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DATA AVAILABILITY

All data employed are publicly available and can be obtained upon request from "Centro de Investigaciones en Recursos Naturales" (CIRN) del Instituto Nacional de Tecnologia Agropecuaria" (INTA) (https://inta.gob.ar/ciderecursosnaturales).

ABSTRACT

Although pesticides are intensively employed in the Pampa region of Argentina, the possibility to perform environmental risk assessment (ERA) remains limited due to the absence of readily available databases to run pesticide fate models and the lack of standardized realistic worst case scenarios. The aim of the current study was to further

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advance capacities for performing probabilistic ERA in the Pampa region by dividing and parameterizing the region into functional soil-climate mapping units (SCU) and defining statistically-based worst-case soil-climate exposure scenarios. Results obtained demonstrate that the SCU selected for a specific modeling exercise should depend on the dissociation constant (Kd) of the pesticide evaluated and whether short-term or long-term pesticide fate modeling and risk assessment is needed. Four regionally representative SCUs were specifically identified for modeling the fate of pesticides with low, high and intermediate values of Kd. Fate modeling of pesticides with an intermediate Kd requires the use of a different SCU for short-term versus long-term pesticide modeling, whereas this distinction is not necessary in the case of pesticides with both low and high Kd. The current definition of realistic worst-case soil-climate scenarios represents a crucial step towards better pesticide fate modeling and exposure assessment in the Pampa region of Argentina.

Key Points

Four soil-climate units were identified as exposure scenarios for the Pampa region The scenario depends on the dissociation constant of the pesticide. The scenario depends on the duration over which the mean concentration is averaged The availability of scenarios should impulse pesticide risk and exposure assessment in the region

KEYWORDS

Agriculture – Pesticide - Exposure Scenarios – Risk Assessment – Water Contamination

INTRODUCTION

Agriculture is a predominant economic activity in Argentina, with grain and feed representing 48.7% of national exports in 2021 (INDEC, 2021). In Argentina, most of the grain production takes place in the Pampa region, a 500.000 km^2 area located in the center-west of the country, which is characterized by temperate climate and deep fertile soils (Moscatelli, 1991). Argentina is the third largest soybean producer worldwide and one of the top ten producers of maize, sunflower and sorghum (FAO, 2021). The widespread adoption of genetically modified crops (GM crops) in the nineties was linked to an intensification of agriculture and an increase in pesticide use (Satorre, 2011). Nowadays, pesticide use per hectare (ha) of cropland is greater in Argentina than in Brazil or than any other countries from the Organization for Economic Cooperation and Development (OECD, 2019).

Considering the large extensions of rural areas that are treated with pesticides each year in the Pampa region, it is crucial to effectively and accurately evaluate the risk these pesticides pose to water quality and aquatic ecosystem health. In most countries, the regulation and management of pesticide products relies on a methodology referred to as "Ecological Risk Assessment" or ERA (Spadotto and Mingoti, 2019). The goal of ERA is to assess the likelihood that adverse ecological effects may occur by comparing the predicted environmental concentrations (PECs) of the pesticide to the concentration below which unacceptable effects will most likely not occur, i.e. the predicted no effect concentrations (PNECs) (Schäfer et al., 2019).

Pesticide authorization procedures generally follow a tiered approach where PECs and potential toxic effects are evaluated in a number of sequential steps. These normally begin with single species laboratory-based toxicity values and worst-case exposure assumptions (first tier) and move on to more complex scenarios (higher tiers) that integrate processes and characteristics occurring in natural ecosystems, such as multi-species and semi-field test systems, as well as more realistic and complex exposure scenarios (Brock et al., 2010; Tiktak et al., 2013 Shäfer et al., 2019). The "exposure assessment" is the process through which PECs are defined. Exposure assessments can be performed based on environmental monitoring surveys (Perez et al., 2021; Rico et al., 2021) but mathematical models are increasingly used to predict the transport and fate of pesticides in the environment and estimate PECs (Tiktak et al., 2013; Teklu et al., 2015; Xie et al. 2018: Zhang et al., 2020).

