

Variability of hydro-chemical response to storm events captured using high-frequency river monitoring in subtropical catchments, southern Brazil

Variabilidade da resposta hidroquímica a eventos de precipitação utilizando monitoramento de alta frequência em bacias hidrográficas subtropicais, sul do Brasil

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ABSTRACT: High-frequency (30 min) data was used to investigate storm responses in two subtropical catchments in the Brazilian Atlantic Forest. We measured discharge, turbidity and conductivity in a 30 km² subsurface-dominated catchment (2012-2013) and in a 48 km² groundwater-dominated catchment (2014-2016). Conductivity was dominated by elements associated with geochemical weathering or atmospheric deposition, but also nutrients such as nitrate. Turbidity was a proxy for suspended sediment. Results showed similar dominant storm event patterns in both catchments. The dominant pattern for turbidity was a positive C-Q relationship with clockwise hysteresis, suggesting a nearby source, while the dominant pattern for conductivity was a negative C-Q relationships with clockwise hysteresis, suggesting storage of solutes in deep groundwater and distant sources (hillside). The negative C-Q pattern for conductivity was stronger and the hysteresis wider in the groundwater-dominated catchment. Hydroclimatic controls were also similar between both catchments, but storm event patterns in the subsurface-dominated catchment were more strongly influenced by antecedent conditions (conditions before the event) that in the groundwater dominated catchment.

Keywords: High-frequency Monitoring; Storm Events; Turbidity; Conductivity.

RESUMO: Dados de alta frequência (30 min) foram utilizados para investigar as respostas de eventos de precipitação em duas bacias hidrográficas subtropicais localizadas no Bioma Mata Atlântica. Foram utilizados dados de vazão, turbidez e condutividade em uma bacia hidrográfica dominada por processos subsuperficial de 30 km² (2012-2013) e de uma bacia hidrográfica dominada por água subterrânea de 48 km² (2014-2016). A condutividade se mostrou associada a elementos do intemperismo geoquímico ou à deposição atmosférica, e também por nutrientes, como o nitrato. Já a turbidez demonstrou ser proxy para a concentração de sedimentos em suspensão. Os resultados mostraram padrões similares de eventos de precipitação nas bacias hidrográficas. O padrão dominante de turbidez foi uma relação C-Q positiva com a histerese no sentido horário, sugerindo uma fonte próxima, enquanto o padrão dominante para a condutividade foi uma relação C-Q negativa também com histerese no sentido horário, sugerindo o armazenamento de solutos provenientes de águas subterrâneas profundas e fontes distantes (encosta). O padrão C-Q negativo para condutividade foi mais forte e a histerese mais ampla na bacia hidrográfica dominada pelas águas subterrâneas. Os controles hidroclimáticos também foram semelhantes nas duas bacias hidrográficas, mas os padrões de eventos de

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precipitação na bacia hidrográfica dominada por processos de subsuperfície foram mais fortemente influenciados pelas condições antecedentes ao evento de precipitação (condições antes do evento) do que na bacia hidrográfica dominada por água subterrânea.

Palavras-chave: Monitoramento de Alta Frequência; Eventos de Precipitação; Turbidez; Condutividade.

INTRODUCTION

Freshwater systems are affected by human activities and anthropogenic climate change in most regions of the world (Wollschläger et al., 2017). River hydrochemistry is characterized by marked time variability controlled by hydrological and biogeochemical factors (Benettin & Van Breukelen, 2017). Hydrologically active periods, particularly flood events, are important because the addition of new water sources during such events mobilizes distinctly new and different sources of nutrients from the catchment (Buda & DeWalle, 2009). Stream hydrochemical dynamics during storm events are a major topic to understand and predict the export of solutes and particulates (Blaen et al., 2016; Van Geer et al., 2016; Fovet et al., 2018; Rode et al., 2016). Storm events are responsible for a disproportionate amount of material transfer compared to base flow (Inamdar et al., 2006; Fellman et al., 2009). The high frequency of data collection during flood event is important to understand the solute dynamics and can help to identify factors influencing dynamic processes and transport (Oeurng et al., 2010). Catchment response to rainfall vary in time and space due to several factors such as soil type, catchment size and morphology, climate and hydrology (Bender et al., 2018; Bowes et al., 2015). Storm events contribute for the major part of the annual flux for several chemical elements, such as phosphorus and dissolved organic carbon (Vidon et al., 2010; Wymore et al., 2019). However, observations of event-scale hydrobiogeochemical transport of nitrate can be highly complex and can vary from one catchment to another (Oeurng et al., 2010). Most existing water quality studies in subtropical catchments focus on baseflow conditions because the weekly to monthly monitoring typically deployed is not adapted to capture storm events dynamics (e.g., Piazza et al., 2018). This is due to the ephemeral nature of storm events, which makes them difficult to monitor. During a storm event, flow and chemistry dynamics vary so quickly that they cannot be captured properly with traditional monthly or weekly monitoring (Horowitz, 2004; Ramos et al., 2015; Lloyd et al., 2016). Capturing the structure of hydrochemical behavior requires a sampling frequency that is comparable to, and possibly higher than, the typical time scale of the hydrologic response (Kirchner et al., 2004). River loads often have to be estimated from continuous discharge data but relatively infrequent sampling of sediment, solute or pollutant concentrations, but now with high-frequency sensors and in situ measurements it's possible to estimate the 'true' load estimate (Ferrant et al., 2013). Monitoring programs with high-frequency techniques are now widespread in temperate regions (Blaen et al., 2016; Ockenden et al., 2016; Rode et al., 2016; Van Geer et al., 2016; Ruhala and Zarnetske, 2017; Haddadchi & Hicks, 2020), but they are scarce in subtropical areas where funding for environmental research is still lacking (Piazza et al., 2018). These high-frequency techniques enable the measurement of physical parameters, such as turbidity (Lawler et al., 2006; Wymore et al., 2019) and conductivity (Penna et al., 2015), at sub-hourly resolutions. Conductivity and turbidity measurements can be associated to other measured catchment elements, such as sediments and nutrients. For example, streamflow conductivity normally reflects the presence of ions in flowing water (Benettin & Van Breukelen, 2017).

