

Investigating the relationships between chemical element concentrations and discharge to improve our understanding of their transport patterns in rural catchments under subtropical climate conditions

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and discharge to improve our understanding of their transport patterns in
rural catchments under subtropical climate conditions
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19

20 Abstract - Solute and particulate elemental concentrations (C) exhibit different 21 responses to changes in discharge (Q), and those relationships are not well 22 understood in subtropical agricultural environments. The objective is to describe 23 the transport processes of different chemical elements during a set of 24 contrasted rainfall events (2011-2015) that occurred in a small rural catchment 25 under subtropical climate. The study was carried out in the Lajeado Ferreira 26 Creek catchment (1.23 km²), southern Brazil. To this end, the concentrations in dissolved organic carbon (DOC), Cl, NO₃, SO₄, ten chemical elements (in 27 28 either dissolved or particulate forms) and suspended sediment concentrations

29 (SSC) were determined. Metric indices were then calculated to characterize their transport patterns: (i) the best fit slope between log-C and log-Q (β), (ii) the 30 31 coefficient of variation of C and Q, (iii) shape of the hysteresis loop and 32 hysteresis index, and (iv) the flushing index. All particulate elements along with the dissolved inorganic phosphorus (PO₄⁻³) were shown to be controlled by the 33 sediment dynamics. Geogenic elements (Fe²⁺, Zn²⁺, Cu²⁺, Mn²⁺, Si⁴⁺) showed a 34 35 dilution effect with increasing Q values, likely because they were mainly 36 transported with subsurface and base flow. Dissolved elements that are mainly supplied with fertilizers (Na⁺ and Cl⁻) as well as DOC showed a dilution effect, 37 38 although they were mainly transported by surface runoff. Finally, a chemostatic behavior was found for those chemical elements (Mg²⁺, K⁺, Ca²⁺, NO₃⁻ and 39 SO₄²⁻) that are supplied by more than one flow pathways. The results 40 41 demonstrate that under subtropical climate conditions, the transport of essential nutrients including PO₄⁻³ and metals (in particulate form), are mainly transported 42 43 with surface runoff. Accordingly, runoff control on cultivated hillslopes should be 44 improved to reduce the potential contaminant supply to the river and to reduce the potentially deleterious impacts that they may cause in downstream regions. 45

46

47 Keywords: rainfall events; export regimes; solutes; metric indexes; water
48 quality

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50

51 1. INTRODUCTION

52 The intensification of agricultural activities and the limited adoption of 53 soil and water conservation practices have increased the formation of surface 54 runoff and accelerated soil erosion (Deuschle et al., 2019; Londero et al., 2018),

sediment, nutrient and metal transport in river systems draining agricultural land 55 around the world (Basu et al., 2010; Minella et al., 2018; Williams et al., 2018). 56 Chemical elements supplied in excess to the streams may originate from 57 58 anthropogenic activities, including agriculture through the supply of fertilizers 59 and agrochemicals (Thomas et al., 2016), or from natural sources, as the result of rock weathering and leaching (Verheven et al., 2015). The relationships 60 61 observed between the chemical element concentrations (C) and water 62 discharge (Q) result from the combined integration of biogeochemical 63 processes, the contribution of the sources, flow pathways, and factors such as lithology, soil type and climate (Godsey et al., 2009; Knapp et al., 2020; 64 65 Rumsey et al., 2017; Verheyen et al., 2015; Von Freyberg et al., 2017). Quantifying these relationships may contribute to improve our understanding of 66 67 the transport of solutes and particulate chemical substances from upper 68 catchment parts to the outlet.

69 The source of each element can be identified by reconstructing the 70 hysteresis phenomenon based on the C - Q relationship (Lloyd et al., 2016; 71 Wymore et al., 2019). Hysteresis analyses have been widely used and 72 progressively improved during the last several decades and they provide a 73 powerful technique for identifying the sources of both particle-bound (Duvert et 74 al., 2010; Lawler et al., 2006; Wymore et al., 2019) and dissolved substances 75 (Lloyd et al., 2016; Williams et al., 2018). Hysteresis occurs when 76 concentrations of an element, observed in either dissolved or particulate form, 77 during the rising stage of the hydrograph differ from those concentrations 78 recorded at the same discharge rate during the falling stage. The hysteresis can 79 be observed by the formation of a loop when plotting C vs Q.

80 There are three main potential interpretations of a given hysteresis loop 81 (Lloyd et al., 2016). Clockwise hysteresis suggests the rapid mobilization of the 82 chemical element of interest and the proximity of its source to the catchment 83 outlet. This situation occurs when higher concentrations are observed during 84 the event rising stage. However, when the loop is counterclockwise (i.e. when 85 the concentration of an element is lower in the rising limb while increasing in the 86 falling limb), the source of the chemical elements is expected to be located far 87 from the catchment outlet. Furthermore, the eight-type hysteresis loop can be a 88 sequence of clockwise and counterclockwise patterns. In addition, Lawler et al. 89 (2006) proposed the hysteresis index (HI) which varies according to the 90 magnitude of the rainfall event itself and, consequently, to the hydrological 91 dynamics of the catchment.

92 Recently, metric indices have been used to evaluate these C - Q 93 relationships, including (i) the best fit slope (β) for the log (C) - log (Q) linear 94 regression (Godsey et al., 2009); (ii) the ratio of the concentration and water 95 discharge coefficients of variation (CV_C/CV_Q) (Thompson et al., 2011); (iii) and a 96 combination of both indicators (Musolff et al., 2015). The combination of both 97 metric indices (β and CV_C/CV_Q) results in an unique structure for the 98 interpretation of transport patterns (Musolff et al., 2015): they can be (i) 99 chemostatic (no change in element concentration with the increase or decrease 100 in Q), (ii) they can show a chemodynamic dilution (as Q increases, the 101 concentration of the chemical element is reduced), (iii) or display a 102 chemodynamic enrichment (increase in the concentration of chemical elements 103 with increasing Q). Besides these types of behavior, the flushing index (FI), which ranges between -1 and 1, guantifies the changes in concentrations 104

105 during a rainfall event (Rose et al., 2018; Vaughan et al., 2019). Negative FI 106 values indicate that concentrations decrease during the hydrograph's rising 107 limb. In contrast, positive FI values indicate increased concentrations during the 108 hydrograph's rising limb. The interpretation of these indices may reveal the 109 different transport patterns of the chemical elements that may be measured 110 during the monitoring of rainfall events.

111 From this new approach, Rose et al. (2018) distinguished the following transport patterns: dilution for geogenic/exogenous elements (Ca²⁺, Mg²⁺, Si⁴⁺, 112 113 Cl⁻, NO₃); constant pattern for biologically associated solutes (carbon and dissolved nitrogen, NH_4^+ , K^+ , PO_4^{3-}); and enrichment for particulate substances 114 115 (suspended solids and total) in a dataset covering 11 years collected in 116 Pennsylvania (USA). Through the CV_C/CV_Q ratio and based on a set of seven-117 year rainfall events monitored in southern Brazil, Piazza et al. (2018) showed 118 that the export dynamics of solutes were similar in agricultural and in native 119 forest catchments. In South Florida, a combined analysis between the CV_C/CV_Q 120 and β showed that total nitrogen (TN) presented a chemostatic behavior while 121 total phosphorus (TP) was chemodynamic; this was due to a combination of 122 fertilizer doses, low P retention in the soil and high storms (Wan et al., 2017).

