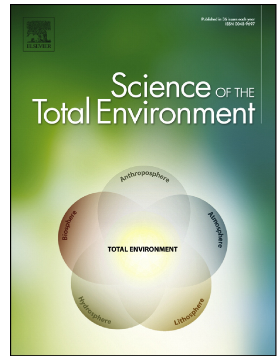
Journal Pre-proof



Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina

VictoriaSoledad Andrade, María Florencia Gutierrez, Luciana Regaldo, Aldo Raul Paira, María Rosa Repetti, Ana María Gagneten

PII: S0048-9697(21)02747-9

DOI: https://doi.org/10.1016/j.scitotenv.2021.147676

Reference: STOTEN 147676

To appear in: *Science of the Total Environment*

Received date: 3 February 2021

Revised date: 20 April 2021

Accepted date: 3 May 2021

Please cite this article as: V. Andrade, M.F. Gutierrez, L. Regaldo, et al., Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina, *Science of the Total Environment* (2021), https://doi.org/10.1016/j.scitotenv.2021.147676

Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina

Andrade, Victoria Soledad[ab]; Gutierrez, María Florencia[acd]; Regaldo, Luciana[ab]; Paira, Aldo Raul[ce]; Repetti, María Rosa[f]; Gagneten, Ana María[a]*

[a]Laboratorio de Ecotoxicología, Departamento de Ciencias Naturales, Facultad de Humanidades y Ciencias, Universidad Nacional del Litoral (UNL), Ciudad Universitaria, Santa Fe (3000), Argentina. [b]Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICET), Nat. Route 168, Km 0, Santa Fe (3000), Argentina. [c]Instituto Nacional de Limnología (INALI-CONICET-UNL), Ciudad Universitaria, Santa Fe (3000), Argentina. [d]Facultad de Bioquímica y Ciencias Biológicas - Escuela Superior de Sanidad "Dr. Ramón Carrillo", UNL, Ciudad Universitaria, Santa Fe (3000), Argentina. [e]Facultad de Ingeniería y Ciencias Hídricas, Universidad Nacional del Litoral (UNL), Ciudad Universitaria, Santa Fe (3000), Argentina. [f]Facultad de Ingeniería Química, UNL, Santiago del Estero 2829, Santa Fe (3000), Argentina.

vandrade@conicet.gov.ar

fgutierrez@inali.unl.edu.ar

lregaldo@fhuc.unl.edu.ar

apaira@inali.unl.edu.a

mrepetti@fiq.unl.edu.ar

*amgagneten@gmail.com. Laboratorio de Ecotoxicología. Facultad de Humanidades y Ciencias. Universidad Nacional del Litoral. Ciudad Universitaria. 3000. Santa Fe. Argentina.

Abstract

An increase in the spatial variability of rainfall is expected due to climate change. This implies increasing rainfall rates during spring and summer in the Pampas region, Argentina, period of maximum application of agrochemicals, which might cause an increase in pesticides and nutrients carried to surface water systems, as runoff by rainfall is one of the main pathways for diffuse pollution. The crops phenological stage can also affect pesticide and nutrient runoff since the applied agrochemicals and soil cover differ in each stage. In this study, we assessed the influence of rainfall and seasonal crop practices on water quality (nutrient and pesticide concentrations) in three streams in the Pampas region, Argentina. Five sampling campaigns were performed before and after three rainfall events during two different seasons of crop practices (SCP1, SCP2) and the physicochemical characteristics of the stream and runoff water were analyzed. The pesticide concentrations in the streams presented a general increase immediately after the rainfall event. Water quality was also affected, as an increase in ammonium, soluble reactive phosphorus (SRP), biological oxygen demand (BOD), and turbidity was observed. The crops phenological stage influenced pesticide and nutrient types and concentrations detected in the streams. During SCP1, mainly characterized by chemical fallow and sowing of soybean and vegetative growth and flowering of corn, ammonium, SRP, BOD, turbidity, and some pesticides, such as metolachlor, showed significantly higher results than those found in SCP2 (grain filling and vegetative growth of soybean and corn sowing). The pesticide concentrations detected in runoff water depended mostly on the pesticide solubility, the lateral slope of the streams, and the percentage of woody riparian vegetation cover. The results obtained show the relevance of assessing the influence of rainfall and crops phenological stages on the dynamics of surface water and on pesticide and nutrient runoff for environmental monitoring.

Keywords: agrochemical; precipitation; phenological stage; diffuse pollution; environmental monitoring

1. Introduction

There is a growing recognition of extreme climates as one of the main consequences of climate change (Marques et al., 2014). In general, it is expected an increase in the spatial variability of rainfall, with a decrease in the subtropics and an increase at higher latitudes (Jeppesen et al., 2009; Knutti and Sedláček, 2013). In the Pampas region, Argentina, an intensification of meteorological events is expected, particularly an increase in rainfall rates during spring and summer, the seasons of maximum application of agrochemicals, which might cause an increase in pesticides and nutrients carried to surface water systems (Barros et al., 2015; Rodrigues Capítulo et al., 2010).

In the last decades, agricultural practices have grown along with the diversification of and the increase in the amounts of the pesticides applied, particularly for the development of genetically modified crops (Benbrook, 2012). In Argentina, this process has taken place mainly in the most fertile areas, such as the Pampas region (Iturburu et al., 2019).

It is known that pesticides can reach freshwater bodies either by leaching, volatilization, or runoff (Jergentz et al., 2005). It is considered that runoff due to rainfall is one of the main ways for agrochemical pollution in surface water bodies (Harrison et al., 2019), which causes environmental degradation in aquatic systems (Isenring, 2010).

Several factors can influence the dynamic of pesticide and nutrient loads in freshwater bodies. Among them, the frequency and intensity of rainfall events and the period of agrochemical application might be highly important (Lefrancq et al., 2017). Another factor of high incidence is the phenological stage of the crops (pre-emergence: chemical fallow and sowing, post-emergence: vegetative growth, flowering, and grain filling) because different compounds are applied for each of them, depending on the fertilization period and on whether the pesticides are pre- and/or post-emergent according to their functions and potentiality to affect the crops.

Although numerous studies of pesticide monitoring have been conducted on field (e.g.: Aparicio et al., 2013; Cruzeiro et al., 2015; Frau et al., 2021; Hasanuzzaman et al., 2018; Jabeen et al., 2015; Kafle et al., 2015; Regaldo et al., 2017; Ronco et al., 2016), rainfall events have been rarely considered. Therefore, the maximum concentrations of pesticides in aquatic environments could have been underestimated (Lefrancq et al., 2017). Moreover, the associated nutrient runoff have been rarely considered in pesticide monitoring, even though several studies have pointed out that nutrient losses by soil erosion and runoff from agricultural lands negatively affects freshwater quality (Fenton and Ó hUallacháin, 2012; Zak et al., 2019). This nutrient input can increase the eutrophication process in freshwater systems and promote the development of algae blooms, which could have a negative impact on the environmental biodiversity (Deelstra et al., 2011). Nowadays, as a consequence of land use changes and global warming, eutrophication constitutes one of the greatest environmental challenges worldwide (Zak et al., 2019).

The aim of this study was to assess the influence of rainfall and the seasonal crop practices on the water quality (measured through nutrient and pesticide concentrations) of three streams in the Pampas region, Argentina. With this purpose, five sampling campaigns were conducted before and after three rainfall events during two different seasons of crop practices (SCP1 and SCP2). The specific aims were: 1) to analyze the influence of the rainfall events on pesticide and nutrient concentrations in stream water, 2) to analyze the influence of the phenological stage of crops on pesticide and nutrient concentrations in stream water, and 3) to analyze the main variables (characteristics of both pesticides and the environment) that determine the number of pesticides and the percentage of total pesticide concentration in runoff water.

The hypotheses for this study were: 1) rainfall events cause an increase in pesticide and nutrient concentrations in stream water; 2) the phenological stage of crops determines the type and concentration of pesticides and nutrients found in water; 3) the side slope, the sub-basin area, the runoff flow, and the riverbank vegetation cover are determining factors for the runoff of pesticides.

2. Materials and methods

2.1 Study area

The study area is located in the central-eastern region of Argentina (Figure 1.a), in the Pampas region, the most fertile plain of Argentina (Rubio et al., 2019). The soil type is Mollisol (great group Argiudoll, subgroups typic and acuic), with silty loam surface texture and silty clay subsurface texture (GeoINTA, 2014). It has a temperate climate with a mean annual temperature of 20 °C (seasonal means: autumn: 19.8, winter: 12, spring: 21.1, summer: 25.2°C, in the period 2018-2019) (EEA-INTA-Rafaela 2018-2019). The study area presents an average annual rainfall of 1100 mm (Rubio et al., 2019) with a higher frequency of heavy rainfall during spring–summer periods (October-March) (Barros et al., 2015). The seasonal means of total monthly rainfall were: autumn:127.2, winter: 18.8, spring: 297.2, summer:194.9 mm month^{-1}, and seasonal maximum daily values were: autumn: 46, winter: 13.4, spring: 104.8, summer: 49.7 mm day^{-1} in the period 2018-2019 (EEA-INTA-Rafaela 2018-2019). In this area, agriculture is the main human activity, largely predominating the soybean cultivation (approximately 40% of land surface), followed by corn (10%), and, to a lesser extent, wheat and sunflower (Dirección Nacional de Estimaciones Agrícolas, INTA Rafaela, 2018, 2019). The remaining land surface correspond mainly to flood areas without agricultural prectices, and also few small towns (< 5000 inhabitants), and routes. The tillage practices for soybean crops are the following: when soybean cultivation is preceded by pastures it is recommended to break the compaction of the subsurface desified layers, if any, with implements such as paraplow, paratill or similar, and then carry out direct sowing. When soybean rotations are carried out with sunflower, sorghum or corn as predecessors, direct sowing or vertical tillage (chisels) is recommended if there are soil densifications (INTA, 2011).

