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Abstract

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

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

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

1 Introduction

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

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

The main crops responsible for the high consumption of agrochemicals are soybean, corn, sugarcane, cotton and rice (SINDIVEG, 2015). Given the associated potential for environmental contamination, studies involving the analysis of pesticide residues demonstrated their occurrence in food (ANVISA, 2016), in the atmosphere (Moreira, et al., 2012; Majewski et al., 2014), in rainfall water (Nogueira et al., 2012; Lima et al., 2020), in soils (Baumgartner et al., 2017; Rheinheimer et al., 2020), in surface and groundwater (Dores et al., 2008), in ocean water (Mercurio et al., 2014), in epilithic biofilms (Fernandes et al., 2019), in fish (Clasen et al., 2018), and even in breast milk (Palma et al., 2014). However, the environmental and human health effects of such exposure will depend on both the level of exposure and the concentration of the substance (Kuperman, et al., 2009; Schäfer & Bundschuh, 2018). Furthermore, in recent years, the removal of riparian vegetation that acted as a natural buffer to trap runoff and sediment originating from cropland may have enhanced the transport of pesticides to water bodies (Becker et al., 2009; Bastos et al., 2018, Fernandes et al., 2019).

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

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

In the Conceição River catchment, the main summer crop is soybean (Glycine max) while, in winter, wheat (Triticum spp.), oats (Avena strigosa) or ryegrass (Lolium multiflorium) are the most widespread crops. Soil management is characterized by no-till planting in more than 85% of the cultivated areas. However, the abandonment of mechanical runoff control practices (e.g. terraces), the implementation of soybean monoculture without crop rotation, the low soil cover achieved by previous crop residues (~ 4 Mg ha^{-1} yr^{-1} of dry matter), and the excessive and uncontrolled traffic of agricultural machinery lead to soil degradation with reduced water infiltration into the soil, thereby increasing runoff and erosion generation (Didoné et al., 2015). In addition, the hydrologically fragile areas are increasingly used for agricultural activities, with riparian forests of insufficient width and following the drainage of wetlands that have lost their functions of runoff buffer and sediment trap. The more detailed effectiveness of conservation systems used in this catchment has been investigated in previous studies conducted by Didoné et al. (2015, 2017).

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

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

2 Methodology

2.1 Study area

The study was conducted in the Conceição River catchment (Fig. 1), located in the northwest part of Rio Grande do Sul, the southernmost state of Brazil. The river monitoring station is located at coordinates 28°27'22 "S and 53°58'24 "W. The catchment has a drainage area of 800 km^2 mainly occupied by cropland (90% of the land use). The region's climate is humid subtropical (Cfa) according to Koppen's (1984) climate classification, with rainfall well distributed throughout the year. Annual rainfall varies between 1750 and 2000 mm, with the heaviest rainfall events taking place in spring (from September to December). The soils are highly weathered and deep (2-5 meters), originating from basalt formations.

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

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

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

In the months prior to the study (i.e. September to December 2016), glyphosate (2 x 2.5 L ha^{-1}), 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}), were used for soybean cultivation (85% of the area), as well for phytosanitary treatment. In January/February 2017, this crop received additional applications of carbendazim (0.5 L ha^{-1}), imidacloprid (120 mL ha^{-1}), tebuconazole (0.5 L ha^{-1}), tetraconazole (0.5 L ha^{-1}), trifloxystrobin (0.4 L ha^{-1}) and propiconazole (100 mL ha^{-1}). Not all of these fungicides are used in soybean cultivation, but between 3 and 5 treatments are performed for general disease control.

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

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

2.2 Hydro-sedimentary monitoring

The hydro-sedimentary dynamics of this catchment have been monitored since 2011. The monitoring strategy was based on rainfall-runoff events using automatic equipments (measuring water level and turbidity) and assisted by manual sample collections with a high frequency during events and at fixed intervals between the events. The variables monitored automatically were precipitation, river water level and turbidity at ten-minute intervals. Then, these data were converted into suspended sediment concentrations (SSC), which were integrated throughout time to calculate the sediment yield (Porterfield, 1977; Didoné et al., 2014).

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

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

Table 1 - Events monitored for pesticide analysis

2.3 Sampling strategy for pesticide analysis

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

Two strategies were used to monitor pesticides in water and suspended sediments samples, considering variations in river water flow during the events. For the quantification of pesticides, the variability of the concentration of substances in water and suspended sediments was also considered. Water samples were collected with a DH48 sampler (Carvalho, 1994) at a distance of two meters from the channel bank. The samples comprised the integration of the vertical variability of the water depth (top-bottom) with depth between 1 - 3 meters according to the river discharge of the event. The samples were always collected at the same location during the different campaigns. Water samples were collected by combining four 300 mL sub-samples collected during each event. The collected water was added in "amber type" bottles with a capacity of 400 mL, and the samples were kept at temperatures below 5 ºC and sent for laboratory analysis. Suspended sediment sampling was done using 20 liter containers that were allowed to settle for 10 days, and then overlying water was siphoned in order to obtain the sediments. Resulting suspended sediment was then dried for analysis.

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

In addition, sediment deposit was also collected and analyzed at the foot of the hillslope. The area is located at coordinates 28°26' 55"S and 53°55'32 "O, with a clayey texture soil (>45%) and an organic matter content of 1.2% (fig. 1). It is estimated that the sedimentary layers of this site were deposited during the last 30 years and originated from erosion of the upslope agricultural areas. In this case, the strategy was to characterize the pesticides in a deposit, which is representative of material transported by erosion, before it reached the drainage systems, as it can be remobilized during future events. The profile was sectioned into four layers: 0-20; 20-40; 40-60 and 60-70 cm, then the samples were processed (sieved and dried) and sent to the laboratory for pesticide analysis.

2.4 Analysis of pesticides in water

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

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

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

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

2.5 Analysis of pesticides in deposited sediment and suspended sediments

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

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

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

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

3 Results and discussion

3.1 Hydro-sedimentary dynamics

Eight events were monitored, and pesticides were detected in half of them. For three events, pesticides were only detected in water, whereas they were detected in suspended sediment only for one event. The hydrological conditions that prevailed during the study period were affected by the magnitude of rainfall-runoff events. Figure 2 indicates the variable magnitude of the events that occurred over the year, and their respective impact on the increase in the river level.