123 In subtropical and tropical climate conditions, the relationship between C 124 and Q is not well known at the event-scale. In these environments the annual 125 average rainfall volume is high as well as the kinetic energy (Ramon et al., 126 2017), which can impact the C - Q relations during rainfall events. However, 127 there is little information on the event scale for these climates. Gwenzi et al. 128 (2017) reports the scarcity of information on the scale of hydrological (Q) and 129 biogeochemistry events for tropical climate, more precisely in Africa. In Brazil,

130 water quality monitoring programs generally collect samples only four times per 131 year following a routine schedule, due to limited human and financial resources 132 applied in this program, where the measurements do not usually occur during 133 events. Few research efforts sought to understand the influence of climate and 134 land use conditions on the dynamics of solute transport under these 135 environmental conditions (Piazza et al., 2018). Agriculture is the main economic 136 activity in the Southern region of Brazil (CONAB, 2019), resulting in a high 137 pressure on natural resources, especially soil and water. Consequently, the 138 environmental impact of this activity must be a constant concern, where the 139 limited adoption of conservationist agriculture associated with the erosive 140 potential of the rains in the region, increase the degree of soil and water 141 degradation (Didoné et al., 2015; Merten et al., 2015). Therefore, it is important 142 to know the hydrological and biogeochemical behavior of rural catchments in a 143 subtropical climate like in southern Brazil, where there is no prior knowledge on 144 the subject.

145 In this study, we aim to investigate the transport processes of different 146 chemical elements during a set of contrasted rainfall events through the 147 analysis of their C - Q relationships. For this purpose, a program to monitor the 148 transport of chemical elements in a small rural catchment representative of 149 those environments found on the Southern Plateau of Brazil and in neighboring 150 regions, under subtropical climate conditions, was established in the period 151 between 2011 and 2015.

152

153 2. MATERIALS AND METHODS

154 2.1 Study area

155 The experimental catchment of the Lajeado Ferreira Creek – Arvorezinha 156 (1.23 km²), is located on the border of the Brazilian southern plateau (Figure 1). 157 This is a typical headwater catchment of the Jacuí River, one of the main 158 tributaries of the Guaíba lake, which supplies drinking water to more than 4 159 million people (Cargnin et al., 2013). Its altitude ranges from 580 to 730 m 160 (Figure 1). The upper third of the catchment has an undulating plateau relief 161 with slopes up to 7%. The middle and lower thirds of the catchment have a 162 much steeper topography with slope gradients often exceeding 15%.

The climate is classified as Cfb (subtropical super-humid with no dry season and warm summer) according to Köppen (Alvares et al., 2013). The average annual rainfall is ca. 1,938 mm (15 years, 2002 - 2016) and erosivity index (EI_{30}) is 9,344 MJ mm ha⁻¹ yr⁻¹ (Ramon, 2017). Rainfall is well distributed over the year, although a wetter season with more rainfall events of high intensity can be identified during the spring season with the frequent occurrence of surface runoff.

170 The soil types in the catchment are Acrisols (57%), Cambisols (10%) and 171 Leptosols (33%). The spatial and temporal variability of land use and soil 172 management was determined using a combination of satellite images and field 173 surveys using a handheld Global Positioning System device. Land use and soil 174 management in 2011 included native forest (15% of the total catchment surface 175 area), reforested zones (23.2%), pasture (6.5%), cropland (soybean + tobacco) 176 under minimum tillage (26%), cropland under conventional tillage (13%), fallow 177 (13%) and other minor uses (3.3%). By 2015, land use and soil management 178 had significantly changed, mainly through an increase in reforested areas 179 (35%), a decrease in cropland under minimum tillage (15%), while the cropland

surface proportion under conventional tillage increased to 24%, and that under
fallow decreased to 2.2%. In contrast, the respective surface areas under native
forest, pasture, and other land uses did not change.

183 2.2 Hydro-sedimentary monitoring

184 The Arvorezinha catchment has been monitored since 2002, with the 185 continuous measurement of flow discharge (Q) and suspended sediment 186 concentrations (SSC) at the outlet of the catchment in a Parshall type flume 187 built in concrete with a 1.83 m width in its narrowest part. Water level and 188 turbidity were recorded through a float-type water level sensor (Thalimedes, 189 OTT HydroMet, Germany) and a turbidimeter (Model SL-2000, Solar®, Brazil), 190 respectively. All automatic equipment recorded data every 10 minutes. SSC 191 data were obtained by the turbidimeter properly calibrated with samples 192 collected manually using an isokinetic sampler (US DH-48) during rainfall-runoff 193 events as proposed by Merten et al. (2014). The 10 min interval data was used 194 to calculate the variations of the sediment yield throughout the year. Rainfall 195 intensity and depth have been measured by means of tipping bucket rain 196 gauges and pluviometers, respectively, and their location is shown in Figure 1. 197 The rainfall of the last five days (R5) before the rainfall events analyzed was 198 computed to reflect the antecedent soil moisture conditions (SILVEIRA et al., 199 2000), which is classified into three classes according to rainfall volume: 1) dry 200 when R5 < 36 mm; 2) field capacity when R5 > 36 and < 53 mm; and 3) 201 saturated when R5 > 53 mm.

The runoff separation (the separation of surface runoff and base flow contributions) was performed for the 16 rainfall events monitored, using the graphical analysis method of Chow et al. (1988). The onset of the surface runoff

is determined by the rise of the hydrograph until the moment when the
discharge returned to values close to those observed just before the rising limb,
thus characterizing the end of the rainfall event.

208

209 2.3 Sampling and chemical analysis

During the rainfall - runoff events, 164 water samples were collected at the catchment outlet using a isokinetic sampler. Duplicate samples were collected, one of them to calculate the sediment concentration following the evaporation method according to Shreve and Downs (2005) and the second sample was used for determining the water chemical composition, which is described in section 2.3.1.

216

217 2.3.1 Chemical analysis

In the laboratory, an aliquot of the sample was filtered at 0.22 µm to characterize the dissolved fraction. The total element concentration was determined in the non-filtered samples. Then, the particulate fraction was obtained through calculating the difference between total and dissolved concentrations.

In the filtered sample, the dissolved organic carbon (DOC) content was determined after mixing an aliquot of the filtered sample with a 1:1 sulphochromic solution incubated in an oven for 4 h at 60°C, with a spectrophotometer at 580 nm. Sulphate ($SO_4^{2^-}$), chlorine (CI^-) and nitrate (NO_3^-) contents were measured with a high-performance liquid chromatography (HPLC) - Sykam S 135 Ion Chromatography System (U.S. EPA, 1997). Finally, the concentration of dissolved Ca²⁺, Cu²⁺, Fe²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, PO₄³⁻, Si⁴⁺,

and Zn²⁺ was quantified by Inductively Coupled Plasma - Optical Emission
Spectrometry (ICP-OES, Perkin-Elmer) directly in the filtered water sample
(U.S. EPA, 1994).

233 Total content in unfiltered samples of water + sediments was assessed 234 after digestion with aqua-regia (U.S. EPA, 1996). In brief, a 20 mL aliquot of 235 unfiltered sample of water + sediment was inserted into Teflon tubes together 236 with 0.5 mL of HCI (37%) and 1 mL of HNO₃ (65%), followed by microwave 237 assisted digestion for 9.5 min at a temperature of 182 °C. After that, Ca, Cu, Fe, 238 K, Mg, Mn, Na, P, Si and Zn were quantified using Inductively Coupled Plasma 239 Optical Emission Spectrometry (ICP-OES, Perkin-Elmer) (U.S. EPA, 1997). 240 Then, particulate contents of these elements were obtained by calculating the 241 difference between total and dissolved contents.

242

243 2.4 Data analysis

The relationship between the element concentrations and the water discharge was evaluated by means of metric indices: slope (β), CV_C/CV_Q, qualitative (loop) and hysteresis index. The analyses were performed for the 16 rainfall events monitored, evaluating the SSC, DOC, NO₃⁻, SO₄²⁻, Cl⁻ and the ten chemical elements analyzed (Ca²⁺, Cu²⁺, Fe²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, Zn²⁺, PO₄⁻³, Si⁴⁺).