In ERA, mathematical models are typically employed in a limited number of standard scenarios, which are combinations of soil, climate and crop parameters to be used in modeling (Tiktak et al., 2013; Teklu et al., 2015; Bach et al., 2017). The use of standardized scenarios helps to harmonize risk assessment calculations and their interpretations (EFSA, 2014). When defining standardized scenarios, the full range of soil-climate conditions existing in a specific area of interest should first be identified. These soil-climate conditions should then be classified into a manageable number of unique soil-climate combinations or scenarios for calculating PECs (Bach et al., 2017). The selected scenarios should represent a realistic worst-case situation (EFSA, 2014), which is often defined as the 90th percentile of the modeled exposure concentrations or PECs in the intended area of use (EFSA, 2010; 2013; USEPA 2019).

Identifying the realistic worst-case scenario involves calculating the basic population of potential pesticide concentrations for the entire soil–climate combinations in a given regulatory area of interest and for a long weather time series. This produces a population of PEC values which can be organized into three different cumulative distribution functions (CDF): a temporal CDF based on the variability of the PECs over the time series, a spatial CDF based on the variability of the PECs amongst the different soil-climate combinations and finally, an overall spatio-temporal CDF which corresponds to the grouping and classification of all the PEC values obtained. The realistic worst-case scenario corresponds to the soil-climate combination whose PEC represents the 90th percentile of the overall spatio-temporal

CDF (Bach et al., 2017; Boesten et al. 2018; Scorza Junior et al., 2018; Oh et al., 2021).

The development of local and regional standardized scenarios is especially needed in Latin America to impulse pesticide fate modeling and probabilistic risk assessment (Casallanovo et al., 2021). Indeed, despite the widespread and intensive use of pesticides in the Pampa region of Argentina, the possibility to perform prospective pesticide ERA remains limited due to the lack of regionally tested pesticide fate models, the absence of readily available databases to run such models, and the lack of standardized realistic worst case scenarios. In a recent study, the possibility to employ the pesticide fate model “Pesticide in Water Calculator” (PWC) in the Pampa region of Argentina was successfully examined, and a sensitivity analysis of the model under regional conditions was performed (D’Andrea et al., 2020). PWC is a field-scale model that allows to simulate pesticide fate into user-defined waterbodies through the selection of different parameters related to pesticide applications, soil, climate, hydrology, and phenology (Young, 2016). PWC is currently used for pesticide registration by the United States of America (USA) and Canada (Health Canada, 2018; 2020; Young, 2019).

The aim of the current study was to further advance capacities for performing probabilistic ERA in the Pampa region of Argentina by pursuing two specific objectives: 1) to divide and parameterize the Pampa region into functional soil-climate mapping units (SCU) for aquatic pesticide fate-modeling with PWC, and 2) to define statistically-based worst-case soil-climate exposure scenarios for ERA exposure assessment.

METHODS

Study area

The Pampa region is a flat plain of about 500,000 km^2 that is characterized by flat or slightly undulated landscapes. The climate of the Pampa region of Argentina is temperate humid, without a dry season and with a very hot summer (Barros et al., 2015). The average annual temperature increases gradually from 14 to 19 ^{o}C from south to north, while the average annual rainfall gradually decreases from 1200 mm to 600 mm from east to west (Rubi Blanchi and Cravero, 2012). Shallow temporary lakes and ponds of fresh or brackish waters are scattered throughout the territory due to the impoverished drainage network and the few slopes (Benzaquen et al., 2017). The biodiversity of these environments is highly specific and dependent on these habitats (Benzaquen et al., 2017).

PWC Model

PWC is a graphic user interface that links the output of two sub-models: the "Pesticide Root Zone Model version 5 (PRZM 5)" and the "Variable Volume Water Body Model (VVWM)”. PRZM 5 is a one-dimensional and dynamic compartmental model that is used to simulate the movement of chemicals in unsaturated soil systems through infiltration, runoff and water erosion within and immediately below the plant root zone. For its part, VVWM is designed to model the fate of chemical substances in a waterbody. It contains a set of mathematical modules that relate the fundamental chemical properties of the pesticide to the limnological parameters responsible for the kinetics of transport of chemical substances in aquatic ecosystems. Additional background information on PWC can be obtained from Young (2016).