The typical data analysis technique to study these high-frequency monitoring data consist in describing the concentration-discharge (C-Q) relationships. Concentration-discharge (C-Q) relationships provide fundamental insight into the mobilization and export of solutes and sediment from watersheds (Chorover et al., 2017). The discharge-sediment and discharge-solute relationships usually present a cyclic form known as hysteresis (Lloyd et al., 2016). During storm events, C-Q relationships form hysteresis loops when a time lag exists between discharge and concentration dynamics (Bowes et al., 2005; Lefrançois et al., 2007; Jiang et al., 2010; Wade et al., 2012; Cerro et al., 2014; Bierozza and Heathwaite, 2015, Lloyd et al., 2016). A clockwise loop is formed by the C-Q relationship when concentration peaks before discharge. Conversely, a counterclockwise loop forms when concentration peaks after discharge. In temperate regions, such patterns have already been identified for water quality parameters, such as turbidity, nitrate, phosphorus and conductivity (e.g. Bowes et al., 2009; Carey et al., 2014; House and Warwick, 1998; Lawler et al., 2006). These loops depend on chemical and

hydrological processes of each catchment (House and Warwick, 1998; Dupas et al., 2015; 2016; Fovet et al., 2018; Jomaa et al., 2018; Vongvixay et al., 2018). In these cases, a clockwise hysteresis, have been explained by transport of readily available elements during the rising stage of the hydrograph (Gao et al., 2007; Smith and Dragovich, 2009), whereas delayed response in the hysteresis indicates a distant source leading to anticlockwise hysteresis patterns (López-Tarazón et al., 2009; Mano et al., 2009; Zhao et al., 2017). The width, magnitude, and direction of these loops also provide insight into how reservoirs of solutes and sediments are stored within the hillslope and exported to fluvial networks (Gellis, 2013; Koenig et al., 2017; Vaughan et al., 2017; Olshansky et al., 2018; Rose et al., 2018).

The development of in-situ sensors to monitor at high-temporal resolution makes feasible a detailed analysis of catchment behavior to storm (Lloyd et al., 2016; Rode et al., 2016; Bierozza et al., 2018). Sets of high-frequency data now allow statistical analyses of hydroclimatic drivers responsible for sediment and nutrient flux in temperate zones (Seeger et al., 2004; Zabaleta et al., 2007; Giménez et al., 2012; Buendia et al., 2016). However, in subtropical regions most of the monitored catchments are ungauged, leaving a gap of understanding considering these complex water quality systems (Piazza et al., 2018). Agriculture in these regions is generally located in fragile environment, either due to mountainous relief or shallow soils, with frequent runoff and subsurface flow pathways. Besides that, crop production in these regions usually do not follow agronomic recommendations regarding environmental protection (Bender et al., 2018).

This study compares high-frequency data sets from two subtropical catchments located in the Atlantic Forest Biome. The aim of this study was to interpret storm event pattern, in term of the proximity of the solute and sediment sources to the stream, in two catchments with similar land use but different hydrology: subsurface dominated or groundwater dominated. To characterize the temporal variability of storm responses we proposed an original method adapted to such data set, combining descriptors of discharge and hydro-chemical responses.

MATERIAL AND METHODS

Study sites

The study sites consisted of two research catchments in Southern Brazil both within the Atlantic Forest Biome (Figure 1). The Concordia catchment (27°10'45.68"S, 49°31'17.41"W) is a 30 km² catchment with a humid subtropical climate, characterized by hot and humid summers and mild and dry winters. Elevation ranges from 340 to 900 m a.s.l. Soil type consists of Ultisols and Cambisols in upper areas and Gleysols in bottomlands. Hydrogeological information indicates free to semi-confined aquifer of regional extension (af2) in the bottom, and semi-confined to confined aquifer of regional extension (as4) in the upper areas (Machado, 2013). Rainfall is evenly distributed throughout the year with summer being the wettest season (December–March). Concordia annual rainfall is around 2000 ± 320 mm (2010-2016). Concordia catchment is composed of 50% of agricultural land, mainly located in bottom and mid slope areas, and native forest (50%) in the uplands. The main agricultural land use types are grassland (20%), planted forest (14%), arable land (12%) and constructed area (4%) (Piazza et al., 2018). Concordia is an agricultural catchment, where farmers grow corn, oat and beans, generally using conventional tillage. A previous study using monthly sampled data from the Concordia catchment showed that El Niño-Southern Oscillation influenced both hydroclimatic and interannual anion dynamics (Piazza et al., 2018).

