



# Sensitivity of river catchments to discharge-controlled dissolved carbon export: a study of eight catchments in southern Patagonia

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**Abstract** Understanding the role of catchment sensitivity to dissolved carbon export to aquatic systems is crucial to predict future changes in carbon fluxes under changing climatic conditions. We present 1-year variations in dissolved organic (DOC) and inorganic carbon (DIC) concentrations and fluxes in eight river catchments differing in size (3–300 km<sup>2</sup>), morphology (steep to flat), and vegetation cover (grassland, forest and peatland) along a precipitation gradient in southern Patagonia, Chile. The results show large differences between catchments in terms of river DOC (2–47 mg L<sup>-1</sup>; 1–44 tons km<sup>-2</sup> year<sup>-1</sup>) and DIC (0.1–38 mg L<sup>-1</sup>; 1–5 tons km<sup>-2</sup> year<sup>-1</sup>) concentrations and fluxes in response to changes in discharge. Small and steep catchments hosting organic rich forest soils and peatlands were the most sensitive and showed the highest and fastest DOC release if evaluated on a per unit area basis. Here, rain events caused a rapid exponential increase in DOC release, while DIC export decreased exponentially. A negative

correlation between DOC and DIC reveals the minor importance of DIC production through mineralization of DOC in most catchments. Catchments hosting large peatlands had low sensitivity to discharged controlled DOC release attributed to their high hydrological buffer capacity. Similarly, flat and relatively dry Patagonian steppe catchments have comparatively low sensitivity but have short-term high release of DOC accumulated during dry periods. In conclusion, morphology, rather than catchment size or vegetation cover, was found to show the major influence on sensitivity to DOC release.

**Keywords** River catchments · Sensitivity to dissolved carbon releases · Controlling factors catchment morphology

## Introduction

River systems are a major component in the global carbon cycle, where they transport and transform carbon between terrestrial and marine environments. There is a large variability in the forms of carbon, both organic and inorganic, across landscapes, and alterations in their fluxes have critical effects on downstream ecosystem function (Tank et al. 2018). Dissolved organic carbon (DOC) is the (by)product of microbial decomposition of organic matter and represents the major link between soil organic carbon (SOC) and aquatic systems (Don and Schulze 2008).

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DOC is considered the most mobile and reactive fraction of soil organic matter (Tank et al. 2018). The importance of DOC for aquatic ecosystems has been extensively discussed, as it affects the mobility and toxicity of metals (e.g., Kalbitz and Wennrich 1998), light attenuation and nutrient availability (e.g., Seekell et al. 2015). Dissolved inorganic carbon (DIC) in river water is composed of dissolved carbon dioxide ( $\text{CO}_2^*$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ions ( $\text{CO}_3^{2-}$ ), but bicarbonate ions predominate at the circumneutral pH of most natural waters (6–8.5). DIC is derived from mineral weathering and the microbiological degradation of organic matter, with both processes releasing  $\text{CO}_2$ . DIC is a biogeochemically important carbon component in fresh water, as it buffers pH, sustains aquatic photosynthesis and biogenic calcification and interacts with other elemental cycles, such as P and Ca (Raymond and Hamilton 2018).

Several factors have been shown to influence DOC export, including land cover and land-use changes (Worrall et al. 2004; Ren et al. 2016; Kritzberg 2017), hydrology and hydrological pathways (Alvarez-Cobelas et al. 2012; Harrison et al. 2005; Hongve et al. 2004), global warming and related climate change (Freeman et al. 2001, 2004), and in-stream DOC cycling (Moody et al. 2013; Cole et al. 2007). DOC export from catchments seems to show a generalized response to changes in discharge. A positive relationship between DOC concentrations in river water and discharge has been shown in many studies—predominantly from northern temperate catchments (e.g., Wen et al. 2020; Broder and Biester 2015; Ågren et al. 2007; Raymond and Seiers 2010; Hope et al. 1994; Ledesma et al. 2015; Cai et al. 2015)—though this relationship has been confirmed across a variety of ecoregions and catchment sizes (Zarnetske et al. 2018). Soil organic layers and riparian zones are considered the main sources of DOC to streams during discharge events, and surface runoff is the main transport pathway (Raymond et al. 2016). Episodic discharge can largely determine the DOC fluxes' seasonality (McClain et al. 2003; Vidon et al. 2010; Pellerin et al. 2012; Inamdar et al. 2006, 2011; Fellman et al. 2009; Catalán et al. 2013; Broder and Biester 2015), and short-term large rainfall as well as snow melt can contribute between 36 and > 50% to the annual DOC export (Hinton et al. 1998; Inamdar et al. 2006; Birkel et al. 2017; Finlay et al. 2006). Broder and Biester

(2015) have shown that DOC concentrations in peatland and forest catchments often increase during high discharge, which is attributed to the connection of carbon pools during rain events.

Discharge also has an influence on DIC export. DIC fluxes have a negative response to increases in river water discharge due to the dilution of groundwater fluxes, the main source of DIC to streams (Rosentreter and Eyre 2019; Wallin et al. 2010; Cai et al. 2015; Shih et al. 2018). However, the connection of soil macropores in catchment soils during high rain events may increase DIC fluxes to the river due to activated ground water influx (e.g., Bass et al. 2013; Öquist et al. 2009).

As DOC and DIC have different sources and transport pathways that are active under different flow regimes, catchment properties (such as dominant vegetation, slope, size) would influence the dynamics of both forms of dissolved carbon and the relative importance of each under different discharge conditions. The synchronous evaluation of the effect of discharge on DOC and DIC export is rare, and most studies to date have been limited to the indirect effects on DOC and DIC production and export attributed to human activities (e.g., nitrogen fertilization, forest management, pollution, and peatland drainage), limiting the conclusions reached about the role of natural processes, such as catchment characteristics.

To evaluate the sensitivity in dissolved carbon export from catchments related to differences in precipitation and discharge patterns, understanding the influence of natural catchment characteristics such as morphology, vegetation cover and size is crucial.

In this study, we investigated DOC and DIC release from eight catchments differing in size, morphology and vegetation cover along a west to the east gradient in precipitation and landscape type in the Magellanic Moorlands in southernmost Patagonia (Chile, 53° S). We aimed to evaluate catchment sensitivity to DOC and DIC export by investigating DOC and DIC concentrations and fluxes as a function of catchment characteristics (size, vegetation cover, morphology). We define catchment sensitivity here as the magnitude of DOC or DIC concentrations and flux changes related to changes in discharge. We hypothesized that morphology and vegetation cover of the catchment, rather than the size of the catchment or of carbon pools, determine the sensitivity of river catchments towards DOC and DIC release.

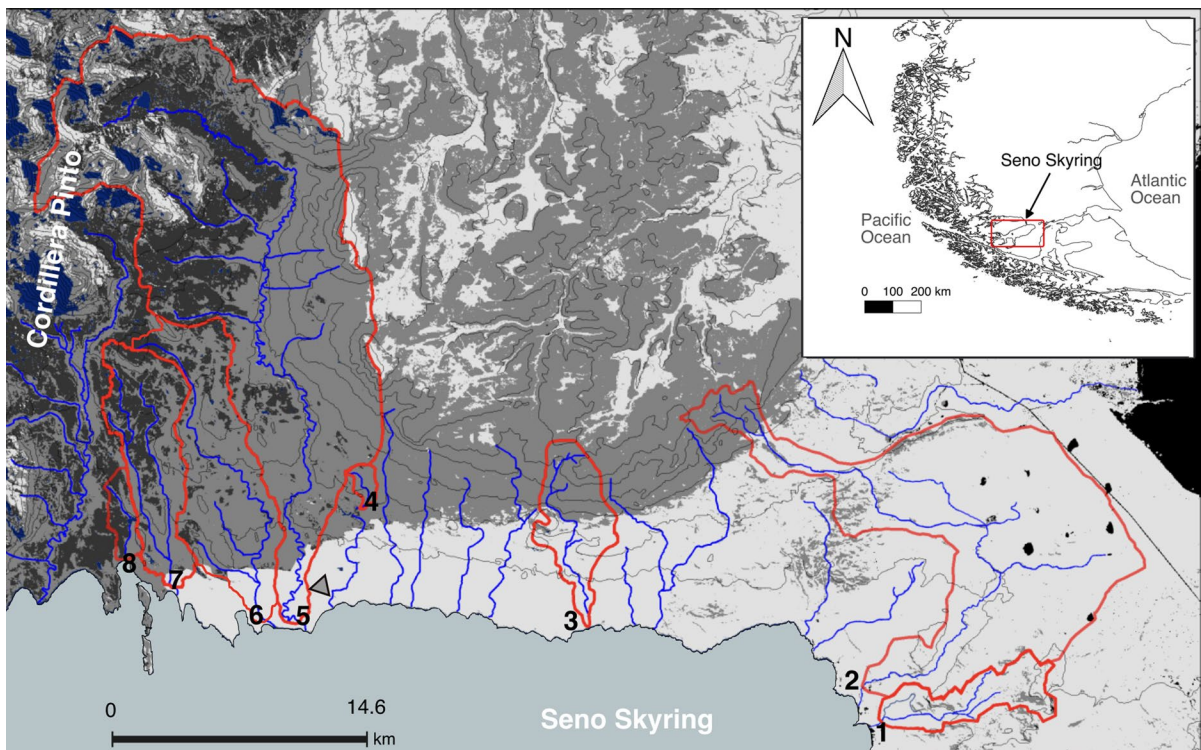
## Material and methods

### Study area and catchments description

The study area (Fig. 1) is located in a remote part of the eastern Andes about 120 km north-west of Punta Arenas, Chile (52° S). All investigated rivers and streams drain into the Seno Skyring. The Seno Skyring area is part of a pronounced large-scale vegetation zonation comprising from the Pacific (Western Andes) to Atlantic Coast, induced by a strong longitudinal precipitation gradient (e.g. Schneider et al. 2003). Within the study area annual precipitation rates decrease from ~2000 mm at the east side of the Andes to 200–400 mm in the semi-arid to arid Patagonian Steppe (Schneider et al. 2003). The mean annual temperature (~6 °C) is relatively constant within the transect, but the inter-annual amplitude of

temperature increases towards the more continental parts (Pisano Valdés 1977), with regular frost events in winter and higher summer temperatures in the drier eastern parts, while frost periods are mostly absent in the west but with even cooler summer temperatures i.e. subpolar oceanic climate Cfk'c, in Köppen classification (Pisano Valdés 1977; Tuhkanen 1992). Mean annual precipitation and temperature in the period 2006 to 2010 were ~740 mm and 6.7 °C (detailed data in Table SM1).