Parametrization of soil-climate units for the Pampa region

As stated in the introduction, to define standardized soil-climate scenarios, it is first necessary to identify the full range of soil-climate conditions existing in the area of interest, and classify them into a manageable number of unique SCUs. In this case, the soil and climate parameters that must be classified are those which need to be entered in PWC in order to simulate the environmental fate of a pesticide. The following sections describe the origin and the nature of the soil and climate data that were employed, as well as the division of the territory that was made, in order to define functional soil-climate mapping units (SCU).

Soil data The soil data required by PWC and included in the scenario definition encompass basic soil characteristics such as the density and the proportion of organic carbon, clay and sand of the soil layers, together with water holding capacity properties (wilting point and field capacity) and parameters corresponding to the curve number and the Universal Soil Loss Equation, which are used to calculate runoff and erosion (USDA, 1986).

A regional soil database specifically designed for application in PWC was constructed based on a 1:2.500.000 national soil database first described by Godagnone and De La Fuente (2014) and adapted for hydrological models by Espíndola et al. (2014). This national database was elaborated using the methodology established by the Global and Nation Soils and Terrain Digital Databases (SOTER), in which the territory is divided into polygons presenting a unique combination of soil and land characteristics including lithology, surface form, slope and parent material (Van Engelen and Wen, 1995). The data corresponding to 77 soil polygons, ranging in surface between 2000 and 20000 km^2, and representing a total of 503.068 km^2 of land from the Pampa region were taken from the georreferenciated national database as a starting point to generate the Pampa region PWC soil database. The data provided by this database included:

The hydrological group, max root depth and albedo of the soil, as well as the number of soil layers and, for each layer, depth, humidity, hydraulic conductivity, erodibility, and content of clay, silt, sand and organic carbon (Godagnone and De La Fuente; 2014; Espíndola et al., 2014).

For each soil horizon, the proportion of soil organic matter was obtained by multiplying the proportion of organic carbon by the van Bemmelen equation factor (1,724) (Eyherabide et al., 2014). Wilting point and field capacity in each soil horizon were calculated using the "Soil Water Characteristics" program (Saxton and Rawls, 2006). The topographic factor (LS), the coverage management factor (C), and the soil conservation practice factor (P) of the USLE were calculated using the USLE-RUSLE software (Gvozdenovich et al., 2015). The curve number values were assigned to fallow and row crop based on the soil hydrological group and according to tables available in the *USDA* Technical Release 55 (*TR-55*) (USDA, 1986). Manning's roughness coefficient was defined from values recommended in PRZM-5 user manual (Young & Fry, 2014). Figure 1 illustrates the hydrological group of the 77 SCUs considered in the analysis, and maps the proportion of sand and organic matter of the first soil horizon.

Climate data The climate data required by PWC and included in the scenario definition are: 1) maximum temperature, 2) minimum temperature, 3) wind speed at 10 m, 4) relative humidity and 5) precipitation. The climate database was built using information from 30 weather stations from the Pampa region for which 30 years of daily data were available for the 1984-2014 period. The study by D'Andrea et al.

(2019) provides the location and detailed information of these 30 weather stations and describes how climate data were thoroughly checked for quality and consistency.

A spatial interpolation was performed on the data from the 30 weather stations in order to generate one climate dataset corresponding to the centroid of each of the soil polygons above described (Figure 2). To achieve this, the centroids of each of the 77 SCU were first determined using the "sf" package version 0.6.3 of the statistical software R. For each of the centroids, a spatial interpolation was then carried out through ordinary kriging using the "variogram" and "variogramfit" routines of the MATLAB software (Mathworks, Natick, MA, USA). An interpolation was performed for all daily values of all variables considered for each of the 30 years comprised within the 1984-2014 period. In total 56,615 interpolations were executed; one per variable and day. Global radiation data series were calculated from interpolated sunshine hours using the Amstrong equation (Penman, 1948). Figure 3 maps the mean annual temperature and total rainfall for each of the 77 SCU considered in the analysis in the 30 years studied.