The Canoas catchment (27°1'16.12"S, 48°39'45.87"W) is located approximately 85 km from Concordia and is closer to the sea (4.5 km versus 90.0 km). The Canoas catchment is 48.1 km² and presents a humid subtropical climate. Elevation ranges from 20-720 m a.s.l. Soil types are composed of Ultisols, Neosols and Cambisols in upper and mid slope areas, and Gleysols and Spodosols in bottomlands. Hydrogeological information indicates free to semi-confined aquifer of regional extension (af2) in the bottom, and aquicludes and aquifers, restricted to fractured areas (na_1) in the upper areas (Machado, 2013). Like in Concordia catchment, rainfall in Canoas is evenly distributed throughout the year with summer being the wettest season. Canoas annual rainfall is 1700 ± 300 mm (2014-2016) (Figure 2). Canoas is covered mainly by native forest (66%), and the main agricultural uses are permanent pasture

(14%), irrigated rice plantations (5%) and planted forests (5%) (Figure 1). The land use in Concordia was calculated using Landsat 5 TM+ images from 2015, and Canoas catchment was calculated using Landsat 5 TM+ images from 2016.

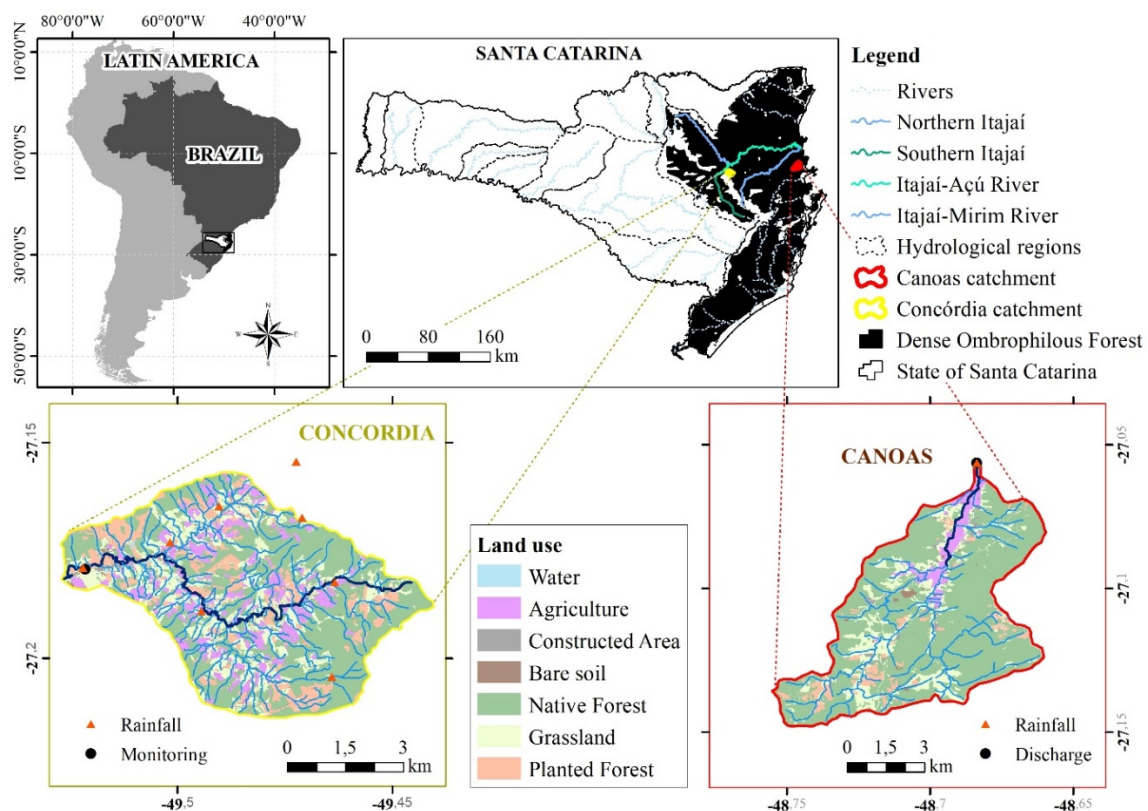


Figure 1. Localization of the Concordia and Canoas catchment, Santa Catarina, Southern Brazil.

Monitoring protocol

We used high-frequency since weekly and monthly sampling is not capable to capture these storm events dynamics in the quarter quality. Concordia high-frequency data comprises two hydrological years (2012-2013), and Canoas three years (2014-2016). We used Hydrolab DS5X probes to measure turbidity and conductivity at 30-minute resolution in both catchments. We monitored hourly rainfall with eight tipping bucket rain gauges distributed throughout the catchments. A pressure transducer Thalimedes OTT was used to record stream flow at a 30 min time step. During the monitoring period discharge measurements were performed quarterly in both catchments, Concordia catchment by Regional University of Blumenau (FURB), and Canoas catchment by EPAGRI/CIRAM, during all the monitoring period. Records (observed vs. registered) were regularly checked during monthly visits. During these two years in Concordia four periods present missing data due problems of maintenance/battery (11/01/2012 to 25/01/2012; 09/05/2012 to 29/05/2012; 28/09/2012 to 01/11/2012; and 03/04/2013 to 26/04/2012). In Canoas the period of 18/08/2016 until 21/08/2016 (turbidity) and 18/08/2016 until 23/09/2019 (conductivity) was discarded due to inconsistent values. In parallel to the high-frequency monitoring, we analyzed several ions (Table 1) at a monthly time step in both catchments. The analysis of this low frequency dataset for Concordia catchment was previously published in Piazza et al. (2018). According to the ion composition (Table 1), for Concordia catchment, Magnesium (Mg^{2+}), Calcium (Ca) and Cl^- accounted for 60% of the conductivity. In Canoas, catchment Chloride (Cl^-), Sodium (Na) and Calcium (Ca) represented 81% of the conductivity. Nitrate represented 8% and 4% of conductivity in Concordia and Canoas, respectively. In Canoas, also 31 samples were measured for suspended sediment mass; the data confirmed a very high correlation with turbidity ($r = 0,96$).