The vegetation zonation in the area is characterized by large mixed coastal blanket- and raised bogs in the western area, followed by temperate evergreen deciduous forest, and finally the semi-arid to arid Fuego-Patagonian steppe to the east (Pisano Valdés 1977). Accompanied by the changes in vegetation, there is a shift from mires and organic-rich peaty soils in the semi-humid areas (histosols) to mollisols in the



**Fig. 1** Map of the research area, showing the distribution of vegetation and localization of rivers (blue) and related catchments (red) along the Seno Skyring area (53° S); Triangle=location of the weather-station AWS “Skyring” (52° 33′ S/71° 58′ W). Sampling sites from east to west, Chorrillo Laguna (1), Río Verde (2), Virgen de Montserrat (3), Río Bosquecillo (4), Río Perez (5), Río Leon (6), Río Nutria (7),

and Río Turba (8). The numbers indicate the approximate location of the sampling point. Colours indicate the distribution of the dominating vegetation with black = vegetation free, dark grey = mires, grey = forest, light grey = (sub-)alpine emerge vegetation and (sub-)alpine grassland (anthropogenic grassland), white = Fuego-Patagonian steppe

eastern semi-arid Patagonian steppe. Forest floors in the area have a high accumulation of organic matter, comprising a large amount of wood debris. Its extent reflects the stage of development of these forests, the human influence and the unfavourable conditions for litter decomposition in Southernmost Patagonia (Gutiérrez et al. 1991). Supplementary material includes detailed information on vegetation, geology and soils (Supplementary Text-1).

Anthropogenic influence in the study area, such as tree cuts and livestock farming, is apparent but only local and decreases from west to east. Most tree cutting dates back to the time of the first European settlements at the end of the nineteenth century.

We investigated eight river catchments—Chorrillo Laguna (CL), Río Verde (RV), Virgen de Montserrat (VM), Río Bosquecillo (RB), Río Perez (RP), Río Leon (RL), Río Nutria (RN) and Río Turba (RT). Catchment sizes vary from <5 to ~300 km<sup>2</sup> and median slopes from ~4 to ~16%. The location and main characteristics of the investigated rivers are shown in Fig. 1 and Table 1.

## Sampling

River water samples were collected throughout the years 2010 and 2011, respectively. The number of samples collected from the rivers varied between 15 and 27 (Table 2). Sampling periods were determined by climatic conditions, especially precipitation regime. The sampling periods include winter, early and late spring, late summer as well as the early autumn phase, in which most climatic- or hydrological events such as summer- and autumn storms and snowmelt occur. Water samples were filtered using a pre-cleaned 0.45 µm nylon single-use syringe filter (Rotilabo®, Carl Roth, Germany). Prior to utilization, filters and PP tubes (50 mL) were pre-rinsed with MilliQ water (18.2 MΩ cm) and with 10 mL of the river water, respectively. Samples were stored cool (<8 °C) and dark prior to analyses. Acidity (pH) and electrical conductivity (EC) were measured directly in the field using a WTW SenTix 41 glass electrode and a TetraCon325 probe (Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany),

**Table 1** Basic information on the studied catchments

| Rivers                    | Sampling site                  | Catchment area (km <sup>2</sup> ) | Slope (%)<br>Median | Dominant vegetation (%) |        |           |
|---------------------------|--------------------------------|-----------------------------------|---------------------|-------------------------|--------|-----------|
|                           |                                |                                   |                     | Peatland                | Forest | Grassland |
| Chorrillo Laguna (CL)     | 52° 36.986' S<br>71° 29.253' W | 23.7                              | 6.7                 | 0                       | 13     | 87        |
| Río Verde (RV)            | 52° 35.820' S<br>71° 30.106' W | 180.5                             | 3.8                 | 0                       | 11     | 89        |
| Virgen de Montserrat (VM) | 52° 33.663' S<br>71° 43.984' W | 27.6                              | 14.8                | 0                       | 50     | 50        |
| Río Bosquecillo (RB)      | 52° 29.740' S<br>71° 55.438' W | 2.7                               | 11.00               | 8                       | 92     | 0         |
| Río Perez (RP)            | 52° 33.114' S<br>71° 58.781' W | 300.8                             | 15.9                | 29                      | 68     | 3         |
| Río Leon (RL)             | 52° 33.210' S<br>71° 59.996' W | 69.5                              | 9.8                 | 13                      | 76     | 12        |
| Río Nutria (RN)           | 52° 31.948' S<br>72° 4.865' W  | 44.7                              | 10.1                | 36                      | 61     | 3         |
| Río Turba (RT)            | 52° 31.005' S<br>72° 7.314' W  | 6.9                               | 10.3                | 83                      | 17     | 0         |

Catchment areas were extracted from pre-processed SRTM 90 m data (Jarvis et al. 2008), while a Landsat data set (NASA Landsat Program, 2011, Landsat ETM+ scene L71229097\_09720030328, L1T, USGS, Sioux Falls, 2003/03/28, available at: <http://glovis.usgs.gov>), offered by the USGS (2011) was further processed with a Hybrid classification as described by Reisen (2006) to gain information about the distribution of the main surface types (mires, forest, (sub-) alpine emerge vegetation and (sub-) alpine grassland, (anthropogenic grassland), Fuego-Patagonian steppe, free vegetation, water/no information). Slope estimates were extracted from a digital elevation map created using data provided by NASA Earth Data server

**Table 2** Summary of the water samples collected

| River                | Total number of samples (2010–2011) | Samples collected during the period 23.10.2010–06.10.2011 |
|----------------------|-------------------------------------|-----------------------------------------------------------|
| Chorrillo Laguna     | 19                                  | 8                                                         |
| Rio Verde            | 20                                  | –                                                         |
| Virgen de Montserrat | 20                                  | –                                                         |
| Rio Bosquecillo      | 27                                  | 19                                                        |
| Rio Perez            | 18                                  | 12                                                        |
| Rio Leon             | 24                                  | –                                                         |
| Rio Nutria           | 23                                  | 12                                                        |
| Rio Turba            | 15                                  | 10                                                        |

23.10.2010–06.10.2011 when continuous discharge data was measured

calibrated by using WTW buffer solutions (technical buffer pH 4.01 and 7.00; conductivity 1000  $\mu\text{S}/\text{cm}$ ).

#### Discharge measurements

Discrete discharge measurements were done each time a water sample was collected. Continuous discharge measurements were done in four of the rivers (CL, RB, RN and RT) between the period (23.10.2010–06.10.2011). Discrete discharge values were determined by means of a Flo-Mate (Model 2000, Marsh McBirney, Inc., USA), while continuous discharges were determined by a Capacitance Water Level Loggers (CWLL, Odyssey, New Zealand, resolution  $\sim 0.8$  mm) installed at rectangle weirs. Due to its large river width, no weir could be installed at RN. Here, the CWLL was installed at a suitable area, where the stream was naturally straightened. The CWLL discharge data were recorded in three-hour intervals. Continuous daily discharge data for RP were obtained from the Ministry of Public Works (Directorate General of Water, Punta Arenas, Chile. <http://snia.dga.cl/observatorio/>, 20.10.2011).

#### Analyses of DOC and inorganic ions

DOC and DIC were analysed by means of a TOC-Analyser (TOC-Analyzer, multi N/C® 2001S, Analytik Jena AG, Germany) via platinum thermo-catalytic combustion. The untreated samples were analysed for DOC and DIC applying the TC-TIC subtraction method. In addition, DOC in approx. 80% of all water samples was additionally measured with the non-purgeable method, where samples were acidified with 2 M HCl to  $\text{pH} < 2$  to remove all inorganic carbon

prior to analysis. Deviations of both methods regarding the DOC concentrations, except those of the Fuego-Patagonian steppe water samples, were less than 10%. As for the latter, DIC values were often as high or even higher as the corresponding DOC concentrations. In this case, only DOC concentrations determined by the non-purgeable method were used. The calibration for DOC measurements was performed using potassium hydrogen phthalate (KHP, DIN 1484), while DIC was calibrated using  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions. Concentrations of Ca, were analysed by means of inductively coupled plasma optical emission spectrometry (ICP-OES, Vista MPX, Varian). Samples for measurement with ICP-OES were acidified with bi-distillate  $\text{HNO}_3$  to  $\text{pH} < 2$ . The standard reference material SRLS-4, SRLS-5 (riverine water, National Research Council of Canada) and Ontario-99 (lake water, Environment Canada) as well as an external KHP solution (DOC concentration  $20 \text{ mg L}^{-1}$ , Bernd Kraft GmbH, Germany) were used for quality control. The detection limit for the DOC was  $0.5 \text{ mg C L}^{-1}$ ,  $3.8 \text{ mg L}^{-1}$  for Ca and repeatability (RSD) always  $< 10\%$ .