250

251 2.4.1 Metric indexes

To obtain the β , all Q and C data were log transformed. Accordingly, a β value was obtained for each element for the 16 rainfall events. A negative β value reflects the decrease of element concentration with the increase of Q,

whereas positive values indicate an increase of both C and Q. When $\beta \sim 0$, it indicates a chemostatic behavior of the element. The chemostatic pattern was defined when the β was considered to be significantly different from zero, at $\alpha =$ 0.05 if Student's *t* statistic | t | > 2 (Helsel and Hirsch, 2002; Rose et al., 2018).

The coefficient of variation of the concentration in each chemical element was calculated (CV_c), as well as the coefficient of variation of water discharge (CV_q). The CV_c/CV_q metric index indicates whether the behavior of the element is chemostatic ($CV_c/CV_q \le 0.5$), or chemodynamic ($CV_c/CV_q > 0.5$). According to Musolff et al. (2015) both β and CV_c/CV_q need to be evaluated in combination.

265 In addition, we also examined hysteresis patterns in dissolved and 266 particulate form of the elements during individual rainfall events, as well as the 267 hysteresis index (HI), with the method of Lawler et al. (2006). The method is 268 based on measuring the width of the hysteresis loop in the central water 269 discharge (Q_{50}) , when there is a 50% increment of the Q compared to the 270 beginning of the rainfall event. The Q₅₀ is calculated with equation 1, based on 271 the minimum (Q_{min}) and maximum water discharge (Q_{max}) values during the 272 rainfall event.

273

274

$$Q_{50} = 0.5 \times (Q_{max} - Q_{min}) + Q_{min} \tag{1}$$

Thus, with the Q_{50} calculated, the chemical element concentration and SCC for the exact corresponding moment was obtained by a coumpound rule of three, using the closest sample collected before and after the Q_{50} time in the rising and falling limbs. Therefore, HI was calculated according to equations 2 and 3, when the concentration in the rising limb - RL is higher than in the falling

280 limb - FL (clockwise hysteresis) and RL < FL (counterclockwise hysteresis),
281 respectively.

$$HI = \left(\frac{RL}{FL}\right) - 1 \tag{2}$$

282

$$HI = \left(\frac{-1}{\frac{RL}{FL}}\right) + 1 \tag{3}$$

283

284 Where: RL is the element concentration in water discharge on the rising 285 limb of the hydrograph and FL is the concentration on the falling limb.

286

The Flushing Index (FI) was calculated according to the method of (Vaughan et al., 2019) (Equation 4). The water discharge and the element concentration had to be normalized, according to equations 5 and 6, respectively.

$$FI = C_{Qpeak,normal} - C_{initial,normal}$$
(4)

290

Where: C_{Qpeak,normal} and C_{initial,normal} are the normalized elements during
the peak and the beginning of each rainfall event, respectively.

293

$$Q_{i,normal} = \frac{Q_i - Q_{min}}{Q_{max} - Q_{min}}$$
(5)

294

$$C_{i,normal} = \frac{C_i - C_{min}}{C_{max} - C_{min}}$$
(6)

295

296 Where: Q_i and C_i are the water discharge and element values at time 297 step i, respectively, Q_{max} and Q_{min} are the maximum and minimum water discharge values during the rainfall event, respectively, and C_{max} and C_{min} are the maximum and minimum concentrations of each element during the rainfall event, respectively.

301

302 **3. RESULTS**

303 3.1 Hydro-sedimentary monitoring and element concentration

304 Table 1 shows the main characteristics of the 16 rainfall events 305 monitored between 2011 and 2015. The peak flow varied from 35 to 3,399 L s⁻¹ 306 while the maximum suspended sediment concentrations fluctuated from 0.1 to 5.4 g L^{-1} . The magnitude of peak flows followed the magnitude of the volume 307 308 and duration of rainfall (Table 1). However, it is important to consider the effect of the previous events on the hydro-sedimentary dynamics, because even with 309 310 low rainfall volume, surface runoff generation, sediment and chemical element 311 transport may occur. The rainfall of the last five days (R5) are presented in 312 Table 1. It can be observed that among all the events analyzed, there was no 313 rainfall at all during the previous five days for four events and for five events the 314 R5 was < 36 mm, corresponding to a dry condition. Five other events were 315 classified as having field capacity humidity, and two rain events considered as 316 saturated soil. The SSC during this period (2011-2015) was not high, except for 317 the events that occurred on 18/09/12 and 12/07/15 (Table 1). According to 318 studies conducted in this catchment between 2002 and 2016, the minimum and maximum SCC recorded values are 0 and 13.7 g L⁻¹, respectively (Minella et 319 al., 2018). However, considering the duration and the surface runoff (Q_{runoff}) of a 320 321 certain event, the sediment yield (SY) may still be high. An example is the event of 20/07/2011 that presented low average SSC (SSC_{ave} - 0.2 g L^{-1}) and a 322

maximum value of 0.6 g L⁻¹, but due to high Q_{runoff} , generated high SY (24.8 ton). The opposite situation was observed for the event that occurred on 12/07/2015, where the SSC_{ave} was higher, but the SY was lower, because the Q_{runoff} was much lower. Annual and event-based hydrographs and sedimentographs during sampling can be found in the supplementary material.

Figure 2 shows the preferential form of transport of each chemical element. A significant proportion of Ca^{2+} , K⁺, Na⁺, and Mg²⁺ transport occurred in dissolved form (47, 41, 39 and 28% respectively). In contrast, Mn, Fe, P, Cu, Si and Zn were mostly transported in particulate form (99, 97, 91, 90, 85 and 79%, respectively).

333

Table 1: Hydro-sedimentary variables monitored during 16 rainfall events from2011 to 2015 in the Arvorezinha catchment.

336

337 3.2 Chemical element exports

338 Table 2 shows the number of rainfall events, the number of samples (n), 339 minimum, average, and maximum concentrations for each element. A large 340 number of samples were collected during the rising, peak and falling limbs of 341 the hydrograph resulting in a total of 164 samples, although for some elements, 342 mainly anions, only the samples of a restricted number of events (n= 7) could 343 be analyzed (Table 2). The analyzed samples cover a wide range of 344 concentrations, due to the variability of rainfall events in terms of magnitude and 345 seasonality.

346

Table 2: Chemicals, total rainfall events, total of samples, maximum, mean and minimum concentration, log (C) – log (Q) regression slopes (\pm SE) and CV_c/CV_Q of dissolved and particulate elements during events from 2011 to 2015 in the Arvorezinha catchment.

- 351
- 352 3.2.1 Dilution patterns

Analyzing separately the metric indices β and CV_C/CV_Q , the following 353 354 results were obtained with $\beta < 0$ significantly different from zero (p < 0.05): 0.32 ± 0.11 for DOC and -0.12 ± 0.03 for Na⁺; where their concentration 355 356 decreased when Q increased (Table 2). Although the β value for Cl was not 357 significantly different from zero (p < 0.06), its value was also < 0. The CV_C/CV_Q 358 values obtained for DOC and Cl^{-} , were 0.83 and 0.58, respectively, which are > 0.5, indicating a chemodynamic pattern (Table 2). In contrast, for Na⁺, the value 359 of CV_C/CV_Q was 0.42, indicating a chemostatic pattern. 360

361

362 3.2.2 Enrichment patterns

363 For SSC and for the concentrations in particulate form of all the chemical elements analyzed, the β values were > 0 (p < 0.05), with the exception of that 364 365 obtained for Zn, which was not statistically different from zero (p < 0.13). This behavior indicates an enrichment (Table 2), and it was also observed for PO_4^{3-1} 366 and Zn^{2+} . Similarly, the CV_C/CV_Q ratio was > 0.5 for all elements in particulate 367 form, SSC, PO₄³⁻ and Zn²⁺, characterizing a chemodynamic pattern. In addition, 368 for some particulate elements (Ca, K, Mg, Mn and Zn) and for $PO_4{}^{3-}$, the 369 370 CV_C/CV_Q ratio is \geq 1, which is classified as a strong chemodynamic pattern.