Table 1. Ion Composition between conductivity and chemical elements monitored in the Concordia (2012-2013) and Canoas (2014-2016) catchment, Southern Brazil.

	Concordia			Canoas		
	Median (mg/l)	mS/m	%	Median (mg/l)	mS/m	%
Cl ⁻	2,68	0,577	18,3	8,14	1,752	44,4
NO ₃ ⁻	2,18	0,251	8,0	1,38	0,159	4,0
PO ₄ ³⁻	0,05	0,005	0,2	0,01	0,001	0,0
SO ₄ ²⁻	2,16	0,180	5,7	1,31	0,109	2,8
Na ⁺	2,2	0,479	15,2	3,91	0,852	21,6
NH ₄ ⁺	0,07	0,029	0,9	0,04	0,016	0,4
K ⁺	1,63	0,306	9,7	0,94	0,177	4,5
Mg ²⁺	3,18	0,693	22,0	1,35	0,294	7,5
Ca ²⁺	4,27	0,634	20,1	3,92	0,582	14,8
		3,154	100,0		3,942	100,0

Data analysis

Because we dedicated a previous study (Piazza et al., 2018) to seasonal to interannual dynamics during baseflow conditions in Concordia catchment, the present paper focuses on storm events. We isolated storm events with the storm detection algorithm developed by Dupas et al. (2016). The start of an event was defined as the first moment with a 5% increase in discharge in 1h and the end time was defined as the first moment with a decrease in discharge lower than <1% in 1 h. We only kept storm events with a discharge increase > 2 m³ s⁻¹ and a discharge decrease after discharge peak > 50%. Then, we computed variables describing flow conditions before and during the events, and C-Q relationships (Table 2) using R (R Development Core Team, 2008).

Table 2. Calculated variables using high-frequency data from Concordia and Canoas catchments, Brazil. X in the first column can represent discharge (Q), turbidity (Turb) or conductivity (SpC).

Variable for X	Variables (Q / Turb / SpC)	Description
X 0_1h	Q, Turb, SpC	Mean X during 1h before storm event
X_24h	Q	Mean X during 24h before storm event
X_7d	Q	Mean X during 7d before storm event
X_30d	Q	Mean X during 30d before storm event
X max	Q, Turb, SpC	Maximum X during storm event
d X	Q, Turb, SpC	X max - X 0_1h
d X max1h	Q	Maximum variation in X in 1h
Trise X	Q	Duration of rising X
Vrise X	Q	Speed of X rise
Wrise X	Q	Cumulative X during rising limb
Hnew X	Turb, SpC	New hysteresis index (normalized, difference)

The loop direction and width were determined with the use of a hysteresis index (HI). Numerous indices have been proposed to describe the shape and direction of hysteresis loops (e.g. Butturini et al., 2008; Lawler et al., 2006). However, the “new” index by Lloyd et al. (2015) was preferred in this study because i) this method includes a normalization phase that allow comparing multiple storm events with different initial discharge and ii) this method relies on a difference rather than a ratio in previous HIs, allowing comparison of storms with different discharge amplitudes. HInew is calculated using storms which have first been normalized using the following equations:

$$\text{Normalised } Q_i = \frac{Q_i - Q_{\min}}{Q_{\max} - Q_{\min}}$$

$$\text{Normalised } C_i = \frac{C_i - C_{\min}}{C_{\max} - C_{\min}}$$

where: Q_i/C_i is the discharge/turbidity or conductivity at timestep i , Q_{min}/C_{min} is the minimum storm parameter value and Q_{max}/C_{max} is the maximum storm parameter value. The new index is calculated as follows:

$$HI_{Q_i} = C_{RL_{Q_i}} - C_{FL_{Q_i}}$$

where: HI_{Q_i} is the index at 50% percentile of discharge (Q), $C_{RL_{Q_i}}$ is the chemical value on the rising limb at percentile i of Q and $C_{FL_{Q_i}}$ is the chemical value at the equivalent point in discharge on the falling limb.

We described storm events dynamics for both catchments for turbidity and conductivity, in terms of 1) variation in concentration, positive or negative, during each event and 2) hysteresis direction, clockwise and counterclockwise. We described storm event hydro-chemical dynamics with four variables: variation of turbidity ($dTurb$), variation of conductivity ($dSpC$), hysteresis turbidity ($HI_{newTurb}$) and hysteresis conductivity (HI_{newSpC}), and analyzed the correlation of these variables with the variables presented in Table 1, describing antecedent and storm even conditions. Correlations were calculated by Pearson, computed in R using the 'corrplot' package.

RESULTS AND DISCUSSION

Hydro-climatic conditions

Total annual rainfall present similar behavior in both study catchments. However, discharge present higher monthly values for Canoas catchment (Figure 2), which is higher in surface area. During the analyzed period of each study site, the highest volumes of precipitation were in summer (January–March) while isolated events were also identified in September and October. Evapotranspiration (ETP) was higher during summer (January–March), and Spring (October - December) (Piazza et al., 2018).