Three sampling sites where selected in three streams of second and third order with independent sub-basins: S1 (31°36'23.4" S, 61°9'34.6" W), S2 (31°34'53.2" S, 61°16'34.2" W) and S3 (31°31'13.7" S, 61°15'55.8" O) (Figure 1.a). The three streams present flow throughout the year. They were selected within a radius of 7 Km in order to ensure that they are equally affected by the rainfall events. The distribution of the aforementioned land uses was similar between the three sub-basins.

2.2 Study design

The study design is summarized in Figure 1.b. Five sampling campaigns were conducted during spring and summer (November 2018 – March 2019) in relation to three rainfall events in two different seasons of crop practices (SCP1 and SCP2). The phenological stage of crops on each SCP are drecribed in Table 1. SCP1 was mainly characterized by chemical fallow and sowing of soybean (pre-emergence) and vegetative growth and flowering of corn (post-emergence), while SCP2 was mainly characterized by grain filling and vegetative growth of soybean (post-emergence) and corn sowing. During SCP1, one sampling campaign was conducted after a rainfall event (Aft1, 23-Nov), and two sampling campaigns were carried out in periods between-rains: one day before the rainfall event (InterBef, 22-Nov) and seven days after the event (InterAft7, 30-Nov). During SCP2, two after-rain sampling campaigns were carried out after two different rainfall events (Aft2, 26-Feb, and Aft3, 6-Mar).

In all sampling campaigns, conductivity (µs cm^{-1}), dissolved oxygen (DO, %), pH, and temperature (°C) were measured in situ (Hanna multiparameter portable meter). Simultaneously, stream water samples were collected (500 mL) to analyze nutrients (ammonium, nitrates, nitrites and soluble reactive phosphorus -SRP-, µg L^{-1}), color (PtCo), turbidity (FTU), biologic oxygen demand (BOD, mg L^{-1}) and chlorophyll *a* (µg L^{-1}), according to APHA (2017).

In each sampling campaign, stream water samples were collected in 1 L glass caramel bottles for pesticide analysis. Runoff water samples (R1, R2, and R3) were also collected in after-rain sampling campaigns (Aft1, Aft2, and Aft3) by burying 1 L bottles, each one with a cover to prevent direct rain water from entering the bottles. Nine bottles (20 cm deep, 79 cm^2 surface, 1.5 L volume) were placed near each one of the sampling points described before (S1, S2, and S3) along the riversides (from 2 to 4 m away from the edge of streams, along 10 m upstream the sampling point) to collect the overland flow from adjacent fields, and a pool of their contents was formed for each site and time. The changes in stream flow after rainfall events did not affect runoff samplers. Sediment samples (500 mL containers) were also collected from the sediment surface (5 cm deep) in water-covered areas of streams with a shovel in every sampling campaign and site for further pesticide analysis.

2.3 Geomorphological and hydrological variables

Rainfall intensity (mm s^{-1}) was estimated with information from SIGA-INTA (Sistema de Información y Gestión Agrometeorológica-INTA) and with the rainfall records from nearby towns (Dirección Provincial de Comunicaciones, Gobierno de Santa Fe). Stream flows were estimated according to Bain and Stevenson (1999).

Runoff flow was estimated through the Soil Conservation Service (SCS) method (Huffman et al., 2013) as follows:

$$Q = \frac{\frac{(I-0.2S)^2}{I+0.8S} \cdot \frac{A10^4}{1000}}{t} \qquad [1]$$

where: Q = runoff flow (m^3 s^{-1}), I = rainfalls (mm), A = basin area (Ha), t = rainfall time (s), S = maximum potential difference between rainfall and runoff (mm), calculated as follows:

$$S = \frac{25400}{CN} - 254 \qquad [2]$$

where: *CN* = curve number. This value was taken from the tables presented by Huffman et al., 2013 for agricultural lands, it depends on soil type, land use, and soil water conditions.

The concentration time, defined as the time required for the water located at the most remote point of the basin to reach the basin outlet (Singh, 1992), was estimated following the SCS method (Huffman et al., 2013) as follows:

$$Tc = L^{0.8} \frac{\left(\frac{1000}{CN} - 9\right)^{0.7}}{4407\ (S_g)^{0.5}} \quad [3]$$

where: *Tc* = concentration time (h), *L* = longest flow length (m), S_g = average watershed gradient (m/m), *CN* = curve number.

The riverbank vegetation cover adjacent to rivers (5 m wide on each side approximately) was estimated by the naked eye along 15 m upstream each sampling site and expressed as the percentage of woody (shrub + tree) and herbaceous cover. The three sampling sites presented riverbank vegetation. Also, Google Earth® aerial photos were used to complement the estimation considering if the riverbank vegetation cover of each sub-basin was similar to the observed at each sampling point. Lateral and longitudinal slopes were calculated for each stream through 1:50.000 topographic charts (Instituto Geográfico Militar, 1959).

2.4 Pesticide analysis

Pesticides in water samples were analyzed by solid phase extraction (SPE) (Min et al., 2008), while pesticides in sediment samples were analyzed following QuEChERS (quick, easy, cheap, effective, rugged, and safe) method (Anastassiades et al., 2003). Afterwards, pesticide concentrations were determined by liquid and gas chromatography-mass spectrometry (LC-MS/MS+GC-MS/MS). For glyphosate, its metabolite aminomethylphosphonic acid (AMPA), and glufosinate determination FMOC-Cl derivatization, SPE cleanup and LC-MS/MS were the approaches (Demonte et al., 2018). The methodologies in all cases were fully validated according with the European Commission guidance document on analytical quality control and method validation procedure for pesticide residues (SANTE/11813/2017). Quantification limit (QL): 0.1 µg L^{-1} and detection limit (DL): 0.03 µg L^{-1} with exception of glyphosate, glufosinate and AMPA: QL: 0.6 µg L^{-1}, DL: 0.18 µg L^{-1} (see SM1).

Pesticides were grouped according to their water solubility as follows: very high: > 100 (VHiSolub), high 10 – 100 (HiSolub), medium 1 – 10 (MedSolub), low 0.1 – 1 (LowSolub), and very low <0.1 mg L^{-1} (VLSolub) (FAO, 2000). Also, they were grouped according to their soil affinity as follows: mobile: 1 – 2 (Mob), moderately mobile: 2 – 3 (ModMob), and slightly mobile: 3 – 4 Log Koc (SlighMob) (FAO, 2000).

2.5 Data analysis

Principal component analysis (PCA) was run to observe the sample distribution with respect to the stream water quality in relation to the effect of rainfall and to the different seasons of crop practices. The explanatory variables (total pesticide concentrations, nutrients, turbidity, BOD, chlorophyll *a*, pH, conductivity, flow, and estimated runoff) were selected in order to avoid collinearity, and excluding those with low explanatory power (contribution < 10%).

To analyze the influence of the rainfall event on stream water quality, a multivariate analysis of variance (MANOVA) was run with one factor including 3 levels (InterBef, Aft1, and InterAft7) with the variables selected in the previous analyses (total pesticide concentration, nutrients, turbidity, BOD, chlorophyll *a*, pH, conductivity, flow, and estimated runoff). For this analysis, only the SCP1 period was considered because this is the only period for which inter-rain information was available. Additionally, for the same period, repeated measures analysis of variance (RMANOVA) was used for each individual variable (nutrients, turbidity, BOD, chlorophyll *a*, pH, conductivity, and DO) to assess its variation in time after the rainfall event. The Tukey post hoc test was applied to check the differences between the sampling campaigns ($p < 0.05$).

To analyze whether the water quality of the streams after the rainfall events (Aft1, Aft2, and Aft3) differs according to the different seasons of crop practices, a one factor MANOVA was performed with 2 levels (SCP1 and SCP2). The intensity of rainfall was included as a covariable and the response variables were the aforementioned (total pesticide concentration, nutrients, turbidity, BOD, chlorophyll *a*, pH, conductivity, flow, and estimated runoff).

One factor analysis of variance (ANOVA) was used to analyze the differences in the environmental variables (nutrients, turbidity, BOD, chlorophyll *a*, pH, conductivity, and DO) for the after-rain sampling campaigns (Aft1, Aft2, and Aft3). The Tukey post hoc test was applied to analyze the differences between sampling campaigns ($p < 0.05$).

To specifically analyze which variable determines the number and percentage of pesticides (response variables) detected in runoff water, a generalized linear model (GLM) with Gaussian adjustment was performed. For this analysis, an initial series of variables were considered as potential predictors: pesticide properties (solubility and mobility) and environmental variables (lateral slope, sub-basin area, percentage of woody riparian vegetation, intensity of rainfall and estimated runoff flow). From these variables, numerous models were tested with one, two or three combined variables. The different models were compared based on the Akaike information criterion (AIC), their statistical significance and the percentage of explanation. The difference between the lowest AIC value and the AIC of all other models (ΔAIC) was also calculated to establish an order of the potential models (Burnham and Anderson, 2002).

3. Results

Table 2 shows environmental, geomorphological and hydrological variables for each site. Overall the three sites were similar with some exceptions: S3 has a larger basin area, higher estimated runoff flow and less flow in the sampling point, S1 has lower DO and lower longitudinal slope. The percentage of woody riverbank cover was higher in S2 (95%) and lower in S3 (10%).

In the stream sediments, different pesticides were detected: bifenthrin, atrazine, metolachlor and glyphosate and its metabolite AMPA, with different trends for each site. As expected, slightly mobile pesticides presented the maximum concentrations: glyphosate: 4 µg Kg^{-1} and AMPA: 10 µg Kg^{-1}, the other pesticides detected were below QL (10 µg Kg^{-1}) (see SM1).

The first component (PC1) of the PCA explains the 29.5% of the total variability and the second component (PC2), the 21.9% (Figure 2.a). In the sample distribution (Figure 2.b) no distinction was observed between sites (S1, S2 and S3). The main differences were observed between the different sampling campaigns. The inter-rain sampling campaigns conducted for the first rainfall event (InterBef and InterAft7) differed from the sampling campaign conducted after said event (Aft1). Also, these sampling campaigns carried out during SCP1 differed from the ones carried out during SCP2 (Aft2 and Aft3). These differences are analyzed in detail in the following sections.

