	0.7	7.0	−16.3	1.0	4.4	V84	1.0	7.1	−16.0	1.3	4.7
V94	0.5	7.1	−15.3	0.6	2.3	V94	0.7	7.3	−15.2	0.8	2.2
V96	0.4	7.1	−14.7	0.5	2.2	V96	0.5	7.3	−13.7	0.6	1.7
V100	0.3	6.9	−14.6	0.5	2.8	V100	0.4	7.0	−8.9	0.5	2.5
19.4.2011						**26.10.2011**					
V0	0.3	6.9	−13.0	0.4	2.4	V0	0.6	7.2	−14.5	0.7	2.3
V8	0.3	7.0	−12.8	0.4	2.1	V8	0.6	7.3	−13.8	0.7	2.0
V24	0.3	6.9	−13.9	0.4	2.5	V24	0.5	7.2	−14.4	0.6	2.1
V39	0.3	6.9	−12.5	0.4	2.0	V39	0.5	7.4	−12.1	0.6	1.3
V48	0.3	6.9	−13.4	0.4	2.4	V48	0.5	7.3	−12.8	0.6	1.5
V55	0.2	6.9	−13.4	0.3	2.0	V55	0.5	7.3	−12.3	0.6	1.6
V64	0.2	6.7	−16.0	0.4	3.1	V64	0.5	7.1	−14.0	0.6	2.7
V68	0.3	6.6	−16.3	0.6	5.8	V68	0.5	7.1	−14.0	0.6	2.5
V75	0.3	6.7	−17.0	0.5	4.1	V75	0.6	7.2	−14.6	0.7	2.5
V79	0.3	6.7	−17.3	0.6	4.8	V79	0.7	7.2	−14.8	0.9	2.7
V84	0.4	6.6	−18.9	0.7	6.2	V84	0.8	7.2	−15.6	0.9	3.1
V94	0.3	6.7	−16.7	0.5	3.8	V94	0.6	7.5	−15.5	0.7	1.3
V96	0.3	6.6	−16.8	0.6	5.3	V96	0.4	7.3	−15.4	0.5	1.3
V100	0.3	6.7	−15.3	0.4	3.3	V100	0.3	7.1	−12.6	0.3	1.2

and 2. The $\delta^{13}C_{DIC}$ values varied between -19 and $-9‰$. At the mouth of the river, the variation was smaller from $-12‰$ in the summer to $-15‰$ in the winter. In April, the $\delta^{13}C_{DIC}$ values showed a weak temporary rise from the winter minimum to $-13.5‰$. The shift was located exactly in the middle of the spring flooding, with a duration of only about 1 week. Throughout most of the year the pH was around 7.5 with a distinct fall during the spring down to 6.6. Alkalinity was also at its minimum of 0.3 mmol/L in the spring, but varied from 0.8 to 1.1 mmol/L throughout the rest of the year. The calculated DIC contents followed the alkalinity closely with a distinct minimum during the spring flooding. Partial pressure of CO_2 varied between 1.2 and 6.8 mbar showing a short-term maximum in April.

The average annual flux of DIC at the mouth of the Vantaanjoki River was approximately 9.1 mol/s, which corresponds to 290,000,000 mol C annually. Even though the

concentration of DIC fell during the spring flooding event, the overall amount of carbon travelling through the river system during this time was 50% of all transported DIC in 2010 and almost 20% in 2011. This was due to the high discharge, which corresponded from 30% (2011) to 70% (2010) of all annual discharge in only 1–2 months.

The sources of dissolved inorganic carbon

Biological organisms prefer the lighter ^{12}C isotope, which becomes enriched in organic material. Bacterial respiration releases this light carbon into water thus decreasing the $\delta^{13}C_{DIC}$ (Barth & Veizer 1999). The $\delta^{13}C$ of organic carbon is approximately $-27‰$ (Deines 1980; Vogel 1993; Schiff et al. 1997). The natural groundwater in the area has been reported having a $\delta^{13}C_{DIC}$ value of approximately $-21‰$ (Kortelainen & Karhu 2006). This value is too low for the DIC in the groundwater to be produced by carbonate weathering in any significant amount. Values of this magnitude have been reported for DIC originated in soil respiration (Doctor et al. 2008; van Geldern et al. 2015).