372 3.2.3 Chemostatic patterns

The concentration of NO₃⁻, SO₄²⁻, Ca²⁺, K⁺, Mg²⁺, Cu²⁺, Fe²⁺, Mn²⁺ and 373 Si⁴⁺ showed little variations with water discharge, because $\beta \sim 0$. All these 374 elements, except for SO_4^{2-} (β = -0.09 ± 0.03, p < 0.01) and Ca^{2+} (β = -0.04 ± 375 376 0.02, p < 0.03), showed no significant difference from zero, at p < 0.05. The 377 chemostatic pattern was confirmed by CV_C/CV_O ratio values ≤ 0.5 for NO₃. SO_4^{2-} , Ca^{2+} , K⁺ and Mg²⁺ (Table 2). However, Cu^{2+} , Fe^{2+} , Mn^{2+} and Si^{4+} were 378 379 associated with a CV_C/CV_O ratio > 0.5, which would indicate a chemodynamic 380 pattern (Table 2).

381 When the two metric indices are combined, it is possible to obtain better 382 insights into the transport patterns of the analyzed elements (Gwenzi et al., 383 2017) (Figure 3). A major part of the elements was characterized by an increase in their concentration with increasing water discharge ($\beta > 0$; $CV_C/CV_Q \ge 0.5$). 384 Furthermore, those elements such as dissolved PO_4^{3-} and Zn^{2+} were among 385 386 those with the strongest chemodynamic behavior ($CV_C/CV_Q \ge 1$). In contrast, those elements with $\beta \sim 0$ and $CV_C/CV_Q < 0.5$ showed a weak relationship 387 between their concentration and the water discharge, mainly Mg²⁺, K⁺, Ca²⁺, 388 NO_3^- and $SO_4^{2^-}$ (Figure 3). Na⁺, Cl⁻ and DOC exhibit a dilution behavior. 389

390

391 3.3 Hysteresis and flushing analysis

The occurrence of a clockwise pattern was more frequent (> 50%) for K⁺, Fe²⁺, Mn²⁺ and Na⁺, SSC and for all particulate elements (Table 3). PO₄³⁻ and particulate Na presented equal proportions of clockwise (50%) and counterclockwise (50%) hysteresis behaviors. All particulate elements and SSC, except for Zn, presented positive HI values. Fe²⁺, Mn²⁺ and particulate Zn,

397 showed negative HI values (-1.18, -0.67 and -1.31, respectively), but the 398 clockwise hysteresis pattern predominated. Among the dissolved chemical 399 elements, only NO_3^- , K⁺, Na⁺, PO_4^{3-} and Si⁴⁺ showed positive HI values, 400 although NO_3^- did not show a well-defined hysteresis pattern (Table 3).

401 For Cl⁻, SO₄²⁻, Ca²⁺, Cu²⁺, Mg²⁺, Si⁴⁺, Zn²⁺ and DOC, a dominance of 402 counterclockwise patterns occurred (> 50%) which is supported by their 403 negative HI values (Table 3). The only exception was observed for DOC and 404 Si⁴⁺ that showed a positive HI value, with the occurrence of a few events with 405 high HI values, resulting in a positive average value.

Similarly, all particulate elements and SSC presented positive FI values, indicating that their concentration increased during the hydrograph's rising limb (Table 3). All the dissolved elements, except for PO_4^{3-} , together with DOC showed negative values for FI (Table 3), indicating that their concentration decreased during the hydrograph's rising limb.

411

Table 3: Chemicals, mean Hysteresis Index (HI) and Flushing Index (FI) values
and percentages of distinct hysteresis patterns during these events monitored
from 2011 to 2015 in the Arvorezinha catchment.

415

When plotting FI *vs* HI, additional information may be derived to improve our understanding of the transport and the sources of these elements during the investigated rainfall events (Figure 4).

In Figure 4a, the elements with negative FI and positive HI are found $(NO_3^-, Si^{4+}, K^+, Na^+ and DOC)$. These elements show a dilution effect and they are supplied by nearby sources, which is particularly well defined for DOC. The

422 dilution effect indicates that this element reaches the river from one of the main 423 flow pathways, which is hypothesized to be surface runoff, since organic carbon 424 concentrations are higher in the topsoil layers. However, the slight 425 predominance of the counterclockwise direction for DOC may be surprising 426 (56%, Table 3), as we expected a clockwise predominance when examining the 427 hysteresis behavior alone without considering other indices (Figure 4a). All 428 other elements are characterized by HI values close to zero, suggesting the 429 absence of well-defined hysteresis patterns (clockwise, counterclockwise, or 430 complex).

All the elements in particulate form, except Zn, SSC and dissolved PO₄³⁻ 431 432 are characterized by an increase in their concentrations during the rising limb 433 (Figure 4b). Furthermore, the source of these elements is expected to be in the 434 vicinity of the catchment outlet, being delivered during the rising limb and 435 depleted during the falling limb (Figure 4b). Particulate Zn is an exception 436 because its main behavior is counterclockwise according to the HI value (its 437 source is expected to be far from the catchment outlet) (Figure 4d). This 438 analysis suggests that at the beginning of an event there is an increase of these 439 element during the rising limb and it is supplied by more distant sources. 440 However, for most events (57%, Table 3), the particulate Zn shows a clockwise 441 pattern. For most events, the HI value was positive and close to zero for Zn. For 442 only two events the HI values were more negative (-4.69 and -5.65 for the 443 events occurred in 01/10/2011 and 20/09/2013, respectively), which makes the 444 result for this element inconclusive.

445 $Cl^{-}, SO_4^{2^-}, Ca^{2^+}, Mg^{2^+}, Cu^{2^+}$ and Mn^{2^+} showed a dilution effect and they 446 are likely supplied by distant sources, well characterized for $Ca^{2^+}, Cu^{2^+}, Mn^{2^+},$

447 Fe²⁺ and Zn²⁺ that present more negative values (-0.22, -0.36, -0.67 and -1.18, 448 respectively) (Figure 4c). The other three elements (Cl⁻, $SO_4^{2^-}$, Mg^{2^+}) were 449 characterized by HI values close to zero (-0.03, -0.05 and -0.06, respectively), 450 suggesting that they are supplied by closer sources during the event, than the 451 other four elements found in Figure 4c.

452

453 **4. DISCUSSION**

454 The rainfall events investigated in the current research covered a 455 pluriannual period, including different seasons and climatic phenomena. The 456 year 2015 was classified as El Niño (NOAA) for Southern Brazil with annual 457 rainfall exceeding 2,498 mm in the study site (Barros, 2016). In the agricultural 458 crop season of 2011/2012, a La Niña phenomenon was registered, which may 459 cause periods of drought in Southern Brazil (NOAA). Therefore, different 460 hydrological behavior occurs in the catchment and they were covered by the 461 period of sampling.

462 The chemical elements that can be strongly adsorbed by clays and iron 463 oxides, were mainly transported in particulate form, including P, Fe and Mn 464 with 91, 97 and 99%, respectively. In contrast, large proportions of ions such as 465 Ca, K and Na were transported in dissolved form (48, 41 and 39%, 466 respectively). However, it should be noted that these values refer to the average 467 value calculated for the entire set of 16 rainfall events (Figure 2). When 468 analyzing the dissolved and particulate proportions for each individual rainfall 469 event, these proportions can be different. Accordingly, during those rainfall 470 events with high SSC, almost 100% of the elements with a high affinity with 471 sediment particles, such as P, Mn, and Fe, were transported in particulate form.

For events with lower sediment concentrations, the proportion of these elements in dissolved form increased. In contrast, elements with a low affinity for sediment particles, such as Ca and K, were mainly transferred in dissolved form whatever the SSC conditions observed during the event.

Three different transport regimes are described for the analyzed elements in the next sections, namely: (i) chemodynamic - enrichment, (ii) chemodynamic – dilution and (iii) chemostatic.

