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1 **Mobilization and transport of pesticides with runoff and suspended sediment during**
2 **flooding events in an agricultural catchment of Southern Brazil**

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17 **Abstract**

18 Brazil is one of the largest consumers of pesticides in the world, and these chemicals
19 present a high contamination risk for the country's water bodies. The mechanisms of
20 mobilization and transport of pesticides from cropland to river systems are controlled by runoff
21 and erosion processes occurring at the catchment scale. In addition to the excessive use of
22 pesticides, the transport processes of these substances are also accelerated by inadequate soil
23 management and the absence of soil conservation measures at the catchment scale. The current
24 research relied on hydrological monitoring to investigate the transport and persistence of
25 pesticides in response to hydrological dynamics. The study was conducted in the Conceição

26 River watershed where runoff and suspended sediment fluxes are continuously monitored at
27 the outlet. This study area is representative of the grain production system in southern Brazil
28 including the application of large amounts of pesticides combined with extensive runoff and
29 erosion problems. Sample collection in the river for pesticide analysis included the analysis of
30 both water and suspended sediment. The sediment deposit analysis was performed in a single
31 location at 4 depths. Results demonstrate the occurrence of pesticides including simazine, 2,4-
32 D, carbendazim, imidacloprid, tebuconazole, propiconazole, tetraconazole and trifloxystrobin
33 in water, while glyphosate and AMPA were detected in suspended sediments, and AMPA and
34 carbendazim were found in sediment deposits. The study demonstrated the strong dependence
35 of the mechanisms of pesticide mobilization and transport in the catchment with the intra and
36 inter-event variability of hydro-sedimentary processes. Pesticide detections can be related to
37 several factors, including the magnitude of the rainfall event, the period of pesticide application
38 or the transport of suspended sediment. All of these factors are correlated, and the mechanisms
39 of transportation play an important role in the connections between sink and sources. The results
40 suggest that pesticide monitoring should take into account the runoff and erosion pathways in
41 each particular catchment, and it should especially include the monitoring of major rainfall
42 events for identifying and quantifying the occurrence of pesticides in the environment. The
43 transport of pesticides indicates to be potentiated by intensive pesticide use, the magnitude of
44 rainfall-runoff events and the absence of runoff control measures (e.g. terracing). These results
45 demonstrate that water and soil conservation techniques should be planned and coordinated at
46 the watershed scale to reduce the connectivity of water and sediment flows from agricultural
47 areas to river systems with the implementation of effective runoff control practices. This will
48 control the mobilization agents (runoff), as well as limit the connection between the sources
49 and the water bodies.

50 **Keywords:** Environmental monitoring, erosion, water, connectivity, no-tillage.

51 **1 Introduction**

52 Use of organosynthetic substances for the control of undesirable insects, weeds and
53 phyto-pathogens (fungi) in agricultural crops has led to the expansion of cultivated areas around
54 the world, as well as to an increase in food production (Steffen et al., 2011). The WHO (2011)
55 defines pesticides as any substance, individually or in a mixture, capable of controlling a pest
56 (insects, fungi, bacteria, viruses) that may pose a risk or inconvenience to populations and the
57 environment. Used pesticides in agriculture include defoliants, desiccants and plant growth
58 regulators or phyto-regulators (FAO - Food and Agriculture Organization of the United Nations,
59 2016). The Brazilian market is the largest user of pesticides in the world, and it occupies the
60 seventh position of consumer per cultivated area (FAO, 2016).

61 According to the Ministry of Agriculture, Livestock and Supply (MAPA, 2019) in 2019
62 alone, about 474 new types of products/formulations were released in the country, and among
63 the 50 most used pesticides, 22 have already been banned in Europe and the United States.
64 According to data from the Brazilian Institute of Environment and Renewable Natural
65 Resources (IBAMA), for the 2017 harvest, use in the country was 540,000 tons. Compared to
66 the last agricultural census (IBGE, 2019), there was a 20.4% increase in pesticide use by farmers
67 compared to the previous year (2018).

68 The main crops responsible for the high consumption of agrochemicals are soybean,
69 corn, sugarcane, cotton and rice (SINDIVEG, 2015). Given the associated potential for
70 environmental contamination, studies involving the analysis of pesticide residues demonstrated
71 their occurrence in food (ANVISA, 2016), in the atmosphere (Moreira, et al., 2012; Majewski
72 et al., 2014), in rainfall water (Nogueira et al., 2012; Lima et al., 2020), in soils (Baumgartner
73 et al., 2017; Rheinheimer et al., 2020), in surface and groundwater (Dores et al., 2008), in ocean
74 water (Mercurio et al., 2014), in epilithic biofilms (Fernandes et al., 2019), in fish (Clasen et
75 al., 2018), and even in breast milk (Palma et al., 2014). However, the environmental and human

76 health effects of such exposure will depend on both the level of exposure and the concentration
77 of the substance (Kuperman, et al., 2009; Schäfer & Bundschuh, 2018). Furthermore, in recent
78 years, the removal of riparian vegetation that acted as a natural buffer to trap runoff and
79 sediment originating from cropland may have enhanced the transport of pesticides to water
80 bodies (Becker et al., 2009; Bastos et al., 2018, Fernandes et al., 2019).

81 Water bodies suffer all the impacts of anthropogenic activities implemented along
82 rivers, in that they receive materials, sediment and pollutants, reflecting the different uses and
83 covers of the soil (Tundisi & Shaskraba, 1999). Factors affecting the fate of agrochemicals in
84 the environment are related to their use, their environmental characteristics and physical-
85 chemical properties (Laabs et al., 2002).

86 Pesticides are transported from cropland to river systems through erosion and transfer
87 of suspended particles from cultivated land, especially on steep and long hillslopes. This is
88 exacerbated when soil is only sparsely covered by vegetation (Rheinheimer et al., 2020). The
89 reduction of the soil cover by vegetation through a low increment of plant residues, and the
90 absence of crop rotation associated with the intensification of farming practices increased soil
91 compaction, which in turn reduced infiltration and generated a loss of the water storage capacity
92 in the soil (Paranhos Filho et al., 2005; Gubiani et al., 2013; Reichert et al., 2016). In addition,
93 once produced locally, runoff may accumulate and concentrate along hillslopes, further
94 accelerating soil erosion downstream (Londero et al., 2018, Deuschle et al., 2019).

95 In the Conceição River catchment, the main summer crop is soybean (*Glycine max*)
96 while, in winter, wheat (*Triticum spp.*), oats (*Avena strigosa*) or ryegrass (*Lolium multiflorum*)
97 are the most widespread crops. Soil management is characterized by no-till planting in more
98 than 85% of the cultivated areas. However, the abandonment of mechanical runoff control
99 practices (e.g. terraces), the implementation of soybean monoculture without crop rotation, the
100 low soil cover achieved by previous crop residues ($\sim 4 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ of dry matter), and the

101 excessive and uncontrolled traffic of agricultural machinery lead to soil degradation with
102 reduced water infiltration into the soil, thereby increasing runoff and erosion generation
103 (Didoné et al., 2015). In addition, the hydrologically fragile areas are increasingly used for
104 agricultural activities, with riparian forests of insufficient width and following the drainage of
105 wetlands that have lost their functions of runoff buffer and sediment trap. The more detailed
106 effectiveness of conservation systems used in this catchment has been investigated in previous
107 studies conducted by Didoné et al. (2015, 2017).

108 The diversity of pesticide molecules may respond differently to a variety of dispersion
109 mechanisms including water, wind, via the trophic chain or with the transport of suspended
110 sediments. In South America, several studies have reported the presence of pesticides in surface
111 waters draining agricultural areas (Lupi et al., 2015; Ronco et al., 2016; Primost et al., 2017).
112 However, there is a lack of knowledge regarding the temporal dynamics affecting the
113 concentrations of these compounds in response to the hydro-sedimentary behavior of
114 catchments (Exterkoetter, et al., 2019).

115 The current research provides an original contribution through the quantification of the
116 persistence of pesticides in the environment, as well as through the design of a strategy for
117 monitoring these compounds considering the pesticide use, timing of application and the
118 connection between agricultural areas and river systems. The objective of the current research
119 is therefore to describe the processes of transport and persistence of pesticides in response to
120 hydrological dynamics, sediment transport and rainfall seasonality at the outlet of an
121 agricultural catchment representative of those areas of intensive farming in Southern Brazil.

122 **2 Methodology**

123 **2.1 Study area**

124 The study was conducted in the Conceição River catchment (Fig. 1), located in the
125 northwest part of Rio Grande do Sul, the southernmost state of Brazil. The river monitoring

126 station is located at coordinates 28°27'22 "S and 53°58'24 "W. The catchment has a drainage
127 area of 800 km² mainly occupied by cropland (90% of the land use). The region's climate is
128 humid subtropical (Cfa) according to Koppen's (1984) climate classification, with rainfall well
129 distributed throughout the year. Annual rainfall varies between 1750 and 2000 mm, with the
130 heaviest rainfall events taking place in spring (from September to December). The soils are
131 highly weathered and deep (2-5 meters), originating from basalt formations.

132 **Figure 1** - Location of the Conceição River catchment in Southern Brazil.

133 The main soil classes found in the catchment are Ferralsols and Nitisols (FAO, 2014),
134 which are rich in iron and kaolinite oxides and, less frequently, Acrisols and Leptosols. The
135 relief of the region is characterized by long hillslopes (300 to 600 m), characterised by convex
136 curvatures, with sediment deposits occurring in the lower section of the slopes. The slopes are
137 smooth at the top (6-9%) and more pronounced (10-14%) in the vicinity of the river systems.

138 The use of pesticides in the region is guided by the agronomic recommendations related to
139 the production of transgenic soybean and winter crops for soil cover, as well as for cattle feeding
140 (oats and ryegrass), or for wheat production. The agronomic recommendations are made by the
141 agrochemical resellers who are regulated by the proficient class council. The instructions of the
142 government's agricultural department through extension workers are limited, in that many
143 employees do not act directly in recommending pesticides.