Pesticide simulation runs

In order to estimate the overall distribution of potential pesticide PECs for the region, simulation runs were performed for 45 different dummy pesticide molecules for a period of 30 consecutive years in the 77 above-described SCUs. Dummy pesticides were selected to illustrate a wide range of degradation and sorption properties to compare the behavior of chemically diverse pesticide molecules amongst SCUs. The physicochemical characteristics of modeled dummy pesticides are presented in Table 1 of Supplementary Materials. Half-life in soil (i.e. DT50) varied from 0.05 to 3000 days, half-life in the water column ranged from 0.2 to 365 days, whereas the pesticide soil-water distribution coefficient (Kd) ranged between 0.07 and

200 490 L/kg. The ranges and combination of physicochemical properties assigned to the dummy pesticides were based on the properties of real pesticides typically employed in grain crops and were obtained from Lewis et al. (2016). It is important to highlight that the goal of the simulations was to compare the PECs obtained in the 77 SCUs following identical applications of a variety of pesticide molecules. The simulations did not aim at modeling real-life pesticide exposures, even though the pesticide pulverizations modeled are based on procedures commonly performed in the Pampa region.

An application rate of 1 kg/ha was fixed for all the simulations to ensure that the same importance was given to all pesticides. In all the simulations, the pesticide was applied before sowing a 29 ha field with a soybean crop. Soybean phenology, i.e. sowing, emergence and harvest dates were defined for the centroid of each SCU based on the phenological calendar corresponding to the region within which the coordinates of the centroid are located. Soybean phenological calendars used for the different subregions of the Pampa are those defined by the Ministry of Agriculture of Argentina (Oficina de Riesgo Agropecuario, 2018). During the simulation, when a soybean crop was considered present on the land (i.e. after the emergence date), canopy interception was set at 0.05 cm, root length at 100 cm and crop height at 80 cm.

To ensure that annual application dates presented similar characteristics amongst years and SCUs, the application date was defined, for each year of the simulation, as the day immediately before the largest rainfall observed in the period ranging from forty to ten days before the sowing date. Accumulated daily precipitation needed to be greater than 3 mm for a specific day to be considered a day with rainfall. Input data used in the section “Watershed and waterbody dimensions” of

PWC were set constant for all runs: (i) area of treated field, 290000 m^2 (29 ha); (ii) fraction of the field cropped, 1; (iii) surface area of waterbody, 8000 m^2 (0.8 ha); and (iv) initial and final depths, 1.5 m. These values were chosen based on an unpublished preliminary study in which the surface area of ponds present over the whole study area was measured on satellital images. The selection of a low, 1.5m depth, was based on the literature (Benzaquen et al., 2017). Values used for both water column and benthic parameters are given in D'Andrea et al. (2020). For their part, water columns and benthic parameters were set according to values found in the literature for Pampean lakes and ponds. Spray efficiency and drift were arbitrarily set at 0.99 and 0.01 in all simulations.

The simulation of the fate of each of the 45 pesticides in the 77 SCUs was performed with the software PWC version 1.52, but repeated model runs were automatized with the software SENSAN, a tool that is included in the PEST software package for parameter estimation and uncertainty analysis of complex environmental computer models (Doherty, 1994). In order to illustrate acute and chronic toxicity scenarios, PWC output data retained for worst-case scenario definition consisted of upper 90th ranked 4-day (4dPEC) and 60-day (60dPEC) annual average pesticide water concentrations.

Percentile-based selection of soil–climate scenarios for multiple pesticides

In accordance with most modern exposure assessment studies (Bach et al., 2017; Boesten, 2018; Scorza Junior et al., 2018), soil-climate scenarios were selected based on the 90th percentile of all 4dPEC and 60dPEC values simulated for the Pampa region. In a spatio-temporal CDF, the overall 90th percentile of a target variable represents a combination of the spatial component and the temporal component of the overall distribution (EFSA 2013, Boesten, 2018, Bach et al., 2017). The risk of exceedance of a given threshold concentration in time and space was considered to be of equal importance in the present study and was set to 20% for both dimensions, in agreement with previous studies (Bach et al., 2017; Scorza Junior et al., 2018; Dowling et al., 2019).