479

480 4.1 Drivers for enrichment patterns

All the elements in particulate form (Ca, Cu, Fe, K, Mg, Mn, Na, P, Si and Zn), as well as SSC and dissolved PO_4^{3-} showed a concentration enrichment with increased discharges. Botter et al. (2019) observed a similar behavior for total phosphorous (Particulate P + PO_4^{3-}), which shows higher concentrations with increasing discharges.

486 Sediment availability for transport is dependent on the kinetic energy of 487 rainfall during previous events and on the occurrence of new sediment pulses, 488 that may be triggered by landslides or channel bank erosion (Wymore et al., 489 2019). As the Arvorezinha catchment did not experience any landslide during 490 the study period, the main sediment supply to the stream is associated with the 491 occurrence of interill and rill erosion in cultivated areas (57% of the total 492 sediment) (Tiecher et al., 2015). However, other potential sources were outlined 493 as delivering a significant proportion of sediment and particle-bound elements. 494 Unpaved roads were shown to provide 23% of the sediment (Tiecher et al., 495 2015) with preferential connections with the river network (Barros, 2016). This 496 high connectivity between the roads and the stream systems allows the quick

delivery of readily available sediment to the stream (Figure 1). These results are consistent with the findings of the current research showing that the sources of particle-bound elements are close from the monitoring station (as these parameters showed a clockwise pattern in > 50% of the events), which may explain the rapid mobilization of the sediment and the elements bound to or contained in the particles (Table 3, Figure 4).

 PO_4^{3-} was the only compound in dissolved form that presented the same 503 504 behavior as the particulate elements (Figure 4). Bender et al. (2018) evaluating 505 the P (dissolved and particulate form) dynamics in the same place of the 506 present study and through eight rain events already verified a strong correspondence between the PO₄³⁻ behavior with its particulate form. This is 507 likely related to the saturation of soils with the use of high doses of phosphate 508 509 fertilizers for tobacco cultivation. Pellegrini et al. (2010) showed that sediment 510 eroded from soils cultivated with tobacco were saturated with phosphates and 511 their desorption capacity was extremely high and fast. The dissolved form of nutrients essential to the development of agricultural crops, such as PO_4^3 , is 512 513 the form that they will be available in the aqueous medium and can trigger new 514 reactions or processes (Tang et al., 2019). In this catchment, a high availability of PO₄³⁻ is found in water and sediments, as already observed in a previous 515 516 study (Bender et al., 2018). A study conducted in France and compiling 40-year 517 records of water quality data from 293 monitoring stations showed that the 518 mitigation of phosphorus pollution reduced the concentrations in this substance 519 and altered the corresponding C – Q slopes (Moatar et al., 2017). Therefore, 520 understanding how the transfer of these elements occurs is of fundamental 521 importance, and is linked to the climatic conditions associated with the

522 characteristics of the catchment responsible for generating runoff and erosive523 processes.

524

525 4.2 Drivers for dilution patterns

526 Fe^{2+} , Zn^{2+} , Cu^{2+} and Mn^{2+} exhibited an increase in their concentration in 527 the rising limb, but during the event, other flow pathways with low concentration 528 in these elements have reached the catchment outlet and contributed to a 529 dilution phenomenon (Figure 3). All these elements displayed counterclockwise 530 patterns, reflecting their supply by sources that are located far from the 531 catchment outlet (Figure 4c).

More specifically, Fe²⁺, Si⁴⁺ and Mn²⁺ are released by natural weathering 532 533 processes and they remain in soluble form in the soil water compartment. 534 Previous studies that examined the hydrological dynamics in the Arvorezinha catchment revealed that subsurface and base flows may supply 60 to 80% of 535 536 the streamflow during a rainfall event in autumn and winter (Barros, 2016; 537 Robinet et al., 2018). Accordingly, the greater frequency of counterclockwise hysteresis behavior patterns may be explained by an important contribution of 538 539 subsurface flow during rainfall events.

540 Dissolved Cu^{2+} and Zn^{2+} showed a similar behavior than Fe^{2+} , Si^{4+} and 541 Mn^{2+} (Figures 3 and 4). The increased concentrations measured at the 542 beginning of the rainfall event were likely due to the release of these elements 543 by weathering processes, as young soils (Acrisols, Cambisols and Leptsols) of 544 basaltic origin are found in this catchment. In addition, in this area, low inputs of 545 Cu^{2+} and Zn^{2+} are expected from the use of fertilizers and agrochemicals

546 (exogenous solutes), which reinforces the different behavior observed 547 compared to that of DOC and dissolved Na⁺ and Cl⁻.

548 Na⁺, Cl⁻ and DOC are preferentially transported with surface runoff, due to their high concentrations in the topsoil layer. The high concentration of Na⁺ 549 550 and CI in water may be explained using inorganic fertilizers for tobacco 551 cultivation (NaNO₃ and KCI), which occupied 15 to 20% of the total catchment 552 surface area between 2011 to 2015. Finally, organic carbon is concentrated in 553 the topsoil layer due to inputs from cover crops; although the levels found may 554 vary depending on land use and soil management (Boix-Fayos et al., 2017; 555 Endale et al., 2017).

556

557 4.3 Chemostatic patterns

In general, Mg^{2+} , K^+ , Ca^{2+} , NO_3^- and SO_4^{-2} showed a very weak C - Q 558 559 relationship. Several sources (anthropogenic and geogenic) may supply these 560 elements, which can come from the storage of these solutes in the soil and by surface runoff. Thus, elements such as K⁺, may not have their concentration 561 562 altered with the increase of Q, because all flow pathways to the river may have 563 similar concentrations, causing no dilution effect nor enrichment with the 564 changes in the water discharge. In White Clay Creek, Pennsylvania – USA, the 565 K^{+} was the only element among those analyzed that presented a chemostatic 566 behavior and a complex hysteresis pattern, as it can be considered a biological solute, geological weathering and additional K⁺ inputs from exogenous sources 567 568 such as fertilizer (Rose et al., 2018). In Arvorezinha catchment, the production 569 of the tobacco requires high inputs of lime and industrial fertilizers (anthropogenic source) containing K^+ , NO_3^- and SO_4^{-2} . Both ions have a low 570

571 bridging energy to clay, oxides, and organic matter, which may facilitate their 572 release into the soil and possibly be transported by subsurface flow towards the 573 catchment outlet. In addition, another fraction of these elements can be carried 574 by surface runoff, due to their higher concentration on the topsoil layer. Na⁺, NH_4^+ , K⁺, Mq^{2+} , Ca^{2+} were already shown to be associated with geogenic 575 576 sources in a study conducted under a subtropical climate in Brazil (Piazza et al., 2018). In Nevada, USA, eight small river catchments were monitored (0.5 to 2.3 577 km²) and during the 8-years study period, Mg²⁺, K⁺, Ca²⁺, Cl⁻, Na⁺ and SO₄⁻² 578 579 revealed a chemostatic behavior under temperate climate, although an opposite situation was observed for NH_4^+ and NO_3^- (Hunsaker and Johnson, 2017). 580

581

582 **5. CONCLUSIONS**

583

584 The results show the strong correspondence between the magnitude of 585 the rainfall event and the preferred form of transportation of the chemical 586 elements. The water discharge is linked to the magnitude of the rainfall event 587 and the generation of surface runoff, the main responsible for the transport of 588 sediment and potential contaminants to the river. This can be attributed to the 589 strong erosive potential of rainfall in subtropical region combined to use and soil 590 management, that have an impact on the hydrological dynamics of the 591 catchment. Practices that may reduce the supply of water (by surface runoff) 592 and sediment to the river network will also minimize the transport of elements in particulate form (Ca, Cu, Fe, K, Mg, Mn, Na, P, Si and Zn), which is the 593 594 preferred form of chemical elements transport in this catchment. In the same

595 way, PO_4^{3-} concentration increased with the surface runoff, having the same 596 behavior of particulate elements, preferentially transferred by surface runoff.