Figure 2 - Representation of the hietograph, hydrograph and sedigraph of the eight monitored events E_1 to E_8.

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

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

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

The runoff formed on the surface captures the soluble or adsorbed pesticides in the transportable solids (Aguiar et al., 2014). In addition, another form of surface water contamination may occur through product leaching, which by proximity to the water beds, combined with favourable topography and intrinsic soil conditions, can reach the river and generate a point source of pollution (Rheinheimer et al., 2020).

3.2 Identification of pesticides in water and sediment

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

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

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

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

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

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

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

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

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

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

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

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

(Fig. 4 and 5). For the May event the maximum concentration of 2,4-D in water was 1.1 µg L^{-1} (Fig. 4).

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

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

Glyphosate and its metabolite AMPA were detected in June during event E_5 (Fig. 5). This period coincides with the beginning of wheat sowing in the region, which is associated with the use of this pesticide. Another factor is the mild temperature observed in autumn, which reduces water evaporation and favors pesticide persistence in the soil for a longer period. This can be observed during event E_5 of 123 mm (June) that resulted in a maximum water flow of 284 m^3 s^{-1}, in response of extensive runoff, leading to a high sediment yield (19.7 t km^{-2}) (tab. 2). This favored the detection of the glyphosate pesticide and its metabolite AMPA at the catchment outlet, although at low levels. The maximum concentrations of glyphosate and AMPA in suspended sediments were 1.0 and 1.6 µg kg^{-1}, respectively (fig.5). Again, the maximum sediment flow occurred before peak flows, and sampling should be intensified during the event rising stage for monitoring pesticides in sediments. This is illustrated in Figure 5 where glyphosate was detected in the sediment during the sediment flow recession, but not in the water flow recession.

The high adsorption coefficients of glyphosate and AMPA on solid particles may be responsible for the fact that the substances were only found in suspended sediment although not in water. Another factor that should be considered is the different properties of pesticides persisting in different ways in the environment. In general, chemical degradation, photochemical reactions and biodegradation may provide the main pathways of pesticide degradation on the soil surface (Sparks, 2003; Capel et al., 2008). These complex dynamics of pesticides in the environment can be observed in Table 2, with the detection of different molecules during the monitored year.

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

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

Figure 6 - Monitoring of 2,4-D pesticides, simazine, tebuconazole, trifloxystrobin tetraconazole, propiconazole carbendazim and imidacloprid in water during the event E_6 of October 10, 2017.

The imidacloprid was detected again in event (E_6) with a concentration of 0.15 µg L^{-1} on October 10, 2017 (Fig. 6C). This pesticide is generally used almost exclusively in soybean cultivation in January/February when this crop is at the stage of grain formation to control different species of bed bugs (*Nezara viridula; Euschistus heros; Piezodorus guildinü*). Imidacloprid persisted in the environment until October well after the harvest that took place in March/April (Fig. 6C). Furthermore, it is also used to a lesser extent in winter crops, in the early stages of oat/wheat development in May and June.

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

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

3.4 Impacts of runoff and erosion on pesticide contamination

When dissolved or particle-bound pesticides were detected during events, their occurrence was confirmed during different flood stages (Figs. 3, 4, 5 and 6). Pesticides were found both in water and in suspended sediment regardless of variations in water flow rates and/or suspended sediment concentration (SSC), (Tab. 2). The occurrence of substances in water and suspended sediment is event-driven and mainly dependent from erosion events combined with the agricultural application schedule. Their detection during different periods throughout the year (Tab. 2) confirms the need for establishing continuous monitoring programmes in order to take into account the impact of both rainfall seasonality and the calendar of farming practices throughout the year (Fig. 2). There is need for hydrological monitoring in catchments of different scales (10^0 to 10^3 km^2), because at these scales it is possible to better understand the impact of agriculture on water resources. For this purpose, high frequency monitoring of precipitation, water flow and concentration of suspended sediments is necessary. In addition, monitoring the losses of solutes (fertilizers and pesticides) during the events must consider the intra and inter-event variability.

Although in Brazil the use of pesticides is initiated in October before the sowing of the spring/summer crops, the presence of imidacloprid during this event (E_6) may be related to the control of aphids (*Metopolophium dirhodum*) and bedbugs (*Dichelops melacanthus*) in wheat and oat crops.

For the E_5 June event (123 mm), the glyphosate and AMPA pesticides were detected in suspended sediment, with respective exports of 0.012 and 0.025 kg (Tab. 3). These low levels can be explained by the degradation processes of these compounds across the catchment. They may interact with other compounds and organisms in the aquatic environment. As the glyphosate molecule is strongly bound to soil colloids and is readily degraded by microorganisms in the environment, the measurement of its levels in the soil is hampered by the nature of their properties (Capel, et al., 2008; Manahan, 2013).

The event E_6 in October 2017 (Fig. 6) reflects the significant supply of runoff to the river systems leading to the detection of higher concentrations of the pesticides tebuconazole, simazine and 2,4-D (E_6). This is due to the more frequent use of pesticides for disease control (e.g. tebuconazole) in winter crops (wheat and oats) during the previous months (August/September). In addition to this, during this same period, areas are prepared for soybean and corn plantation, for which simazine and 2,4-D herbicides are used. The highest 2.4-D contamination was found in soybean and winter crop production areas. The occurrence of these substances in water and suspended sediment is likely event-driven and mainly dependent on the occurrence of erosion events combined with the agricultural application schedule as observed in another agricultural catchment of Southern Brazil (Rheinheimer, et al., 2020; Lima et al., 2020). In addition, these authors found a relationship between pesticide concentrations and the size of the area considered, with the dominance of dissolved pesticide fractions at the catchment outlet. This may explain the concentrations observed during the event E_5 characterised by higher water flows but during which only two pesticides were detected, while during the event E_6 characterised by lower water flows, a large diversity of pesticides was detected.