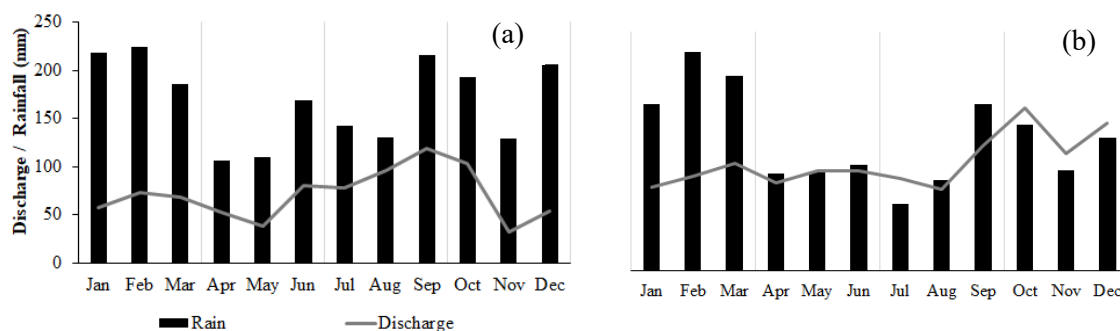


Figure 2. Monthly rainfall (mm) and discharge (mm) for (a) Concordia (2010-2016) and (b) Canoas (2014-2016) catchment, Santa Catarina, Southern Brazil.

The term 'storm' is used here to refer to a complete hydrological event with rising and recession limbs (Oeurng et al., 2010). The distribution of storm events is not seasonal with events happening all year (Figure 3). In total, the storm detection algorithm identified 56 events for Concordia and 84 for Canoas, i.e. 28 storm events per year each in catchment. Total discharge and annual distribution were different in the catchments: discharge in Canoas was higher than in Concordia (note however that the study periods were different) and the distribution of discharge was more skewed in Concordia, indicating a flashier hydrology in the later (Figure 4). Mean turbidity ($Turb$) in Concordia was slightly higher (76.5 NTU) than Canoas (74.6 NTU) but they did not show statistical difference, using ANOVA test ($\alpha=0,05$). Mean conductivity (SpC) in Canoas catchment presented higher concentrations (93 $\mu S/cm$) compared to Concordia (59 $\mu S/cm$) showing statistical difference, using ANOVA test ($\alpha=0,05$).

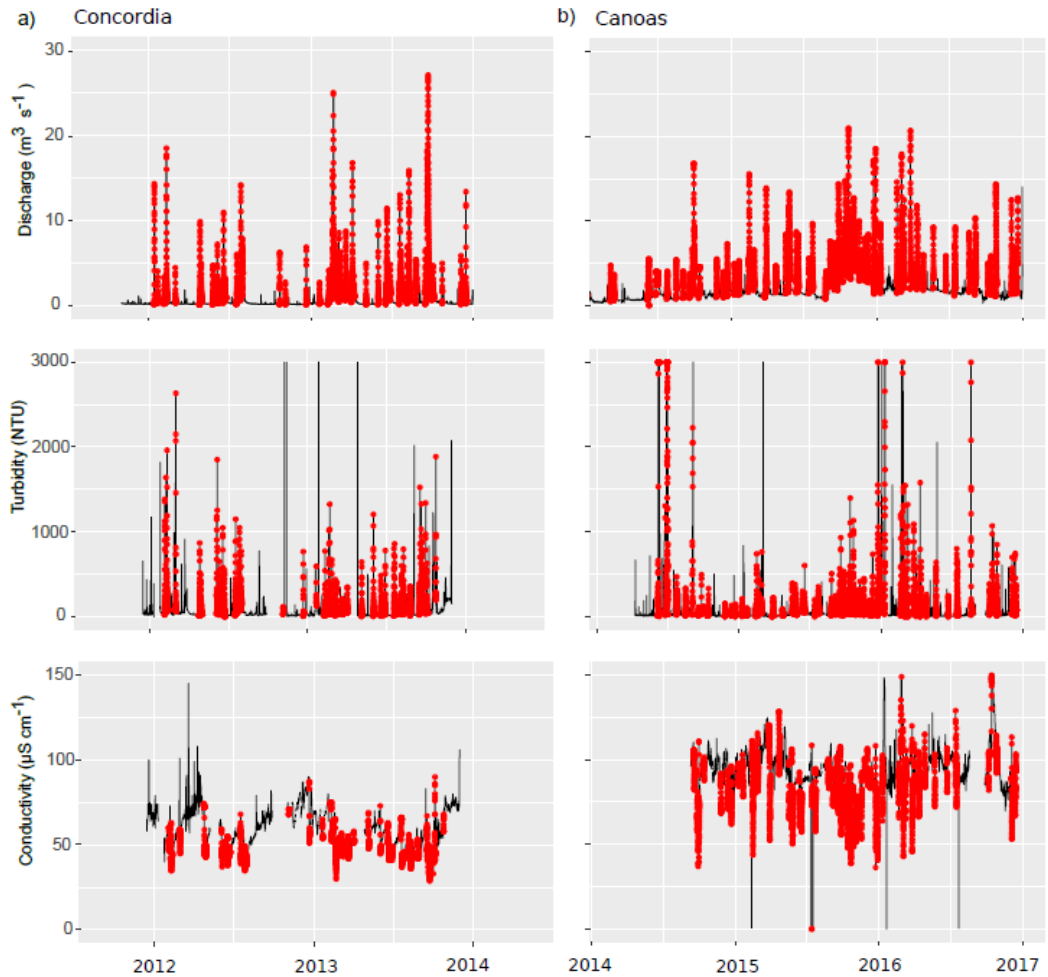


Figure 3. Temporal variations of discharge, turbidity, conductivity in (a) Concordia (2012- 2013) and (b) Canoas (2014-2016), Santa Catarina, Southern Brazil. The storm events are highlighted in red.