597 Most of the dissolved chemical elements are associated to both element sources (geogenic/anthropogenic) and flow pathways (base, subsurface and 598 599 surface flow). Thus, elements that are not preferably transported by surface runoff, such as geogenic (Fe²⁺, Zn²⁺, Cu²⁺, Mn²⁺ and Si⁴⁺), reduce their 600 601 concentration with the increase in water discharge, and the dilution process 602 occurs. DOC, Na⁺ and Cl⁻ also have a dilution regime export (concentrations 603 decrease with the increase of Q). However, their source is anthropogenic 604 through fertilization and soil organic matter and mainly transported by the 605 surface runoff.

The chemostatic regime export is linked to chemical elements that are supplied by more than one flow pathway (Mg^{2+} , K^+ , Ca^{2+} , NO_3^- and SO_4^{2-}), due its potential contribution by both geogenic and anthropogenic source.

Overall, the results show that despite a small data set, it was possible to understand the transport of some important chemical elements (nutrients, geochemicals and metals) in a subtropical environment and it could be better understood when the different metric indices were used together. These insights are fundamental to design strategies to control surface runoff and erosive process, because as we have observed, they seem to be the main responsible for the chemical elements transport in this region.

616

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618

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626 **7. REFERENCES**

627

Alvares, C.A., Stape, J.L., Sentelhas, P.C., De Moraes Gonçalves, J.L.,
Sparovek, G., 2013. Köppen's climate classification map for Brazil.
Meteorol. Zeitschrift 22, 711–728. https://doi.org/10.1127/09412948/2013/0507

Barros, C.A.P. de, 2016. Dinâmica Dos Escoamentos Na Modelagem Da
Produção De Sedimentos Em Uma Pequena Bacia Rural. PhD thesis.
Federal University of Santa Maria.

Basu, N.B., Destouni, G., Jawitz, J.W., Thompson, S.E., Loukinova, N. V.,
Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., Rao,
P.S.C., 2010. Nutrient loads exported from managed catchments reveal
emergent biogeochemical stationarity. Geophys. Res. Lett. 37, 1–5.
https://doi.org/10.1029/2010GL045168

Bender, M.A., dos Santos, D.R., Tiecher, T., Minella, J.P.G., de Barros, C.A.P.,
Ramon, R., 2018. Phosphorus dynamics during storm events in a
subtropical rural catchment in southern Brazil. Agric. Ecosyst. Environ. 261,
93–102. https://doi.org/10.1016/j.agee.2018.04.004

Boix-Fayos, C., Martínez-Mena, M., Cutillas, P.P., de Vente, J., Barberá, G.G.,
Mosch, W., Navarro Cano, J.A., Gaspar, L., Navas, A., 2017. Carbon
redistribution by erosion processes in an intensively disturbed catchment.
Catena 149, 799–809. https://doi.org/10.1016/j.catena.2016.08.003

- Botter, M., Burlando, P., Fatichi, S., 2019. Anthropogenic and catchment
 characteristic signatures in the water quality of Swiss rivers: A quantitative
 assessment. Hydrol. Earth Syst. Sci. 23, 1885–1904.
 https://doi.org/10.5194/hess-23-1885-2019
- Cargnin, A.P., De Aveline Bertê, A.M., De Oliveira Lemos, B., De Oliveira, S.B.,
 2013. Atlas socioeconômico do Rio Grande do Sul: quinze anos
 acompanhando as transformações do estado. Geo UERJ 2.
 https://doi.org/10.12957/geouerj.2013.8200
- 656 Chow, V. Te, Maidment, D.R., Mays, L.W., 1988. Aplied Hydrology, McGraw-657 Hil. ed.
- 658 CONAB, 2019. Acompanhamento da Safra Brasileira. Cia. Nac. Abast. 5, 1– 659 113.
- Deuschle, D., Minella, J.P.G., Hörbe, T. de A.N., Londero, A.L., Schneider,
 F.J.A., 2019. Erosion and hydrological response in no-tillage subjected to
 crop rotation intensification in southern Brazil. Geoderma 340, 157–163.
 https://doi.org/10.1016/j.geoderma.2019.01.010
- Didoné, E.J., Minella, J.P.G., Merten, G.H., 2015. Quantifying soil erosion and
 sediment yield in a catchment in southern Brazil and implications for land
 conservation. J. Soils Sediments 15, 2334–2346.
 https://doi.org/10.1007/s11368-015-1160-0

Duvert, C., Gratiot, N., Evrard, O., Navratil, O., Némery, J., Prat, C., Esteves,
M., 2010. Drivers of erosion and suspended sediment transport in three
headwater catchments of the Mexican Central Highlands. Geomorphology
123, 243–256. https://doi.org/10.1016/j.geomorph.2010.07.016

- Endale, D.M., Potter, T.L., Strickland, T.C., Bosch, D.D., 2017. Sediment-bound
 total organic carbon and total organic nitrogen losses from conventional
 and strip tillage cropping systems. Soil Tillage Res. 171, 25–34.
 https://doi.org/10.1016/j.still.2017.04.004
- 676 Godsey, S.E., Kirchner, J.W., Clow, D.W., 2009. Concentration-discharge
- 677 relationships reflect chemostatic characteristics of US catchments. Hydrol.

678 Process. 23, 1844–1864. https://doi.org/10.1002/hyp.7315

- Gwenzi, W., Chinyama, S.R., Togarepi, S., 2017. Concentration-discharge
 patterns in a small urban headwater stream in a seasonally dry waterlimited tropical environment. J. Hydrol. 550, 12–25.
 https://doi.org/10.1016/j.jhydrol.2017.04.029
- Helsel, D.R., Hirsch, R.M., 2002. Statistical Methods in Water Resources,
 Studies in Environmental Sciences. United States Geological Survey.
 https://doi.org/10.13140/RG.2.2.36048.10248

Hunsaker, C.T., Johnson, D.W., 2017. Concentration-discharge relationships in
headwater streams of the Sierra Nevada, California. Water Resour. Res.

- 688 53, 7869–7884. https://doi.org/10.1002/2016WR019693
- Knapp, J.L., Freyberg, J. von, Studer, B., Kiewiet, L., Kirchner, J., 2020.
 Concentration-discharge relationships vary among hydrological events,
 reflecting differences in event characteristics. Hydrol. Earth Syst. Sci.

692 Discuss. 1–27. https://doi.org/10.5194/hess-2019-684

- 693 Lawler, D.M., Petts, G.E., Foster, I.D.L., Harper, S., 2006. Turbidity dynamics 694 during spring storm events in an urban headwater river system: The Upper Sci. 695 Tame, West Midlands, UK. Total Environ. 360. 109–126. 696 https://doi.org/10.1016/j.scitotenv.2005.08.032
- Lloyd, C.E.M., Freer, J.E., Johnes, P.J., Collins, A.L., 2016. Technical Note:
 Testing an improved index for analysing storm discharge-concentration
 hysteresis. Hydrol. Earth Syst. Sci. 20, 625–632.
 https://doi.org/10.5194/hess-20-625-2016
- Londero, A.L., Minella, J.P.G.G., Deuschle, D., Schneider, F.J.A.A., Boeni, M.,
 Merten, G.H., 2018. Impact of broad-based terraces on water and sediment
 losses in no-till (paired zero-order) catchments in southern Brazil. J. Soils
 Sediments 18, 1159–1175. https://doi.org/10.1007/s11368-017-1894-y
- 705 Merten, G.H., Araújo, A.G., Biscaia, R.C.M., Barbosa, G.M.C., Conte, O., 2015.
- No-till surface runoff and soil losses in southern Brazil. Soil Tillage Res.
 152, 85–93. https://doi.org/10.1016/j.still.2015.03.014
- Merten, G.H., Horowitz, A.J., Minella, J.P.G., Moro, M., 2014. Determinação da
 concentração de sedimentos em suspensão em rios com o uso de
 turbidímetro. Porto Alegre, Brasil.
- Minella, J.P.G., Merten, G.H., Barros, C.A.P., Ramon, R., Schlesner, A., Clarke,
 R.T., Moro, M., Dalbianco, L., 2018. Long-term sediment yield from a small
 catchment in southern Brazil affected by land use and soil management
 changes. Hydrol. Process. 32, 200–211. https://doi.org/10.1002/hyp.11404