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

It was observed that the coincidence of the pesticide application period with the monitoring of erosion rainfall-runoff event is crucial to detect these substances. Accordingly, monitoring during high flow periods is not sufficient, as regular monitoring should also be conducted taking into consideration the timing of pesticide application. This observation is also confirmed by data provided in Tables 2 and 3, where the Q_{max} and Q_0 are lower during E_6 compared to other events (e.g. in June - E_5) with higher water flows. The event (E_6) with water flow and sediment yield 44 and 22 % lower in relation to the event maxims (E_5), represents the highest amount of substance detected. Increased humidity may cause an increased risk of various fungal diseases, so that this situation may require additional pesticide applications. Accordingly, an indirect risk for transport via sediment movement may occur, and add to the direct risk of contamination due to spray drift (Fernandes et al., 2019).

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

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

After the crop harvesting, soils are left uncultivated (during two months) ~until the next crop. Furthermore, in some fields, the use of animals (cattle) in winter reduces the vegetation cover. It is during this period that crop residues offer the lowest soil cover and increase the potential for erosion. However, overall, the implementation of no-till practices results in a denser vegetation cover than other tillage practices (e.g. conventional plow). This has further contributed to the reactivity with which events can impact water flow rates as observed in October (fig. 6 - A, B, C). Furthermore, the increase in rainfall recorded in October (Tab. 2; Fig.6) generated extensive runoff and suspended sediment transport, and pesticides were likely transported to the river systems during this period. This is consistent with October being the period with the highest rainfall volumes in the region based on rainfall records for the last 50 years (Embrapa, 2012). The average rainfall erosivity index for the region is 8,800 MJ mm ha-1 h-1 (Cassol et al., 2007), which reflects the rainfall-runoff events.

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

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

Based on water and sediment discharges, the export of different pesticides in water and suspended sediments was calculated. The variability and the temporal dynamics of water and suspended sediment flows and pesticide concentrations for each event were considered. From the pesticide concentrations determined at the measured time flows (water and sediment), the pesticide concentrations with the discharges (liquid/solid) over time were integrated to calculate the loads of pesticides. The loads are presented in Table 3 with the calculation of these loads both in water and sediment.

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

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

When quantifying the pesticides in water (Tab. 3), values of 7.3 and 2.9 kg were found for imidacloprid, after the occurrence of 140 and 123 mm in April (E_3) and October (E_6), respectively. When analysing the events of May (E_4) and October (E_6), with respective precipitations of 80 and 123 mm, losses of 13.3 and 15.7 kg of 2,4-D in water were quantified (Tab. 3). However, no pesticides in suspended sediments were detected, which also probably reflects their chemical properties. For instance, 2,4-D is a very weakly sorbing compound with a very low Koc (Tab. 4). It is therefore not surprising that it was not found adsorbed to suspended solids. This indicates that even during major rainfall events, the dynamics of pesticides in suspended sediment may not follow that of water flows. The hydrophobic pesticides have a low solubility adhering to lipophilic substances present in the aquatic system and sediments. Concentration of soluble pesticides in water, is generally low, partly due to the effect of dilution (Inoue et al., 2006; Cabrera et al., 2008).

Sediment sorption and desorption processes act as the main pesticide retention processes for hydrophobic pesticides (Ramsey et al. 2005; Inoue et al., 2006). Sorption and desorption are dynamic processes in which molecules are continuously transferred between the solution and the soil surface. The different intermolecular forces that can attract molecules at the interface and subsequently retain them at the surface are hydrophobic bonds, hydrogen bonds, van der Waals forces, and ionic and covalent bonds, depending on the type of existing soil colloids (Inoue et al. 2006; Oliveira Jr. and Regitano, 2009). This can explain why pesticides may remain in the environment for weeks or even months after their application (Gibbons et al., 2015).

3.6 Occurrence of pesticides in sediment deposits

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

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

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

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

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

4 Conclusions

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

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

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

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

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

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

Declarations

Ethical Approval

Not applicable.

Consent to Participate

Not applicable.

Consent to Publish

Not applicable.

Authors Contributions

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

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

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

The author Renato Zanella, read and made scientific suggestions relevant to the manuscript.

The author Osmar Damian Prestes, read and approved the final manuscript

The author Olivier Evrard, read and corrected English technical terms in addition to helping in the preparation of the final version of the manuscript, as well as responses to reviewers.

The authors made relevant technical and scientific contributions to the manuscript. All authors read and approved the final manuscript

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Competing Interests

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

Availability of data and materials

All data generated or analysed during this study are included in this published article (and its supplementary information files).