144 In the months prior to the study (i.e. September to December 2016), glyphosate (2 x 2.5 L
145 ha⁻¹), 2,4-D (1.5 L ha⁻¹), simazine (5 L ha⁻¹), imidacloprid (120 ml ha⁻¹) and carbendazim (0.5
146 L ha⁻¹), were used for soybean cultivation (85% of the area), as well for phytosanitary treatment.
147 In January/February 2017, this crop received additional applications of carbendazim (0.5 L ha⁻¹)
148 ¹), imidacloprid (120 mL ha⁻¹), tebuconazole (0.5 L ha⁻¹), tetraconazole (0.5 L ha⁻¹),
149 trifloxystrobin (0.4 L ha⁻¹) and propiconazole (100 mL ha⁻¹). Not all of these fungicides are

150 used in soybean cultivation, but between 3 and 5 treatments are performed for general disease
151 control.

152 After the soybean harvest (March/April-2017), the areas remained under fallow for 40
153 days and then (in May/June-2017), glyphosate (2.5 L ha⁻¹), 2,4 - D (1.5 L ha⁻¹), simazine (5 L
154 ha⁻¹), imidacloprid (120 ml ha⁻¹) were again used to sow the winter crops (wheat/oats - 70% of
155 the area). Later (in June, July and August 2017), imidacloprid (120 ml ha⁻¹), carbendazim (0.5
156 L ha⁻¹), tebuconazole (0.5 L ha⁻¹), tetraconazole (0.5 L ha⁻¹), trifloxystrobin (0.4 L ha⁻¹) and
157 propiconazole (100 ml ha⁻¹) were used for phytosanitary treatments. For the cultivation of
158 wheat, 2 to 3 treatments are carried out and, for oats, at least one application was made, for
159 disease control.

160 In August and September 2017, pesticides were used as glyphosate (2 x 2.5 L ha⁻¹), 2,4
161 - D (1.5 L ha⁻¹), simazine (5 L ha⁻¹), imidacloprid (120 ml ha⁻¹) during the maize crop cycle
162 (5% of the area). Furthermore, from September to December 2017, glyphosate (2 x 2.5 L ha⁻¹),
163 2,4 - D (1.5 L ha⁻¹), simazine (5 L ha⁻¹), imidacloprid (120 ml ha⁻¹) and carbendazim (0.5 L ha⁻¹)
164 ¹), were used again to implement the 2017/2018 soybean crop, using the same sequence of
165 pesticides and crops as in 2017. The soybean sowing window can be wide, as it will depend on
166 the previous crop (wheat/oats) as well as the type of cultivar.

167 **2.2 Hydro-sedimentary monitoring**

168 The hydro-sedimentary dynamics of this catchment have been monitored since 2011.
169 The monitoring strategy was based on rainfall-runoff events using automatic equipments
170 (measuring water level and turbidity) and assisted by manual sample collections with a high
171 frequency during events and at fixed intervals between the events. The variables monitored
172 automatically were precipitation, river water level and turbidity at ten-minute intervals. Then,
173 these data were converted into suspended sediment concentrations (SSC), which were

174 integrated throughout time to calculate the sediment yield (Porterfield, 1977; Didoné et al.,
175 2014).

176 The flow rate was obtained by measuring the water level with a pressure limnigraph and
177 converted into a flow rate using the key curve height/discharge conducted by the National Water
178 Agency (ANA). The SSC was measured with a DH48-type sampler at variable intervals during
179 significant events during both the rising and falling limbs of the flood. Duplicate water samples
180 were collected during the events, one was used for the determination of the SSC through the
181 methodology of Shreve & Downs (2005), and the other for pesticide analysis. In addition to
182 manual sampling, the use of a turbidimeter increased the temporal resolution of the SSC
183 measurements. It was calibrated using simultaneously measured SSC data (Merten et al. 2013).
184 More information on monitoring techniques and their applications are provided by Didoné
185 (2015, 2017).

186 During the monitoring period (2011-2018) of the Conceição River catchment, an
187 average of eight significant rain events were monitored each year, which contributed on average
188 to 70% of the total annual sediment flux. For this study, pesticides were monitored during eight
189 of the main events that occurred during the thirteen-month period of interest (from January
190 2017 to January 2018; Tab. 1).

191 **Table 1** - Events monitored for pesticide analysis

192 *2.3 Sampling strategy for pesticide analysis*

193 Pesticides were analyzed in the collected water and suspended sediment samples.
194 Samples were also collected during low-water stages between events to characterize fluxes
195 during periods when river flow is mainly supplied with sub-surface and underground water.

196 Two strategies were used to monitor pesticides in water and suspended sediments
197 samples, considering variations in river water flow during the events. For the quantification of
198 pesticides, the variability of the concentration of substances in water and suspended sediments

199 was also considered. Water samples were collected with a DH48 sampler (Carvalho, 1994) at
200 a distance of two meters from the channel bank. The samples comprised the integration of the
201 vertical variability of the water depth (top-bottom) with depth between 1 - 3 meters according
202 to the river discharge of the event. The samples were always collected at the same location
203 during the different campaigns. Water samples were collected by combining four 300 mL sub-
204 samples collected during each event. The collected water was added in "amber type" bottles
205 with a capacity of 400 mL, and the samples were kept at temperatures below 5 °C and sent for
206 laboratory analysis. Suspended sediment sampling was done using 20 liter containers that were
207 allowed to settle for 10 days, and then overlying water was siphoned in order to obtain the
208 sediments. Resulting suspended sediment was then dried for analysis.

209 Individual samples were grouped after examining the hydrograph (water flow $\text{m}^3 \text{s}^{-1}$)
210 and sedigraph (sediment SSC g L^{-1}) of each event. The samples were grouped according to the
211 analysis of the liquid and solid discharges considering the values of these variables during the
212 event as a whole. The suspended sediment samples were grouped and dried in an oven with
213 forced air circulation at a temperature of 40 °C for evaporation of the water, until obtaining dry
214 sediment. The drying time to obtain the sediment varied between 2-3 days. After water
215 evaporation, the suspended sediment was immediately removed from the oven. The suspended
216 sediments were crushed and sieved to 2 mm for subsequent analysis.

217 In addition, sediment deposit was also collected and analyzed at the foot of the hillslope.
218 The area is located at coordinates 28°26' 55"S and 53°55'32 "O, with a clayey texture soil
219 (>45%) and an organic matter content of 1.2% (fig. 1). It is estimated that the sedimentary
220 layers of this site were deposited during the last 30 years and originated from erosion of the
221 upslope agricultural areas. In this case, the strategy was to characterize the pesticides in a
222 deposit, which is representative of material transported by erosion, before it reached the
223 drainage systems, as it can be remobilized during future events. The profile was sectioned into

224 four layers: 0-20; 20-40; 40-60 and 60-70 cm, then the samples were processed (sieved and
225 dried) and sent to the laboratory for pesticide analysis.

226 **2.4 Analysis of pesticides in water**

227 The water samples were analyzed in the Pesticide Residue Analysis Laboratory (LARP-
228 UFSM). The analytical solutions for each standard were prepared individually at a
229 concentration of 0.1 g L⁻¹ in HPLC grade methanol. These solutions were stored in amber glass
230 bottles at -20 °C (Ferrer et al., 2011).

231 In order to reduce the matrix effect, the water samples were vacuum-filtered in cellulose
232 acetate or nylon membrane (0.45 µm) (Lazartigues et al., 2011) and kept under refrigeration at
233 4 °C. For pesticide multiresidue determination in water samples, a solid phase extraction (SPE)
234 was performed based on the methods described by Lazartigues et al. (2011) and Donato et al.
235 (2015), with a Phenomenex StrataTM X 33 µm cartridge (6 mL/200 mg). The cartridges were
236 conditioned using acetonitrile (2 mL), methanol (2 mL) and ultrapure water (2 mL). A water
237 sample of 200 mL was percolated, then the cartridge was washed with water (3 mL) and dried
238 for 20 min with air flow. The analytes were eluted with methanol (1 mL), acetonitrile (1 mL)
239 and water (1 mL). After extraction, the samples were analyzed for 70 pesticides by liquid
240 chromatography with tandem mass spectrometry (LC-MS/MS). Validation parameters obtained
241 using spiked blank water samples are presented in table 6 in in Supplementary Material.

242 For the determination of glyphosate and AMPA in water, NaOH extract and FMOC (9-
243 fluorenylmethoxycarbonyl) derivation were used. The compounds were identified by
244 comparing retention times, against a reference standard (Martins-Júnior, 2009).

245 To determine the loads of the respective pesticides in the water during the events, their
246 concentrations were multiplied by the respective river water flows. Accordingly, it was possible
247 to quantify the loads of pesticides during each monitored event.

248 **2.5 Analysis of pesticides in deposited sediment and suspended sediments**

249 Deposited sediment samples were analyzed for glyphosate and AMPA at the
250 Laboratoire Santé Environnement Hygiène de Lyon (CARSO-France), while the other
251 pesticides in suspended sediments were analyzed in LARP-UFSM.

252 For pesticide multiresidue determination in soil and sediment samples, 10 ± 0.1 g of the
253 samples dry were weighed directly into polypropylene centrifuge tubes with a capacity of 50
254 mL and extracted using a modified QuEChERS method (Martins et al., 2014; Kemmerich et
255 al., 2015). Afterwards, the samples were agitated for 20 sec in vortex. After this step, 10 mL of
256 acetonitrile containing 1% acetic acid were added, shaking manually and vigorously for 1 min.
257 In the sequence, anhydrous magnesium sulphate (3.0 g) and anhydrous sodium acetate (1.7 g)
258 were added to the tubes. The tubes were then shaken manually for about 1 min and centrifuged
259 at 4000 rpm for 8 min. Afterwards, 1 mL of the supernatant was transferred to a 2 mL vial and
260 analyzed by LC-MS/MS (Köck-Schulmeyer et al., 2013). Validation parameters obtained using
261 spiked blank soil and sediment samples are presented in table 7 and in Supplementary Material.

262 The determination of glyphosate and AMPA in sediments was performed by liquid
263 chromatography with fluorimetric detection after a derivatization step. The compounds were
264 identified by comparing retention times, in a characteristic wavelength pair, against a reference
265 standard (Ghanem et al., 2007; Lacina et al., 2012).