Therefore, the first step of the analysis consisted in building, for every dummy pesticide evaluated, the overall, as well as the spatial and temporal CDFs of all annual 4dPEC and 60dPEC values to determine the percentile corresponding to every annual value obtained over the 30-year simulation period. Then, for each modeled pesticide, the SCUs which PECs corresponded to the 89 and 90th overall percentiles were selected. The 89th percentile was considered together with the 90th percentile, so as to obtain enough SCUs to choose from in the next step, and to ensure that the resulting scenario was conservative enough. Once this initial set of SCUs was selected, the number of potential scenarios was further reduced by restricting the selection to SCUs presenting both a spatial and a temporal percentile ranging between the 75th and 85th position. Again, the range of selection was slightly extended on both sides of the 80th percentile criteria, to obtain enough adequate SCUs to select from in the next step. The above described analysis was performed in parallel for 4dPEC and 60dPEC values, so that a pool of candidate soil-climate scenarios was obtained for both endpoints.

All above described analyses were performed separately for each dummy pesticide because the spatial pattern of the predicted exposure concentrations is likely to differ amongst pesticides given that the relation between soil parameters, substance fate parameters and predicted environmental concentrations is non-linear (Tiktak et al., 2013). In the final step of the analysis, the SCUs selected for all dummy pesticides were compared, and those with the largest selection frequency were considered as candidate scenarios. As stated above, this analysis was performed separately for 4dPEC and 60dPEC values to examine whether selected scenarios were similar in terms of acute and chronic periods.

RESULTS

To estimate the overall distribution of potential pesticide PECs in the Pampa region, the upper 90th ranked 4-days and 60-days annual average pesticide water concentrations were determined for 30 consecutive years and 45 dummy pesticides in 77 SCUs of the Pampa region. In total, 103,950 simulations were carried out using the PWC model (45 pesticides * 30 years * 77 SCUs). Figure 4 illustrates the relative proportion of applied pesticide which enters the waterbody through either erosion, runoff or spray drift, according to the model for each dummy pesticide. This figure clearly shows that molecules with a high Kd reach surface waters mainly through erosion, whether molecules with a low Kd enter the water through runoff.

SCUs producing PEC values equivalent to the 90th percentile of all PECs were identified using the percentile-based selection protocol described above (see methods). 41 (4dPEC) and 34 (60dPEC) of the 77 examined SCUs were selected for at least one dummy pesticide, when applying this selection protocol. However, of these SCUs, about half were selected in the case of only four pesticides or less, meaning that their potential to illustrate various chemical classes in a region-wide exposure assessment was limited. Overall, when considering all tested dummy pesticides, the cartographic units presenting the largest frequency of selection were only selected in the cases of 33-36% of the dummy pesticides, i.e. for 15 (4dPEC) and 16 (60dPEC) of the 45 pesticides tested.

In an attempt to identify SCUs representative of different chemical groups, dummy pesticides were gathered according to either their soil half-life, their water half-life, or their Kd, and the representativeness of selected SCUs was assessed for each group of pesticide (data not shown). The largest level of representativeness was obtained when dummy pesticides were grouped according to their Kd, with some SCUs presenting selection frequencies as high as 78 - 88% for some categories (Table 1). Indeed, if only mobile pesticides with a Kd lower than 2.5 are considered, it is possible to identify an SCU (*A300_140*) with 4dPEC values that is representative of the 90th percentile of all PECs for 78% of the 14 dummy pesticides in this category. When considering 60dPECs for the same group of pesticides, four SCUs are equally representative with a range of selection frequencies corresponding to 42 - 57% of the pesticides (Table 1). Nevertheless, as one of these four SCUs is the SCU number *A300_140* that was identified as the most representative in the case of 4dPECs, it is recommendable, for greater practicality, that SCU *A300_140* is selected as the pampean scenario to be employed for both short term (4dPEC) and long term (60dPEC) pesticide fate modeling and exposure assessment of low Kd pesticides (Kd < 2.5). The SCU *A300_140* is located in the northeast of the Pampa region (Fig. 5) and its main soil type is typic hapludert (vertisol), which is classified as hydrological group D (Table 1).

In the case of pesticides with an intermediate soil binding affinity (3 < Kd < 15), the most frequently selected SCUs differed whether 4dPECs or 60dPECs were considered, and no single SCUs could be identified that was representative of both time averages. For this reason, the SCU *A373_72* was selected as the most representative in the case of short term concentrations (4dPECs) with a selection frequency of 72.7%, whereas, the SCU *A318_525* was selected for long term concentrations (60dPEC) with a selection frequency of 72.8% (Table 1). The SCU *A373_72* is located in the center south of the Pampa region (Fig. 5), its main soil type is typic natraquoll (mollisol), which is classified as hydrological group D (Table 1). For its part, SCU *A318_525* is located in the north east of the region (Fig. 5), its main soil type is vertic argiudoll (mollisol) and it also belongs to hydrological group D (Table 1).