The winter and summer samples portray typical characteristics of base flow originated water with distinctly higher pH and DIC concentration than the spring samples (Figure 2). This finding is in agreement with higher base flow content in the summer and winter discharge of the river (Niinikoski et al. 2016).
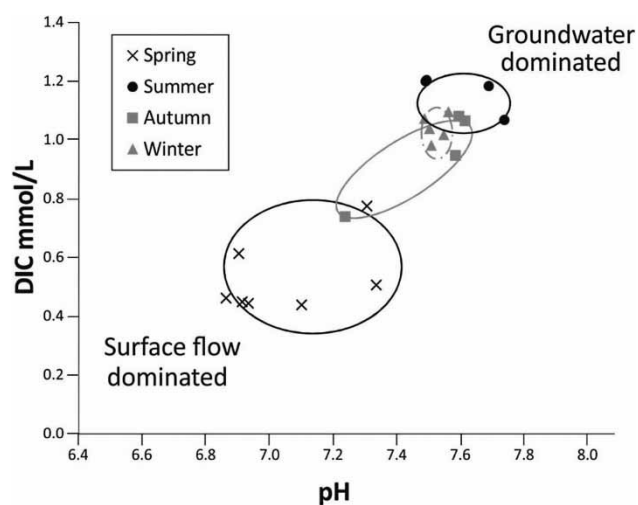
Table 2 | Carbon isotope, pH and alkalinity analyses and the calculated contents of DIC and pCO_2 from the mouth of the river (sampling point V0)

Date	Alkalinity mmol/L	pH	$\delta^{13}C_{DIC}$ ‰ VPDB	DIC mmol/L	$p(CO_2)$ mbar
4.2.2010	1.0	7.6	-15.1	1.1	1.8
15.3.2010	0.9	7.5	-13.4	1.0	1.7
6.4.2010	0.3	7.1	-14.5	0.4	1.8
27.4.2010	0.4	7.3	-12.5	0.5	1.3
24.5.2010	0.7	7.3	-14.3	0.8	2.1
7.7.2010	1.1	7.5	-11.8	1.2	2.3
6.8.2010	1.1	7.7	-12.3	1.2	1.4
5.9.2010	1.0	7.6	-13.0	1.1	1.5
13.10.2010	1.0	7.6	-13.4	1.1	1.6
22.12.2010	0.9	7.5	-13.2	1.0	1.9
27.1.2011	0.9	7.5	-14.7	1.0	1.8
8.3.2011	1.0	7.5	-15.6	1.1	2.0
5.4.2011	0.7	7.1	-14.5	0.9	3.6
9.4.2011	0.4	6.9	-14.5	0.6	3.6
11.4.2011	0.3	6.9	-13.7	0.5	2.9
12.4.2011	0.3	6.9	-14.3	0.4	2.5
19.4.2011	0.3	6.9	-15.3	0.4	2.4
14.6.2011	1.1	7.5	-12.0	1.2	2.3
11.7.2011	1.0	7.7	-12.8	1.1	1.2
12.9.2011	0.9	7.6	-14.3	0.9	1.4
26.10.2011	0.6	7.2	-14.5	0.7	2.3

Figure 2 | A graph showing contents of DIC against the pH. Base flow and surface flow dominated water types have distinct characteristics on this graph.

Since the Vantaanjoki River receives a significant amount of base flow, it also has a significant DIC input originated from soil respiration. The decrease in $\delta^{13}C_{DIC}$ between 90 and 70 km from the sea (Figure 3) coincides well with the decrease in $\delta^{18}O$ and δ^2H associated with a base flow pulse found by Niinikoski et al. (2016).

In the summer and winter, the overall concentration of DIC is at its highest, which is due to a large proportion of base flow (Figure 4). In the autumn, the DIC concentration is lower, as there is more surface flow in the river water brought on by increased precipitation also visible in the discharge (Figure 4).