3.1 Rainfall event: effects on stream water quality

The rainfall event affected significantly the stream water quality: in SCP1 period, the water quality of the after-rain sampling campaign (Aft1) was significantly different from the sampling campaigns performed before (InterBef) and seven days after that rainfall event (InterAft7) (MANOVA $p < 0.001$ $F = 297.8$). There were no statistically significant differences between these last two inter-rain sampling campaigns (Figure 2.b).

Among the environmental variables analyzed, the ammonium concentration increased significantly after the rainfall event and decreased seven days later (RMANOVA $p = 0.016$). SRP decreased significantly after the rainfall event and tended to decrease seven days later (RMANOVA $p = 0.003$). Nitrite and nitrate concentrations were not affected significantly by the rainfall event and showed different patterns between sites

(RMANOVA p = 0.69 and 0.74, respectively). Turbidity increased significantly and BOD tended to increase after the rainfall event, and both decreased seven days later (RMANOVA p = 0.006 and 0.007 respectively). Chlorophyll *a* decreased and pH increased significantly after the rainfall event and both tended to decrease seven days later (RMANOVA p = 0.005 and 0.03 respectively). Conductivity and DO decreased in all sites the day after the rainfall event (Table 3).

Pesticide concentration in stream water increased after the rainfall event and decreased seven days later in all sites. Only atrazine showed a different pattern, as it decreased after the rainfall event (Figure 3). The observed increase in pesticide concentrations after the rainfall event was mostly due to VHiSolub pesticides (+310%), followed by MedSolub pesticides (+280%). After seven days, both VHiSolub and MedSolub pesticides decreased in similar proportions (-86% and -87%, respectively). Nevertheless, the relative concentration (% of total pesticide concentration) of VHiSolub pesticides was higher (Bef1: 74%, Aft1: 92%, and Aft7: 75%) than MedSolub pesticides (Bef1: 1.3%, Aft1: 1.5%, and Aft7: 1.1%) (Figure 3). Regarding pesticide mobility in soil (Log Koc), the increase in pesticide concentrations after the rainfall event was mostly due to Mob pesticides (+622%), followed by ModMob pesticides (+374%), and lastly, SlighMob pesticides (+68%). After seven days, Mob pesticides were not detected (-100%), ModMob pesticides decreased in -85% and SlighMob pesticides, in -69%. Nevertheless, the relative concentration of Mob pesticides was lower (Bef1: 4%, Aft1: 10%, and Aft7: 0%) than ModMob pesticides (Bef1: 46%, Aft1: 65%, and Aft7: 55%) and SlighMob pesticides (Bef1: 50%, Aft1: 25%, and Aft7: 45%) (Figure 3).

3.2 Phenological stage: effects on stream water quality

No pattern was observed in relation to the rainfall intensity of the different rainfall events in water quality, this is why the rainfall intensity was used as a covariable for the analysis of the phenological stage effects described below. Significant differences were observed in relation to the different seasons of crop practices, as Aft1 was conducted during SCP1 period and Aft2 and Aft3 during SCP2 (MANOVA, $p < 0.001$ $F = 4719.6$). SCP1 sampling campaign (mainly defined by soybean pre-emergence and, to a lesser extent, corn post-emergence) showed higher SRP, ammonium, BOD, turbidity (ANOVA p = 0.007, 0.001, <0.001 and 0.07, respectively) (Table 4), and VHiSolub and ModMob pesticides, mostly metolachlor and s-metolachlor, pre-emergence herbicides applied during chemical fallow.

3.3 Runoff water

Candidate GLMs for the number and percentage of pesticides detected in runoff water showed that the sub-basin area, the solubility and the percentage of woody riverbank vegetation were the main predictors. All the models tested with these variables were statistically significant (see SM2).

From the results obtained from the comparisons between the GLMs, the final models for the number and percentage of pesticides that include the three mentioned variables are described in Table 5. In both models, the area of the sub-basin and the solubility were positively correlated with the response variables (the greater the area and solubility, the greater the number and percentage of pesticides detected in water). On the contrary, the coverage of woody riverbank vegetation (trees + shrubs) was negatively correlated, which indicates that this factor would act as a barrier, limiting the number and percentage of pesticide runoff into the water body.

4. Discussion

4.1 Rainfall event: effects on stream water quality

The rainfall event had a substantial effect on stream water quality. The observed increase in turbidity and ammonium after the event could be due to an input of allochthonous organic matter (OM) and to soil particles carrying the nutrients associated (Fenton and Ó hUallacháin, 2012). In these sense, Shang et al. (2018)

reported that the basins with high proportion of agricultural land use presented large proportion of soil derived and OM in the United States. In the present study, the rainfall event also produced an increase in BOD, similarly to the findings by Almada et al. (2019), who argued that this could be due to the increase in oxygen consumption for the decomposition of the allochthonous OM carried by rainfall.

The concentration of most pesticides in stream water increased in all sites after the rainfall event, and decreased after 7 days. These findings show a clear connection between pesticide concentration in stream water and rainfall events. Lefrancq et al. (2017) found a similar tendency in a high-frequency monitoring of seven pesticides in France. They reported that the pesticide concentrations increased after all runoff events, concluding that significant pesticide export can occur during a single event. This information should be considered for the design of pesticide monitoring, as these environments are highly dynamic systems, and if variables such as rainfall and application periods are not considered, the environmental pesticide concentrations can be underestimated, and with it, the environmental risk of these compounds (Holvoet et al., 2007; Lefrancq et al., 2017).

On the other hand, atrazine concentration in stream water decreased after the rainfall event, which indicates that it could have a different pollution pathway, such as leaching, as its potential for polluting groundwater is widely known (Jablonowski et al., 2011; Mudhoo and Garg, 2011; Schwab et al., 2006), and its potentiality for leaching on Argentine pampas soils have been reported (Bedmar et al., 2004; Montoya et al., 2006). More recently, Portocarrero et al. (2019) surveyed atrazine concentrations in groundwater from sugarcane production in Tucumán (Argentina), detecting it in 77% of the samples. The land use and the hydrogeological factors are known to be conditionating of groundwater pollution. The potential risk for groundwater pollution increases when the soils are permeable and the layers are superficial (APVMA, 2004). The importance of developing agricultural practices that mitigate the pollution of aquifers is highlighted; this is particularly important considering that groundwater is the main source of water for human consumption in rural areas.

Atrazine herbicide has been frequently detected in surface water (Bradley et al., 2017; Caron et al., 2012), which could be due to its extensive use worldwide (Jablonowski et al., 2011). This pesticide is also the most frequently recorded in Argentinian basins. Regaldo et al. (2017) detected it in 94% of the stream samples collected in a region nearby the study area, where we detected atrazine in 100% of the stream water samples, just like Frau et al. (2021) who also detected it in 100% of samples collected in Pampean streams linked to intensive agricultural pollution in Santa Fe province, De Gerónimo et al. (2014) also detected it in more than 80% of the water samples in the Pampas region in Buenos Aires province, and Mac Loughlin et al. (2021), who monitored the impact of intensive peri-urban horticultural practices in a stream in the same province, detected it in 100 % of samples along 2 years, highlighting that it can be considered a pseudo-persistent pollutant. In Argentina atrazine is the second pesticide most employed (Ministerio de Salud de la República Argentina, 2014) mainly for corn, the second crop in the region (10% of the land surface, Dirección Nacional de Estimaciones Agrícolas, INTA Rafaela, 2018, 2019). INTA (1997) recommends to aply atrazine from presowing to early post-emergence of corn, these applications being previous or coinciding with these sampling times performed in relation to the first rainfall event during SCP1 period, where the corn crops were in vegetative growth and flowering stages. The frequent detection of atrazine could also be due to its relatively high solubility, slow hydrolysis, and relatively high persistence in soil (half-life in soil: 146 d) (IUPAC, 2019). Moreover, its repeated and long-term application can cause accumulation in soils and it can persist for several years, constituting a long-term threat to the environment (Vonberg et al., 2014). Although atrazine is banned in the European Union as well as in other countries (Sass and Colangelo, 2006), in Argentina is one of the most widely used herbicides (Aparicio et al., 2015).

The increase in pesticide concentrations detected after the rainfall event was observed mainly for VHiSolub pesticides, such as glyphosate, its metabolite AMPA, metolachlor, and s-metolachlor, and Mob pesticides, such as 2.4-D, imazethapyr, and haloxyfop. Soil affinity (Log Kow) and solubility are the properties that most affect their runoff potential, as several authors have concluded (Chen et al., 2019; Elias et al., 2018; Jurado et al., 2012). Nevertheless, there are some contradictions on these patterns. For example, glyphosate and its metabolite AMPA were detected in 93 and 100% of stream water samples, respectively, despite being SlighMob. The high solubility and wide use of glyphosate could increase its risk for surface water pollution, being one of the most frequently detected pesticides in surface waters (Annett et al., 2014; Battaglin et al., 2014; Perez et al., 2017; Primost et al., 2017; Ronco et al., 2016). Moreover, Sasal et al. (2015) found that the fertilization with phosphorus resulted in an increase in glyphosate runoff. Borggaard and Gimsing (2008) stated that soil structure, mineral composition, pH, and rainfall are the main factors that affect glyphosate soil affinity.

4.2 Phenological stage: effects on stream water quality

The phenological stage of crops had a considerable influence on the water quality of the streams. The after-rain SCP1 sampling campaign, mainly defined by soybean pre-emergence and, to a lesser extent, corn post-emergence, showed concentrations of ammonium and SRP significantly higher than those observed for after-rain SCP2 sampling campaigns, mainly characterized by soybran post-emergence and corn sowing. This might be due to the application of diammonium phosphate (DAP) during or before soybean sowing, recommended by INTA-Rafaela for soils with nutrient deficiency, mostly in this area of the middle east of Santa Fe province (INTA, 2011). DAP fertilizer has been described as rapidly mobile in runoff (Hart et al., 2004); moreover, its potentiality for runoff has been reported to be much higher than single superphosphate (SSP) both in laboratory (Nash et al., 2003) and field studies (Nash et al., 2004). P mobilization through runoff from agricultural basins has been largely reported (Fenton and Ó hUallacháin, 2012; Hart et al., 2004). In fact, surface runoff has been recognized as the main P pollution pathway from agricultural lands (Pärn et al., 2012). In the aforementioned studies, particular attention was paid to runoff events occurring close to fertilizer applications, being these high P loses called incidental mobilizations (Hart et al., 2004).