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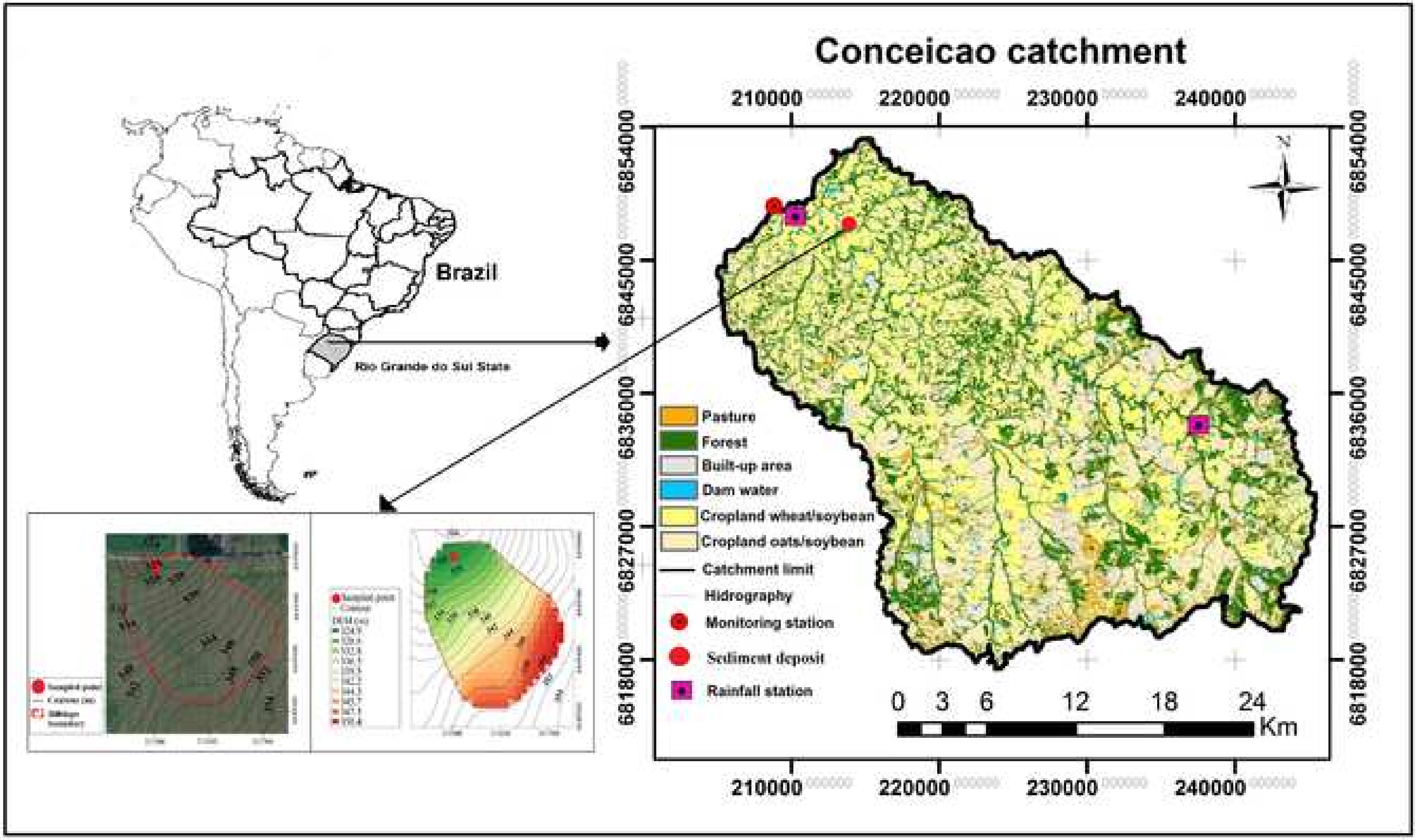
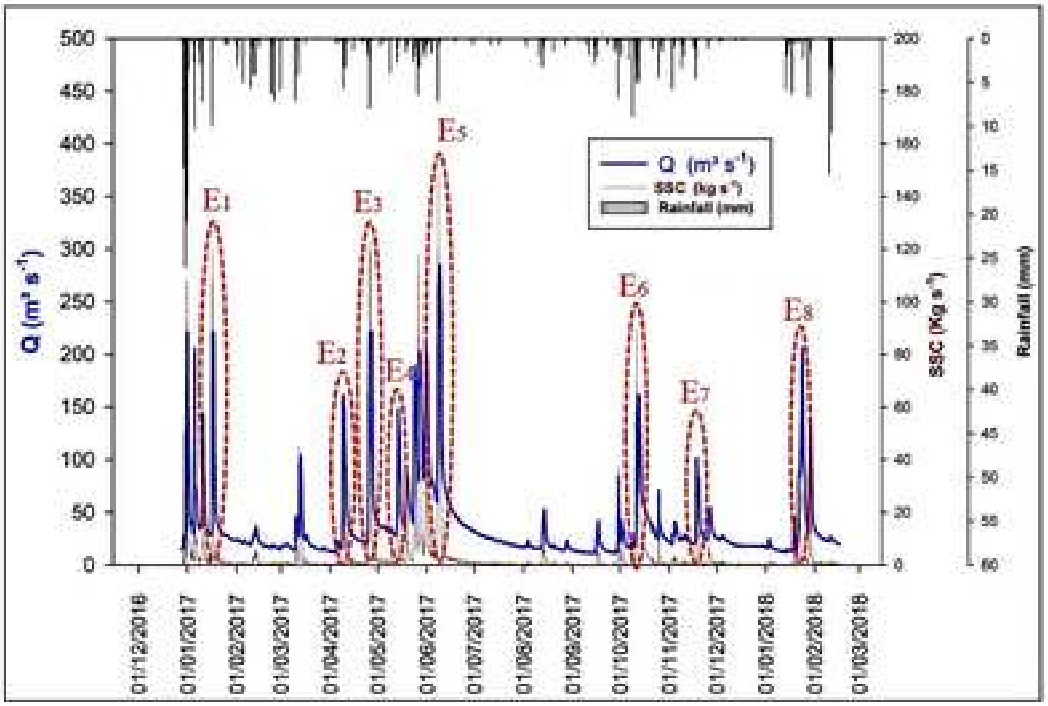
Figure 1



Conceicao catchment
Brazil
Rio Grande do Sul State
210000
220000
230000
240000
6854000
6845000
6836000
6827000
6818000
Pasture
Forest
Built-up area
Dam water
Cropland wheat/soybean
Cropland oats/soybean
Catchment limit
Hidrography
Monitoring station
Sediment deposit
Rainfall station
0 3 6 12 18 24
Km

Figure 2



Q (m³ s⁻¹)
SSC (Kg s⁻¹)
Rainfall (mm)
Q (m³ s⁻¹)
SSC (kg s⁻¹)
Rainfall (mm)
E1
E2
E3
E4
E5
E6
E7
E8
01/12/2016
01/01/2017
01/02/2017
01/03/2017
01/04/2017
01/05/2017
01/06/2017
01/07/2017
01/08/2017
01/09/2017
01/10/2017
01/11/2017
01/12/2017
01/01/2018
01/02/2018
01/03/2018