266 From the determination of the respective pesticide concentrations in suspended
267 sediment during the monitored events, the sediment discharges were integrated throughout time
268 to calculate the sediment yield of each event. It was then possible to quantify the fluxes of
269 particle-bound pesticides for each event monitored.

270 **3 Results and discussion**

271 **3.1 Hydro-sedimentary dynamics**

272 Eight events were monitored, and pesticides were detected in half of them. For three
273 events, pesticides were only detected in water, whereas they were detected in suspended

274 sediment only for one event. The hydrological conditions that prevailed during the study period
275 were affected by the magnitude of rainfall-runoff events. Figure 2 indicates the variable
276 magnitude of the events that occurred over the year, and their respective impact on the increase
277 in the river level.

278 **Figure 2** - Representation of the hietograph, hydrograph and sedigraph of the eight
279 monitored events E₁ to E₈.

280 As observed (Fig. 2), there was much variability of event characteristics during the
281 hydrological year. They are associated with contrasted liquid/solid discharges that can be
282 influenced by several independent hydrologic processes, which affect in turn water flows and
283 suspended sediment supply to rivers.

284 Weather conditions, topography and agricultural management practices, among others,
285 may affect the fate of pesticides in the environment (Spadotto et al., 2004). The volume,
286 intensity and frequency of rainfall have a great influence on the transportation and loss of
287 agrochemicals through runoff and the percolation of water in the soil.

288 The drainage of pesticides can be a direct process of contamination of surface water
289 (Aguiar et al., 2014). Authors such as Fernandes et al., 2019 and Rheinheimer et al., 2020 warn
290 of pesticide contamination of water sources, and their implication in long distance and hillslope
291 transport that favors runoff. Furthermore, Queiroz et al., (2011) state that the runoff process is
292 more prominent in situations where rainfall intensity is much higher than the soil's capacity to
293 absorb water. From this runoff formation dynamics, the pollution process begins with the
294 agrochemicals following the mass flow, and this is in line with some physical-chemical
295 characteristics of the active substance of each product (Castro et al., 2006).

296 The runoff formed on the surface captures the soluble or adsorbed pesticides in the
297 transportable solids (Aguiar et al., 2014). In addition, another form of surface water
298 contamination may occur through product leaching, which by proximity to the water beds,

299 combined with favourable topography and intrinsic soil conditions, can reach the river and
300 generate a point source of pollution (Rheinheimer et al., 2020).

301 **3.2 Identification of pesticides in water and sediment**

302 For the events monitored, several pesticides used on crops grown during the year were
303 detected in the river (Tab. 2). This indicates that there is an annual flow of different molecules
304 being transported from agricultural fields to water courses dissolved in runoff and/or associated
305 with eroded sediments.

306 **Table 2** - Evaluation of water, suspended sediment and pesticide losses during the
307 monitored events.

308 The detection of pesticides was variable from one flood event to the next depending on
309 the event monitored (Fig. 2 and Tab. 2) and it varied with the seasons throughout the year.
310 Pesticide substances were only detected during half of the events whereas no substances were
311 found at all during four events, neither in water nor in suspended sediment. This can likely be
312 related to the dynamics of each pesticide in the environment, as well as to factors related to its
313 application, land use, soil management, runoff generation, sediment redistribution processes
314 and connectivity between hillslopes and river systems. The combination of all these factors can
315 likely explain the presence/absence of a pesticide in the environment for longer or shorter time
316 periods.

317 **3.3 Intra-event and inter-event variability of pesticide detection**

318 Pesticides were detected in four of the eight monitored events. In the event monitored
319 on April 24 (fig. 3), only imidacloprid was found with maximum concentrations of $0.180 \mu\text{g L}^{-1}$.
320 ¹. After the soybean harvest in April, pesticide use on cropland is low, as the implementation
321 of winter crops only starts in May, which lasts for the entire month of June.

322 **Figure 3** - Monitoring of imidacloprid in water during the event of April 24, 2017.

323 During the rising stage of the event, the highest concentration of sediments occurred when
324 the water flow reached its maximum level. Later, during the recession stage, the sediment load
325 was reduced. Thus, the maximum sediment flow occurred before the maximum water flow. In
326 the event shown in Figure 3, imidacloprid was found in water, and its highest concentrations
327 occurred during the highest water flow. During the recession of events with lower flows, this
328 pesticide was not detected showing the occurrence of a strong intra-event variability.

329 The presence of pesticides in the water and sediments in suspension originates from soil
330 erosion. Pesticides can also be transported through terrestrial/underground water flow,
331 especially for the most hydrophilic pesticides. Many of these compounds found in water are
332 considered hydrophilic and are expected to be transported in the dissolved phase. In addition,
333 leaching to aquifers can be amplified due to the precipitation regime in these areas (Kevin and
334 Victor, 2014).

335 The movement of pesticides in water in clayey soils is very slow due to the small porosity
336 and reduced water transport capacity. However, these soils have a good bacterial load that
337 contributes to the degradation of these compounds (Aguiar et al., 2017). In general, the
338 compounds are transported by surface and groundwater flows, both in soluble form and
339 adsorbed in colloidal particles (Chesnaux and Allen, 2008).

340 During the event that occurred on May 13, 2017 (80 mm rainfall), the 2,4-D molecule
341 was detected in water (fig. 4). During this event, different concentrations of 2,4-D were found
342 in water at different water flows, with maximum levels of 1.2 microgram per liter ($\mu\text{g L}^{-1}$).

343 **Figure 4** - Monitoring of 2,4-D pesticide in water during a rain event on May 13, 2017.

344 Due to the initial growing stage of crops with a low soil cover associated with soil
345 compaction, a large volume of water and suspended sediment was generated and supplied to
346 river systems with maximum water flows of 150 and 260 $\text{m}^3 \text{s}^{-1}$ respectively in May and June

347 (Fig. 4 and 5). For the May event the maximum concentration of 2,4-D in water was $1.1 \mu\text{g L}^{-1}$
348 $^{-1}$ (Fig. 4).

349 In early June when an intensified use of pesticides occurred, other compounds were
350 found in suspended sediments. For the event monitored on June 7, 2017 (fig. 5), the presence
351 of two pesticides in suspended sediment, glyphosate and its metabolite AMPA, were detected.

352 **Figure 5** - Monitoring of the glyphosate pesticide and its AMPA metabolite in suspended
353 sediments during the event of June 7, 2017.

354 Glyphosate and its metabolite AMPA were detected in June during event E₅ (Fig. 5). This
355 period coincides with the beginning of wheat sowing in the region, which is associated with the
356 use of this pesticide. Another factor is the mild temperature observed in autumn, which reduces
357 water evaporation and favors pesticide persistence in the soil for a longer period. This can be
358 observed during event E₅ of 123 mm (June) that resulted in a maximum water flow of 284 m^3
359 s^{-1} , in response of extensive runoff, leading to a high sediment yield (19.7 t km^{-2}) (tab. 2). This
360 favored the detection of the glyphosate pesticide and its metabolite AMPA at the catchment
361 outlet, although at low levels. The maximum concentrations of glyphosate and AMPA in
362 suspended sediments were 1.0 and $1.6 \mu\text{g kg}^{-1}$, respectively (fig.5). Again, the maximum
363 sediment flow occurred before peak flows, and sampling should be intensified during the event
364 rising stage for monitoring pesticides in sediments. This is illustrated in Figure 5 where
365 glyphosate was detected in the sediment during the sediment flow recession, but not in the water
366 flow recession.

367 The high adsorption coefficients of glyphosate and AMPA on solid particles may be
368 responsible for the fact that the substances were only found in suspended sediment although not
369 in water. Another factor that should be considered is the different properties of pesticides
370 persisting in different ways in the environment. In general, chemical degradation,
371 photochemical reactions and biodegradation may provide the main pathways of pesticide

372 degradation on the soil surface (Sparks, 2003; Capel et al., 2008). These complex dynamics of
373 pesticides in the environment can be observed in Table 2, with the detection of different
374 molecules during the monitored year.

375 Fernandes et al., (2019) detected concentrations of glyphosate and AMPA in epilithic
376 biofilms and showed that they varied with the season (from 90 to 305 $\mu\text{g kg}^{-1}$ for glyphosate
377 and from 50 to 240 $\mu\text{g kg}^{-1}$ for AMPA, in fall and spring, respectively) and that they were
378 strongly influenced by the amount of herbicide applications. In the current research, these
379 compounds were only detected during a single event (Fig. 5) at maximum concentrations of 1.1
380 and 1.8 $\mu\text{g kg}^{-1}$ for glyphosate and AMPA, respectively. Sampling techniques were different in
381 the study of Fernandes et al., (2019), who considered a combined intra- and inter-event period
382 that was characterised by concentrations of up to 670 times greater than in the current study.
383 Already, Lima et al., (2020) monitored an agricultural catchment and analyzed water and
384 passive sampling (Polar Organic Chemical Integrative Sampler – POCIS) collection. They
385 detected the same pesticides as in the current research, with similar concentrations of 2,4-D,
386 simazine, carbendazim, tebuconazole and imidacloprid. It is important to point out that the
387 methods used by Fernandes et al. (2019) and Lima et al. (2020) were different from those used
388 in the current study, and each method has its own advantages and drawbacks. In addition,
389 different topographic contexts were investigated in these studies.

390 During another similar event that occurred in October 2017 (Fig. 6) the pesticides 2,4-D,
391 simazine tebuconazole, tetraconazole, trifloxystrobin, propiconazole, carbendazim and
392 imidacloprid were detected in the water. A much larger number of compounds was detected
393 during this event that took place in October 2017 compared to the previous events (Fig. 6).

394 **Figure 6** - Monitoring of 2,4-D pesticides, simazine, tebuconazole, trifloxystrobin
395 tetraconazole, propiconazole carbendazim and imidacloprid in water during the event E₆ of
396 October 10, 2017.

397 The imidacloprid was detected again in event (E₆) with a concentration of 0.15 µg L⁻¹ on
398 October 10, 2017 (Fig. 6C). This pesticide is generally used almost exclusively in soybean
399 cultivation in January/February when this crop is at the stage of grain formation to control
400 different species of bed bugs (*Nezara viridula*; *Euschistus heros*; *Piezodorus guildinii*).
401 Imidacloprid persisted in the environment until October well after the harvest that took place
402 in March/April (Fig. 6C). Furthermore, it is also used to a lesser extent in winter crops, in the
403 early stages of oat/wheat development in May and June.