The increase in nutrients, BOD and turbidity observed for the SCP1 can be related to a higher erosion and OM input due to the unprotected soil in soybean fields during pre-emergence. Rainfall events are expected to increase in frequency and intensity during spring and summer in the Pampas region (Barros et al., 2015; Rodrigues Capítulo et al., 2010). In this scenario, the risk of erosion of unprotected fields increases considerably. In this sense, Michael et al. (2005) simulated the expected increase in rainfall intensity through a numerical model and found that soil erosion might increase under current land uses. In addition, it is expected that this increase in erosion and the consequent input of OM and nutrients foster eutrophication of surface water and increase the risk of algal bloom development (Neal and Heathwaite, 2005).

The SCP1 samples presented higher concentrations of metolachlor and s-metolachlor, pre-emergence herbicides applied during chemical fallow for soybean (INTA, 2011) and in pre-sowing and pre-emergence of corn (INTA, 1997). Although metolachlor is moderately mobile from soil, it was pointed out by several authors as one of the most frequently detected pesticides in stream water (Caron et al., 2012; Glinski et al., 2018; Vialle et al., 2013). In the present study, we detected it in 93% of stream water samples, which could be due to its very high solubility and wide use (Rector et al., 2003).

4.3 Runoff water

The main pesticide properties that may affect their runoff potential were pesticide mobility and solubility, as it was previously mentioned. Nevertheless, solubility seemed to have a greater incidence in the pesticides detected in runoff water. Chen et al.

(2019) pointed out that the runoff rate of pesticides with higher solubility tends to be greater. However, Nakano et al. (2004) reported that pesticide runoff depended more on their mobility than on their solubility, since they detected high concentrations of the herbicide dymron, which has low solubility but moderate mobility. In a meta-analysis, Elias et al. (2018) pointed out that highly soluble pesticides tend to be detected in high concentrations in runoff water, while pesticides with high soil affinity tend to be detected in lower concentrations, but are more persistent. In this sense, Willis and Mcdowell (1983) established that the greater the persistence, the longer the pesticide is available to runoff forces. In the present work, this seems to have been the case of the insecticide mirex, which although its application was forbidden in Argentina in 2005 (Law 26.011, 2005), it is a persistent compound with a half-life of between 1 and 10 years (IUPAC, 2019).

The environmental variables that presented greater explanatory power of the percentage and number of pesticides in runoff water were the sub-basin area and the woody riverbank cover. The reception sub-basin area is a parameter usually considered to model the potential pesticide runoff to surface waters (e.g.: Berenzen et al., 2005; Ippolito et al., 2015). This variable has also been widely employed to test the input of carbon, nitrogen and phosphorus to surface waters from agricultural areas (e.g.: Deelstra et al., 2011; Graeber et al., 2012; Neal and Heathwaite, 2005; Shang et al., 2018; Xu et al., 2016). In general, it is considered that the larger the area of the receiving sub-basin, the greater the pool of these potentially dragged compounds and the greater the number of point sources thereof (Neal and Heathwaite, 2005; Shang et al., 2018).

Vegetation buffer strips have been recently evaluated and employed to mitigate the pollution of surface water by runoff of nutrients and pesticides from agricultural areas (Prosser et al., 2020). These buffer strips not only provide habitat for wildlife and host beneficial predators of pests and pollinators (Schweiger et al., 2005; Wratten et al., 2012), but the vegetation can also retain the suspended solids that runoff water carries and the pesticides and nutrients adsorbed on them (Sweeney and Newbold, 2014). Moreover, the vegetation increases the infiltration and retention capacity of runoff water, due to the relatively high porosity of the root zone. There, pesticides and nutrients can be sorbed into soil particles or OM, transformed by microorganisms, sequestered by plants, or percolate into deeper soil horizons (Prosser et al., 2020). The type of vegetation of the buffer strips is one of the main factors that determine their efficiency (Prosser et al., 2020). In the present study, the woody riverbank cover was negatively correlated with the number and percentage of pesticides detected in runoff water, which could indicate that it acted as a buffer area with greater efficiency than herbaceous coverage areas. In congruence, Lowrance et al. (1997) reported that riparian forest buffer zones can further increase the retention efficiency of a strip of herbaceous. The effectiveness of the latter can be largely limited by factors such as width and coverage (Hill, 2018). Moreover, the trees can increase the infiltration and retention capacity of the buffer zone (Senbayram et al., 2012), being the slow transport of runoff water through these areas of great importance to guarantee the biogeochemical processes that mitigate the runoff of pesticides and nutrients (Arora et al., 2010).

5. Conclusions

Pesticide and nutrient runoff is influenced by many factors. Rainfall events may be determinants of their concentrations in stream water, and the phenological stage of the crops could be also of great importance in relation to the products applied for each stage and the degree of lack of protection of the soil. It is necessary to continue studying these hypotheses in nonmanipulated conditions to contribute to monitoring and mitigation measures design. Factors such as solubility and mobility of pesticides, the receiving sub-basin area, and the type of riverbank vegetation cover could be determinants of pesticide runoff. All these factors must be considered both in the design of environmental monitoring, in order to avoid underestimating the environmental concentrations of these compounds, and in the design of mitigation measures for runoff of agrochemicals. In addition, it is necessary to continue developing studies under realistic conditions to study more deeply the influence of these factors on pesticides and nutrients pollution. Finally, it is imperative to continue analyzing the interaction between both agrochemical runoff and climate change environmental problematics, as both showed to be deeply related and are between the greatest environmental challenges worldwide.

Acknowledgments: We thank M.S. Piacenza (INALI-CONICET-UNL) for his assistance during samplings and M.C. Mora (INALI-CONICET-UNL) for her assistance in nutrients analyses.

Fundings: This work was supported by Universidad Nacional del Litoral (Research Project CAI+D 2016: PI50120150100001LI, PI: L. Regaldo, and CAI+D Orientado 2017: 1-11, PI: A.M. Gagneten) and Agencia Nacional de Promoción Científica y Tecnológica (Research Project PICT 2016-1605, PI: M.F. Gitierrez).

Journal Pre-proof

6. References

Almada, H.K.S., Silvério, D.V., Macedo, M.N., Maracahipes-Santos, L., Zaratim, E.C.P., Zaratim, K.P., Maccari, A., Nascimento, M.R., Umetsu, R.K., 2019. Effects of geomorphology and land use on stream water quality in southeastern Amazonia. Hydrol. Sci. J. 64, 620–632. https://doi.org/10.1080/02626667.2019.1587563

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce. J. AOAC Int. 86, 412–31. https://doi.org/https://doi.org/10.1093/jaoac/86.2.412

Annett, R., Habibi, H.R., Hontela, A., 2014. Impact of glyphosate and glyphosate-based herbicides on the freshwater environment. J. Appl. Toxicol. 34, 458–479. https://doi.org/10.1002/jat.2997

Aparicio, V., De Gerónimo, E., Hernández, K., Pérez, D., Portocarrero, R., Vidal, C., 2015. Los plaguicidas agregados al suelo y su destino en el ambiente, 1st ed. Ediciones INTA, Buenos Aires.

Aparicio, V.C., De Gerónimo, E., Marino, D., Primost, J., Carriquiriborde, P., Costa, J.L., 2013. Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins. Chemosphere 93, 1866–1873. https://doi.org/10.1016/j.chemosphere.2013.06.041

APHA, American Public Health Association. 2017. Standard Methods for the Examination of Water and Wastewater, 23th ed. American Public Health Association, American Water Works Federation. Water Environment Association, Washington, D.C.

Arora, K., Mickelson, S.K., Helmers, M.J., Baker, J.L., 2010. Review of Pesticide retention processes occurring in buffer strips receiving agricultural runoff. J. Am. Water Resour. Assoc. 46, 618–647. https://doi.org/10.1111/j.1752-1688.2010.00438.x

Australian Pesticides and Veterinary Medicines Authority (APVMA). 2004. The reconsideration of approvals of the active constituent atrazine, registrations of products containing atrazine, and their associated labels Including additional assessments. October, p.70. Canberra, Australia.

Bain, M.B., Stevenson, N.J., 1999. Aquatic habitat assessment: common methods. American Fisheries Society, Bethesda, Maryland.

Barros, V.R., Boninsegna, J.A., Camilloni, I.A., Chidiak, M., Magrín, G.O., Rusticucci, M., 2015. Climate change in Argentina: Trends, projections, impacts and adaptation. Wiley Interdiscip. Rev. Clim. Chang. 6, 151–169. https://doi.org/10.1002/wcc.316

Battaglin, W.A., Meyer, M.T., Kuivila, K.M., Dietze, J.E., 2014. Glyphosate and its degradation product AMPA occur frequently and widely in U.S. soils, surface water, groundwater, and precipitation. J. Am. Water Resour. Assoc. 50, 275–290. https://doi.org/10.1111/jawr.12159

Bedmar, F., Costa, J.L., Suero, E., Gimenez, D., 2004. Transport of Atrazine and Metribuzin in Three Soils of the Humid Pampas of Argentina 1. Weed Technol. 18, 1–8. https://doi.org/10.1614/wt-02-056

Benbrook, C.M., 2012. Impacts of genetically engineered crops on pesticide use in the U.S. – the first sixteen years. Environ. Sci. Eur. 24, 1–13. https://doi.org/10.1186/2190-4715-24-24

Berenzen, N., Lentzen-Godding, A., Probst, M., Schulz, H., Schulz, R., Liess, M., 2005. A comparison of predicted and measured levels of runoff-related pesticide concentrations in small lowland streams on a landscape level. Chemosphere 58, 683–691. https://doi.org/10.1016/j.chemosphere.2004.05.009

Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: areview. Pest Manag. Sci. 64, 441–456. https://doi.org/10.1002/ps.1512

Bradley, P.M., Journey, C.A., Romanok, K.M., Barber, L.B., Buxton, H.T., Foreman, W.T., Furlong, E.T., Glassmeyer, S.T., Hladik, M.L., Iwanowicz, L.R., Jones, D.K., Kolpin, D.W., Kuivila, K.M., Loftin, K.A., Mills, M.A., Meyer, M.T., Orlando, J.L., Reilly, T.J., Smalling, K.L., Villeneuve, D.L., 2017. Expanded Target-Chemical Analysis Reveals Extensive Mixed-Organic-Contaminant Exposure in U.S. Streams. Environ. Sci. Technol. 51, 4792–4802. https://doi.org/10.1021/acs.est.7b00012

Burnham, K.P., Anderson, D.R., 2002. Model Selection and Multimodel Inference: A Practical Information- Theoretic Approach, 2nd ed. Springer, New Jork.