Figure 3

Click here to access/download;Figure;Figure 3.JPG

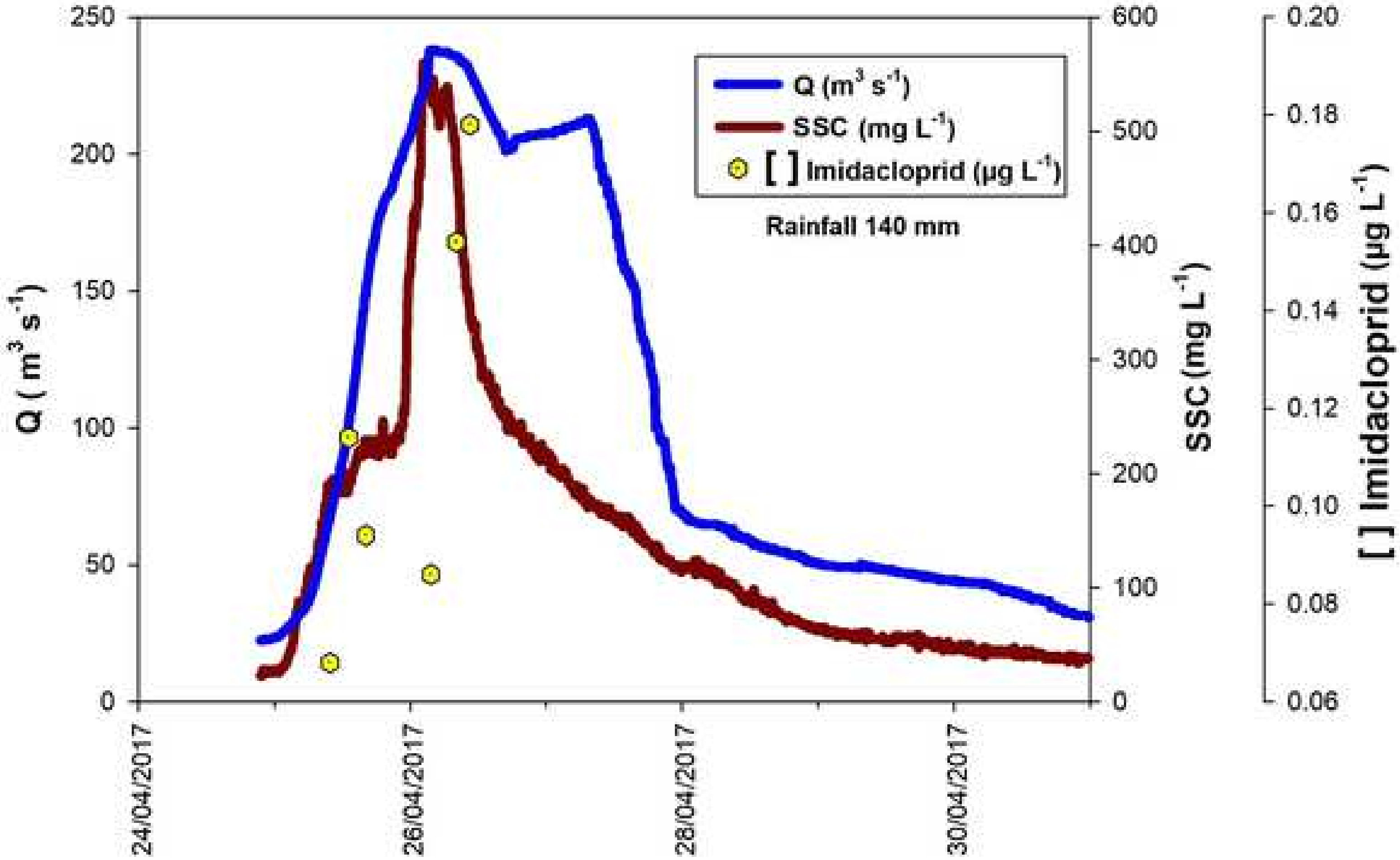