#### Method to evaluate the relation between DOC and DIC concentrations and discharge

We applied an empirical model to determine if the changes in discharge (Q) produce dilution or connection of DOC pools increasing the export. To do this, we calculated the slope ( $\beta$ ) of the  $\ln(\text{DOC})-\ln(Q)$  linear regression (Godsey et al. 2009). According to Godsey et al. (2009) (Eq. 1,  $\ln-\ln$ ), a negative  $\beta$ -value represents decreasing material flux with increasing water flux (i.e. dilution), while a positive  $\beta$ -value

indicates increasing material flux with increasing water flux. If  $\beta$  is  $\approx 0$  the catchment behaves chemostatically, that is, the system keeps concentrations constant as discharge varies. Using Student's *t* test we determined whether  $\beta$  was significantly different from reference slope of zero. Therefore, we used the mentioned approach to determine the type of relation between DOC and discharge and whether this relation is significant. Logarithmic transformed data allows a better comparison between variables with different magnitude, such as discharge in the studied the catchments. Thus, we used the results of the linear regression on logarithmic data to make comparisons of the relations between DOC concentrations and discharge among catchments. In addition to the  $\ln(\text{DOC})-\ln(Q)$ , we tested a linear regression model on DOC concentrations— $\ln(Q)$  (Eq. 2, semi- $\ln$ ) and a power-law model (Eq. 3) to determine (based on the residual sum-of-squares RSS value) differences in the accuracy of the different methods. Based on the results of the linear regression models we evaluated the catchments based on their sensitivity (i.e., the magnitude of response in terms of DOC concentrations due to changes in discharge).

$$\ln(y) = \beta \times \ln(x) + c \quad (1)$$

$$y = \beta \times \ln(x) + c \quad (2)$$

$$y = a \times x^{-b} \quad (3)$$

where  $y$  is DOC concentration,  $x$  is discharge,  $\beta$  is the slope of the regression line,  $c$  is the  $y$ -intercept and  $a$  and  $b$  are constants.

The same analyses were done for pH, conductivity, DIC and Ca concentrations. All the logarithmic transformation mentioned in the text as “logarithm” are natural logarithms ( $\ln$ ). All analyses were performed using R software (R Development Core Team 2019).

#### Calculation of DOC fluxes

Export of DOC was calculated according to the Eq. 4, to provide the best estimate of load based on available continuous discharge data (Walling and Webb 1985; Littlewood 1995). This method has been used in studies on (annual) DOC fluxes from different catchments (e.g., Hope et al. 1997; Clark et al. 2007; Strohmeier et al. 2013).

$$F = K \times Q_r \left( \frac{\sum_{i=1}^n C_i Q_i}{\sum_{i=1}^n Q_i} \right) \quad (4)$$

where,  $F$  is the total solute (i.e. DOC) load based on a certain time period,  $K$  is the conversion factor (numbers of seconds in the corresponding time period),  $Q_r$  is the mean discharge over the period of continuous record,  $Q_i$  is the instantaneous discharge at sampling time  $i$ ,  $C_i$  is the instantaneous concentration of solute in sample  $i$ , and  $n$  is the numbers of samples.

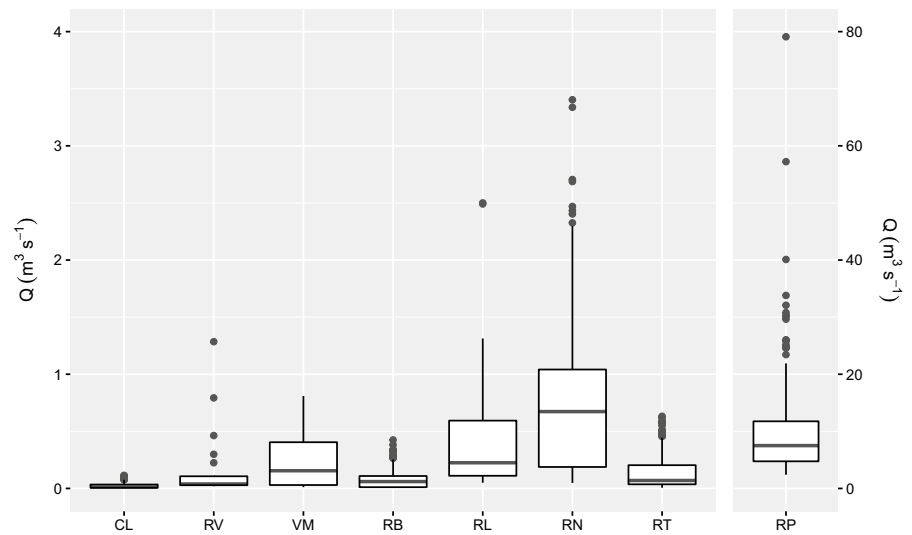
Equation 4 was applied here to calculate short term and annual DOC and DIC fluxes per catchment area. The short term DOC and DIC fluxes were calculated for the summer period 2010 (low precipitation; 12.03.—16.04.2010) and the early spring period 2011 (high precipitation; 17.09.—06.10.11), based on continuous and interpolated daily discharge data of the eight Patagonian watersheds (CL, RV, VM, RB, RL, RP, RN, RT). Annual DOC and DIC fluxes were calculated for the five watersheds (CL, RB, RP, RN, RT) where continuous discharge data were available. Continuous discharge measurements do not cover a whole year (16 days are missing). To estimate the annual discharge (365 days), we first calculated the export of carbon per day based on a period of 349 days.

## Results

### Discharge

Discharge varied between rivers and throughout the year (Figs. 2 and SM1). The easternmost rivers, which are flatter and dominated by grassland, had the lowest median discharges ( $0.012 \text{ m}^3 \text{ s}^{-1}$  and  $0.039 \text{ m}^3 \text{ s}^{-1}$ , respectively). In contrast, the river with the largest catchment (RP) had the highest discharge of all studied rivers ( $7.5 \text{ m}^3 \text{ s}^{-1}$ ), which was up to 620 times higher than those of easternmost rivers CL and RV, although its catchment size was only 12 and  $\sim 2$  times larger, respectively. The river with the smallest, steep and forested catchment (RB) and the main peatland-draining river (RT) had median discharge values of  $0.06$  and  $0.07 \text{ m}^3 \text{ s}^{-1}$ , while the discharge of the other rivers (VM, RL and RN) ranged between  $0.155$  and  $0.673 \text{ m}^3 \text{ s}^{-1}$ . See the seasonal patterns in discharge in Fig. SM1 in the supplementary material.

**Fig. 2** Annual discharge of the eight study rivers. Box plots for CL, RB, RN, RT and RP are based on continuous and punctual measurements while RV, VM and RL only in punctual measurements. More information in the text. In box plots: horizontal lines in the rectangle indicate the median, top and bottom of the rectangle indicate the third and first quartile respectively; whiskers show maximum and minimum; and individual points are outliers



#### Annual and temporal variation in conductivity, pH and concentrations of DIC and DOC

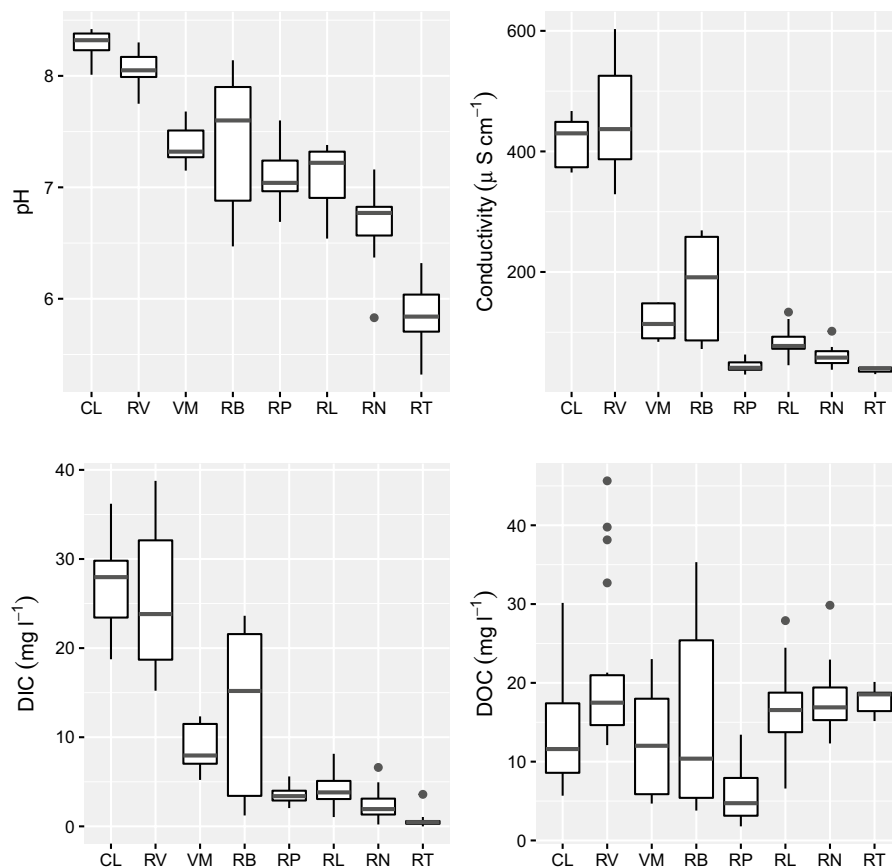
The median annual conductivity values ranged between 40 and 437  $\mu\text{S cm}^{-1}$ , with minimum and maximum values of ca. 30  $\mu\text{S cm}^{-1}$  (RT and RP) and 603  $\mu\text{S cm}^{-1}$  (RV), respectively. Conductivity values increased west to east, with the lowest values in peatland-draining rivers and higher values in those draining carbonate sediments (Fig. 3). Annual pH values generally increased from west to the east (Fig. 3). The main peatland-draining river (RT) had a median pH of 5.8 and a minimum of 5.3, while the eastern rivers (CL and RV) had median values between 8.0 and 8.3 attributed to the carbonate sediments in their catchments.

Annual DIC concentrations also increased from west to the east (Fig. 3). The lowest median values were found in the peatland-draining river (RT; 0.5  $\text{mg C L}^{-1}$ ), while the highest were found in the rivers draining catchments underlain by carbonate sediments in the semiarid Patagonian steppe (CL and RV, 28 and 23.8  $\text{mg C L}^{-1}$ ). The median DIC of VM, RP, RL, RN and RT decreased in this order from  $\sim 8$  to 2  $\text{mg C L}^{-1}$ . Only the steepest and smallest river RB, which is located in the middle of the west–east transect and had an annual median of 15  $\text{mg C L}^{-1}$ , broke this pattern. Throughout the year, two main seasonal patterns can be observed (Fig. 4). In the eastern rivers (CL, RV and VM),

DIC concentrations decreased from March until July–August (winter) and increased again from September–October (spring). The western rivers RP, RL and RN had relatively constant DIC values throughout the year, with only a slight decrease in April and September and a slight increase in November.