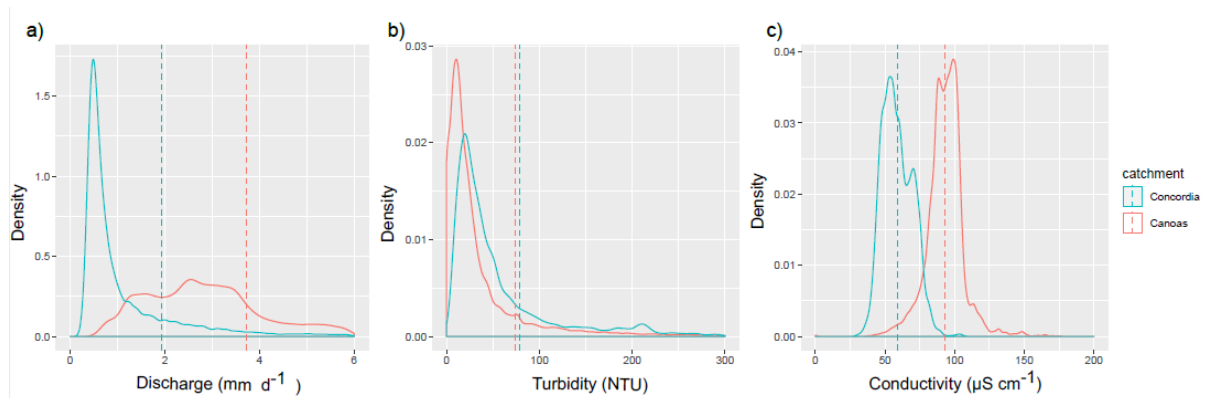


Figure 4. Statistical distribution of (a) discharge (mm/d-1), (b) Turbidity (NTU), and conductivity (SpC - mS cm-1) for Concordia (2012- 2013) and Canoas (2014-2016) catchment, Southern Brazil. Vertical lines represent medians.

Storm event dynamics

The dominant pattern for turbidity (Figure 5) was an increasing turbidity at the beginning of the storm event, as turbidity variation was always positive (> 0) (100% for both catchments), and with clockwise hysteresis ($HI > 0$) (98% of the time for Concordia and 95% for Canoas) (Figure 6). According to Ferrant et al. (2013), during these periods, a combination of rainfall events generating subsurface flows should transfer a part of the soil into the stream. Clockwise hysteresis patterns are produced when a particular element has a higher concentration during the rising stage of a flood hydrograph, compared

with the falling stage (Oeurng et al., 2010). This means that the nutrient is rapidly transported to the sampling point during the storm event, implying that the nutrient load is coming from either within the river channel itself, or from a catchment source that is rapidly transported to the river (Bowes et al., 2009). Sediment sources generally are close to the stream due to agriculture and were mobilized fastly into it. The underlying transport mechanisms may be the remobilisation of streambed sediment or bank erosion. The clockwise pattern suggests proximal sources with rapid exhaustion (Sherriff et al., 2016; Wymore et al., 2019). This accretion pattern has been previously observed elsewhere for turbidity (Williams, 1989; Asselman, 1999; Lawler et al., 2006).

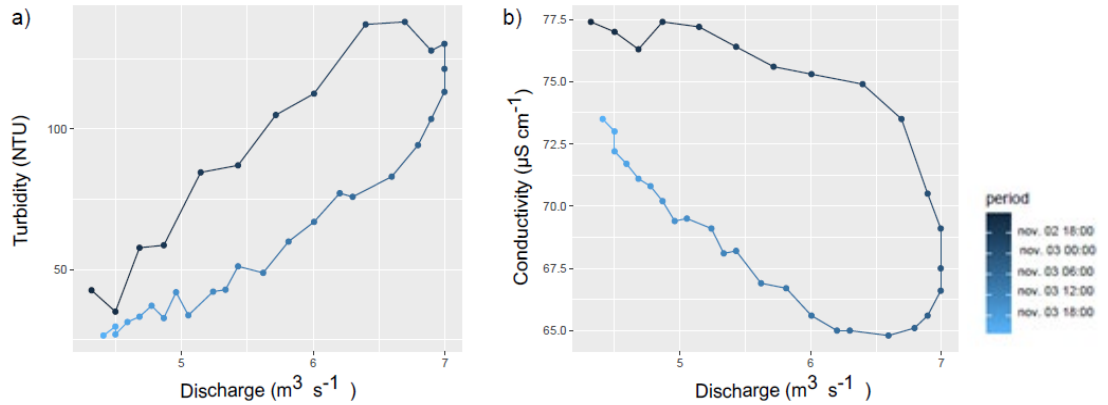


Figure 5. Hysteresis pattern for a typical storm event on 03-11-2015 in Concordia catchment for (a) turbidity, and (b) conductivity.