404 Regarding tetraconazole belonging to the triazole substance group, it has been widely used
405 in Southern Brazil to combat soybean rust and it is generally combined with the pesticides of
406 the azoxystrobin group. The presence of this pesticide was detected in samples collected in
407 October 2017 in the current research (Fig. 6A), and it may be associated with its use for wheat
408 cultivation, or it may originate from soybean areas cultivated in the period from December to
409 March.

410 Another pesticide found was tebuconazole at maximum concentrations of 0.10 µg L⁻¹ in
411 October 2017 (Fig. 6B). The tebuconazole is recommended by ANVISA to be used for soybean
412 cultivation, which may explain its persistence in water even longer periods after its use (Fig.
413 6).

414 **3.4 Impacts of runoff and erosion on pesticide contamination**

415 When dissolved or particle-bound pesticides were detected during events, their
416 occurrence was confirmed during different flood stages (Figs. 3, 4, 5 and 6). Pesticides were
417 found both in water and in suspended sediment regardless of variations in water flow rates
418 and/or suspended sediment concentration (SSC), (Tab. 2). The occurrence of substances in
419 water and suspended sediment is event-driven and mainly dependent from erosion events
420 combined with the agricultural application schedule. Their detection during different periods
421 throughout the year (Tab. 2) confirms the need for establishing continuous monitoring

422 programmes in order to take into account the impact of both rainfall seasonality and the calendar
423 of farming practices throughout the year (Fig. 2). There is need for hydrological monitoring in
424 catchments of different scales (10^0 to 10^3 km²), because at these scales it is possible to better
425 understand the impact of agriculture on water resources. For this purpose, high frequency
426 monitoring of precipitation, water flow and concentration of suspended sediments is necessary.
427 In addition, monitoring the losses of solutes (fertilizers and pesticides) during the events must
428 consider the intra and inter-event variability.

429 Although in Brazil the use of pesticides is initiated in October before the sowing of the
430 spring/summer crops, the presence of imidacloprid during this event (E₆) may be related to the
431 control of aphids (*Metopolophium dirhodum*) and bedbugs (*Dichelops melacanthus*) in wheat
432 and oat crops.

433 For the E₅ June event (123 mm), the glyphosate and AMPA pesticides were detected in
434 suspended sediment, with respective exports of 0.012 and 0.025 kg (Tab. 3). These low levels
435 can be explained by the degradation processes of these compounds across the catchment. They
436 may interact with other compounds and organisms in the aquatic environment. As the
437 glyphosate molecule is strongly bound to soil colloids and is readily degraded by
438 microorganisms in the environment, the measurement of its levels in the soil is hampered by
439 the nature of their properties (Capel, et al., 2008; Manahan, 2013).

440 The event E₆ in October 2017 (Fig. 6) reflects the significant supply of runoff to the
441 river systems leading to the detection of higher concentrations of the pesticides tebuconazole,
442 simazine and 2,4-D (E₆). This is due to the more frequent use of pesticides for disease control
443 (e.g. tebuconazole) in winter crops (wheat and oats) during the previous months
444 (August/September). In addition to this, during this same period, areas are prepared for soybean
445 and corn plantation, for which simazine and 2,4-D herbicides are used. The highest 2,4-D
446 contamination was found in soybean and winter crop production areas. The occurrence of these

447 substances in water and suspended sediment is likely event-driven and mainly dependent on the
448 occurrence of erosion events combined with the agricultural application schedule as observed
449 in another agricultural catchment of Southern Brazil (Rheinheimer, et al., 2020; Lima et al.,
450 2020). In addition, these authors found a relationship between pesticide concentrations and the
451 size of the area considered, with the dominance of dissolved pesticide fractions at the catchment
452 outlet. This may explain the concentrations observed during the event E₅ characterised by
453 higher water flows but during which only two pesticides were detected, while during the event
454 E₆ characterised by lower water flows, a large diversity of pesticides was detected.

455 According to the European Union (EU) legislation, concentrations of individual
456 pesticides in drinking water should not exceed 0.1 µg L⁻¹, and the maximum concentration of
457 all compounds in a sample should not exceed 0.5 µg L⁻¹. In this sense, it is observed that the
458 samples collected in the Conceição River catchment did not meet the drinking water standards
459 according to the European legislation. Following the ordinance 2.914/2011 that establishes the
460 potability parameters for drinking water in Brazil, the concentrations of Simazine e.g. found in
461 all the samples analysed in the current research did not exceed the maximum limit allowed (2
462 µg L⁻¹), and therefore respected the Brazilian legislation. A comparison between European and
463 Brazilian toxicity limit references of the main pesticides observed in the Conceição River basin
464 is provided in Table 8 in the Supplementary Material.

465 It was observed that the coincidence of the pesticide application period with the
466 monitoring of erosion rainfall-runoff event is crucial to detect these substances. Accordingly,
467 monitoring during high flow periods is not sufficient, as regular monitoring should also be
468 conducted taking into consideration the timing of pesticide application. This observation is also
469 confirmed by data provided in Tables 2 and 3, where the Q_{max} and Q₀ are lower during E₆
470 compared to other events (e.g. in June - E₅) with higher water flows. The event (E₆) with water
471 flow and sediment yield 44 and 22 % lower in relation to the event maxims (E₅), represents the

472 highest amount of substance detected. Increased humidity may cause an increased risk of
473 various fungal diseases, so that this situation may require additional pesticide applications.
474 Accordingly, an indirect risk for transport via sediment movement may occur, and add to the
475 direct risk of contamination due to spray drift (Fernandes et al., 2019).

476 The mean runoff coefficient in the Conceição river catchment was estimated to 6 %
477 (Didoné t al., 2014). The main sources of suspended sediment are cropland areas corresponding
478 to 60 % of sediment production (Tiecher et al., 2018). We can therefore infer that among the
479 total quantities of pesticides used in the crops, only a small fraction is transported to the river
480 system, with 0.006 % reaching the outlet for the monitored events. The quantification of
481 pesticides in suspended sediment at the catchment outlet may be complicated by the long
482 transport times and biotic/abiotic degradation processes. Rheinheimer et al., (2020) who
483 monitored different locations within an agricultural catchment observed that pesticide levels
484 vary across the catchment with different concentrations observed at the outlet compared to
485 upper locations. Lima et al., (2020) observed the same behavior in secondary tributaries.
486 Suspended sediment transiting at the outlet during the event of interest did not necessarily travel
487 directly from the cropland to the outlet, and they may instead consist of material deposited at
488 the footslopes and resuspended during the event. In contrast to particle-bound substances,
489 pesticides in water are transported much faster across the catchment.

490 Although most soils of the Conceição River catchment show a relatively low sensitivity
491 to erosion due to the high clay content ($> 400 \text{ g kg}^{-1}$ clay), the strong soil compaction, as well
492 as the low vegetation cover observed in a large part of the catchment have accelerated erosion
493 processes as well as water and pollutant water flows in rivers.

494 After the crop harvesting, soils are left uncultivated (during two months) ~until the next
495 crop. Furthermore, in some fields, the use of animals (cattle) in winter reduces the vegetation
496 cover. It is during this period that crop residues offer the lowest soil cover and increase the

497 potential for erosion. However, overall, the implementation of no-till practices results in a
498 denser vegetation cover than other tillage practices (e.g. conventional plow). This has further
499 contributed to the reactivity with which events can impact water flow rates as observed in
500 October (fig. 6 - A, B, C). Furthermore, the increase in rainfall recorded in October (Tab. 2;
501 Fig.6) generated extensive runoff and suspended sediment transport, and pesticides were likely
502 transported to the river systems during this period. This is consistent with October being the
503 period with the highest rainfall volumes in the region based on rainfall records for the last 50
504 years (Embrapa, 2012). The average rainfall erosivity index for the region is 8,800 MJ mm ha-
505 1 h-1 (Cassol et al., 2007), which reflects the rainfall-runoff events.

506 Overall, according to Carneiro et al., (2015) and Di Souza & Da Silva, (2016) only 20%
507 of the amount of pesticides used in crops can reach surface waters, but in practice this
508 proportion is relatively low due to the occurrence of mechanisms (e.g. adsorption) limiting the
509 mobility of pesticide molecules in the soil. Other mechanisms include the variability of
510 transports depending on the scale considered, the presence of riparian forests and the installation
511 of conservation measures which may impact pesticide transport rates in the environment. To
512 reduce these effects, appropriate agricultural techniques should be applied for the conservation
513 of these resources, such as terracing, contour lines, no-till and crop rotation (Didoné et al.,
514 2015). All these measures reduce runoff and also erosion, which are the main modes of pesticide
515 transport. Soil and crop management, in addition to runoff control practices, is indicated as the
516 best alternative for controlling pesticide pollution (Bertoluzzi et al. 2006; Silva et al. 2011).

517 **3.5 Estimation of the flux of pesticides associated with suspended sediment and dissolved** 518 **in water**

519 Based on water and sediment discharges, the export of different pesticides in water and
520 suspended sediments was calculated. The variability and the temporal dynamics of water and
521 suspended sediment flows and pesticide concentrations for each event were considered. From

522 the pesticide concentrations determined at the measured time flows (water and sediment), the
523 pesticide concentrations with the discharges (liquid/solid) over time were integrated to calculate
524 the loads of pesticides. The loads are presented in Table 3 with the calculation of these loads
525 both in water and sediment.

526 **Table 3** - Quantification of pesticides found in water and suspended sediments.

527 It is important to note that the delivery of pesticides to the river systems occurs
528 differently when associated with sediments. This depends on the ability of the rainfall-runoff
529 events to transport suspended sediment over long distances. When these compounds may be
530 found in water, their occurrence is detected on multiple occasions during the agricultural year.