The median DOC concentrations varied between 4.7 and 18.5  $\text{mg C L}^{-1}$  (Fig. 3). Higher median values (16.5 to 18.5  $\text{mg C L}^{-1}$ ) were found in the western rivers, where peatlands cover a large part of the catchments (i.e., RL, RN and RT) and RV. The eastern rivers CL, VM and RB (without RV) had lower annual median DOC concentrations (10.4–12  $\text{mg C L}^{-1}$ ), with the larger river (RP) having the lowest median (4.7  $\text{mg C L}^{-1}$ ). The eastern rivers, which were dominated by grassland (Patagonian-steppe) vegetation, had a larger range in DOC concentrations. Here, DOC concentrations differ by a factor of 5.3 and 9.3 (e.g., CL and RB, respectively) compared to the western rivers (e.g., RT and RL), which differ by factors of 1.3 and 4. RB, the river with the smallest and steepest forest-dominated catchment, had the largest variation. All the studied rivers exhibited an increase in DOC concentrations from June to September (spring) followed by a decline from October to March/April (summer) in the eastern rivers (Fig. 5), whereas the western rivers (RN, RL, RP and RT) had increasing DOC concentrations from January to May (summer).

**Fig. 3** Annual data for pH, conductivity, DIC and DOC concentrations of the eight study rivers. In box plots: horizontal lines in the rectangle indicates the median, top and bottom of the rectangle indicate the third and first quartile respectively; whiskers show maximum and minimum; and individual points are outliers



#### Relationship between discharge, DOC, DIC and hydrochemical parameters (Ca, pH, EC)

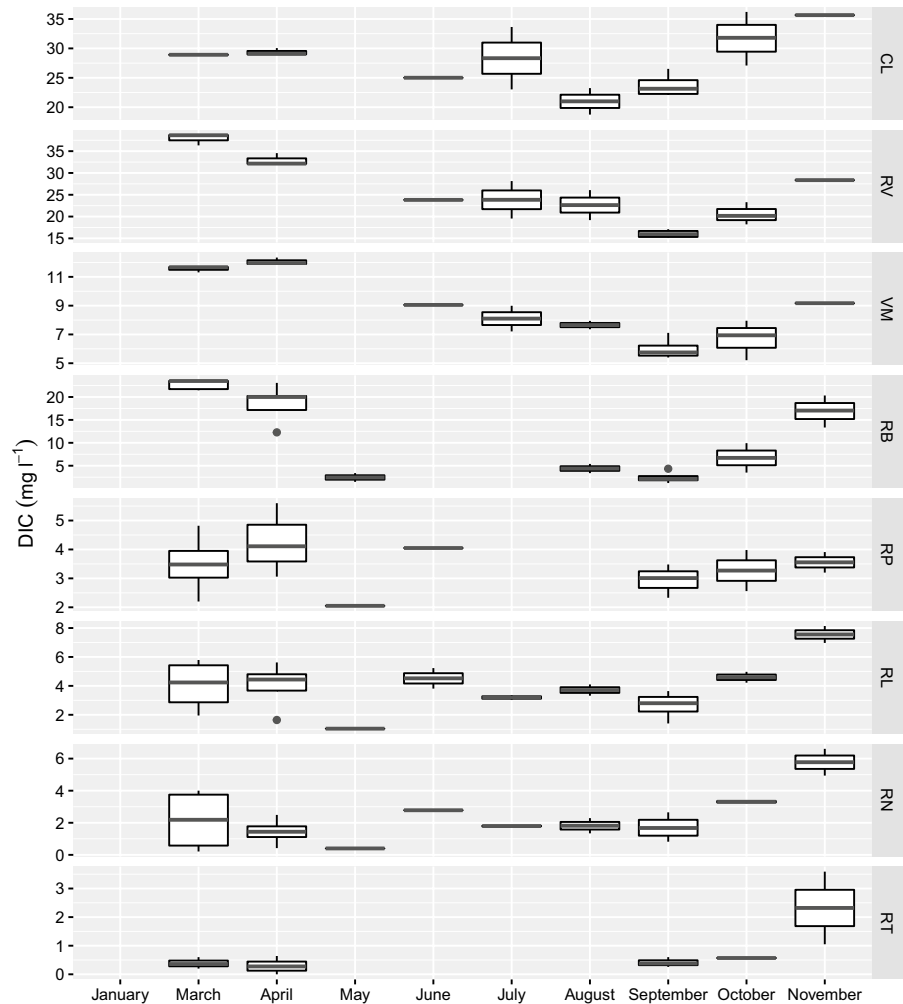
Across all sites, the linear regression slope ( $\beta$ ) on  $\ln$  (DOC concentrations) was positive (between 0.07 and 0.5), with  $r^2$  values between 0.25 and 0.95 (Table 3). Student's *t* test showed that the slopes of CL, RV, VM, RB, RL, RN and RT were significantly different from zero ( $\alpha=0.01$ ), which means that the DOC concentration generally increased with discharge. For the largest river (RP), Student's *t* test was significant, with  $\alpha=0.05$  and a  $r^2$  of 0.25 (Table 3) (Fig. 6). In flat river catchments dominated by peatlands (mainly RN and RT), the low slope of the regression between DOC and discharge indicates that DOC concentrations here varied little across the range of discharge. In contrast, the rivers with steep, forest-dominated catchments had the highest regression slope, i.e., a strong increase in DOC concentrations with discharge, and the highest  $r^2$  values (0.95 and 0.97 for VM and RB, respectively), indicating the strongest

relationship between DOC concentrations and discharge. In rivers with watersheds in the Patagonian steppe as well as RL, the rates of increase in DOC concentrations with discharge and  $r^2$  were lower than those in the steep catchments. RP (the largest river with the largest catchment) exhibited the lowest  $r^2$  ( $\sim 0.3$ ), indicating a weak increase in DOC concentrations with discharge.

The regression slopes on  $\ln$  (DIC)– $\ln$  (Q) were negative and significantly different from zero ( $\alpha=0.01$ ) for CL, RV, VM, RB, RP, RL and RN, with  $r^2$  values between  $-0.60$  and  $-0.96$  (Table 3 and Fig. 7). The negative relation between DIC and Q means that DIC concentrations decrease with discharge, indicating dilution of groundwater by surface run-off during high discharge and that there are no DIC pools connected during high surface run-off. For the peatland-draining river (RT), the regression slope was negative and different from zero at  $\alpha=0.05$  and  $r^2=-0.42$ , indicating dilution. Notably, a high dilution effect was caused by discharge in



**Fig. 4** Monthly data of DIC concentration in the eight study rivers. Only months for which data is available are represented. Notice different y-axis for every river



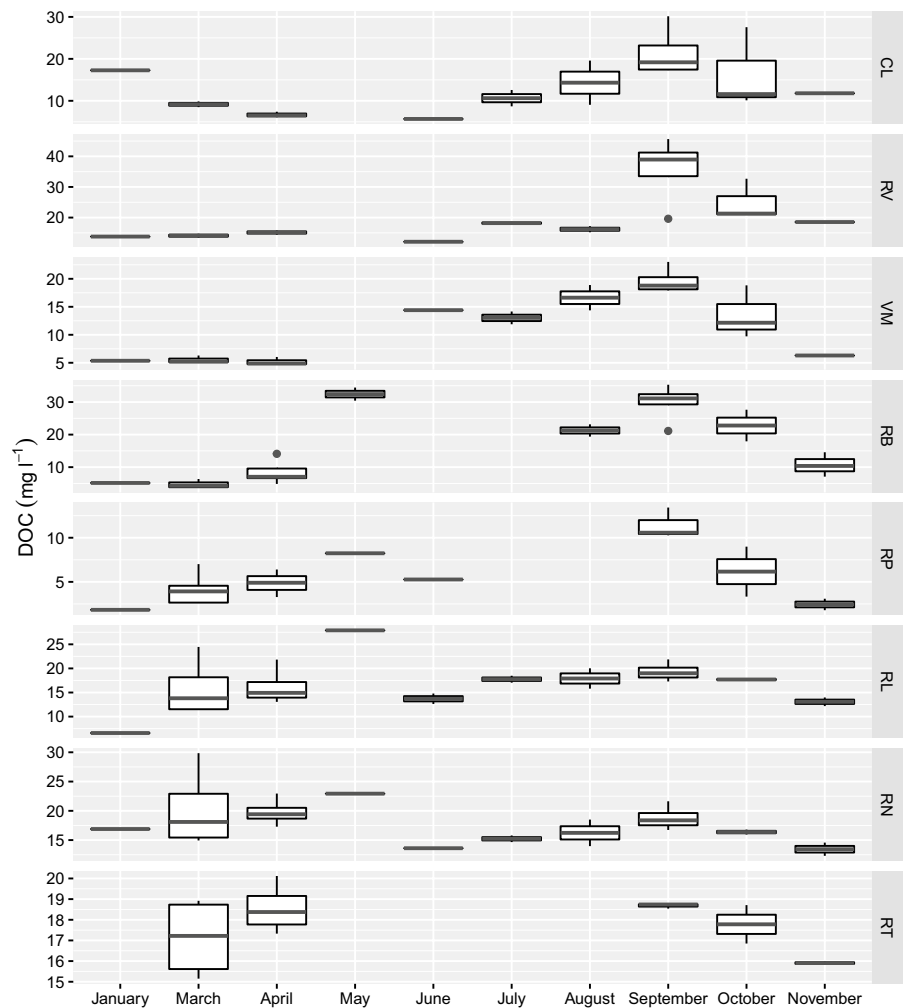
DIC concentrations in the steep forested catchment (RB), as indicated by the higher (negative) slope. The dilution effect was slightly lower in the catchments dominated by peatlands (RN and RT) and those with dominant mixed vegetation (RP and RL). In the rivers of the Patagonian steppe, the dilution of DIC concentrations due to increased discharge was generally low.