Moatar, F., Abbott, B.W., Minaudo, C., Curie, F., Pinay, G., 2017. Elemental
properties, hydrology, and biology interact to shape concentrationdischarge curves for carbon, nutrients, sediment, and major ions. Water
Resour. Res. 53, 1270–1287. https://doi.org/10.1002/2016WR019635

Musolff, A., Schmidt, C., Selle, B., Fleckenstein, J.H., 2015. Catchment controls
on solute export. Adv. Water Resour. 86, 133–146.
https://doi.org/10.1016/j.advwatres.2015.09.026

Pellegrini, J.B.R., Dos Santos, D.R., Gonçalves, C.S., Copetti, A.C.C.,
Bortoluzzi, E.C., Tessier, D., 2010. Impacts of anthropic pressures on soil
phosphorus availability, concentration, and phosphorus forms in sediments
in a Southern Brazilian watershed. J. Soils Sediments 10, 451–460.
https://doi.org/10.1007/s11368-009-0125-6

727 Piazza, G.A., Dupas, R., Gascuel-Odoux, C., Grimaldi, C., Pinheiro, A., 728 Kaufmann, V., 2018. Influence of hydroclimatic variations on solute 729 concentration dynamics in nested subtropical catchments with 730 635. heterogeneous landscapes. Sci. Total Environ. 1091-1101. 731 https://doi.org/10.1016/j.scitotenv.2018.03.394

Ramon, R., 2017. Kinetic energy measurement of rainfall and defining a pluvial
index to estimate erosivity in Arvorezinha/RS. Master thesis. Federal
University of Santa Maria.

Ramon, R., Minella, J.P.G., Merten, G.H., de Barros, C.A.P., Canale, T., 2017.
Kinetic energy estimation by rainfall intensity and its usefulness in
predicting hydrosedimentological variables in a small rural catchment in
southern Brazil. Catena. https://doi.org/10.1016/j.catena.2016.07.015

Robinet, J., Minella, J.P.G., de Barros, C.A.P., Schlesner, A., Lücke, A.,
Ameijeiras-Mariño, Y., Opfergelt, S., Vanderborght, J., Govers, G., 2018.
Impacts of forest conversion and agriculture practices on water pathways in
Southern Brazil. Hydrol. Process. 32, 2304–2317.
https://doi.org/10.1002/hyp.13155

Rose, L.A., Karwan, D.L., Godsey, S.E., 2018. Concentration-discharge
relationships describe solute and sediment mobilization, reaction, and
transport at event and longer timescales. Hydrol. Process. 32, 2829–2844.
https://doi.org/10.1002/hyp.13235

Rumsey, C.A., Miller, M.P., Schwarz, G.E., Hirsch, R.M., Susong, D.D., 2017.
The role of baseflow in dissolved solids delivery to streams in the Upper
Colorado River Basin. Hydrol. Process. 31, 4705–4718.
https://doi.org/10.1002/hyp.11390

Shreve, E.A., Downs, A.C., 2005. Quality-Assurance Plan for the Analysis of
Fluvial Sediment by the U.S. Geological Survey Kentucky Water Science
Center Sediment Laboratory. Geol. Surv. Open-File Rep. -1230. 35.

SILVEIRA, L., CHARBONNIER, F., GENTA, J.L., 2000. The antecedent soil
moisture condition of the curve number procedure. Hydrol. Sci. J. 45, 3–12.
https://doi.org/10.1080/02626660009492302

758 Tang, X., Li, R., Wu, M., Zhao, W., Zhao, L., Zhou, Y., Bowes, M.J., 2019. 759 Science of the Total Environment In fl uence of turbid fl ood water release 760 on sediment deposition and phosphorus distribution in the bed sediment of 761 Three Gorges. Sci. Total Environ. 657, 36-45. the 762 https://doi.org/10.1016/j.scitotenv.2018.12.011

Thomas, Z., Abbott, B.W., Troccaz, O., Baudry, J., Pinay, G., 2016. Proximate
and ultimate controls on carbon and nutrient dynamics of small agricultural
catchments. Biogeosciences 13, 1863–1875. https://doi.org/10.5194/bg-131863-2016

Thompson, S.E., Basu, N.B., Lascurain, J., Aubeneau, A., Rao, P.S.C., 2011.
Relative dominance of hydrologic versus biogeochemical factors on solute
export across impact gradients. Water Resour. Res. 47, 1–20.
https://doi.org/10.1029/2010WR009605

Tiecher, T., Caner, L., Minella, J.P.G., Santos, D.R. dos, 2015. Combining
visible-based-color parameters and geochemical tracers to improve
sediment source discrimination and apportionment. Sci. Total Environ.
527–528, 135–149. https://doi.org/10.1016/j.scitotenv.2015.04.103

U.S. EPA, 1997. Method 300.1, Revision 1.0: Determination of Inorganic Anions
in Drinking Water by Ion Chromatography. Washington, DC.

U.S. EPA, 1996. EPA Method 3050B, Revision 2: Acid Digestion of Sediments,
Sludges, and Soils. Washington, DC.

U.S. EPA, 1994. Method 200.7, Revision 4.4: Determination of macro and trace
elements in rare earth magnesium cast iron by inductively coupled plasma
atomic emission spectrometry. Washington, DC.

782 Vaughan, M.C.H., Bowden, W.B., Shanley, J.B., Vermilyea, A., Schroth, A.W.,

2019. Shining light on the storm: in-stream optics reveal hysteresis of
dissolved organic matter character. Biogeochemistry 143, 275–291.
https://doi.org/10.1007/s10533-019-00561-w

Verheyen, D., Van Gaelen, N., Ronchi, B., Batelaan, O., Struyf, E., Govers, G.,
Merckx, R., Diels, J., 2015. Dissolved phosphorus transport from soil to
surface water in catchments with different land use. Ambio 44, 228–240.
https://doi.org/10.1007/s13280-014-0617-5

Von Freyberg, J., Studer, B., Kirchner, J.W., 2017. A lab in the field: Highfrequency analysis of water quality and stable isotopes in stream water and
precipitation. Hydrol. Earth Syst. Sci. 21, 1721–1739.
https://doi.org/10.5194/hess-21-1721-2017

Wan, Y., Wan, L., Li, Y., Doering, P., 2017. Decadal and seasonal trends of
nutrient concentration and export from highly managed coastal catchments.

796 Water Res. 115, 180–194. https://doi.org/10.1016/j.watres.2017.02.068

Williams, M.R., Livingston, S.J., Penn, C.J., Smith, D.R., King, K.W., Huang, C.
hua, 2018. Controls of event-based nutrient transport within nested
headwater agricultural watersheds of the western Lake Erie basin. J.
Hydrol. 559, 749–761. https://doi.org/10.1016/j.jhydrol.2018.02.079

Wymore, A.S., Leon, M.C., Shanley, J.B., McDowell, W.H., 2019. Hysteretic
response of solutes and turbidity at the event scale across forested tropical
montane watersheds. Front. Earth Sci. 7.
https://doi.org/10.3389/feart.2019.00126

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Figure 1 – Location of the study site in Brazil and the hydro-sedimentary
monitoring within the catchment.

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Figure 2 – Average distribution of chemical elements in dissolved and
particulate forms during the rainfall events monitored from 2011 to 2015.

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Figure 3: Plot of log (C) – log (Q) regression slope – β versus CV_C/CV_Q for all elements determined in the current study. The plotted values correspond to the mean of those measurements conducted on all the samples analyzed during the 2011 – 2015 period. Error bars represent ± 1 Standard Error β . SSC: suspended sediment concentration; DOC: dissolved organic carbon.