531 When quantifying the pesticides in water (Tab. 3), values of 7.3 and 2.9 kg were found
532 for imidacloprid, after the occurrence of 140 and 123 mm in April (E₃) and October (E₆),
533 respectively. When analysing the events of May (E₄) and October (E₆), with respective
534 precipitations of 80 and 123 mm, losses of 13.3 and 15.7 kg of 2,4-D in water were quantified
535 (Tab. 3). However, no pesticides in suspended sediments were detected, which also probably
536 reflects their chemical properties. For instance, 2,4-D is a very weakly sorbing compound with
537 a very low K_{oc} (Tab. 4). It is therefore not surprising that it was not found adsorbed to
538 suspended solids. This indicates that even during major rainfall events, the dynamics of
539 pesticides in suspended sediment may not follow that of water flows. The hydrophobic
540 pesticides have a low solubility adhering to lipophilic substances present in the aquatic system
541 and sediments. Concentration of soluble pesticides in water, is generally low, partly due to the
542 effect of dilution (Inoue et al., 2006; Cabrera et al., 2008).

543 Sediment sorption and desorption processes act as the main pesticide retention processes
544 for hydrophobic pesticides (Ramsey et al. 2005; Inoue et al., 2006). Sorption and desorption
545 are dynamic processes in which molecules are continuously transferred between the solution
546 and the soil surface. The different intermolecular forces that can attract molecules at the

547 interface and subsequently retain them at the surface are hydrophobic bonds, hydrogen bonds,
548 van der Waals forces, and ionic and covalent bonds, depending on the type of existing soil
549 colloids (Inoue et al. 2006; Oliveira Jr. and Regitano, 2009). This can explain why pesticides
550 may remain in the environment for weeks or even months after their application (Gibbons et
551 al., 2015).

552 **3.6 Occurrence of pesticides in sediment deposits**

553 In the sediment deposition profile, two compounds were found (Tab. 4) including
554 carbendazim (0-20 cm) and AMPA (0-70 cm). AMPA was detected at relatively high
555 concentrations of 222 $\mu\text{g kg}^{-1}$ up to 70 cm depth.

556 **Table 4** - Evaluation of pesticides in a deposited sediment profile at the bottom of a
557 cultivated hillslope.

558 The detection of pesticides in sediment deposits at the bottom of the hillslopes can be
559 explained by the accumulation of sediments over the years, which is accelerated by the absence
560 of soil conservation practices implemented in the region (Tab. 4). Furthermore, a fraction of the
561 pesticide applied may have migrated vertically with water through the soil profile. The most
562 plausible explanation for the absence of glyphosate in the sediment layers may be related to its
563 higher rate of degradation in the environment through the action of light, temperature and
564 microorganisms.

565 In a comparative study between leaching and surface losses of glyphosate in agricultural
566 soils, Queiroz et al., (2011) proved that the greatest losses occurred through leaching, especially
567 during erosive rainfall early after the application of the product. Although the preferential flow
568 is mainly vertical, the fact that torrential rains occurred may have caused clogging of the soil
569 macropores, facilitating the formation of surface runoff. In this way, it can be inferred that the
570 occurrence of AMPA found down to 70 cm depth (Tab. 4) can be due to leaching through the
571 profile as well as to sediment deposition over time.

572 Regarding carbendazim (Tab. 4), although its sorption coefficient (K_{oc}) is much lower
573 than that of AMPA, its detection in the upper deposited sediment layer only may be due to the
574 frequency/time of its use. In addition, the vegetation cover may have prevented a greater contact
575 with the soil, favoring its degradation in this environment, which limited its movement through
576 the profile. This demonstrates that the concentrations of these compounds can be similar in
577 agricultural environments, but changes in concentrations can occur at different observation
578 scales (Keesstra et al., 2018, Lima et al., 2020). The monitoring conducted in the current
579 research demonstrates that pesticide mobilization does not depend only on the amount and time
580 of application, but also on the hydrological processes that control the dynamics of intra and
581 inter-event water flow.

582 **4 Conclusions**

583 To be successful in detecting pesticides in catchments, sampling campaigns should be
584 conducted with a sufficient frequency in order to capture the seasonality of rainfall events (both
585 intra and inter-event variations) and their impact on the variations of liquid/solid discharges in
586 river systems. The calendar of pesticide use throughout the year should also be taken into
587 account to cover periods of increased pesticide use in agricultural areas.

588 A strong connection was found between the applied chemicals and those found in the
589 receiving systems after rainfall-runoff events. This relationship cannot be explained by
590 individual events alone, but it is instead controlled by the succession of events, in addition to
591 underground water flow regime.

592 The highest concentrations of pesticides in water occurred during the rising stage of
593 events, which indicate that they mainly originate from runoff. Regarding the pesticide fraction
594 bound to sediment, it is also necessary to prioritize sediment collection during the rising stage
595 when pesticide is the most likely to be detected in sediment.

596 There is a connection between agrochemicals used during cultivation and those detected
597 in water flow, indicating that current soil conservation practices are insufficient to limit water,
598 sediment and pesticide transfers from hillslopes to the river systems. To limit this potential
599 supply of pesticides to the river systems, the implementation of effective soil conservation
600 practices concerted at the catchment scale is recommended in order to limit water flow and
601 sediment connectivity and the associated pesticide transport across these intensively cultivated
602 landscapes.

603 Despite the absence of detection of AMPA and glyphosate at the outlet, AMPA was
604 detected in sediment deposits at the bottom of a hillslope showing the transport and persistence
605 of this metabolite in agricultural catchments. Among the total amount of pesticides used in the
606 crops, only 0.006 % reached the outlet mainly under dissolved form in water, and an even lower
607 fraction was found to be associated with sediments. An exception to this finding is the detection
608 of AMPA in deep sediment deposits.

609 The monitoring of the highest flow events showed that they were not characterised by
610 the highest pesticide transports. More detailed studies are needed to establish technical
611 guidelines for further limiting pesticide residue levels found in the environment in order to
612 conserve soil and water resources. To this end, there is a need for hydrological monitoring in
613 catchments of different scales to better understand the impact of pesticide use on the quality of
614 water resources. High frequency monitoring of hydro-sedimentary variables is required to
615 quantify the losses of solutes (fertilizers and pesticides) considering both intra and inter-event
616 variability.

617 **Declarations**

618 **Ethical Approval**

619 Not applicable.

620 **Consent to Participate**

621 Not applicable.

622 **Consent to Publish**

623 Not applicable.

624 **Authors Contributions**

625 The author Elizeu Jonas Didoné, developed the study in the field and wrote the first
626 version of the manuscript. He also made the corrections proposed by the reviewers.

627 The author Jean Paolo Gomes Minella, helped in the interpretation of the data and made
628 technical suggestions for the new version of the manuscript.

629 The author Tales Tiecher, read and made scientific suggestions relevant to the manuscript.

630 The author Renato Zanella, read and made scientific suggestions relevant to the
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632 The author Osmar Damian Prestes, read and approved the final manuscript

633 The author Olivier Evrard, read and corrected English technical terms in addition to
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636 The authors made relevant technical and scientific contributions to the manuscript. All
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642 **Competing Interests**

643 The authors declare that they have no competing interests" in this section.

644 **Availability of data and materials**

645 All data generated or analysed during this study are included in this published article (and
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926