In the early summer, the $\delta^{13}C_{DIC}$ values show a clear rise, followed by a decreasing trend in the late summer and autumn (Figure 4). The $\delta^{13}C_{DIC}$ values decline gradually reaching their minimum before the spring flooding
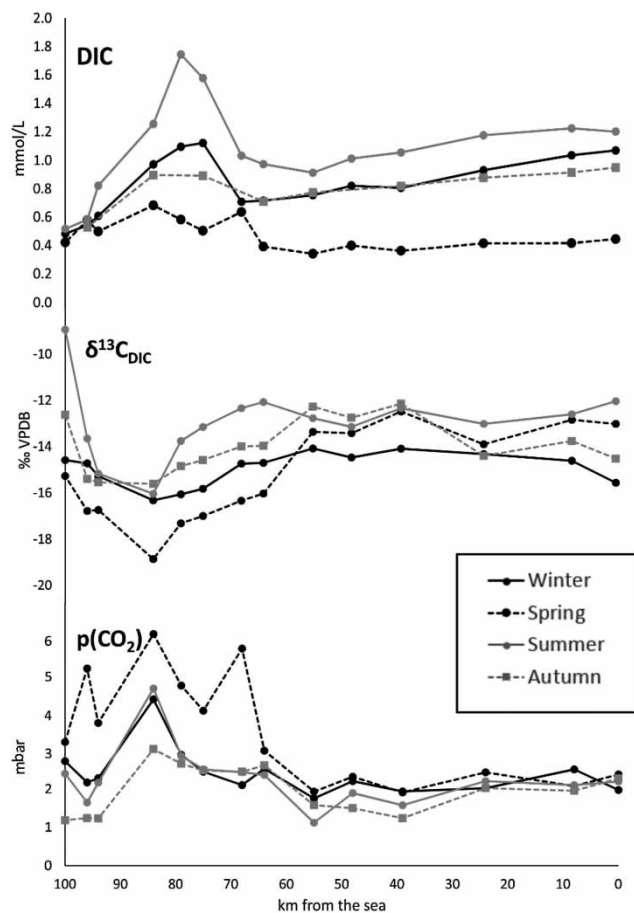
Figure 3 | DIC contents, p(CO₂) and $\delta^{13}C_{DIC}$ along the flowpath of the main channel of the Vantaanjoki River.

(Figure 4). A similar trend is seen in the pH. These long-term changes can be interpreted to be related to soil respiration, adding ^{12}C-enriched carbon to the DIC pool and lowering the pH (Figure 4). In harmony with the pH drift, the pCO₂ rises steadily from early summer to the spring flooding.

In addition to increased flow and relatively low DIC contents, the spring flooding event is characterized by a decrease in the pH and a short local maximum in $\delta^{13}C_{DIC}$. Typical range for DIC contents in precipitation is from 1–5×10^{-5} mol/L (Stumm & Morgan 1996). These contents are too small to account for the DIC found during the spring flooding event. Apparently, snowmelt collects carbon originating from soil respiration, when it travels through fields and forests before entering the river channel (Figure 4).

In the catchment of the Vantaanjoki River most, if not all, DIC is derived from soil respiration, either via base flow, or flushed by the spring flooding waters from the surrounding fields and forests. The changes in the isotopic composition of the DIC are described below.