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Figure 4: Plots of median hysteresis index versus median flushing index for chemical across all sampled rainfall events from 2011 to 2015. SSC: suspended sediment concentration; DOC: dissolved organic carbon. HI and FI values are normalized considering their maximum value equal to 1.

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Data	Т	R	R5	Q _{total}	Q_{base}	Q _{runoff}	Q_{peak}	С	SSC_{peak}	SSC _{ave}	SY
Dala	min			mm			L s⁻¹	%	g L	-1 -	ton
20/07/2011	1340	127	44	92.7	37.5	55.2	3399.4	43.4	0.6	0.2	24.8
01/10/2011	350	17	0	0.81	0.61	0.2	57.7	1.2	0.2	0.1	0.1
05/07/2012	1460	95	0	16.5	10.6	6.2	536.4	6.4	0.4	0.2	2.4
26/08/2012	2040	27	15	1.0	0.9	0.1	44.2	0.5	0.2	0.1	0.3
09/09/2012	540	26	0	9.1	8.9	0.2	35.6	0.7	0.3	0.1	0.1
18/09/2012	430	110	27	44.3	19.3	25	1470.8	22.7	5.3	1.1	20.6
12/03/2013	480	27	58	5.6	4.7	0.9	235.6	3.4	0.2	0.1	0.6
24/08/2013	*	64	16	0.9	**	**	45.5	**	0.1	0.1	0.1
20/09/2013	1980	84	18	47.6	22.2	25.4	785.3	30.2	2.2	0.7	70.6
26/10/2013	245	36	52	6.3	3.6	2.7	463.6	7.5	1.0	0.4	3.3
19/03/2014	430	34	35	2.1	1.3	0.9	125.9	2.5	0.7	0.3	0.9
23/07/2014	950	83	0	26.7	17.0	9.7	1034.5	11.7	1.1	0.2	6.4
06/09/2014	390	42	8	7.4	5.2	2.2	258.4	5.2	0.4	0.2	1.2
30/09/2014	950	42	51	20.2	12.5	7.7	520.5	18.2	0.2	0.1	1.9
08/07/2015	1370	48	36	19.7	17.8	1.9	536.4	4.0	0.3	0.1	2.2
12/07/2015	*	87	86	22.5	17.0	5.5	599.5	6.3	5.4	0.4	6.6

Table 1: Hydro-sedimentary variables monitored during events from 2011 to 2015 in the Arvorezinha catchment.

* Events that lasted more than one day. ** This event was long, and the rainfall was of low intensity; accordingly, during the period of sampling, the flow level did not rise. T = duration of the rainfall, R = rainfall depth, R5 = antecedent rainfall of the last five days, Q_{total} = total flow, Q_{base} = total base flow, Q_{runoff} = total surface runoff; Q_{peak} = peak flow, C = surface runoff coefficient, SSC_{peak}= peak suspended sediment concentration, SSC_{ave}= average suspended sediment concentration, SY= sediment yield.

Table 2: Chemicals, total rainfall events, total of samples, maximum, mean and minimum concentration, log (C) – log (Q) regression slopes (\pm SE) and CV_o/CV_Q of dissolved and particulate elements during events from 2011 to 2015 in the Arvorezinha catchment.

Chemical	Events	Data	Maximum	Mean	Minimum	β	CV_C/CV_Q
SSC	16	164	4.4	0.3	0.0	0.52 (± 0.08) [†]	1.16
DOC	15	114	10.4	1.8	0.0	-0.32 (± 0.11) [†]	0.83
Dissolved							
Cl	7	53	16.4	3.0	0.6	-0.10 (± 0.05)	0.58
NO ₃ ⁻	7	53	2.7	1.2	0.4	-0.06 (± 0.03)	0.23
SO4 ²⁻	7	53	5.3	2.7	0.6	-0.09 (± 0.03) [†]	0.24
Ca ²⁺	16	164	4333.7	2183.8	660.9	-0.04 (± 0.02) [†]	0.16
Cu ²⁺	16	142	31.6	2.1	0.0	0.05 (± 0.06)	1.05
Fe ²⁺	16	163	2034.6	303.7	0.0	0.07 (± 0.12)	0.89
K⁺	16	164	4548.3	2611.6	534.0	-0.01 (± 0.02)	0.13
Mg ²⁺	16	164	1273.3	743.0	297.5	-0.02 (± 0.01)	0.11
Mn ²⁺	16	126	22.0	3.6	0.0	0.08 (± 0.09)	0.74
Na⁺	16	143	4492.4	1210.7	0.0	-0.12 (± 0.03) [†]	0.42
PO4 ³⁻	16	150	642.5	27.7	0.0	0.23 (± 0.08) [†]	1.41
Si ⁴⁺	16	163	10223.6	1621.7	0.0	0.01 (± 0.08)	0.63
Zn ²⁺	16	164	77.7	10.6	0.3	$0.14 (\pm 0.06)^{\dagger}$	0.70
Particulate							
Ca	12	105	72709	2191.3	0.0	0.62 (± 0.11) [†]	2.05
Cu	11	95	98.6	12.3	0.0	0.35 (± 0.14) [†]	0.96
Fe	12	118	111452.0	13408.7	290.3	$0.66 (\pm 0.07)^{\dagger}$	0.97
К	12	103	28784.1	3218.0	0.0	$0.46 (\pm 0.09)^{\dagger}$	1.02
Mg	12	110	18021.1	1710.1	0.0	0.51 (± 0.08) [†]	1.10
Mn	12	118	4631.5	472.5	9.0	$0.77 (\pm 0.08)^{\dagger}$	1.03
Na	11	89	9438.0	1376.1	0.0	0.45 (± 0.15) [†]	0.99
Р	12	114	1936.1	203.8	0.0	$0.60 (\pm 0.07)^{\dagger}$	0.90
Si	12	112	53759.4	9383.1	0.0	$0.65 (\pm 0.08)^{\dagger}$	0.91
Zn	11	81	489.4	25.3	0.0	0.20 (± 0.13)	1.48

SSC: suspended sediment concentration - g L⁻¹; DOC: dissolved organic carbon (mg L⁻¹); Cl⁻, NO₃⁻, SO₄²⁻ are expressed in mg L⁻¹, whereas the other elements are expressed in μ g L⁻¹, SE: standard error. [†]Significant different from zero at *p* < 0.05.

Chemical	HI	FI	% Clockwise	% Counterclockwise	%Complex
SSC	1.48	0.75	85	15	0
DOC	2.63	-0.09	44	56	0
Dissolved					
Cl	-0.03	-0.20	43	57	0
NO ₃ ⁻	0.03	-0.34	43	43	14
SO4 ²⁻	-0.05	-0.38	43	57	0
Ca ²⁺	-0.22	-0.38	38	62	0
Cu ²⁺	-0.36	-0.08	36	64	0
Fe ²⁺	-1.18	-0.15	54	46	0
K ⁺	0.05	-0.04	54	38	8
Mg ²⁺	-0.06	-0.30	38	68	0
Mn ²⁺	-0.67	-0.04	67	33	0
Na⁺	0.01	-0.71	55	45	0
PO ₄ ³⁻	0.69	0.28	50	50	0
Si ⁴⁺	0.05	-0.67	46	54	0
Zn ²⁺	-1.43	-0.10	23	77	0
Particulate					
Mg	1.16	0.59	80	20	0
Ca	0.56	0.38	80	20	0
Cu	1.02	0.44	89	11	0
Mn	1.80	0.66	90	10	0
Fe	1.18	0.67	80	20	0
Na	0.24	0.30	50	50	0
К	0.42	0.51	70	30	0
Р	0.86	0.63	80	10	10
Si	1.36	0.59	100	0	0
Zn	-1.31	0.59	57	43	0

Table 3: Chemicals, mean Hysteresis Index (HI) and Flushing Index (FI) values and percentages of distinct hysteresis patterns during these events monitored from 2011 to 2015 in the Arvorezinha catchment.

SSC: suspended sediment concentration; DOC: dissolved organic carbon