Finally, in the case of pesticides that tightly bind to the soil (Kd > 50), the SCU *A240_582* came out as highly representative of this group of pesticides, being selected for 77.8 and 88.9% of the 18 pesticides present in the group, in the case of 4dPECs or 60dPECs, respectively (Table 1). It is interesting to note that SCU *A311_231* is equally representative as *A240_582* in the case of 4dPECs, but as *A240_582* is also widely selected for 60dPECS, it is more convenient to use this SCU, as it can be employed for both short term and long term pesticide modeling. The SCU *A240_582* is located in the center west of the Pampa region (Fig. 5) and its main soil type is entic haplustoll, which is classified as hydrological group B (Table 1).

DISCUSSION

The present study identified twelve different SCUs as potential candidates for realistic worst case scenarios modeling of PECs in the Pampa region of Argentina. Results obtained demonstrated that scenarios reached a larger representativeness of the whole region when selected scenarios were based on both the Kd of the pesticide and the duration of the time averaged PECs considered. Based on these criteria, a final set of four SCUs were selected as representatives of the Pampa Region and are recommended for pesticide fate modeling at the regional level. This is the first time to our knowledge that statistically-based standardized worst case scenarios are developed for the Pampa region. The availability of such scenarios is critical to impulse pesticide fate modeling and probabilistic risk assessment in the region.

The pesticide fate model PWC was employed in the current study. Recently, the possibility to employ this model in the Pampa region was examined by performing a sensitivity analysis of PWC using regional conditions (D'Andrea et al., 2020). Consistent with the observations made in the present study, the sensitivity analysis highlighted the fact that PWC is highly sensitive to the soil adsorption coefficient (Kd) of the modelled pesticide (D'Andrea et al., 2020). Based on the evidence gathered, we propose the use of four distinct SCUs for worst case scenarios modeling of PECs in the Pampa region of Argentina. The SCU selected for a specific modeling exercise should depend on the Kd of the pesticide evaluated and whether short term or long term pesticide fate modeling and exposure assessment is required: 1) SCU *A300_140* for both short and long term modeling of pesticides with a Kd inferior to 2.5. 2) SCU *A373_72* for short term modeling and SCU *A318_525* for long term modeling of pesticides with a Kd between 3 and 15, and 3) SCU *A240_582* for both short and long term modeling of pesticides with a Kd superior to 50.

The pesticide fluxes generated within an agrosystem are largely governed by the movement of water and the hydrologic and hydraulic characteristics of the catchment (Payraudeau and Gregoire, 2012). Surface runoff and soil erosion from treated fields that occur soon after pesticide application have been identified as the main processes resulting in fast and intense contamination peaks in surface waters (Peyrard et al., 2016). Surface runoff occurs whenever the rate of water inflowing on the ground surface exceeds the rate of infiltration and the surface storage capacity is exceeded (Holvoet et al., 2007). It usually starts as a laminar sheet flow that channelizes into a concentrated turbulent flow after a certain travel length. For its part, soil erosion by water is the detachment of soil particles from the soil surface and their subsequent transport into runoff water (Reichenberger et al., 2007). Sorbing pesticides (high Kd) reach surface waters mainly through erosion, whether non-sorbing molecules (low Kd) enter the waterbody in solution in runoff water (Fig. 4). This is because a pesticide with a large Kd will be tightly bound to eroded soil particles and move together with it, whereas a pesticide molecule with a low Kd will remain in solution and follow the water movement (Boyd et al., 2003; Holvoet et al., 2007; Duus Børgesen et al., 2015).