Figure 1

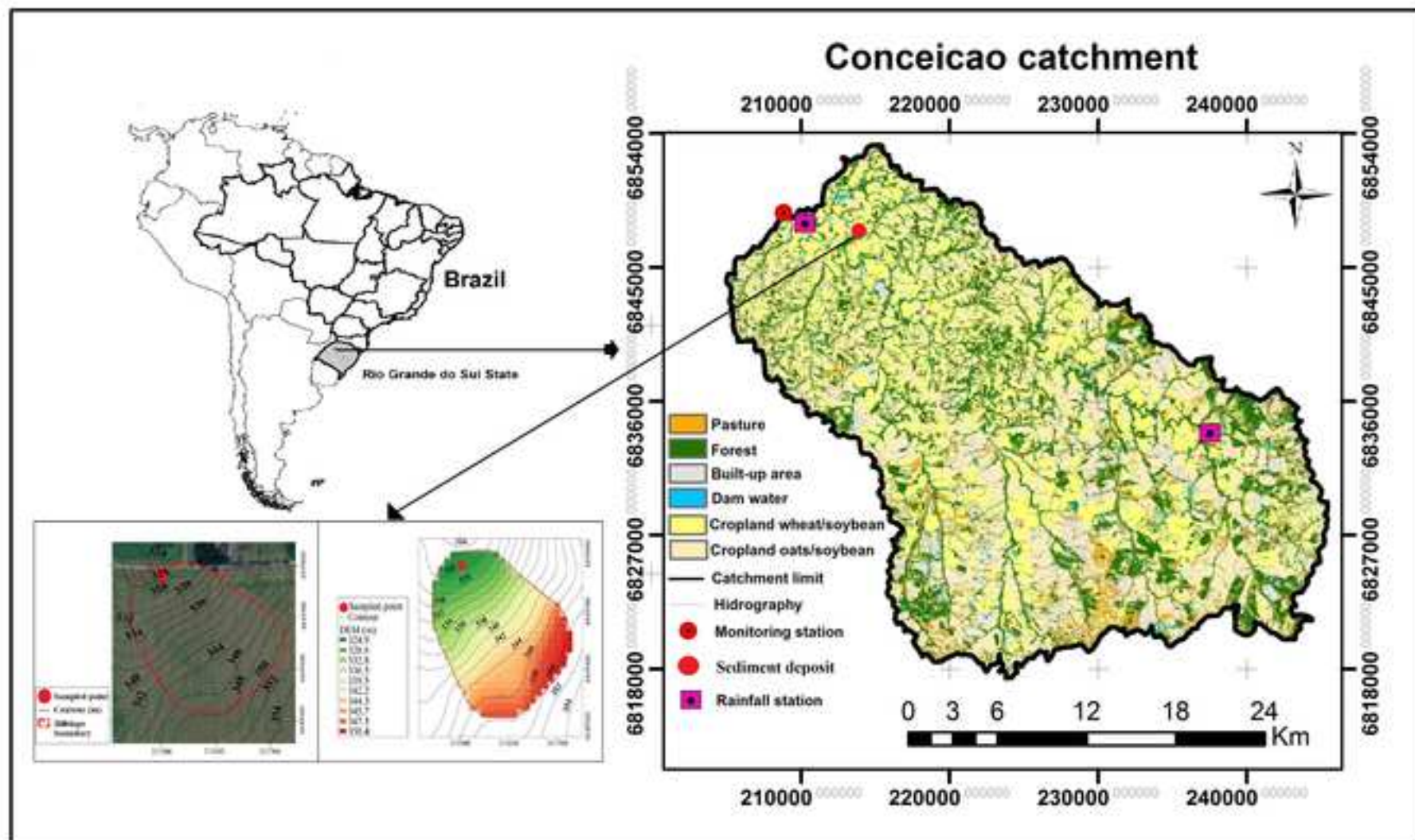


Figure 2

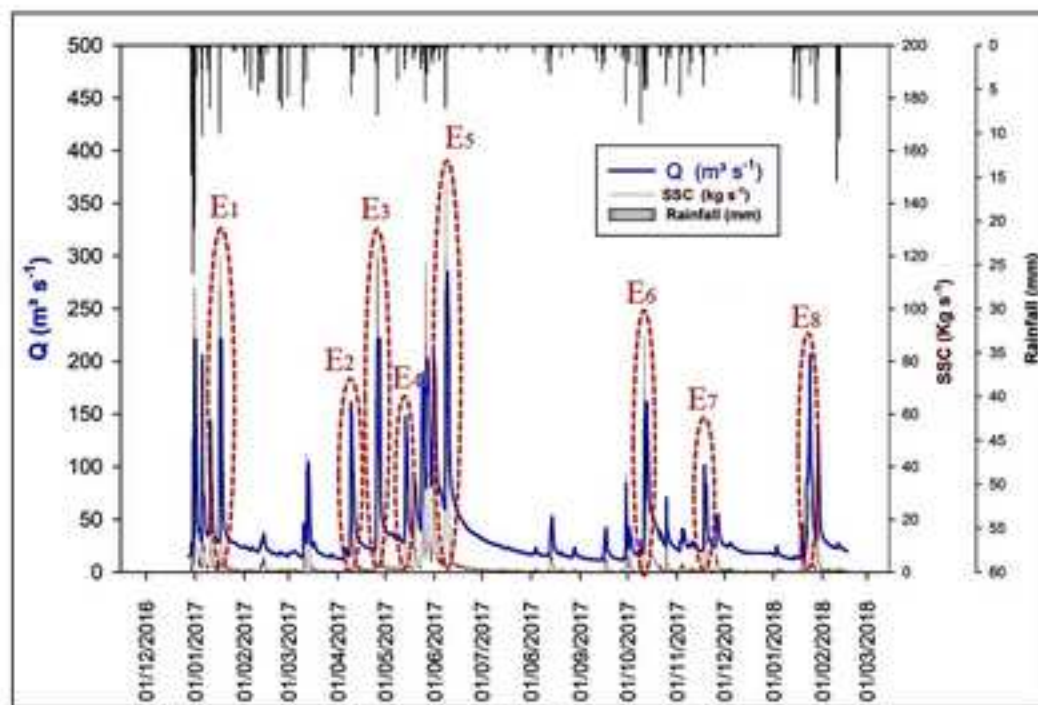


Figure 3

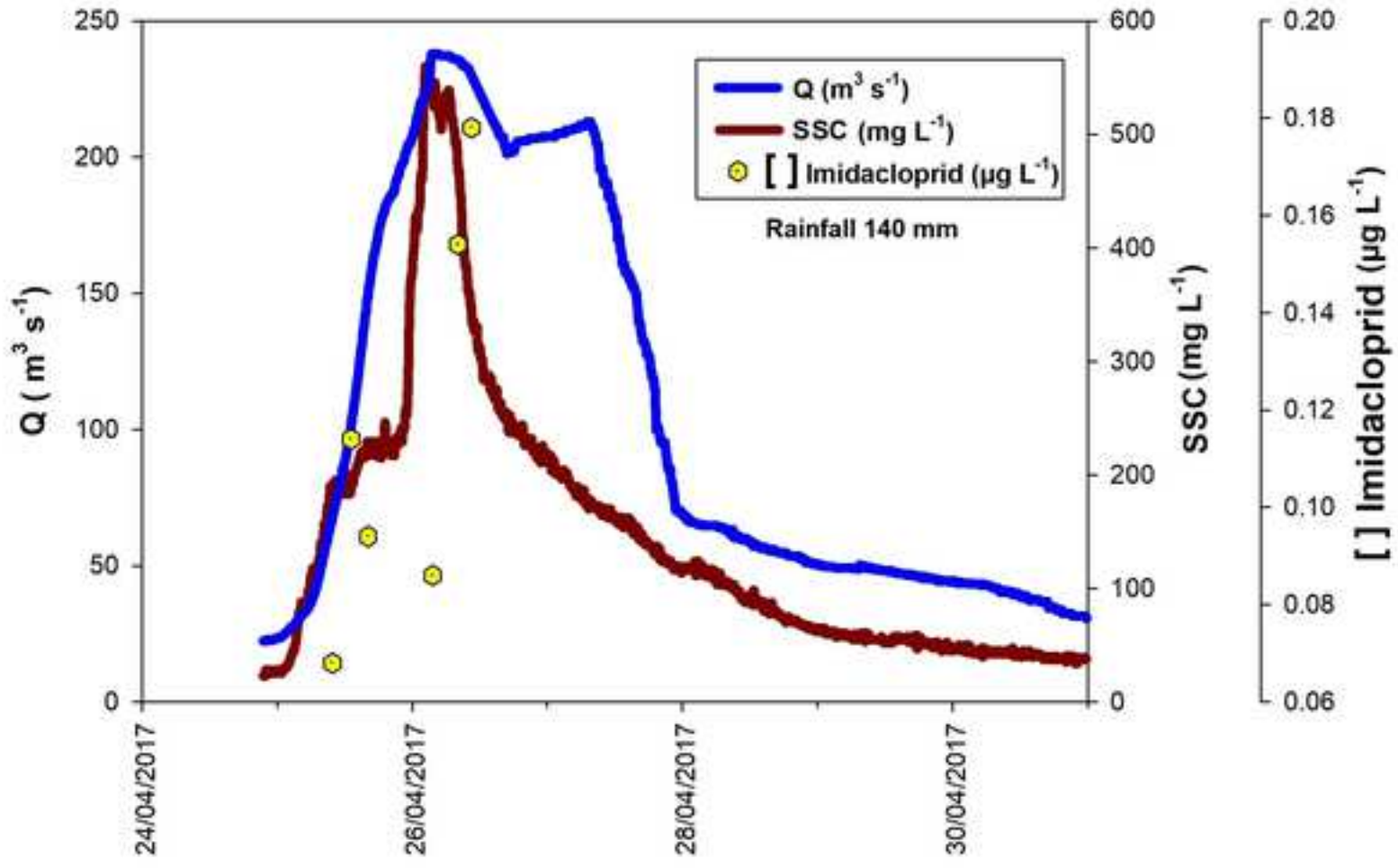


Figure 4

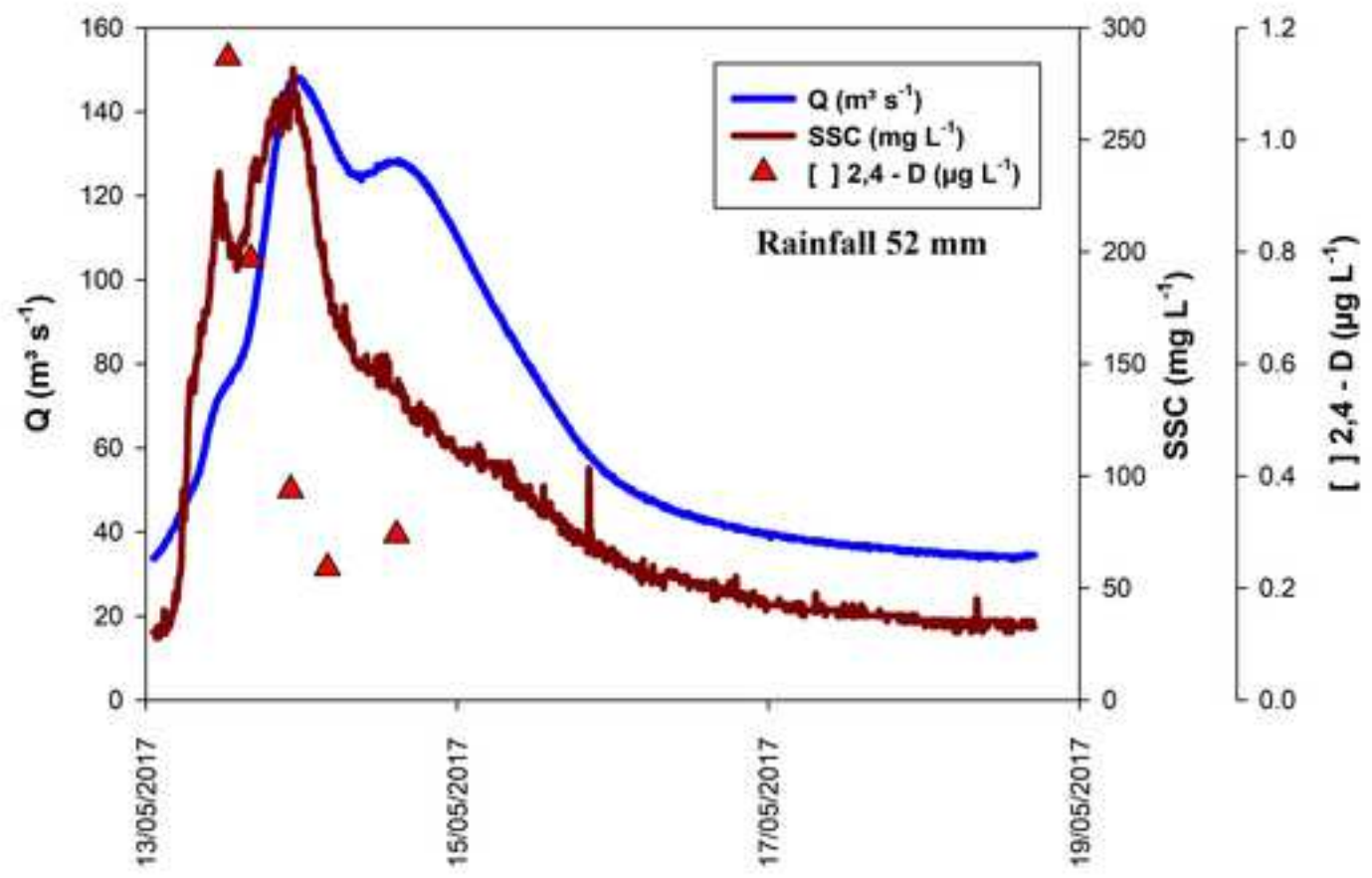


Figure 5

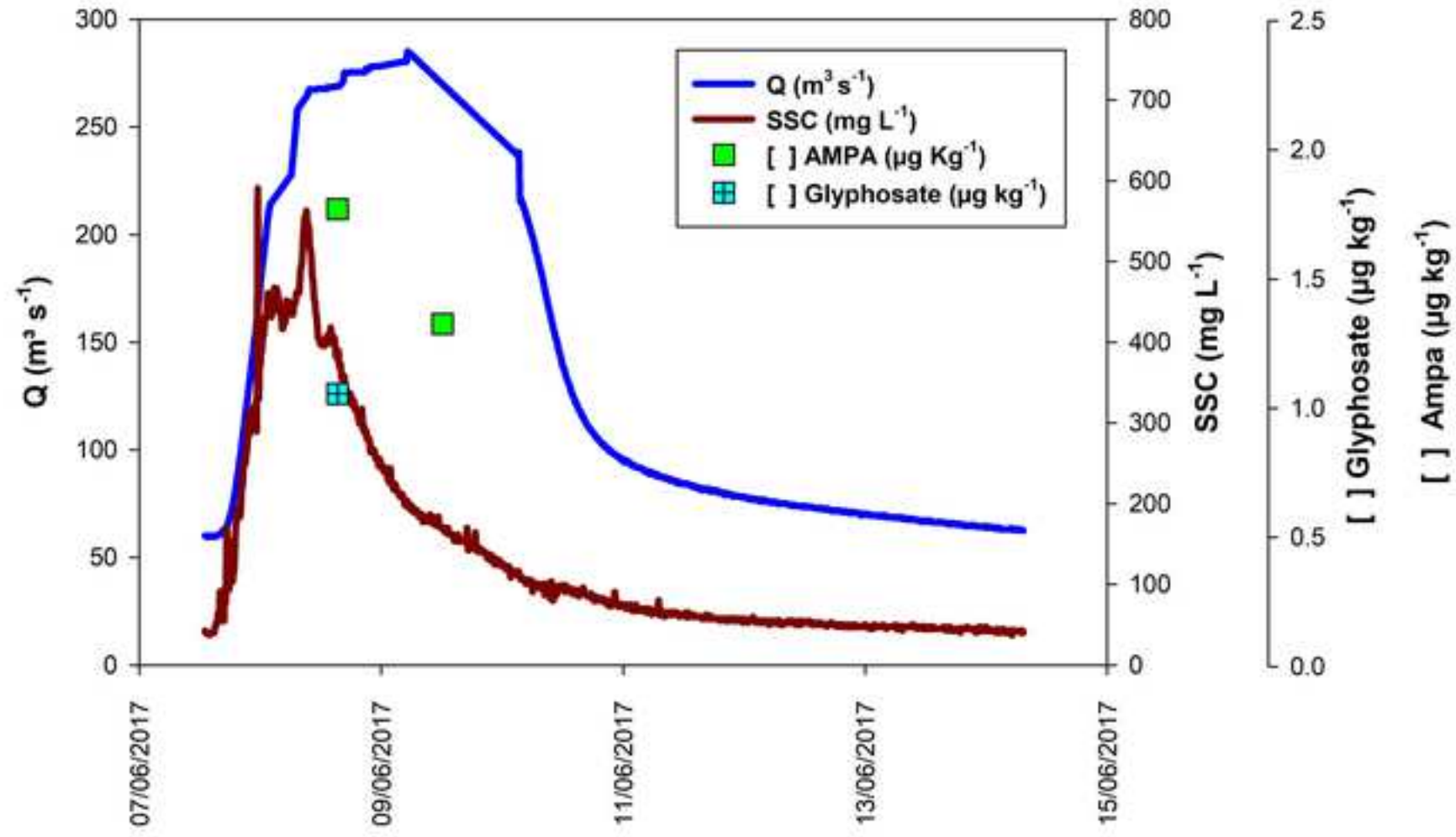


Figure 6A

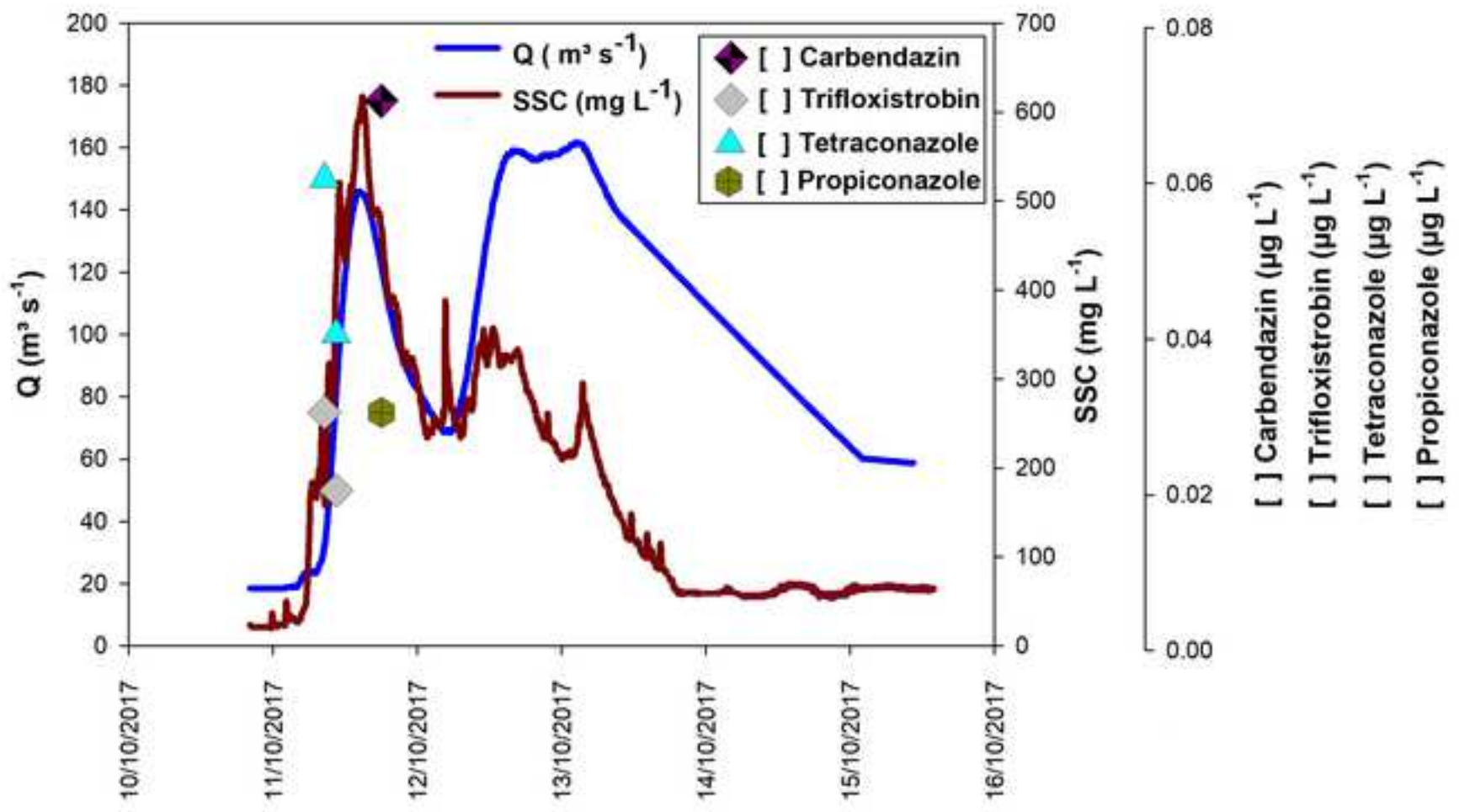


Figure 6B

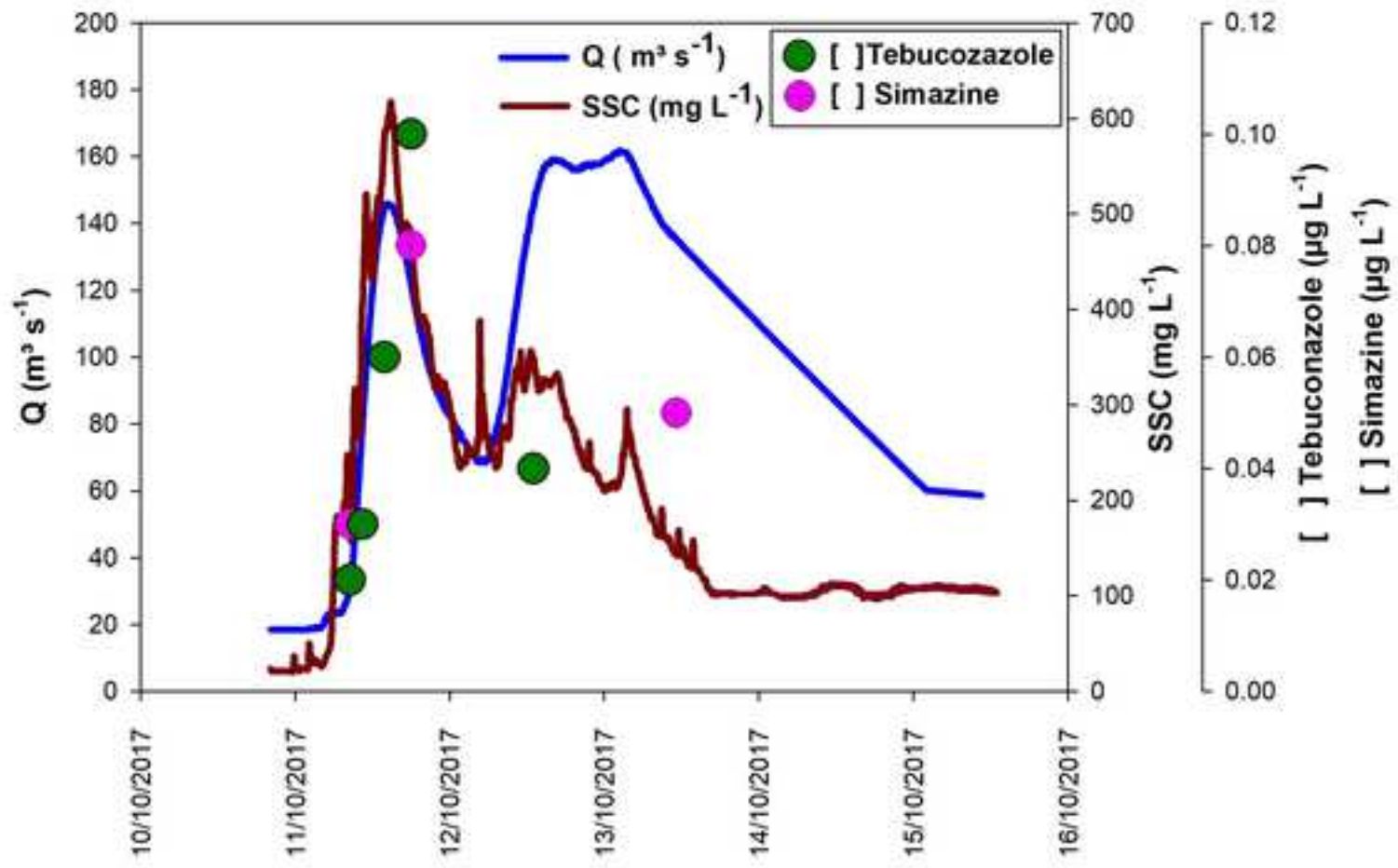


Figure 6C

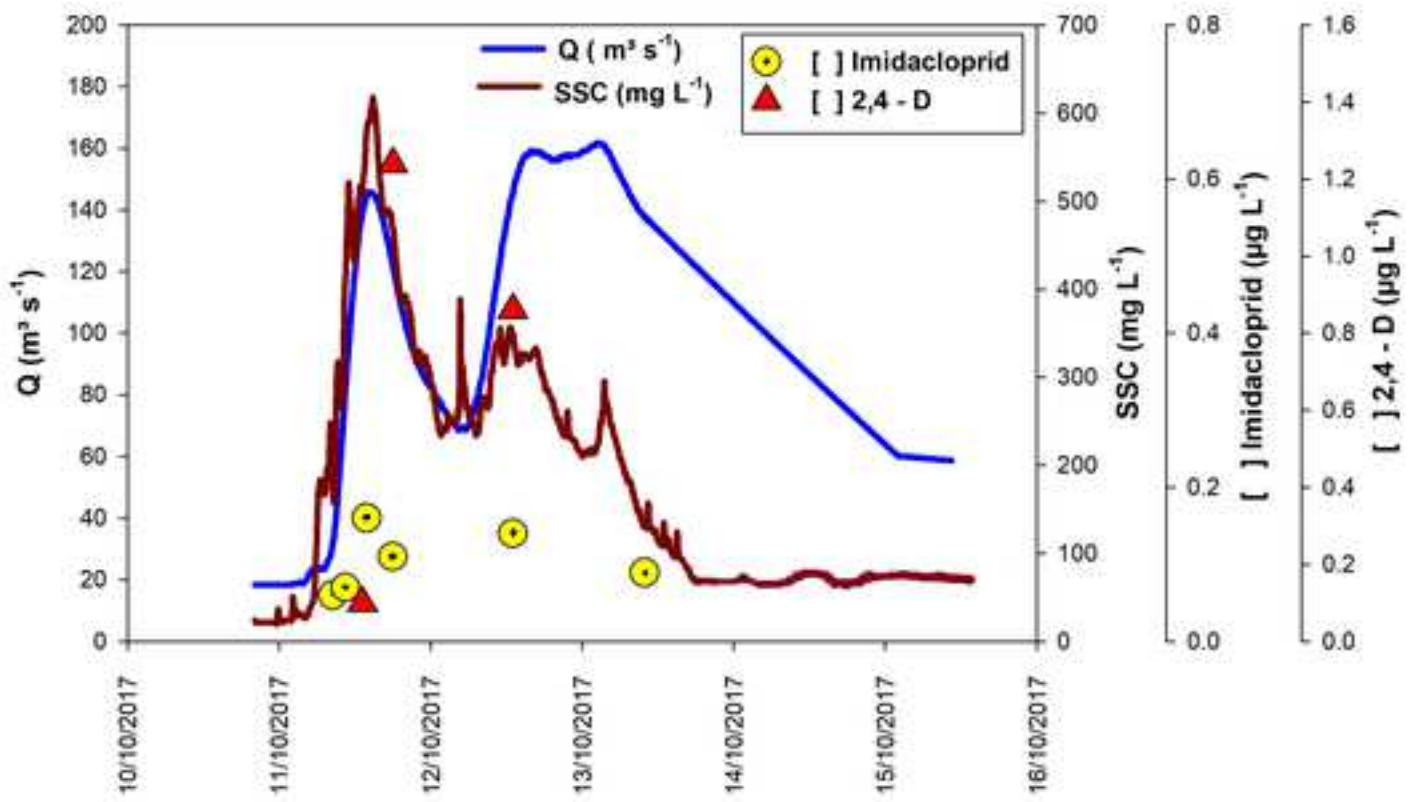


Figure Captions

Figure 1 - Location of the Conceição River catchment in Southern Brazil.

Figure 2 - Representation of the hietograph, hydrograph and sedigraph of the eight monitored events E₁ to E₈.

Figure 3 - Monitoring of imidacloprid in water during the event of April 24, 2017.

Figure 4 - Monitoring of 2,4-D pesticide in water during a rain event on May 13, 2017.

Figure 5 - Monitoring of the glyphosate pesticide and its AMPA metabolite in sediments during the event of June 7, 2017.

Figure 6 - Monitoring of 2,4-D pesticides, simazine, tebuconazole, trifloxystrobin tetraconazole, propiconazole carbendazim and imidacloprid in water during the event E₆ of October 10, 2017.

Table 1 - Events monitored for pesticide analysis