Caron, E., Lafrance, P., Auclair, J.C., 2012. Temporal evolution of atrazine and metolachlor concentrations exported in runoff and subsurface water with vegetated filter strips. Agron. Sustain. Dev. 32, 935-943. https://doi.org/10.1007/s13593-012-0087-8

Chen, C., Guo, W., Ngo, H.H., 2019. Pesticides in stormwater runoff—A mini review. Front. Environ. Sci. Eng. 13, 1–72. https://doi.org/10.1007/s11783-019-1150-3

Cruzeiro, C., Pardal, M.Â., Rocha, E., Rocha, M.J., 2015. Occurrence and seasonal loads of pesticides in surface water and suspended particulate matter from a wetland of worldwide interest—the Ria Formosa Lagoon, Portugal. Environ. Monit. Assess. 187, 1–21. https://doi.org/10.1007/s10661-015-4824-8

De Gerónimo, E., Aparicio, V.C., Bárbaro, S., Portocarrero, R., Jaime, S., Costa, J.L., 2014. Presence of pesticides in surface water from four sub-basins in Argentina. Chemosphere 107, 423–431. https://doi.org/10.1016/j.chemosphere.2014.01.039

Deelstra, J., Øygarden, L., Blankenberg, A.G.B., Eggestad, H.O., 2011. Climate change and runoff from agricultural catchments in Norway. Int. J. Clim. Chang. Strateg. Manag. 3, 345–360. https://doi.org/10.1108/17568691111175641

Demonte, L.D., Michlig, N., Gaggiotti, M., Adam, C.G., Beldoménico, H.R., Repetti, M.R., 2018. Determination of glyphosate, AMPA and glufosinate in dairy farm water from Argentina using a simplified UHPLC-MS/MS method. Sci. Total Environ. 645, 34–43. https://doi.org/10.1016/j.scitotenv.2018.06.340

EEA-INTA-Rafaela, 2018-2019. Informes Agrometereológicos. Instituto Nacional de Tecnología Agropecuaria, Estación Experimental Agropecuaria Rafaela, Argentina. https://inta.gob.ar/documentos/boletin-agrometeorologico-mensual-inta-rafaela-listado-de-informes-mensuales (accessed 8.3.21).

Elias, D., Wang, L., Jacinthe, P.A., 2018. A meta-analysis of pesticide loss in runoff under conventional tillage and no-till management. Environ. Monit. Assess. 190, 1–17. https://doi.org/10.1007/s10661-017-6441-1

FAO, 2000. Food and Agriculture Organization of the United Nations. Assessing soil contamination: A reference manual [WWW Document]. URL http://www.fao.org/3/X2570E/X2570E00.htm (accessed 9.14.20).

Fenton, O., Ó hUallacháin, D., 2012. Agricultural nutrient surpluses as potential input sources to grow third generation biomass (microalgae): A review. Algal Res. 1, 49–56. https://doi.org/10.1016/j.algal.2012.03.003

Frau, D., Gutierrez, M.F., Regaldo, L., Saigo, M., Licursi, M., 2021. Plankton community responses in Pampean lowland streams linked to intensive agricultural pollution. Ecol. Indic. 120, 1–12. https://doi.org/10.1016/j.ecolind.2020.106934

GeoINTA, 2014. Mapa de suelos de la Provincia de Santa Fe [WWW Document]. Inst. Nac. Tenología Agropecu. URL http://www.geointa.inta.gob.ar/2014/05/22/mapa-de-suelos-de-la-provincia-de-santa-fe/ (accessed 9.3.19).

Glinski, D.A., Purucker, S.T., Van Meter, R.J., Black, M.C., Henderson, W.M., 2018. Analysis of pesticides in surface water, stemflow, and throughfall in an agricultural area in South Georgia, USA. Chemosphere 209, 496–507. https://doi.org/10.1016/j.chemosphere.2018.06.116

Graeber, D., Gelbrecht, J., Pusch, M.T., Anlanger, C., von Schiller, D., 2012. Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. Sci. Total Environ. 438, 435–446. https://doi.org/10.1016/j.scitotenv.2012.08.087

Harrison, S., McAree, C., Mulville, W., Sullivan, T., 2019. The problem of agricultural 'diffuse' pollution: Getting to the point. Sci. Total Environ. 677, 700–717. https://doi.org/10.1016/j.scitotenv.2019.04.169

Hart, M.R., Quin, B.F., Nguyen, M.L., 2004. Phosphorus Runoff from Agricultural Land and Direct Fertilizer Effects: A Review. J. Environ. Qual. 33, 1954–1972. https://doi.org/10.2134/jeq2004.1954

Hasanuzzaman, M., Rahman, M.A., Islam, M.S., Salam, M.A., Nabi, M.R., 2018. Pesticide residues analysis in water samples of Nagarpur and Saturia Upazila, Bangladesh. Appl. Water Sci. 8, 4–9. https://doi.org/10.1007/s13201-018-0655-4

Hill, A.R., 2018. Landscape hydrogeology and its influence on patterns of groundwater flux and nitrate removal efficiency in riparian buffers. J. Am. Water Resour. Assoc. 54, 240–254. https://doi.org/10.1111/1752-1688.12606

Holvoet, K., Seuntjens, P., Mannaerts, R., De Schepper, V., Vanrolleghem, P.A., 2007. The dynamic water-sediment system: Results from an intensive pesticide monitoring campaign. Water Sci. Technol. 55, 177–182. https://doi.org/10.2166/wst.2007.086

Huffman, R.L., Fangmeier, D.D., Elliot, W.J., Workman, S.R., 2013. Soil and Water Conservation Engineering, 7th ed. American Society of Agricultural and Biological Engineers, St Joseph, Michigan.

Instituto Geográfico Militar, 1959. Cartas topográficas 1:50.000. Ejército Argentino.

INTA (Instituto Nacional de Tecnología Agropecuaria), 1997. Guia practica para el cultivo de maiz. Fundación ArgenINTA, Buenos Aires.

INTA (Instituto Nacional de Tecnología Agropecuaria), 2011. Guia practica para el cultivo de soja. Fundación ArgenINTA, Buenos Aires.

Ippolito, A., Kattwinkel, M., Rasmussen, J.J., Schäfer, R.B., Fornaroli, R., Liess, M., 2015. Modeling global distribution of agricultural insecticides in surface waters. Environ. Pollut. 198, 54–60. https://doi.org/10.1016/j.envpol.2014.12.016

Isenring, R., 2010. Pesticides and the loss of biodiversity. How intensive pesticide use affects wildlife populations and species diversity. Pesticide Action Network

Europe, London, U.K.

Iturburu, F.G., Calderon, G., Amé, M.V., Menone, M.L., 2019. Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region of Argentina: Legacy and current use chemicals contribution. Sci. Total Environ. 691, 476–482. https://doi.org/10.1016/j.scitotenv.2019.07.044

IUPAC, 2019. International Union of Pure and Applied Chemistry. Pesticides Properties DataBase [WWW Document]. URL https://sitem.herts.ac.uk/aeru/iupac/index.htm (accessed 9.24.20).

Jabeen, F., Chaudhry, A.S., Manzoor, S., Shaheen, T., 2015. Examining pyrethroids, carbamates and neonicotenoids in fish, water and sediments from the Indus River for potential health risks. Environ. Monit. Assess. 187, 1–11. https://doi.org/10.1007/s10661-015-4273-4

Jablonowski, N.D., Schäffer, A., Burauel, P., 2011. Still present after all these years: Persistence plus potential toxicity raise questions about the use of atrazine. Environ. Sci. Pollut. Res. 18, 328–331. https://doi.org/10.1007/s11356-010-0431-y

Jeppesen, E., Kronvang, B., Meerhoff, M., Søndergaard, M., Hansen, K.M., Andersen, H.E., Lauridsen, T.L., Liboriussen, L., Beklioglu, M., Özen, A., Olesen, J.E., 2009. Climate Change Effects on Runoff, Catchment Phosphorus Loading and Lake Ecological State, and Potential Adaptations. J. Environ. Qual. 38, 1930–1941. https://doi.org/10.2134/jeq2008.0113

Jergentz, S., Mugni, H., Bonetto, C., Schulz, R., 2005. Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina. Chemosphere 61, 817–826. https://doi.org/10.1016/j.chemosphere.2005.04.036

Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012. Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context. Sci. Total Environ. 440, 82–94. https://doi.org/10.1016/j.scitotenv.2012.08.029

Kafle, B.K., Pokhrel, B., Shrestha, S., Raut, R., Dahal, B.M., 2015. Determination of Pesticide Residues in Water and Soil Samples From Ansikhola. Int. J. Geol. Earth Environ. Sci. 5, 119–127. https://cibtech.org/J-GEOLOGY-EARTH-ENVIRONMENT/PUBLICATIONS/2015/Vol_5_No_2/11-JGEE-015-DAHAL-DETERMINATION.pdf

Knutti, R., Sedláček, J., 2013. Robustness and uncertainties in the new CMIP5 climate model projections. Nat. Clim. Chang. 3, 369–373. https://doi.org/10.1038/nclimate1716

Law 26.011, 2005. Convenio de estocolmo sobre contaminantes organicos persistentes. http://servicios.infoleg.gob.ar/infolegInternet/anexos/100000-104999/102996/norma.htm (accessed 8.23.20).