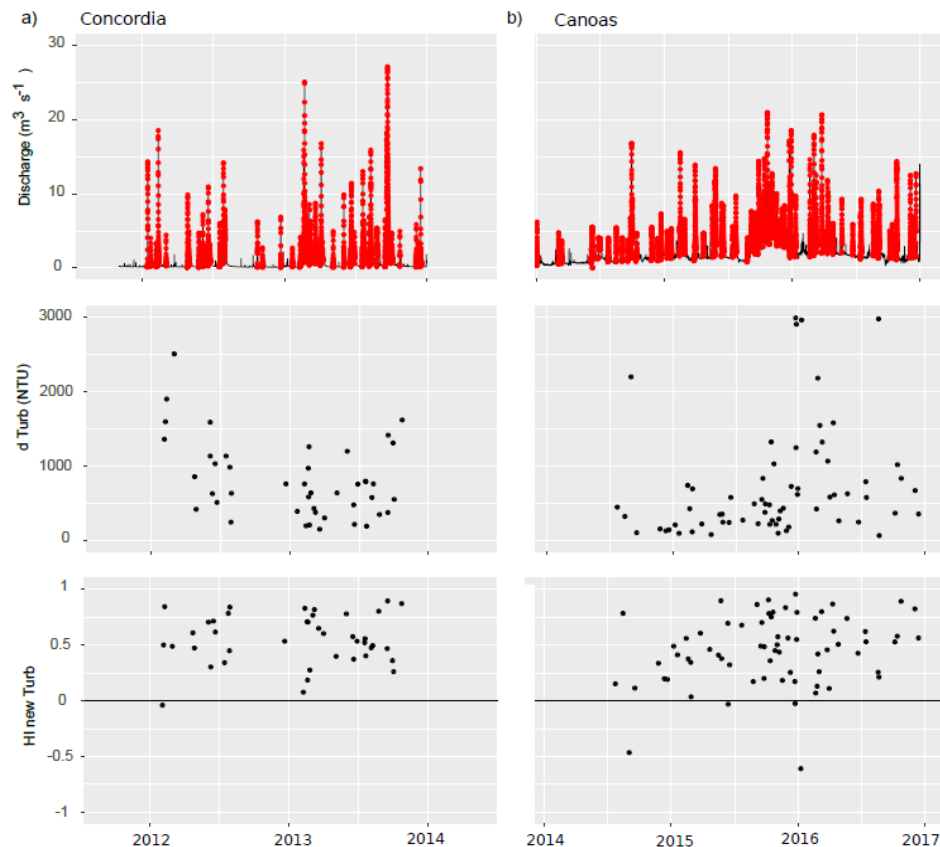


Figure 6. Variation of discharge ($\text{m}^3 \text{s}^{-1}$), $d\text{Turb}$ (NTU), and $\text{HI}_{\text{new Turb}}$ on (a) Concordia (2012-2013) and (b) Canoas (2014-2016) catchment, Southern Brazil.

On the other hand, the dominant pattern for conductivity (Figure 5) was a dilution at the beginning of the storm event, as conductivity variations were most of the time negative (< 0) (96% of the time for Concordia and 90% for Canoas), and with clockwise hysteresis ($\text{HI} > 0$) (80% of the time

for Concordia and 91% for Canoas) (Figure 7). The dilution of conductivity and the hysteresis loop were more pronounced in the Canoas catchment compared to Concordia (Figure 7).

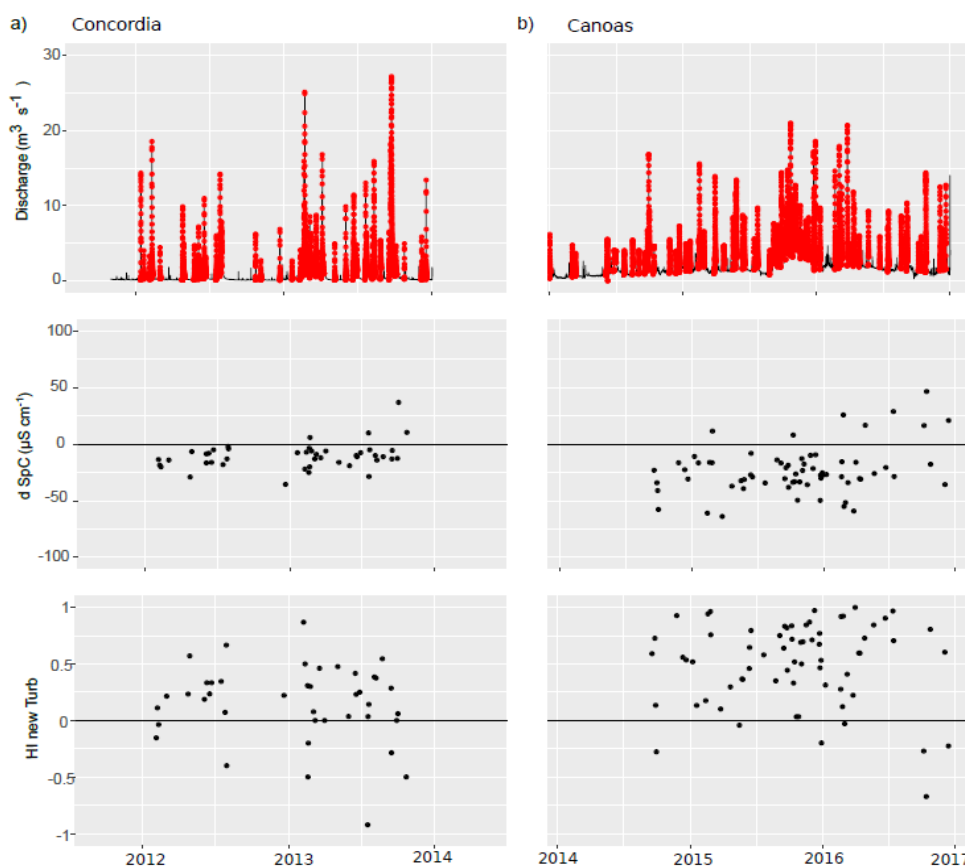


Figure 7. Variation of discharge ($\text{m}^3 \text{s}^{-1}$), d SpC ($\mu\text{S/cm}$), and HI new SpC on (a) Concordia (2012-2013) and (b) Canoas (2014-2016) catchment, Southern Brazil.