Atmospheric effect

The $\delta^{13}C_{DIC}$ values in the river water were approximately 7‰ more positive than those in the surrounding groundwater (Tables 1 and 2). This difference could be due to three effects, namely carbonate weathering or photosynthesis or atmospheric effects. Carbonate weathering is not a plausible cause, since there are negligible carbonates in the bedrock and soil of the catchment (Pekkala 1997). It would also be expected that an effect from carbonate weathering would be most visible during the winter, when the river is mostly ice covered, and surface flow and primary production are shut down. In contrast, the $\delta^{13}C_{DIC}$ of the river water shows the lowest values during the winter at all measurement points within 60 km from the mouth of the river (Figure 3). This agrees better with photosynthesis or atmospheric effects being the cause of the difference between the $\delta^{13}C_{DIC}$ values of groundwater and river water, since in the winter this effect would be smaller due to the ice cover. During the winter, photosynthesis is shut down, and even though the $\delta^{13}C_{DIC}$ values during this time are at a low level, they still are higher than those in
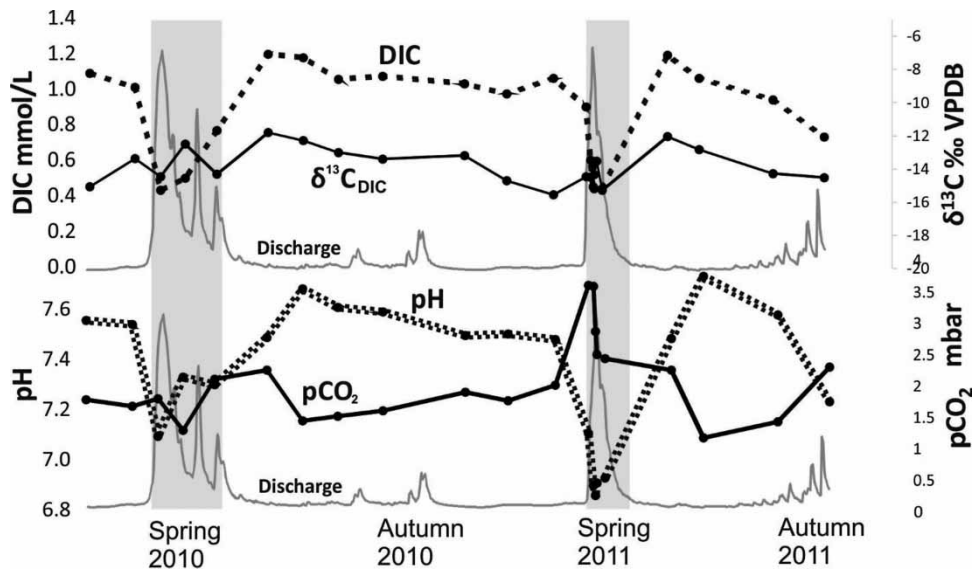
Figure 4 | The annual cycles in DIC contents, $\delta^{13}C_{DIC}$, pH, p(CO_2) and discharge at the end of the flowpath.

the local groundwater. Ruling out carbonate weathering and photosynthesis leaves atmospheric exchange as the most probable cause for the perceived difference in the $\delta^{13}C_{DIC}$ values.

The CO_2 in the atmosphere has a $\delta^{13}C$ value of -8% (Keeling *et al.* 2005) and complete equilibration with the atmosphere results in $\delta^{13}C_{DIC}$ values close to zero, although the exact value depends on temperature (Barth & Veizer 1999). However, in the case of the Vantaanjoki River, there is very little time for complete exchange with the atmosphere, since the mean residence time of the surface flow component in the river is only 2 months (Niinikoski *et al.* 2016), which appears to be insufficient for complete equilibration (Mook 1970). The pond in the beginning of the flow path has the most evaporated water (Niinikoski *et al.* 2016) and it shows the most positive $\delta^{13}C_{DIC}$ values, indicating prolonged carbon isotope exchange with the atmosphere. However even here the equilibration is not complete.

Another way the atmosphere can affect the isotopic composition of DIC in river water is by degassing. The lighter isotope is more readily lost into the atmosphere (Keeling *et al.* 2005) hence the remaining DIC tends to become enriched in ^{13}C. CO_2 degassing into the atmosphere can amount to even 50% of stream carbon flux (Wallin *et al.* 2012). The calculated pCO_2 values of the river water range