Lefrancq, M., Jadas-Hécart, A., La Jeunesse, I., Landry, D., Payraudeau, S., 2017. High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts. Sci. Total Environ. 587–588, 75–86. https://doi.org/10.1016/j.scitotenv.2017.02.022

Lowrance, R., Vellidis, G., Wauchope, R.D., Gay, P., Bosch, D.D., 1997. Herbicide transport in a managed riparian forest buffer system. Am. Soc. Agric. Eng. 40, 1047–1057. doi: 10.13031/2013.21357

Mac Loughlin, T.M., 2021. Distribución de plaguicidas y sus efectos ecotoxicológicos en sistemas acuáticos. Impactos ambientales de las actividades agrícolas-productivas sobre la sustentabilidad del ecosistema. Ph. D. Thesis. Facultad de Ciencias Exactas. Universidad Nacional de La Plata. http://sedici.unlp.edu.ar/

Marques, S.C., Primo, A.L., Martinho, F., Azeiteiro, U.M., Pardal, M.Â., 2014. Shifts in estuarine zooplankton variability following extreme climate events: A comparison between drought and regular years. Mar. Ecol. Prog. Ser. 499, 65–76. https://doi.org/10.3354/meps10635

Michael, A., Schmidt, J., Enke, W., Deutschländer, T., Malitz, G., 2005. Impact of expected increase in precipitation intensities on soil loss - Results of comparative model simulations. Catena 61, 155–164. https://doi.org/10.1016/j.catena.2005.03.002

Min, G., Wang, S., Zhu, H., Fang, G., Zhang, Y., 2008. Multi-walled carbon nanotubes as solid-phase extraction adsorbents for determination of atrazine and its principal metabolites in water and soil samples by gas chromatography-mass spectrometry. Sci. Total Environ. 396, 79–85. https://doi.org/10.1016/j.scitotenv.2008.02.016

Ministerio de salud de la República Argentina, 2014. Los plaguicidas en Argentina. Tema: Serie de salud ambiental N° 14 [WWW Document]. URL http://www.msal.gob.ar/images/stories/bes/graficos/0000000341cnt-14-Plaguicidas_Argentina.pdf (accessed 9.23.20).

Montoya, J.C., Costa, J.L., Liedl, R., Bedmar, F., Daniel, P., 2006. Effects of soil type and tillage practice on atrazine transport through intact soil cores. Geoderma. 137, 161–173. https://doi.org/10.1016/j.geoderma.2006.08.007

Mudhoo, A., Garg, V.K., 2011. Sorption, Transport and Transformation of Atrazine in Soils, Minerals and Composts: A Review. Pedosphere. 21, 11–25. https://doi.org/10.1016/S1002-0160(10)60074-4

Nakano, Y., Miyazaki, A., Yoshida, T., Ono, K., Inoue, T., 2004. A study on pesticide runoff from paddy fields to a river in rural region - 1: Field survey of pesticide runoff in the Kozakura River, Japan. Water Res. 38, 3017–3022. https://doi.org/10.1016/j.watres.2004.02.013

Nash, D., Hannah, M., Clemow, L., Halliwell, D., Webb, B., Chapman, D., 2004. A field study of phosphorus mobilisation from commercial fertilisers. Aust. J. Soil Res. 42, 313–320. https://doi.org/10.1071/SR03062

Nash, D., Hannah, M., Clemow, L., Halliwell, D., Webb, B., Chapman, D., 2003. A laboratory study of phosphorus mobilisation from commercial fertilisers. Aust. J. Soil Res. 41, 1201–1212. https://doi.org/10.1071/SR03062

Neal, C., Heathwaite, A.L., 2005. Nutrient mobility within river basins: A European perspective. J. Hydrol. 304, 477–490. https://doi.org/10.1016/j.jhydrol.2004.07.045

Pärn, J., Pinay, G., Mander, Ü., 2012. Indicators of nutrients transport from agricultural catchments under temperate climate: A review. Ecol. Indic. 22, 4–15. https://doi.org/10.1016/j.ecolind.2011.10.002

Perez, D., Okada, E., Aparicio, V., Menone, M., Costa, J.L., 2017. Seasonal and spatial variations of glyphosate residues in surface waters of El Crespo stream, Buenos Aires province, Argentina, in: EGU General Assembly 2017. Geophysical Research Abstracts.

Portocarrero, R., Aparicio, V., de Gerónimo, E., Costa, J.E., 2019. Soil properties of sugarcane fields controlling triazine leaching potential. Soil Res. 57, 729–737 https://doi.org/10.1071/SR18342

Primost, J.E., Marino, D.J.G., Aparicio, V.C., Costa, J.L., Carriquiriborde, P., 2017. Glyphosate and AMPA, “pseudo-persistent” pollutants under real-world agricultural management practices in the Mesopotamic Pampas agroecosystem, Argentina. Environ. Pollut. 229, 771–779. https://doi.org/10.1016/j.envpol.2017.06.006

Prosser, R.S., Hoekstra, P.F., Gene, S., Truman, C., White, M., Hanson, M.L., 2020. A review of the effectiveness of vegetated buffers to mitigate pesticide and nutrient transport into surface waters from agricultural areas. J. Environ. Manage. 261, 110210. https://doi.org/10.1016/j.jenvman.2020.110210

Rector, R.J., Regehr, D.L., Barnes, P.L., Loughin, T.M., 2003. Atrazine, S -metolachlor, and isoxaflutole loss in runoff as affected by rainfall and management. Weed Sci. 51, 810–816. https://doi.org/10.1614/2002-07

Regaldo, L., Gutierrez, M.F., Reno, U., Fernández, V., Gervasio, S., Repetti, M.R., Gagneten, A.M., 2017. Water and sediment quality assessment in the Colastiné-Corralito stream system (Santa Fe, Argentina): impact of industry and agriculture on aquatic ecosystems. Environ. Sci. Pollut. Res. 25, 6951–6968. https://doi.org/10.1007/s11356-017-0911-4

Rodrigues Capítulo, A., Gómez, N., Giorgi, A., Feijoó, C., 2010. Global changes in pampean lowland streams (Argentina): Implications for biodiversity and functioning. Hydrobiologia 657, 53–70. https://doi.org/10.1007/s10750-010-0319-3

Ronco, A.E., Marino, D.J.G., Abelando, M., Almada, P., Apartin, C.D., 2016. Water quality of the main tributaries of the Paraná Basin: glyphosate and AMPA in surface water and bottom sediments. Environ. Monit. Assess. 188, 1–13. https://doi.org/10.1007/s10661-016-5467-0

Rubio, G., Lavado, R.S., Pereyra, F.X., 2019. The Soils of Argentina. Springer, Madison, USA. https://doi.org/10.1007/978-3-319-76853-3

SANTE/11813/2017, 2017. guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed. European Commission (EC).

Sasal, M.C., Demonte, L., Cislaghi, A., Gabioud, E.A., Oszust, J.D., Wilson, M.G., Michlig, N., Beldoménico, H.R., Repetti, M.R., 2015. Glyphosate loss by runoff and its relationship with phosphorus fertilization. J. Agric. Food Chem. 63, 4444–4448. https://doi.org/10.1021/jf505533r

Sass, J.B., Colangelo, A., 2006. European Union bans atrazine, while the United States negotiates continued use. Int. J. Occup. Environ. Health 12, 260–267. https://doi.org/10.1179/oeh.2006.12.3.260

Schwab, A.P., Splichal, P.A., Banks, M.K., 2006. Persistence of atrazine and alachlor in ground water aquifers and soil. Water. Air. Soil Pollut. 171, 203–235. https://doi.org/10.1007/s11270-005-9037-2

Schweiger, O., Maelfait, J.P., Van Wingerden, W., Hendrickx, F., Billeter, R., Speelmans, M., Augenstein, I., Aukema, B., Aviron, S., Bailey, D., Bukacek, R., Burel, F., Diekötter, T., Dirksen, J., Frenzel, M., Herzog, F., Liira, J., Roubalova, M., Bugter, R., 2005. Quantifying the impact of environmental factors on arthropod communities in agricultural landscapes across organizational levels and spatial scales. J. Appl. Ecol. 42, 1129–1139. https://doi.org/10.1111/j.1365-

2664.2005.01085.x

Senbayram, M., Chen, R., Budai, A., Bakken, L., Dittert, K., 2012. N2O emission and the N2O /(N2O + N2) product ratio of denitrification as controlled by available carbon substrates and nitrate concentrations. Agric. Ecosyst. Environ. 147, 4–12. https://doi.org/10.1016/j.agee.2011.06.022

Shang, P., Lu, Y.H., Du, Y.X., Jaffé, R., Findlay, R.H., Wynn, A., 2018. Climatic and watershed controls of dissolved organic matter variation in streams across a gradient of agricultural land use. Sci. Total Environ. 612, 1442–1453. https://doi.org/10.1016/j.scitotenv.2017.08.322

Singh, V.P., 1992. Elementary hydrology, 1st ed. Prentice-Hall, New Jersey.