During storm events, conductivity was slowly diluted by shallow flow paths with a low concentration of solutes (Figure 5). This explains the larger decrease in conductivity and larger loops in Canoas compared to Concordia (Figure 7). The Canoas catchment is closer to the sea with higher influence of the seaspray indicating a higher concentration of ions (and also conductivity) during baseflow. However, these higher concentrations are rapidly diluted during storm events. One possible contribution, near Canoas outlet, is the occurrence of rice plantations producing overland and wetland flow responsible for this dynamic.

In conclusion, both catchments exhibited similar storm event response patterns, which suggests that they are driven by the same dominant processes (general patterns). The dominant pattern for turbidity was a positive C-Q relationship with clockwise hysteresis, while the dominant pattern for conductivity was a negative C-Q relationships with clockwise hysteresis.

Hydroclimatic controls storm hydro-chemical dynamics

The correlation table (Figure 8) reveals the main drivers of the storm event dynamics. Both catchments presented similar variations of turbidity and hysteresis loop shape at storm event level. The variation of turbidity was positively correlated with the maximum variation in discharge in one hour ($dQ_{\text{max}1\text{h}}$) and speed of discharge rise ($V_{\text{rise}Q}$) (Figure 8). Wider hysteresis on conductivity than on turbidity indicate a near source, which in our case could be the losses from agricultural soils during large storm events. The correlation is different for conductivity, as antecedent flow conditions (conditions before the event) seems to have a larger influence in Concordia than in Canoas, as positive correlation with mean discharge of 30 days before storm event ($Q_{30\text{d}}$) was found. This hypothesis was also corroborated with $HI_{\text{new}SpC}$ which demonstrated that in Concordia previous flow conditions have stronger effect (negative), such as $Q_{24\text{h}}$, $Q_{1\text{h}}$ and $TriseQ$, than in Canoas.



Figure 8. Correlation table for (a) Concordia (2012- 2013) and (b) Canoas (2014-2016) catchment, Santa Catarina, Southern Brazil.

Conductivity responds differently to antecedent conditions (conditions before the event) between both catchments. The suggestion of a larger storage of solutes in Canoas groundwater is associated with its downstream localization in the river network, close to the sea, which led to less variability in the solute export, whereas in Concordia, the amount of solute is smaller and the storage of elements highly varies from one event to another, due to production/exhaustion mechanisms. In particular, groundwater fluctuation in the riparian zone near the catchment outlet and in a relatively shallower zone may be critical factors contributing to stream water solutes (Ohte et al., 2003). Various studies have reported that nutrients are flushed out of the landscape during hydrologically active periods particularly during flood events, while they are retained in drier periods (Creed et al., 1996; Sickman et al., 2003; Burns, 2005; Rozemeijer and Broers, 2007). According to Cerro et al. (2014) and Penna et al. (2015), depending on regions, the composition of the shallow water, also responsible for variations in conductivity, may be enriched with different solutes. The clockwise direction involves dilution during the falling limb related to the contribution of riparian denitrified water (Oehler et al., 2007).

Long-term nutrient concentration datasets are a key resource for environmental scientists, catchment managers and policy-makers because they permit analyses of nutrient trends, loads, nutrient behavior and the effectiveness of past nutrient migration and supporting data for future management decisions regarding issues of eutrophication and nutrient control (Burt, 2003). Considering Alewell et al. (2004) which have assessed how much of the heterogeneity of solution concentrations is lost because of temporal integration of measurements, using high-resolution measurements (daily interval) of ion concentrations in runoff and soil solution, they have concluded that high-resolution measurements are considered to be too expensive compared with the gain of information. However, the authors explain that these conclusions apply neither to agriculturally used systems nor to extreme hydrological conditions. As suggestion we encourage next experiments to analyze conductivity in different river compartments: ie. groundwater, runoff, rainfall water. Such measurements would give important information about the water origins at the river basin's outlet for hydrograph separation (e.g. Matsubayashi et al., (1993), Pellerin et al. (2008), Longobardi et al. (2018), Cano-Paoli et al. (2019)).

CONCLUSIONS

This study examines the variations in water quality parameters during storm events in two subtropical catchments. This storm event analysis showed that despite the different characteristics, such as soil, vegetation, proximity to the sea, catchments present the same hysteresis behavior for

turbidity which is controlled by the same driver on the two catchments, i.e. erosion close to the stream mainly due to agricultural lands. For conductivity a slightly difference was found on the two catchments. Conductivity on Concordia is more influenced by ancient conditions (conditions before the event), due to a smaller storage of ions in that catchment compared to Canoas. Antecedent conditions and storm characteristics control storm dynamics in a similar way in both catchments, but the strength of these controls differ between Canoas and Concordia. The use of high temporal resolution hydrological data has allowed us a detailed analysis of storm events in subtropical to streams, providing a comparison of storms within and between catchments.

One limitation of the present study is the similarity of the both studied catchments considering the hydrogeological system in which they are. Other monitors on different catchments (subtypes of the Atlantic Forest) could provide different responses of processes which were not so explicit in this manuscript, since both catchments were the only available systems with high-frequency data in proximal years.

Another consideration for future analysis, since conductivity is not an expensive parameter, is to add this measurement to every monitoring stations dealing with soil erosion. With these suggestions it will be possible to help answering management issues of land erosion related to conductivity and consequently with sediment transfer dynamics in a sub-tropical and agricultural environment, providing fundamental data for further analysis, such as modelling.

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