between 1.2 and 3.7 mbar at the mouth of the river, being clearly higher than atmospheric pCO_2 (Figure 5). Even higher values are reached upstream (Figure 3). The initial pCO_2 of the local groundwater base flow can be estimated to be about 12 mbar, calculated from the groundwater analyses presented by Kortelainen & Karhu (2006). Even in the winter, when base flow is the dominant water component in the river (Niinikoski *et al.* 2016), the pCO_2 of the river water remains at 2–3 mbar, corroborating rapid CO_2-loss to the atmosphere.
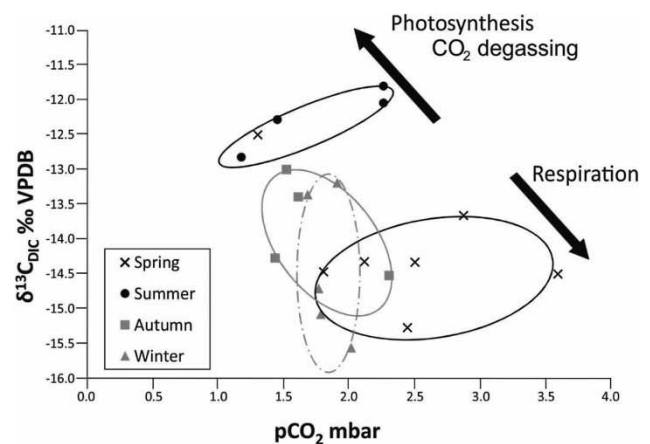

Figure 5 | A graph showing pCO_2 and $\delta^{13}C_{DIC}$ at the mouth of the river divided by seasons. Summer samples indicate possible photosynthesis or CO_2 degassing.

There is a distinct rise in $\delta^{13}C_{DIC}$ values in the summer samples and a decrease in the pCO_2 in the river water (Figure 5). These changes can indicate either photosynthesis or CO_2 degassing (Telmer & Veizer 1999). There is no way of differentiating between the two by using the measured parameters. Therefore the presence of photosynthesis is not confirmed by these results, but it can have a significant effect on the inorganic carbon balance of boreal surface waters (Jonsson et al. 2001). It can be concluded that CO_2 degassing is taking place, at least to some extent, since the pCO_2 of the river water is higher than atmospheric.

Human induced changes

Two point contamination sources, a wastewater purification facility and a sawmill, are located between the sampling points at 96 km and 84 km. All measured parameters show distinct changes in this interval (Figure 3). These include an increase in the DIC and pCO_2 values, as well as a decrease in the $\delta^{13}C_{DIC}$. These changes suggest local addition of DIC from an organic source. This would lead to increases in the DIC and pCO_2 and to a decrease in the $\delta^{13}C_{DIC}$, caused by the decomposition of organic carbon, with $\delta^{13}C$ of approximately $-27‰$, into the inorganic form. There are two possible causes for the changes in the carbon contents: One is the wastewater purification facility releasing organic matter into the river channel, and the other is stronger base flow bringing soil respiration originated DIC. The latter is supported by a base flow pulse described by Niinikoski et al. (2016), but it can also be a combination of these two effects. The rest of the point contamination sources are located further down along the flow path, but no significant changes in these parameters can be observed.

The first carbon flushed into the river channel during the spring flooding event is likely affected by carbonate weathering, suggested by a small positive 1‰ peak in the $\delta^{13}C_{DIC}$ values in the beginning of the flooding period (spring 2011, Figure 3). This event could be related to carbonate containing liming product spread on the fields before snowmelt. The purpose of liming is to raise the pH of the soil to make it better suited for agricultural purposes. The carbonate used for liming is derived from sedimentary sources with normal marine $\delta^{13}C$ values of about 0‰. However, this effect of human activity appears to be minor.

CONCLUSIONS

As most surface waters, the Vantaanjoki River serves as a source for atmospheric CO_2. The DIC in the river is mostly derived from soil respiration and brought to the river by base flow and during spring flooding surface flow as well. Significant quantities of carbon travel through the river system during the spring flooding, when carbon derived from soil respiration is flushed into the river by snowmelt. The isotopic composition of DIC is mainly controlled by respiration and degassing of CO_2. Photosynthesis cannot be confirmed, and it is unlikely considering the short residence time of the water. There are no signs of carbonate weathering, and there are also negligible sources for carbonates in the catchment. Wastewater purification facilities may be a local source of organic carbon into the river, but in the overall carbon contents of the river they are not significant.

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