For DIC concentrations, the linear regression indicate that an increase in discharge dilutes the calcium concentration and lowers pH and conductivity values (Tables SM2, SM3 and SM4, respectively). Regarding the influence of discharge, the regression slopes were not significantly different from zero for pH and conductivity in the Patagonian steppe rivers (CL and RV), as well as for pH of VM or for conductivity in the peatlands-draining river (RT). Similar to what we found for DOC and DIC concentrations,

the rivers with catchments dominated by steep forest (specifically RB) have a strong correlation between Ca concentrations, pH and conductivity and discharge (Tables SM2, SM3 and SM4).

For most of the rivers and variables studied here, the results provided by the three models (i.e., ln–ln, semiln and power-law) were similar, and the related conclusions reached in terms of catchment sensitivity were the same. However, there were some differences between the fitting of the models among rivers and solutes (e.g., DOC, DIC, Ca). For example, for the DOC regressions (Table 3), the power law had a slightly lower RSS for most rivers than the other models, whereas VM and especially RB had lower RSS in the semiln model. For the DIC/discharge regressions (Table 3), ln–ln and power-law had similar or better performance than the semiln for all rivers.

**Fig. 5** Monthly data of DOC concentrations in the eight study rivers. Only months for which data is available are represented. Notice different y-axis for every river

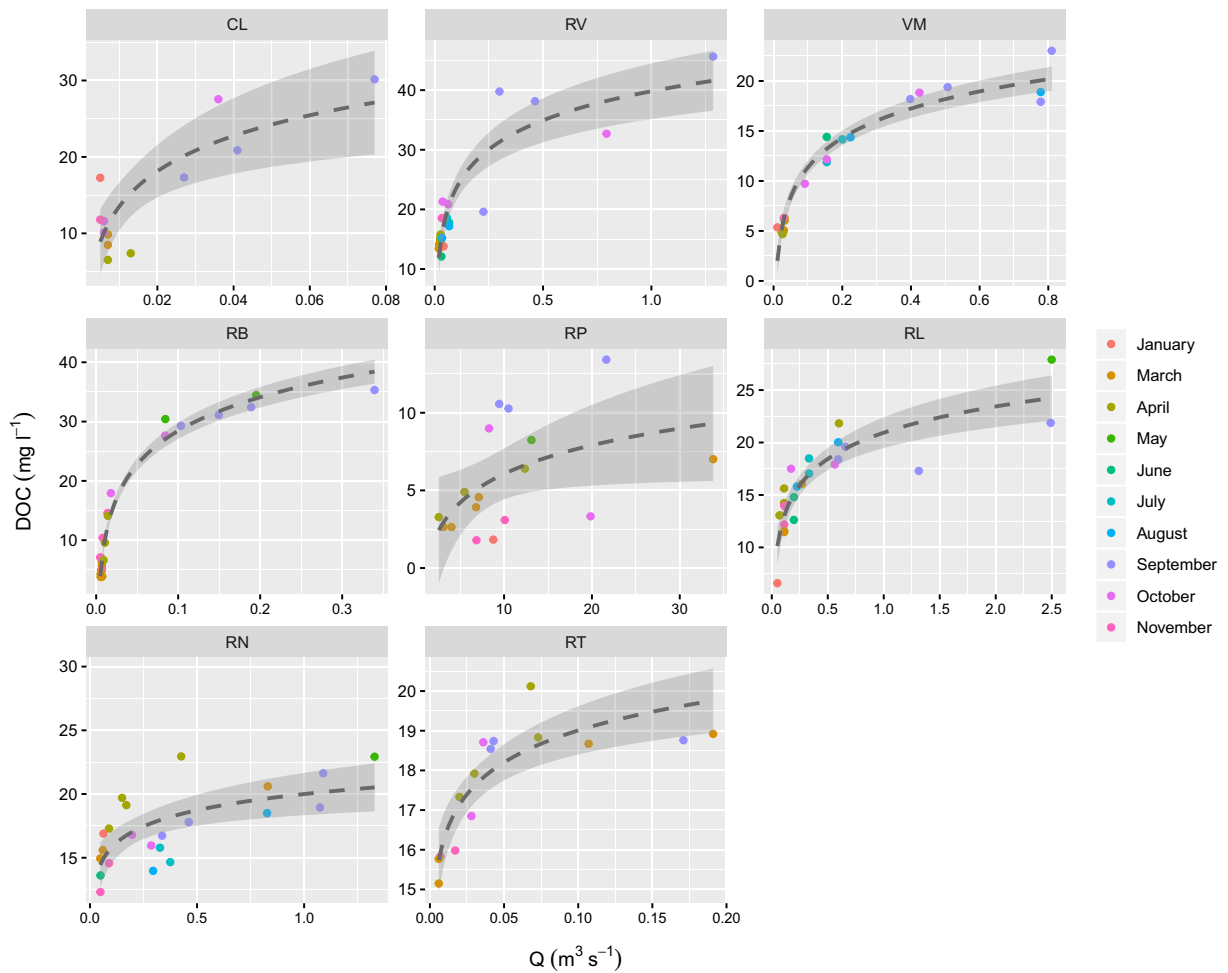


### Fluxes and export of DOC and DIC

The total annual DOC fluxes varied between 34 and 3833 Mg. The easternmost river in the semiarid Patagonian steppe (CL) had the smallest and the river with the largest catchment (RP) the highest annual DOC fluxes (Table 4). When DOC fluxes are related to catchment size (i.e., DOC exports), the easternmost river (CL) had the smallest ( $1.4 \text{ Mg year}^{-1} \text{ km}^{-2}$ ), and the river with the steep forest-dominated and smallest catchment (RB) had the highest DOC fluxes ( $44 \text{ Mg year}^{-1} \text{ km}^{-2}$ ) ( $2.7 \text{ km}^2$ ). The largest river (RP) and the rivers with peatland-dominated catchments (RN and RT) had intermediate values between 13 and  $20 \text{ Mg year}^{-1} \text{ km}^{-2}$ . Annual fluxes of total DIC ranged between 3 and 1459 Mg, with the smallest values for peatland-dominated catchment (RT) and

the highest values again for RP (Table 4). When the DIC fluxes were expressed in relation to catchment size, the smallest value corresponded to RT and the highest to RP. Unlike the DOC fluxes, the smallest catchment of RB did not have the highest DIC fluxes after being corrected for the catchment size.

Monthly DOC fluxes varied widely, ranging from 0.1 to 150 Mg in summer and 2.8–365 Mg in spring (Table 5), indicating that DOC fluxes were highest in spring. The lowest values were found for the small steep forested catchment (RB) in summer and for the easternmost river in semiarid Patagonian steppe (CL) in spring, while the highest values were generally (summer and spring) found for RP with its large catchment (RP). The difference between spring and summer varied between the rivers, being on average 20 times higher for the eastern rivers (CL, RV, VM



**Fig. 6** DOC concentrations versus discharge ( $Q$ ) in the eight study rivers. Discontinuous lines indicate the logarithmic regression and grey shadows show the confidence interval (0.95)

and RB) than for the western rivers (RP, RL, RN and RT). The smallest difference (1.5-fold) was found for RP with its large catchment, while the maximum difference (136-fold) was gain found for the small steep forested RB catchment.

The peatland-draining river (RT) generally had the lowest DIC fluxes, while the highest corresponded to the river with the largest catchment (RP; summer and spring). Monthly DIC fluxes varied from 0.07 to 72 Mg in summer and 0.06–94 Mg in spring (Table 5), indicating that the DIC fluxes were more similar in spring and summer than the DOC fluxes. For example, for RB, with its small steep forested catchment, this difference was 68 times lower and between 3 to 8 times lower than the easternmost

rivers (VM, RV and CL). The rivers with a high proportion of peatlands in their catchments (RN and RT) indicate slightly higher differences between spring and summer for the DIC fluxes compared to the DOC fluxes.

## Discussion

Our regression analysis results indicate a significant relation between DOC and DIC concentrations and discharge for most of the rivers (Table 3). Therefore, determining which factors control the discharge patterns will help to identify which underlying processes and catchment characteristics affect the sensitivity

**Table 3** Regression slopes ( $\beta \pm \text{std. error}$ ), significance of the Student's t-test (Sign.), residual sum-of-squares (RSS) and coefficient of determination ( $r^2$ ) of the linear regression on  $\ln$ - $\ln$  transformed data as well as the coefficient of determination of the linear regression and RSS were only discharge (Q) is  $\ln$  transformed

| Rivers | In (DOC)-ln (Q)                         |      |                | DOC-Q <sup>-b</sup> |                |     | ln (DIC)-ln (Q)                         |      |                | DIC-Q <sup>-b</sup> |                |     |
|--------|-----------------------------------------|------|----------------|---------------------|----------------|-----|-----------------------------------------|------|----------------|---------------------|----------------|-----|
|        | Slope ( $\beta \pm \text{std. error}$ ) | Sign | r <sup>2</sup> | RSS                 | r <sup>2</sup> | RSS | Slope ( $\beta \pm \text{std. error}$ ) | Sign | r <sup>2</sup> | RSS                 | r <sup>2</sup> | RSS |
| CL     | 0.39 ± 0.11                             | **   | 0.56           | 196                 | 0.67           | 224 | 182                                     | ***  | 0.80           | 44                  | 0.76           | 45  |
| RV     | 0.28 ± 0.03                             | ***  | 0.83           | 294                 | 0.83           | 313 | 291                                     | ***  | 0.73           | 338                 | 0.66           | 402 |
| VM     | 0.40 ± 0.02                             | ***  | 0.95           | 47                  | 0.95           | 38  | 42                                      | ***  | 0.80           | 18                  | 0.82           | 20  |
| RB     | 0.54 ± 0.05                             | ***  | 0.86           | 509                 | 0.97           | 92  | 293                                     | ***  | 0.99           | 91                  | 0.93           | 125 |
| RP     | 0.47 ± 0.21                             | *    | 0.25           | 159                 | 0.26           | 145 | 150                                     | ***  | 0.79           | 2                   | 0.80           | 3   |
| RL     | 0.23 ± 0.03                             | ***  | 0.71           | 114                 | 0.77           | 97  | 108                                     | ***  | 0.77           | 20                  | 0.69           | 19  |
| RN     | 0.11 ± 0.03                             | ***  | 0.47           | 98                  | 0.46           | 99  | 97                                      | ***  | 0.59           | 20                  | 0.59           | 20  |
| RT     | 0.07 ± 0.01                             | ***  | 0.76           | 8                   | 0.75           | 8   | 8                                       | *    | 0.42           | 9                   | 0.18           | 8   |