Sweeney, B.W., Newbold, J.D., 2014. Streamside forest buffer width needed to protect stream water quality, habitat, and organisms: a literature review. J. Am. Water Resour. Assoc. 50, 560–584. https://doi.org/10.1111/jawr.12203

Vialle, C., Sablayrolles, C., Silvestre, J., Monier, L., Jacob, S., Huau, M.C., Montrejaud-Vignoles, M., 2013. Pesticides in roof runoff: Study of a rural site and a suburban site. J. Environ. Manage. 120, 48–54. https://doi.org/10.1016/j.jenvman.2013.02.023

Vonberg, D., Hofmann, D., Vanderborght, J., Lelickens, A., Köppchen, S., Pütz, T., Burauel, P., Vereecken, H., 2014. Atrazine Soil Core Residue Analysis from an Agricultural Field 21 Years after Its Ban. J. Environ. Qual. 43, 1450–1459. https://doi.org/10.2134/jeq2013.12.0497

Willis, G.H., Mcdowell, L.L., 1983. Pesticides in Agricultural Runoff and Their Effects on Downstream Water Quality. Environmetal Toicology Chem. 1, 267–279. https://doi.org/10.1002/etc.5620010402

Wratten, S.D., Gillespie, M., Decourtye, A., Mader, E., Desneux, N., 2012. Agriculture , Ecosystems and Environment Pollinator habitat enhancement : Benefits to other ecosystem services. "Agriculture, Ecosyst. Environ. 159, 112–122. https://doi.org/10.1016/j.agee.2012.06.020

Xu, B., Li, J., Huang, Q., Gong, Q., Li, L., 2016. Impacts of land use patterns and typhoon-induced heavy rainfall event on dissolved organic matter properties in the South Tiaoxi River, China. Environ. Earth Sci. 75. https://doi.org/10.1007/s12665-016-5413-z

Zak, D., Stutter, M., Jensen, H.S., Egemose, S., Carstensen, M. V., Audet, J., Strand, J.A., Feuerbach, P., Hoffmann, C.C., Christen, B., Hille, S., Knudsen, M., Stockan, J., Watson, H., Heckrath, G., Kronvang, B., 2019. An Assessment of the Multifunctionality of Integrated Buffer Zones in Northwestern Europe. J. Environ. Qual. 48, 362–375. https://doi.org/10.2134/jeq2018.05.0216

CRediT author statement

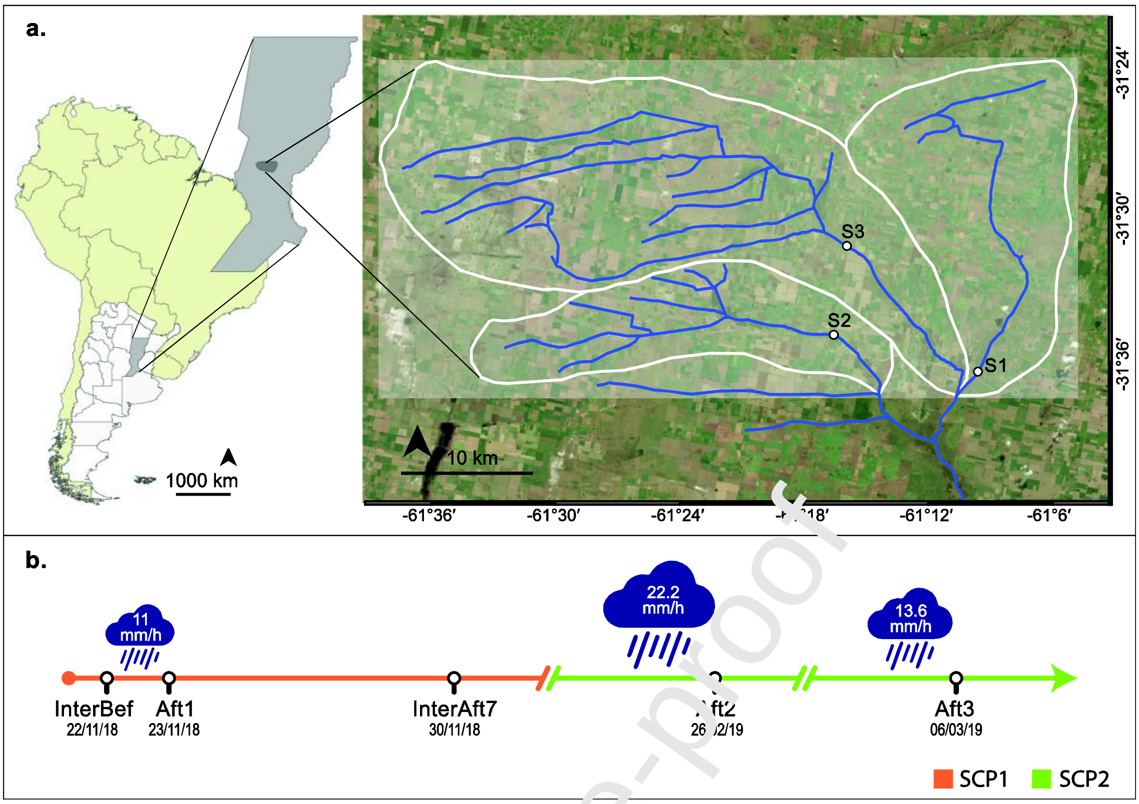
Andrade, Victoria Soledad: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **Gutierrez, María Florencia:** Conceptualization, Methodology, Formal analysis, Funding acquisition, Writing - review & editing. **Regaldo, Luciana:** Funding acquisition, Writing - review & editing. **Paira, Aldo Raul:** Methodology, Writing - review & editing. **Repetti, María Rosa:** Data curation, Writing - review & editing. **Gagneten, Ana María:** Conceptualization, Methodology, Project administration, Supervision, Funding acquisition, Writing - review & editing.

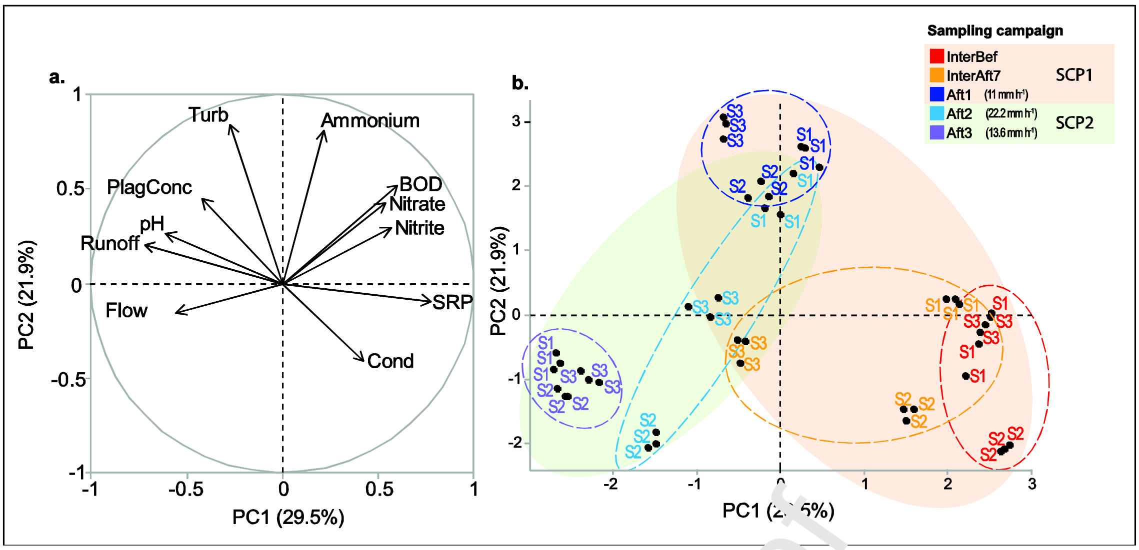
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Ana María Gagneten


a.
1000 km
10 km
S1
S2
S3
-61°36′
-61°30′
-61°24′
-61°12′
-61°6′
-31°24′
-31°30′
-31°36′
b.
11 mm/h
22.2 mm/h
13.6 mm/h
InterBef 22/11/18
Aft1 23/11/18
InterAft7 30/11/18
Aft3 06/03/19
SCP1
SCP2


a.
Turb
Ammonium
PlagConc
BOD
Nitrate
Nitrite
pH
Runoff
Flow
SRP
Cond
PC2 (21.9%)
PC1 (29.5%)
b.
Sampling campaign
InterBef
InterAft7
Aft1 (11 mm h⁻¹)
Aft2 (22.2 mm h⁻¹)
Aft3 (13.6 mm h⁻¹)
SCP1
SCP2
PC2 (21.9%)

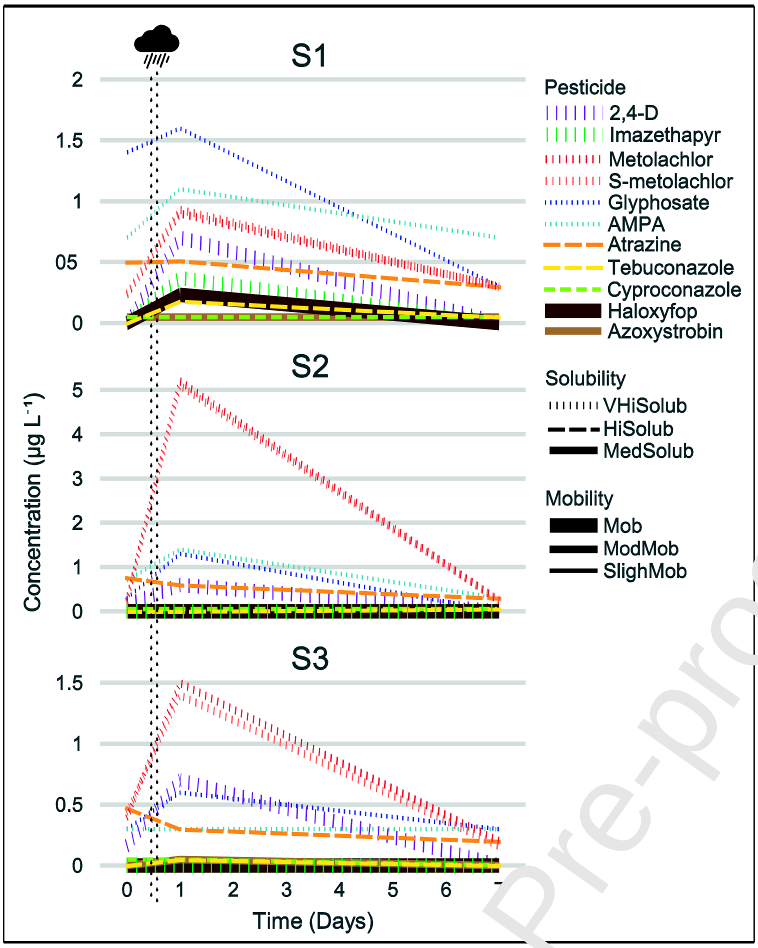

S1
S2
S3
Concentration (µg L⁻¹)
Time (Days)
2
1.5
1
05
0
5
4
3
2
1
0
1.5
1
0.5
0
0 1 2 3 4 5 6
Pesticide
2,4-D
Imazethapyr
Metolachlor
S-metolachlor
Glyphosate
AMPA
Atrazine
Tebuconazole
Cyproconazole
Haloxyfop
Azoxystrobin
Solubility
VHiSolub
HiSolub
MedSolub
Mobility
Mob
ModMob
SlighMob

Figure Captions

Figure 1. a. Study area. South America, Argentina, Santa Fe province and the three sampling sites (S1, S2 and S3) with their independent sub-basins; **b.** Sampling campaigns timeline showing the study design in relation to three rainfall events (intensity specified in the cloud drawing) with two different seasons of crop practices (SCP1, SCP2) (time line color). Five samplings were carried out: two samplings in inter rain periods: one day before the first rainfall event (InterBef) and seven days after the event (InterAft7), and three after-rain samplings: one day after each rainfall event (Aft1, Aft2 and Aft3).