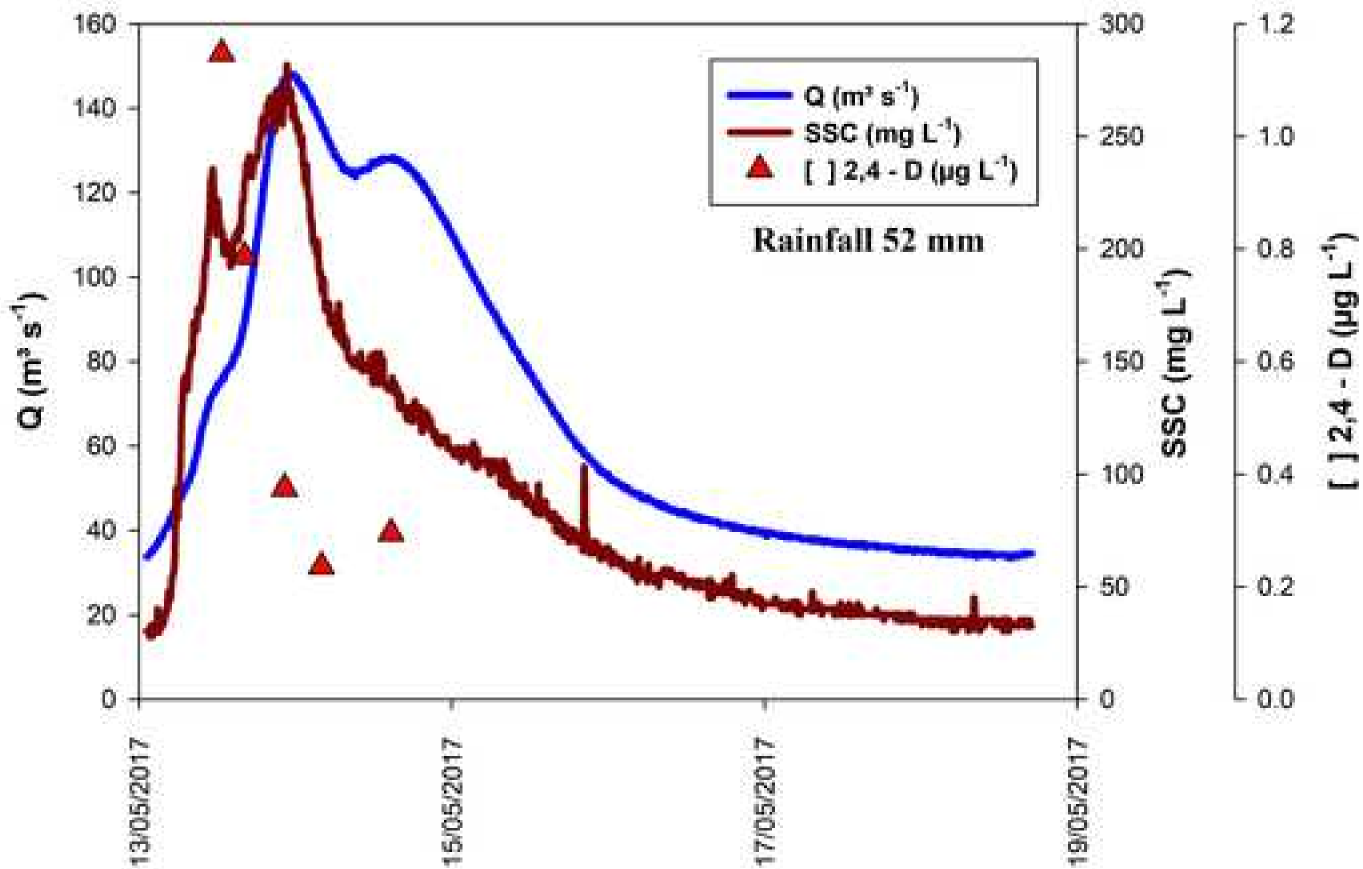
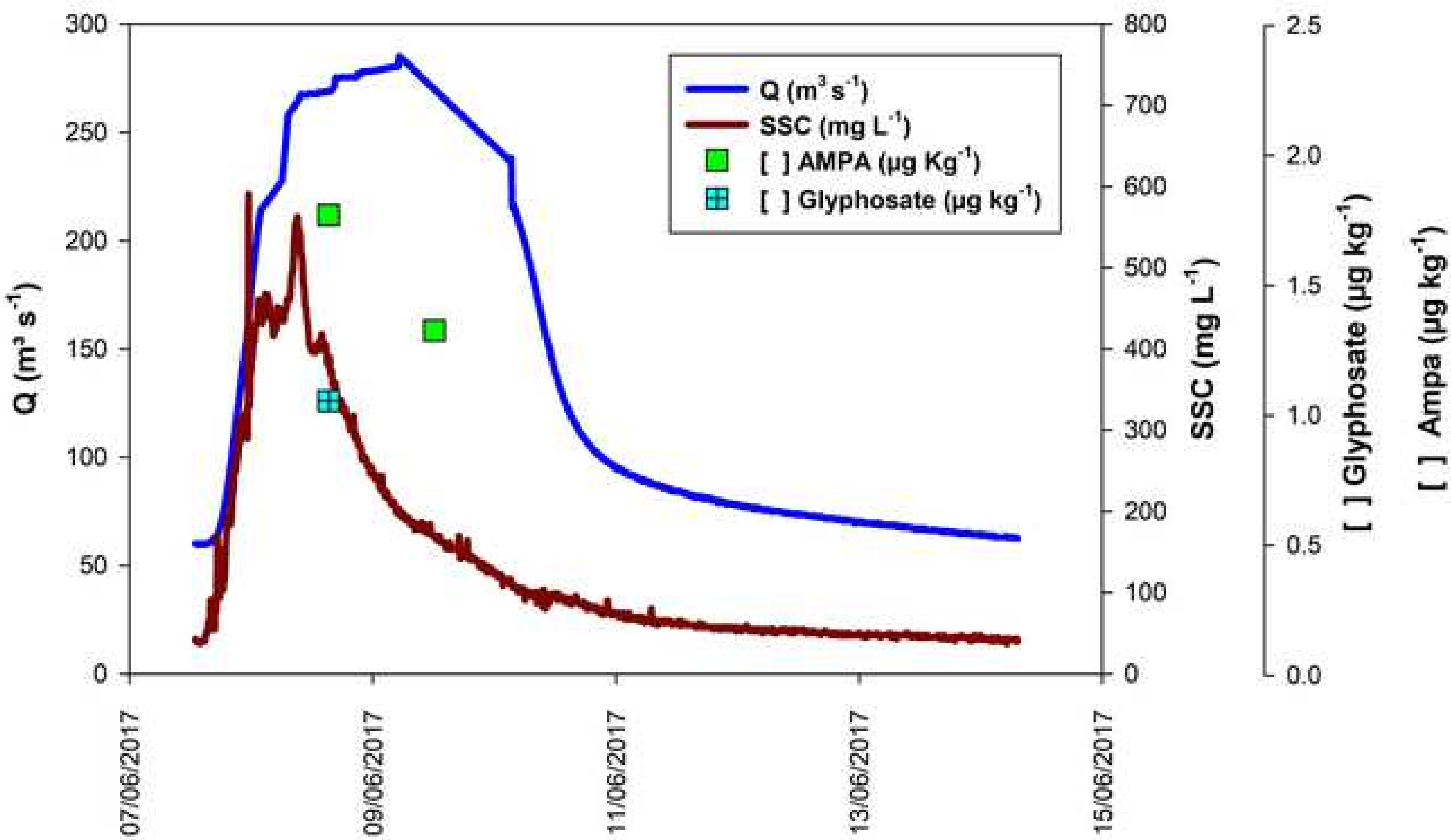