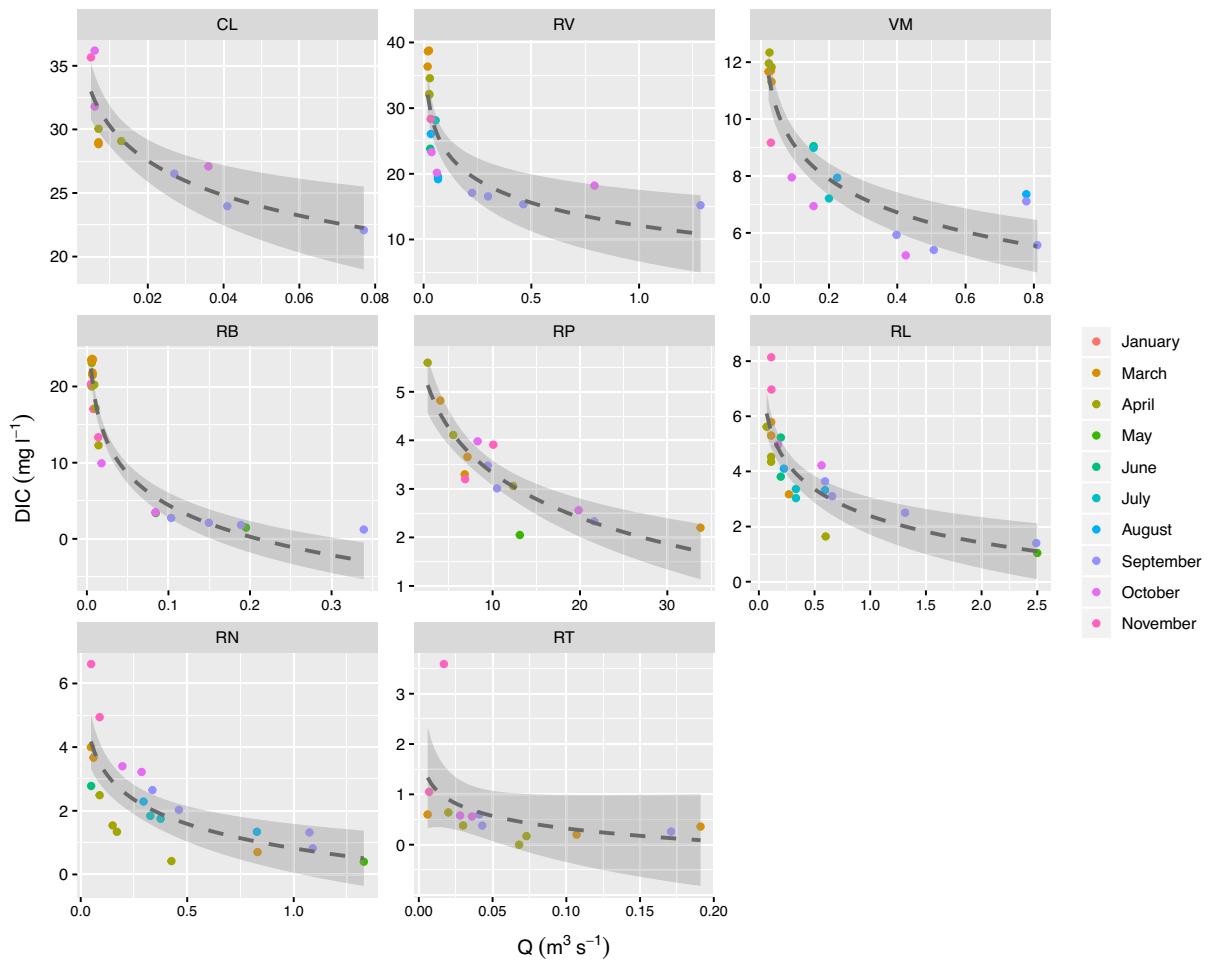
For the power-law (no-linear model) only RSS are provided. Student's t-test significance < 0.05 indicates that the  $\beta$  is significantly different from zero. Statistical significance \*\*\*0.001, \*\*0.01, \*0.05

for DOC and DIC release. Our limited discharge data limit the interpretation of the discharge data. While five of the rivers were continuously monitored over almost a year, from the other three rivers, only discrete discharge measurements were available. Therefore, conclusions based on discharge data of rivers with only discrete measurements must be taken as indications of general discharge characteristics only. Similarly, the number of catchments studied here is too small to statistically assess the general relationships between catchment characteristics (i.e., dominant vegetation, slope, catchment size and geology) and DOC and DIC release patterns. Thus, our interpretation of catchment sensitivity to DOC release is valid for the investigated catchments.

#### Precipitation gradient- and catchment type-controlled discharge

The west to the east Seno Skyring transect has a pronounced climate divide in terms of precipitation. Schneider et al. (2003) demonstrated that precipitation east of the Andes depends mainly on the intensity of westerly winds and that areas closest to the Andes receive the highest amount of precipitation. Accordingly, precipitation rates drop on the eastern side of the Andes to 25% and 8% relative to the maximum observed at sea level within the Andes (i.e., from ~10,000 mm to 500 mm within ~100 km; Schneider et al. 2003). The annual median discharge in the studied rivers (Fig. 2) reflects this spatial decrease in precipitation rates. The catchments of the westernmost rivers RL and RN, with the exception of RP (in the semihumid lowland area), exhibit the highest annual discharge. The rivers of the Patagonian steppe (CL and RV) experience semiarid to arid conditions known to be dominant along the Atlantic Coast, which results in generally low median annual discharge.

It is not surprising that RP had the highest annual median discharge given the large catchment area (300 km<sup>2</sup>) but also because its catchment area extends over the mountains towards the west, where precipitation is significantly higher than at the eastern sites. Seasonal differences in precipitation influence the seasonality in discharge (Fig. SM1). The hyperhumid catchments where large peatlands dominate (especially RT and RN, 83 and 36% peatlands, respectively) had more constant discharge than the



**Fig. 7** DIC concentrations versus discharge (Q) in the eight study rivers. Discontinuous lines indicate the logarithmic regression and grey shadows show the confidence interval (0.95)

**Table 4** Annual DOC and DIC fluxes and export of the five different rivers where the continuous discharge was measured

|                                                | Units                                | CL   | RB   | RP    | RN   | RT   |
|------------------------------------------------|--------------------------------------|------|------|-------|------|------|
| Catchment size                                 | km <sup>2</sup>                      | 23.7 | 2.7  | 300.8 | 44.7 | 6.9  |
| Avg. Q                                         | m <sup>3</sup> s <sup>-1</sup>       | 0.04 | 0.12 | 17.21 | 1.16 | 0.23 |
| Avg. DOC                                       | mg l <sup>-1</sup>                   | 18.3 | 16.9 | 6.1   | 17.4 | 17.7 |
| Total DOC exported in 1 year (365 days)        | Mg yr <sup>-1</sup>                  | 34   | 118  | 3833  | 742  | 136  |
| DOC exported in relation to the catchment size | Mg km <sup>-2</sup> yr <sup>-1</sup> | 1.4  | 44   | 13    | 17   | 20   |
| Avg. DIC                                       | mg l <sup>-1</sup>                   | 29.0 | 12.3 | 3.2   | 2.9  | 0.9  |
| Total DIC exported in 1 year (365 days)        | Mg yr <sup>-1</sup>                  | 34   | 6    | 1459  | 51   | 3    |
| DIC exported in relation to the catchment size | Mg km <sup>-2</sup> yr <sup>-1</sup> | 1.4  | 2    | 5     | 1    | 0.5  |

Patagonian steppe-dominated catchments, where discharge mostly occurs at the end of the winter during snowmelt. In addition to wetter conditions, peatlands

work as hydrological buffers, smoothing the variability in discharge (Lennartz and Liu 2019; Ahmad et al. 2020). Discharge in the two forested catchments in

**Table 5** Short-term DOC and fluxes at low and high discharge

|                           | Discharge/period | Avg. Q (m <sup>3</sup> s <sup>-1</sup> ) | Avg. (mg L <sup>-1</sup> ) |      | Total fluxes within 30 days (Mg) |      | Factor of difference in summer and spring fluxes |     |
|---------------------------|------------------|------------------------------------------|----------------------------|------|----------------------------------|------|--------------------------------------------------|-----|
|                           |                  |                                          | DOC                        | DIC  | DOC                              | DIC  | DOC                                              | DIC |
| Chorrillo Laguna (CL)     | Low/summer       | 0.01                                     | 7.7                        | 29.2 | 0.2                              | 0.7  | 15                                               | 4   |
|                           | High/spring      | 0.04                                     | 24.0                       | 24.9 | 2.8                              | 2.6  |                                                  |     |
| Rio Verde (RV)            | Low/summer       | 0.02                                     | 15.2                       | 35.4 | 1.0                              | 2.2  | 69                                               | 12  |
|                           | High/spring      | 0.63                                     | 39.1                       | 16.3 | 65.8                             | 26.6 |                                                  |     |
| Virgen de Montserrat (VM) | Low/summer       | 0.02                                     | 5.4                        | 11.8 | 0.4                              | 0.8  | 71                                               | 9   |
|                           | High/spring      | 0.52                                     | 19.9                       | 5.5  | 27.5                             | 7.4  |                                                  |     |
| Rio Bosquecillo (RB)      | Low/summer       | 0.01                                     | 5.8                        | 21.6 | 0.1                              | 0.4  | 136                                              | 2   |
|                           | High/spring      | 0.16                                     | 31.2                       | 2.3  | 13.5                             | 0.8  |                                                  |     |
| Rio Perez (RP)            | Low/summer       | 15.66                                    | 4.7                        | 3.8  | 150.1                            | 72.3 | 2                                                | 1.3 |
|                           | High/spring      | 12.27                                    | 10.8                       | 3.2  | 365.1                            | 94.3 |                                                  |     |
| Rio Leon (RL)             | Low/summer       | 0.14                                     | 16.7                       | 3.9  | 5.4                              | 1.4  | 10                                               | 5   |
|                           | High/spring      | 1.02                                     | 19.4                       | 3.1  | 54.9                             | 6.4  |                                                  |     |
| Rio Nutria (RN)           | Low/summer       | 0.29                                     | 21.3                       | 1.3  | 14.9                             | 0.8  | 2                                                | 3   |
|                           | High/spring      | 0.52                                     | 18.0                       | 2.2  | 25.9                             | 2.3  |                                                  |     |
| Rio Turba (RT)            | Low/summer       | 0.09                                     | 18.3                       | 0.3  | 4.1                              | 0.07 | 0.8                                              | 0.9 |
|                           | High/spring      | 0.07                                     | 18.7                       | 0.5  | 3.2                              | 0.06 |                                                  |     |