Figure 2. PCA on stream water quality of the three streams (S1, S2 and S3) in the sampling campaigns made in the inter-rain periods: InterBef and InterAft7, and after-rain: Aft1, Aft2 and Aft3 (dashed ellipses), in both seasons of crop practices (SCP1, SCP2) (colored ellipses). **a.** Correlation circle. **b.** Sample distribution according to sampling times and sites. PlagConc: total concentration of pesticides, Turb: turbidity, BOD: biologic oxygen demand, SRP: soluble reactive phosphorus, Cond: conductivity.

Figure 3. Pesticide concentrations (μg L^{-1}) in the three streams (S1, S2 and S3) water one day before (InterBef) and one (Aft1) and seven days after (InterAft7) the rainfall event. Solubility (line pattern): Very high: > 100 (VHiSolub), High: 10 – 100 (HiSolub), medium: 1 – 10 mg L^{-1} (MedSolub). Mobility (line thickness): Mobile: 1 – 2 (Mob), Moderately mobile: 2 – 3 (ModMob), Slightly mobile: 3 – 4 Log Koc (SlighMob).

Table1

Table 1. Phenological stages of crops developed in the study area in the two seasons of crop practices (SCP) studied: SCP1 (InterBef, InterAft7, and Aft1), SCP2 (Aft2 and Aft3). * indicates double cropping soybean cultivation following wheat.

Land surface %	Crop	Seasons of Crop Practices (SCP)	
		SCP1	SCP2
40%	**Soy**	Chemical fallow Sowing	1° Grain filling * 2° Vegetative growth
10%	**Corn**	Vegetative growth Flowering	Sowing
<10%	**Wheat**	Sowing	* 2° Soy
	Sunflower	Flowering - Grain filling	-

Journal Pre-proof

Table 2. Ranges and values of environmental, geomorphological and hydrological variables for the three sampling sites.

			S1	S2	S3
Environmental variables	Ammonium (µg L^{-1})		32.4 - 307	0 - 174.3	0 - 208.4
	Nitrite (µg L^{-1})		11.4 - 105.4	3 - 55.3	6.4 - 59
	Nitrate (µg L^{-1})		84 - 1954	0 - 800	80 - 602
	SRF (µg L^{-1})		923.6 - 1791.4	951.4 - 2070	1011.4 - 2168.6
	Chlorophyll *a* (µg L^{-1})		0 - 12	0 - 9.4	2.4 - 11.5
	BOD (µg L^{-1})		8.2 - 43.1	6.3 - 46.3	6.7 - 45.9
	Turbidity (FTU)		28 - 90	7 - 98	33 - 128
	Conductivity (µs cm^{-1})		235 - 614	519 - 1837	341 - 887
	Dissolved oxygen (%)		41.4 - 64.2	72.1 - 81.5	62.8 - 73.8
	pH		6.9 - 7.9	7.2 - 7.8	7.7 - 8.4
Geomorphological and hydrological variables	Stream order		2°	3°	3°
	Basin area (m^2)		27.9	19.2	57.2
	Longitudinal slope (%)		0.04	0.11	0.1
	Side slope (%)		0.2	0.33	0.17
	Woody riverbank cover (%)		40	95	10
	Time of concentration (h)		113.1	74.4	107.3
	Flow ($m^3 s^{-1}$)	InterBef	3.5	2.9	1.1
		Aft1	5.8	7.1	2.8
		InterAft7	6.5	3.7	3.8
		Aft2	4.6	9.6	1.3
		Aft3	12.0	9.6	3.3
	Estimated runoff flow ($m^3 s^{-1}$)	Aft1	0.28	0.19	0.57
		Aft2	0.34	0.24	0.71
		Aft3	0.46	0.32	0.95

***** S1: Site 1; S2: Site 2; S3: Site 3; InterBef: one day before the first rainfall event; InterAft7: seven days after the first rainfall event; Aft1, Aft2, and Aft3: one day after each of the three rainfall events.

Table 3. Mean values and standard deviation of environmental variables of the three sites (S1, S2, and S3) in samplings related to the first rainfall event.

	Ammonium ($\mu g\ L^{-1}$)	Nitrite ($\mu g\ L^{-1}$)	Nitrate ($\mu g\ L^{-1}$)	SRP ($\mu g\ L^{-1}$)	Chlorophyll *a* ($\mu g\ L^{-1}$)
InterBef	95.3 ± 83.5	42.1 ± 10.0	614.3 ± 184.3	**1997.5 ± 186.5**	**10.4 ± 2.1**
Aft1	**215.8 ± 72.0**	31.5 ± 3.9	648.9 ± 111.8	1348.1 ± 78.2	5.0 ± 0.4
InterAft7	24.8 ± 21.5	50.5 ± 44.6	848.9 ± 770.6	1244.8 ± 25.1	3.2 ± 0.4
	BOD ($\mu g\ L^{-1}$)	Turbidity (FTU)	Conductivity ($\mu s\ cm^{-1}$)	Dissolved oxygen (%)	pH
InterBef	40.4 ± 5.6	26.3 ± 18.6	821.3 ± 183.5	66.5 ± 14.7	**7.3 ± 0.4**
Aft1	45.1 ± 1.8	**97.3 ± 24.0**	512.0 ± 349.0	59.9 ± 17.3	7.8 ± 0.4
InterAft7	**31.1 ± 2.6**	55.9 ± 7.3	964.0 ± 758.4	68.3 ± 4.7	7.7 ± 0.6

*InterBef: one day before the rainfall event; Aft1: the day after the event; InterAft7: seven days after the event. Bold font: significant differences ($p < 0.05$).

Table 4. Mean values and standard deviation of environmental variables of the three sites (S1, S2, and S3) one day after three different rainfall events.

	Ammonium ($\mu g\ L^{-1}$)	Nitrite ($\mu g\ L^{-1}$)	Nitrate ($\mu g\ L^{-1}$)	SRP ($\mu g\ L^{-1}$)	Chlorophyll *a* ($\mu g\ L^{-1}$)
Aft1	**215.8 ± 72.0**	31.5 ± 3.9	648.9 ± 111.8	**1348.1 ± 78.2**	5.4 ± 1.0
Aft2	42.8 ± 43.1	53.5 ± 37.9	755.6 ± 976.4	1035.5 ± 89.7	**8.4 ± 1.8**
Aft3	25.6 ± 24.9	7.6 ± 3.9	100.8 ± 87.3	1031.9 ± 50.6	4.5 ± 1.3
	BOD ($\mu g\ L^{-1}$)	Turbidity (FTU)	Conductivity ($\mu s\ cm^{-1}$)	Dissolved oxygen (%)	pH
Aft1	**45.1 ± 1.8**	97.3 ± 24.0	512.0 ± 349.0	59.9 ± 17.3	7.8 ± 0.4
Aft2	10.7 ± 1.1	67.7 ± 27.4	698.0 ± 201.8	71.9 ± 6.9	7.7 ± 0.0
Aft3	7.1 ± 1.0	45.4 ± 11.8	375.0 ± 130.4	64.5 ± 16.6	7.8 ± 0.1

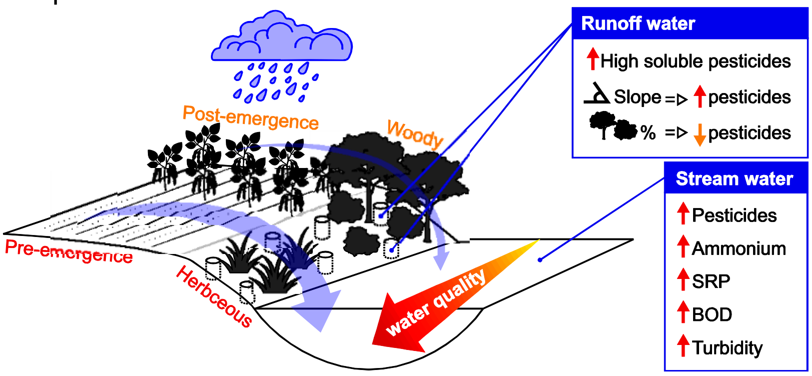
*Aft1, Aft2 and Aft3: sampling campaigns conducted after three rainfall events. Bold font: significant differences ($p < 0.05$).

Table 5. Final models indicating the variables with the highest explanatory power of the number and percentage of pesticides detected in runoff water.

Final Models				
	b	**SE**	**T**	**p(T)**
Pesticide number				
BasinArea (ha)	0.19	0.05	4.03	0.005
HighSolub (µg L $^{-1}$)	0.74	0.21	3.53	0.01
WoodyRiv (%)	-0.06	0.02	-3.35	0.01
Pesticide percentage				
BasinArea (ha)	1.04	0.26	4.03	0.005
HighSolub (µg L $^{-1}$)	4.12	1.17	3.53	0.01
WoodyRiv (%)	-0.36	0.11	-3.35	0.01

b: slope of the correlation; SE: standard error; T: statistic of the model; p(T): significance value of the variable; BasinArea: sub-basin area; HighSolub: VHiSolub+HiSolub pesticides; WoodyRiv: woody riverbank cover.

Graphical abstract



Highlights

- An increase in rainfalls is expected in the agricultural Pampas due to climate change
- Runoff by rainfalls is the main drift way of agrochemicals to surface water bodies
- Pesticides, nutrients, BOD & turbidity increased after rain, pre-emergence being worst
- Pesticides in runoff water depended on solubility, slope, and woody riparian flora %
- Design environmental monitoring considering rainfalls and crops phenological stage