Events	Time (hours)	R (mm)	Q _{Max} (m ³ s ⁻¹)	Sediment yield (SY) (t. km ⁻²)	% (SY) year	Number of water samples	Number of sediment samples
E ₁ - 16/01/17	83	85	220.3	10.9	8.1	3	10
E ₂ - 09/04/17	100	119	160.7	5.0	3.7	3	12
E ₃ - 24/04/17	140	140	221.8	13.2	10.0	6	20
E ₄ - 13/05/17	122	80	147.9	4.1	3.1	5	15
E ₅ - 07/06/17	156	123	284.6	19.7	14.7	5	23
E ₆ - 10/10/17	138	123	161.7	11.7	8.7	6	25
E ₇ - 25/11/17	109	45	54.8	1.1	0.8	3	17
E ₈ - 23/01/18	106	68	206.7	4.5	3.1	6	23

R=Rainfall; Q=Flow rate; SY= Sediment yield

Table 2 - Evaluation of water, sediment and pesticide losses during the monitored events.

Events monitored	Ppt (mm)	SY (t km ⁻²)	Q _{Max} (m ³ s ⁻¹)	Pesticides detected	
				Water	Sediments
E ₁ - 16/01/2017	85	10.9	220.3	nd	nd
E ₂ - 09/04/2017	119	5.0	160.7	nd	nd
E ₃ - 24/04/2017	140	13.2	221.8	Imidacloprid	nd
E ₄ - 13/05/2017	80	4.1	147.9	2,4-D	nd
E ₅ - 07/06/2017	123	19.7	284.6	nd	AMPA
E ₆ - 10/10/2017	123	11.7	161.7	nd	Glyphosate
				2,4-D	nd
				Simazine	nd
				Tebuconazole	nd
				Tetraconazole	nd
				Trifloxistrobin	nd
				Propiconazole	nd
				Carbendazim	nd
				Imidacloprid	nd
				Simazine	nd
E ₇ - 25/11/2017	45	1.1	54.8	nd	nd