Low discharge corresponds to measures done in late summer 2010 and includes storm events. High discharge corresponds to measures done in early spring 2011 including snow melt. “Avg. Q”, “Avg. DOC”, and “Avg. DIC” correspond to average discharge, DOC or DIC concentrations during the measuring period

the middle of the transect (the steep and forested VM and RB catchments) indicates intermediate behaviour, with a precipitation maximum at the end of winter and storm events in April.

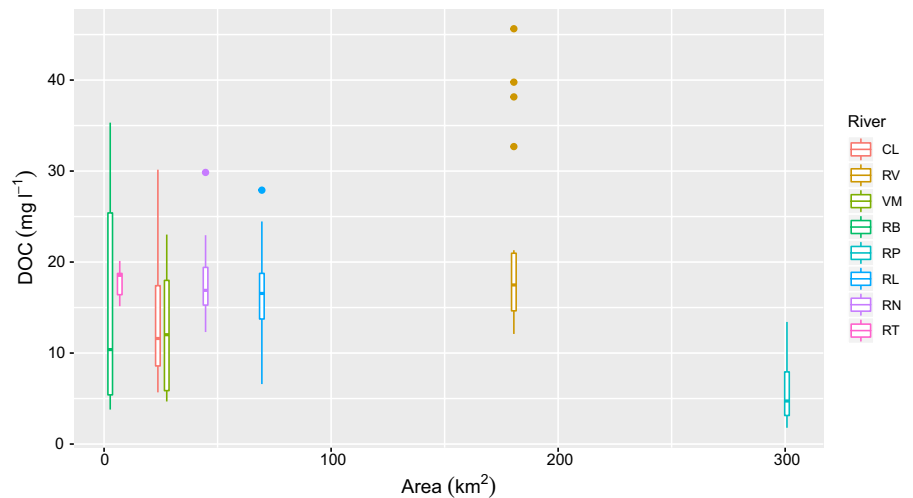
The small size of the catchment area of RB caused relatively low absolute annual discharge, as expected from its position in our east–west transect. However, the size-normalized annual median discharge of RB (i.e., relative discharge) was substantially higher than that for all eastern rivers. Moreover, the steep slopes of the small RB catchment caused a rapid increase in discharge when the intensity of precipitation changed, as indicated by the frequent outliers during periods of low (April) and high (August) discharge (Figs. 2, SM1).

The effect of catchment size on DOC concentrations and exports

DOC concentrations for most of the rivers were measured at the river mouth close to Seno Skyring (Fig. 1). These samples best indicate the effect of

the catchment size in terms of DOC export to the marine environment. However, processing of DOC within stream could at least partly remove, degrade or add DOC, affecting the DOC fluxes from the catchments alone (Moody et al. 2013). A study performed in a catchment in northern England (UK) estimates an annual DOC loss between 48 and 69%, strongly coupled to solar radiation patterns (Moody et al. 2013). According to this study, the majority of DOC loss occurs within days (Moody et al. 2013) due to the rapid degradation of fresh organic matter. These results might imply that catchment size could control DOC concentrations, where smaller catchments will exhibit higher DOC stream water concentrations than larger catchments due to relatively lower catchment residence time and DOC degradation. We compared the DOC concentrations of the individual rivers here as a function of catchment size (Fig. 8) with the aim of evaluating to what extent catchment size is a major factor for DOC concentration and flux patterns in our rivers. Our results did not show any clear indication

**Fig. 8** DOC concentrations for the eight study rivers plotted according to the catchment area. In box plots: horizontal lines in the rectangle indicates the median, top and bottom of the rectangle indicate the third and first quartile respectively; whiskers show maximum and minimum; and individual points are outliers

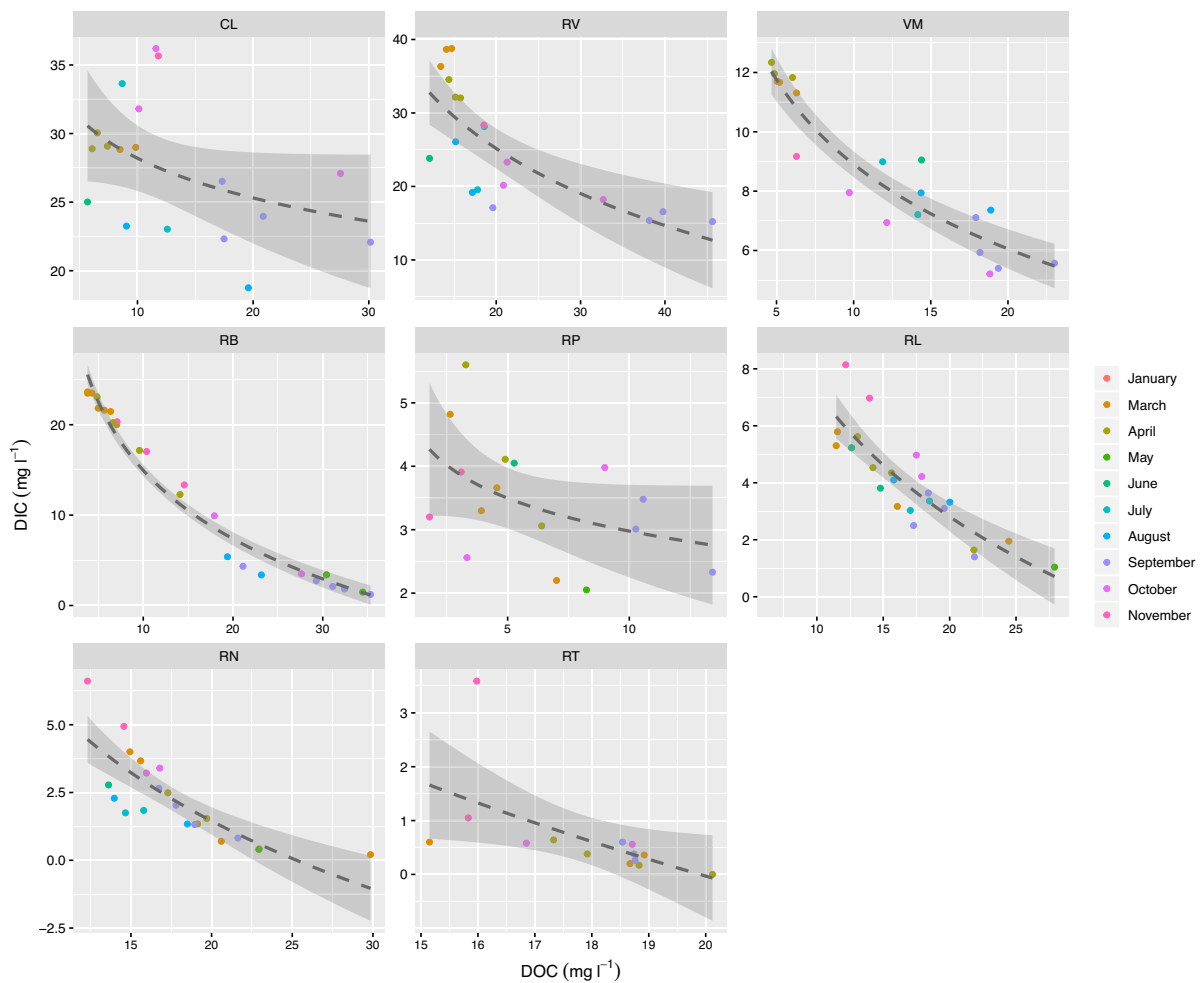


suggesting that DOC concentrations in our rivers were mainly determined by catchment size (Fig. 8). In contrast, mean DOC concentrations were similar for rivers with large differences in catchment size (7 to 180 km<sup>2</sup>, RT, RN, RL and RV). The lack of such a relationship suggests that factors other than catchment size affect the DOC concentrations in rivers, such as land use, vegetation cover, morphology or DOC composition (degradability) (Laudon et al. 2011; Harms et al. 2016; Aguilera and Melack 2018; Soares et al. 2019). Moreover, if DIC dynamics were driven predominantly by losses of DOC attributed to OM degradation, a positive relationship between DOC and DIC concentrations should have been observed. Instead, the negative relationship between DOC and DIC concentrations in most rivers indicates that DOC degradation in the catchments and streams is of minor importance here (Fig. 9). The effect of in-stream DOC degradation leading to an increase in the proportion of DIC (or CO<sub>2</sub>) was suggested to be negligible for catchments in cold (boreal) areas with a low residence time of water in the system (Wallin et al. 2010; Liu et al. 2022). DOC in our rivers is predominantly coloured and refractory, typical for such boreal landscapes, and thus less prone for rapid photochemical or microbial degradation, so that within river losses of DOC had no major influence here. We found that in terms of unit area, small catchments (e.g., RB and RT) and especially mountainous catchments (RB) are very efficient DOC exporters (Mattsson et al. 2005; Ågren et al. 2007; Hilton et al. 2011). This is

in line with Liu et al. (2022), who found that small river networks are DOC export-dominated systems, while very large river networks (stream order 7–9) are DOC reaction-oriented systems.