Figure 4



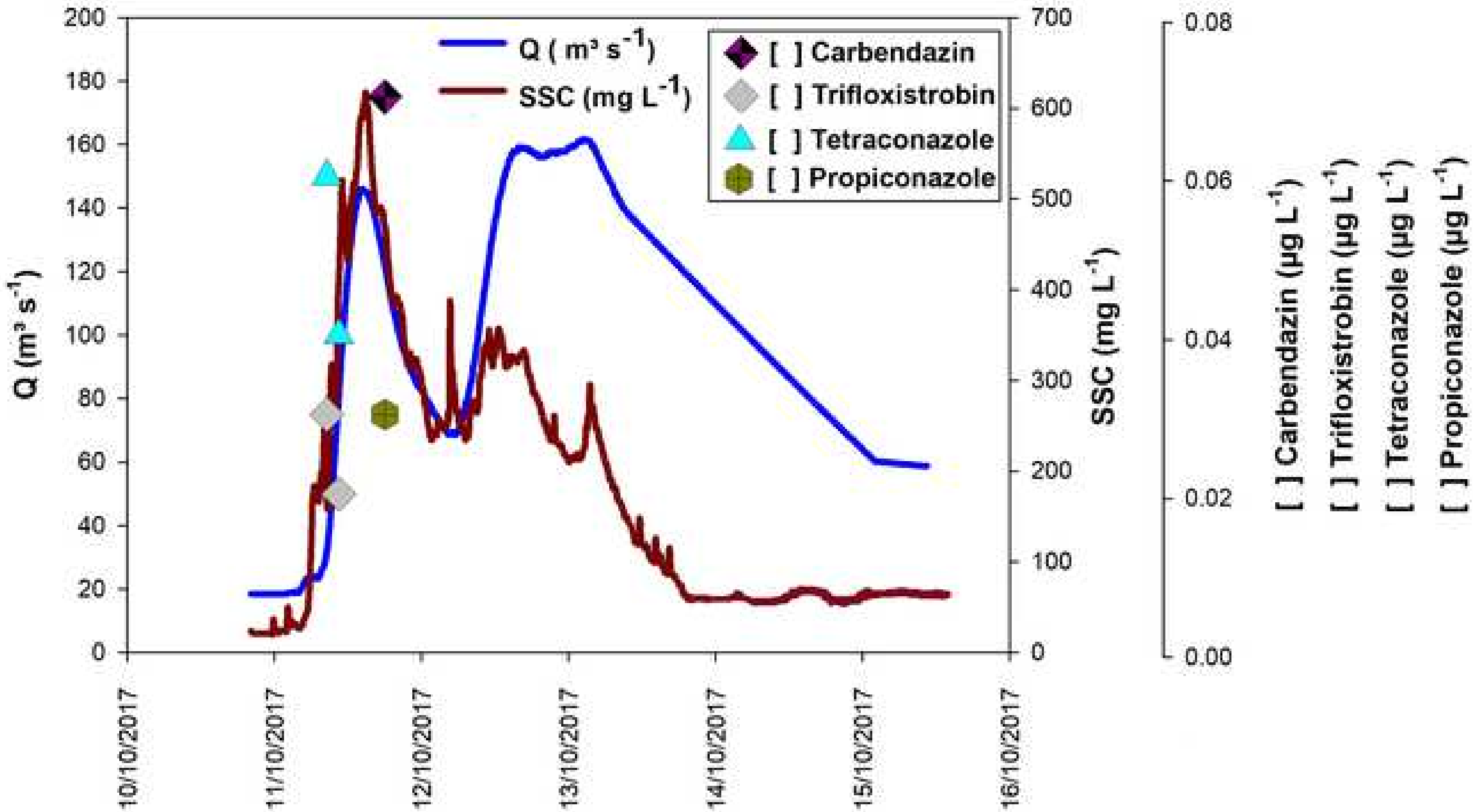
Q (m³ s⁻¹)
SSC (mg L⁻¹)
[ ] 2,4 - D (µg L⁻¹)
Rainfall 52 mm
Q (m³ s⁻¹)
SSC (mg L⁻¹)
[ ] 2,4 - D (µg L⁻¹)
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300
0.0
0.2
0.4
0.6
0.8
1.0
1.2
13/05/2017
15/05/2017
17/05/2017
19/05/2017

Figure 5



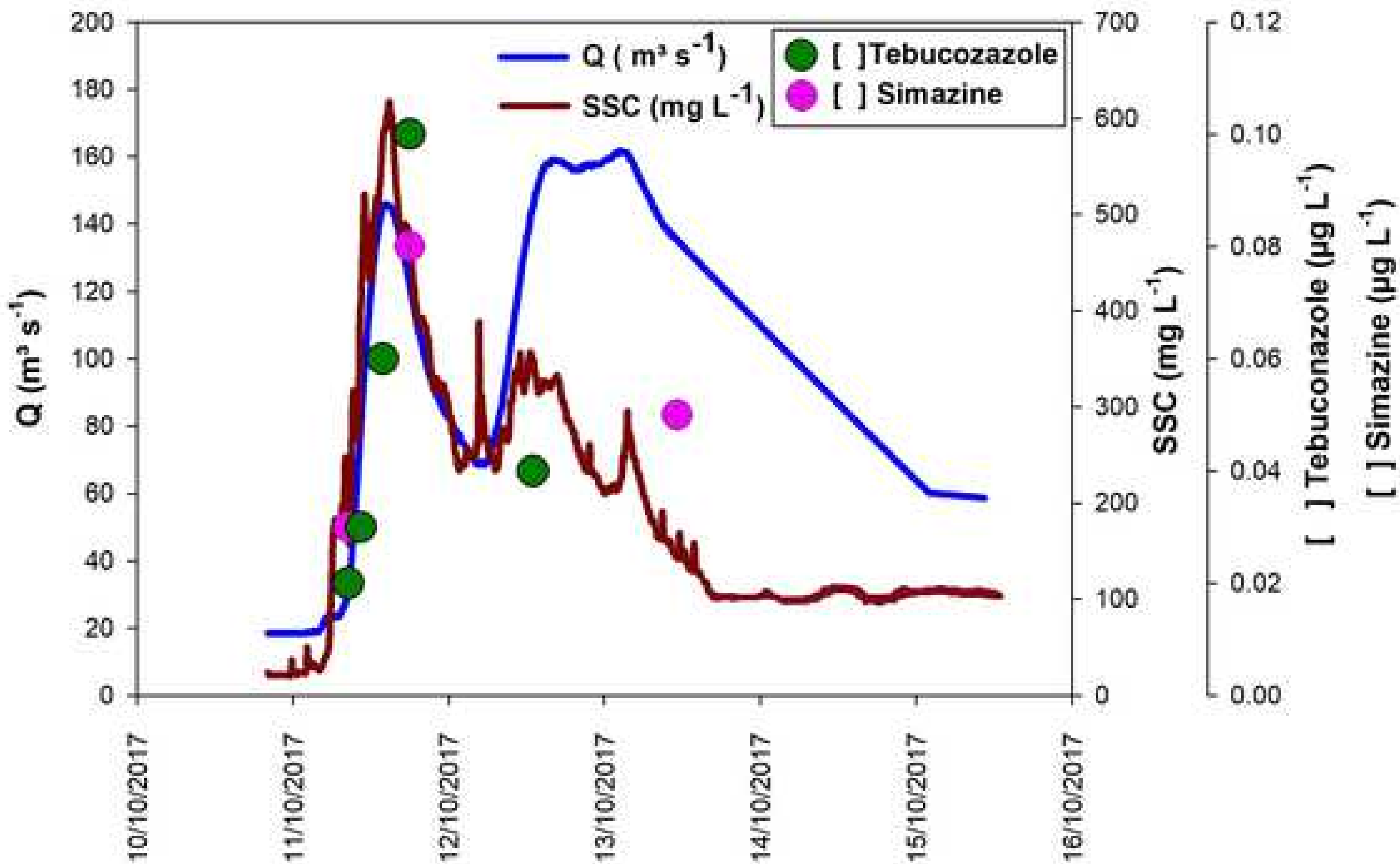
Q (m^3 s^{-1})
SSC (mg L^{-1})
[ ] AMPA (µg Kg^{-1})
[ ] Glyphosate (µg kg^{-1})
300
250
200
150
100
50
0
800
700
600
500
400
300
200
100
0
2.5
2.0
1.5
1.0
0.5
0.0
Q (m^3 s^{-1})
SSC (mg L^{-1})
[ ] Glyphosate (µg kg^{-1})
[ ] Ampa (µg kg^{-1})
07/06/2017
09/06/2017
11/06/2017
13/06/2017
15/06/2017