E ₈ - 23/01/2018	68	4.5	206.1	nd	nd

SY= Sediment yield; Q Max = Maximum flow; nd = not detected

Table 3 - Quantification of pesticides found in water and suspended sediments

Events monitored	Q₀ (m³ s⁻¹)	Pesticides detected	Quantity associated with water (kg)	Quantity associated with sediments (kg)
E ₁ - 16/01/2017	28.7	-	-	-
E ₂ - 09/04/2017	30.8	-	-	-
E ₃ - 24/04/2017	20.9	Imidacloprid	7.3	-
E ₄ - 13/05/2017	29.3	2,4-D	13.3	-
E ₅ - 07/06/2017	59.6	AMPA	-	0.025
		Glyphosate	-	0.012
E ₆ - 10/10/2017	17.7	2,4-D	15.7	-
		Simazine	5.6	-
		Tebuconazole	0.9	-
		Tetraconazole	0.3	-
		Trifloxistrobin	0.1	-
		Propiconazole	0.2	-
		Carbendazim	0.5	-
		Imidacloprid	2.9	-
E ₇ - 25/11/2017	23.8	-	-	-
E ₈ - 23/01/2018	28.2	-	-	-

Q₀= Initial flow; E_{1,2,3 ...}= Events monitored

Table 4 - Evaluation of pesticides in a sediment deposition profile at the bottom of a hillslope.

Depth (cm)	0-20	20-40	40-60	60-70	*Sorption coeficiente (koc) mL g ⁻¹	*Half-lives (Persistence in the soil- days)
	----- Levels of detected pesticides (µg kg ⁻¹) -----					
AMPA	315	2016	226	225	500-5000	119-958
Carbendazim	64	-	-	-	200	350

*Barceló and Hennion, 1997