The role of catchment sensitivity in dissolved carbon release

We define catchment sensitivity here as the magnitude of the response in terms of dissolved carbon concentrations in the river related to changes in discharge. Catchment sensitivity here is defined by the slope and the  $r^2$  value of the linear regression model on the logarithmic data of DOC and DIC concentrations, which means that the extent of DOC and DIC concentration increase with increasing discharge defines sensitivity (the steeper the slope is, the higher the sensitivity). The results provided by the three regression models tested (i.e., linear ln–ln, semiln and power-law) lead to the same conclusions in terms of sensitivity (comparison of statistical models is provided in Supplementary Text-2). Based on  $r^2$ , it is possible to quantify the strength of the relationship between discharge and DOC and DIC, where a higher  $r^2$  indicates greater strength and a more consistent relationship. Similar information is provided by the ratios of DOC and DIC fluxes between low- and high-precipitation periods (Table 4). Accordingly, highly sensitive catchments, such as steep forested catchments (RB or VM), show an exponential and consistent increase in DOC release with increasing discharge (Fig. 6, high slope  $\beta$  and  $r^2 > 0.9$ ); concurrently, the DIC release



**Fig. 9** DIC concentrations versus DOC concentrations in the eight study rivers. Discontinuous lines indicate the logarithmic regression and grey shadows show the confidence interval (0.95)

shows a consistent decrease (Fig. 7 high slope  $\beta$  and  $r^2 \sim 0.9$ ). This behaviour suggests a change in the predominant flow paths and the contribution of carbon pools. During periods of high discharge and intense surface run-off, shallow soil organic carbon pools contribute the largest amount of DOC, whereas during periods of low discharge, slow water movement through mineral soil horizons mainly leach smaller DOC and larger DIC pools.

The seasonal differences found in water chemistry between periods of low- and high-flow conditions can be explained by these different flow paths. In summer, low DOC concentrations and high conductivity might indicate flow paths through mineral soil horizons where the water can slowly percolate. The

high cation (max. Ca concentration  $\sim 30 \text{ mg L}^{-1}$ ) and DIC concentrations, which are positively correlated, during low discharge might be related to the dissolution of the coquina carbonate sediments underlying the soils in those catchments (SERNAGEOMIN S 2003). In contrast, during events of high runoff in spring, high DOC concentrations and low cation concentrations indicate preferential and fast flow through organic matter-rich surface soils, which is supported by the strong negative correlation between DOC and Ca concentrations ( $r^2 = -0.85$  and  $-0.96$ , VM and RB, respectively), the strong positive relation between DOC concentrations and discharge (Fig. 6), and the negative relation between DIC and Ca concentrations and discharge (Figs. 7 and SM2). With its



steep slopes, small catchment and organic matter-rich soils, RB is a typical example of fast DOC flushing and simultaneous peaking with discharge (Butturini and Sabater 2000), confirming that hydrological functioning can provide a first-order control on stream water DOC concentrations in small homogenous catchments (Laudon et al. 2011). The release of DOC exerts a dilution effect on DIC concentrations (Cai et al. 2015), becoming the main dissolved carbon form in river water. Moreover, RB has a short length and thus short flow time, which additionally minimizes in-stream processes of DOM removal (e.g., microbial consumption and photodegradation). The maximum thresholds are  $\sim 0.1$  and  $\sim 0.2 \text{ m}^3 \text{ l}^{-1}$  in RB and RV, respectively), where a further increase in discharge does not cause a further increase in DOC concentrations (i.e., all DOC pools connected) (Fig. 6) indicates the approximate capacity of the system to mobilize DOC.

In contrast, less sensitive catchments, such as the largest river RP or rivers with catchments dominated by large peatlands in the lowlands (RT and RN), do not show a strong and consistent relation between increasing discharge and DOC concentrations, despite the dilution of DIC concentrations with increasing discharge. The peatland-draining river (RT) showed a consistent and significant increase in DOC with increasing discharge ( $r^2=0.75$ ). Due to the hydrological buffering of peatlands, the generally very high organic carbon pool and the absence of a mineral DIC pool, the difference in DOC release between high and low discharge is comparatively small here, and the relation between discharge and DIC release is weak. Although the relationship between DOC and DIC concentrations is more consistent than in the other studied catchments, the narrow range of variation in DIC concentrations limits its relevance (Fig. 9). Annual fluxes in RT indicate that even under natural conditions and without human disturbance, rivers with lowland coastal catchments hosting peatlands and forested peatlands in hyperhumid regions are a constant but less variable source of DOC to the marine system (e.g., Dillon and Molot 1997; Bishop et al. 2004; Connolly et al. 2018).

In the case of RP, the large size of the catchment and its extension to mountainous areas (maximum elevation:  $\sim 1200$  m), which are almost free of vegetation and soil, might be the main reasons for the weak relationship between DOC and discharge.

Thus, the effect of increased DOC concentrations due to surface run-off in the flat parts of this catchment might be diluted by the abundant discharge of headwater, which is poor in DOC. The weak relationship between DOC and DIC concentrations (Fig. 9) and the strong negative correlation between discharge and DIC concentrations (Fig. 7) suggest that during high surface runoff, DIC concentrations are diluted by precipitation (Cai 2003; Wallin et al. 2010), and flow paths through mineral soil or bedrock are minor, which is supported by the relatively low EC, pH, DIC and calcium concentrations here.

The two catchments in the semiarid Patagonian steppe CL and RV and the RL catchment with its mixed composition of grassland, forest and peatland vegetation in the hyperhumid region (RL) show a positive but less consistent relationship (medium  $\beta$  values and  $r^2$  values between 0.66 and 0.83) between DOC (and DIC) concentrations and discharge and can be grouped here as medium-sensitive (Figs. 6 and 7). Their high maxima in DOC and DIC concentrations can be explained by their flat catchments and related soil and vegetation characteristics. In the Patagonian steppe, the meadow areas represent habitats of high fertility. Due to favourable temperatures, soil microbial activity increases during summer, favouring the production of DOC. Dry conditions, especially as a result of intense wind, limit intensive soil leaching and therefore also the export of DOC to streams during dry months. In spring, however, the meadows receive water from the steppe and adjacent hills during snowmelt. This results in intensive flushing of DOC pools accumulated during the dry period and high peak DOC concentrations ( $30$  and  $45 \text{ mg L}^{-1}$  for CL and RV, respectively). Both catchments have generally higher pH, DIC and electrical conductivity values than any other of the studied rivers. The source of Ca and DIC here is attributed to the dissolution of the underlying Quaternary and Tertiary sediments (SERNAGEOMIN S 2003), especially during low discharge periods, when rain can infiltrate deep mineral horizons and surface runoff is of minor importance (Figs. 7 and SM2, SM3). The high concentrations of Cl and  $\text{SO}_4$  (data not shown) are to a high extent attributed to the high fluxes of sea spray and evaporation in the lower parts of both catchments, both caused by the permanently high wind speed in this area (Schneider et al. 2003). Therefore, cation concentrations are up to ten times higher than those

detected in RN and RT. In both rivers, the changes in discharge do not affect conductivity (Table SM3 in supplementary material), indicating that the flow through mineral soil layers is likely of minor influence here. Sodium concentrations correlate positively with Cl concentrations ( $r^2=0.97$ ) and DOC ( $r^2=0.95$ ), which indicates that DOC, Na, and Cl are simultaneously leached from the upper soil horizons. In this context, it is not clear if and how high salt/Cl concentrations reduce dissolved organic matter solubility through coiling and precipitation effects (Riedel et al. 2012; Strehse et al. 2018).

The catchment of the medium-sensitivity river in the hyperhumid region, RL, is dominated by forest (76%), followed by peatlands and grasslands in similar proportions. We assume that the DOC discharge relationship of RL resembles that shown by Laudon et al. (2011) for a mixed vegetation catchment in Sweden, where the combination of peatland and forest soil DOC pools influences DOC fluxes and water chemistry by producing a switch in the DOC sources. During low flow conditions, stream water DOC might be dominated by DOC originating from peatland sources, while the steady and exponential increase in DOC concentrations driven by small increases in discharge indicates the change in surface run-offs, with forested areas being the major source of DOC release (similar to RB and VM). During low flow conditions, the higher DOC and lower DIC and cation concentrations in RL compared to the forest-dominated catchments (such as RB) support the dominant peatland origin of the DOC. Similar to RB and VM, there is a threshold above which an increase in discharge does not cause an additional increase in DOC concentrations. The slope of the linear regression model is, however, lower than that for the forest-dominated catchments—with no or low proportions of peatlands, underlining the hydrological buffer capacity of peatlands.

## Conclusions

Our study on discharge-controlled DOC and DIC release from eight river catchments in southern Patagonia indicates that morphology rather than catchment size or vegetation cover has a major influence on DOC release sensitivity if evaluated

on a per unit area basis. Accordingly, steep catchments hosting organic rich forest soils and peatlands are most sensitive and have the highest and fastest relative DOC release, especially during heavy rain events. In contrast, these catchments show relatively low release of DIC (<6%) due to minor water flow through the mineral soil section and short water retention times. The negative correlation between DOC and DIC in most of our catchments indicates that DIC production by mineralization of DOC is of minor importance here. Peatlands have low sensitivity to discharged controlled DOC release attributed to their high hydrological buffer capacity, which results in the almost constant release of DOC and DIC. Flat and relatively dry Patagonian steppe catchments have comparatively low sensitivity but have short-term high release of accumulated DOC if rain events follow dry periods. Regarding the expected future increase in the frequency of heavy rain events as well as the increasing occurrence of dry periods, our results imply that small and steep catchments, rather than large and flat catchments, will face a strong increase in DOC release. Due to low catchment residence times and dominant surface flow paths, DIC export to rivers appears to be less affected.

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**Data availability** All data use in this publication is provided in form of figures or tables. On request it could be sent in numerical format.

**Code availability** Not applicable.

**Declarations**

**Conflict of interest** The authors declare that there is no conflict of interest.

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