Figure 6A



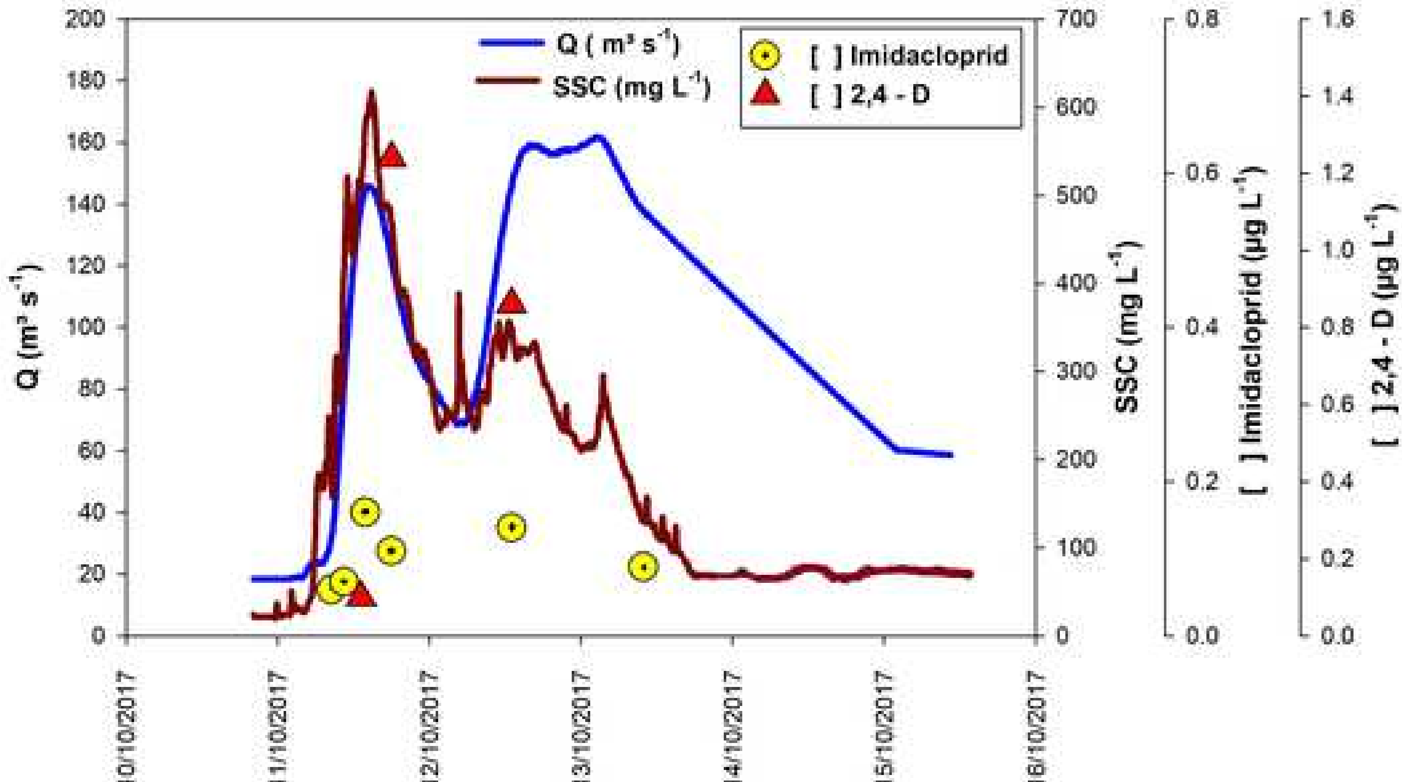
Q (m³ s-1)
SSC (mg L-1)
[ ] Carbendazin
[ ] Trifloxistrobin
[ ] Tetraconazole
[ ] Propiconazole
Q (m³ s-1)
SSC (mg L-1)
[ ] Carbendazin (µg L-1)
[ ] Trifloxistrobin (µg L-1)
[ ] Tetraconazole (µg L-1)
[ ] Propiconazole (µg L-1)
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400
500
600
700
0.00
0.02
0.04
0.06
0.08
10/10/2017
11/10/2017
12/10/2017
13/10/2017
14/10/2017
15/10/2017
16/10/2017

Figure 6B



Q (m³ s-1)
SSC (mg L-1)
[ ]Tebucozazole
[ ] Simazine
Q (m³ s-1)
SSC (mg L-1)
[ ] Tebuconazole (µg L-1)
[ ] Simazine (µg L-1)
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400
500
600
700
0.00
0.02
0.04
0.06
0.08
0.10
0.12
10/10/2017
11/10/2017
12/10/2017
13/10/2017
14/10/2017
15/10/2017
16/10/2017

Figure 6C



Q (m³ s⁻¹)
SSC (mg L⁻¹)
[ ] Imidacloprid
[ ] 2,4 - D
Q (m³ s⁻¹)
SSC (mg L⁻¹)
[ ] Imidacloprid (µg L⁻¹)
[ ] 2,4 - D (µg L⁻¹)
0
20
40
60
80
100
120
140
160
180
200
700
600
500
400
300
200
100
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
10/10/2017
11/10/2017
12/10/2017
13/10/2017
14/10/2017
15/10/2017
16/10/2017

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 E_1 to E_8.

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 E_6 of October 10, 2017.

Table 1

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

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
				nd	Glyphosate
E_6 - 10/10/2017	123	11.7	161.7	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

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

Events monitored	Q_0 ($m^3 s^{-1}$)	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	-	-	-

Q_0= 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