The hydrologic soil group (HSG) refers to the classification of soils based on their runoff producing characteristics. In the present study, all SCUs selected for low Kd pesticides had soils belonging to group D, which includes clay soils with very low infiltration rates and is the HSG presenting the highest runoff potential (USDA, 2009). It is logical for SCUs with group D soils to represent worst case scenarios for low Kd molecules considering that non-sorbing pesticides remain dissolved in water and reach the waterbody almost entirely though surface runoff. The large majority of SCUs identified as candidate worst-case scenarios for pesticide with a Kd lower than 2.5 were located in the northeast of the Pampa region, where average annual temperatures are highest. They either presented relatively flat soils with a rich content of clay (slope < 2 %) or soils with a thin argillic horizon (aquic arguidolls) and a steeper slope (between 2 and 5 %). They also presented an elevated content of silt, a factor which makes them prone to structural degradation by compaction and, thereby, surface runoff (Reichenberger et al., 2007).

In the case of low Kd pesticides, the two SCUs that were selected as potential scenarios for 4dPECs also came out as possible scenarios for 60dPECs, together with two other SCUs that were equally representative in terms of their selection frequencies (Table 1). This means that, in the case of low Kd molecules, the same SCU can be used as worst case scenarios for both short term and long term average concentrations. This observation is likely due to the fact that pesticide movements based on fast transport mechanisms such as surface runoff are characterized by fast and intense contamination peaks triggered by rainfall events (Peyrard et al., 2016; Belles et al., 2019). Whereas most part of the pesticide transfer to the waterbody occurs through fast-flow events, fast transport mechanisms also cause the build-up of a transient pesticide pool in the saturated zone, which sustains low level pesticide concentrations by leaching over considerable periods of time (Leu et al, 2004; Belles et al., 2019). In this context, 4dPECs will mostly be dependent on fast-flow associated peak concentrations, whereas residual slow water movements may affect 60dPEC. The fact that the same SCUs were selected as worst-case scenarios for both 4dPEC and 60dPEC, either indicates that both components of the pesticide flux are influenced in a similar manner by land and climate variables or that the large peak values override any other influences on PECs.

In the case of pesticides with a high Kd (>50), all selected SCUs are located to the west of the Pampa region and have soils belonging to HSG group B. They also exhibit elevated sand contents, high values of soil erodibility (USLE factor K), and they present a slope of 2-5%, which is somewhat elevated for the Pampa plain. Because strongly binding pesticides (high Kd) are essentially mobilized through water erosion and reach the waterbody bonded to eroded soil particles, soil erodibility was clearly an important factor in the selection of worst-case SCUs for these molecules. For this category of pesticides, two SCUs were equally representative as potential scenarios for 4dPECs with selection frequencies of 77.8%. One of these, SCU *A240_582*, also was selected for 60dPEC values for the large majority of high Kd pesticides, with a selection frequency of 88.9%. As was the case for low Kd pesticides, the fact that the same SCU was selected as worst-case scenarios for both

4dPEC and 60dPEC either indicates that short-term and long-term pesticide transfer to the waterbody are similarly influenced by land and climate variables, or that rainfall associated acute events override low-level chronic discharge of pesticides into the waterbody.

As opposed to what was observed for both low and high Kd pesticides, it was not possible to identify an SCU that could be used for both 4dPEC and 60dPEC in the case of pesticide with a Kd value between 3 and 15. Indeed, none of the SCU selected for 4dPEC and 60dPEC coincided, suggesting that short-term and long term pesticide transfer to the waterbody are either governed by different processes or that land and climate variables affect the leading transfer route in different manners. It is logical that pesticide flux and fate is more complex for this category of pesticides, as the molecules it includes reach water bodies by both erosion (i.e. bonded to soil particles) and runoff (i.e.in solution in water). In runoff water, although both the dissolved and particle-bound pesticides are considered as mobile fractions, they each travel through different transport pathways (Wu et al., 2004). For vertical transport, the water-soluble pesticides are assumed to be most mobile, while for lateral transport, pesticides bound to particles of different sizes differ in their settling velocity and therefore their transport distances and deposition patterns (Krein and Schorer, 2000; Wu et al., 2004; Walker, 2001). As for all pesticide Kd categories, further complexity may also be introduced by the initial moisture content of soil, the interactions between soil properties and climate, temporal variations in weather conditions and rainfall characteristics (Le Bissonais et al., 1995; Sandin et al., 2018).

Because the amount of eroded soil lost from a field is usually small compared with the runoff volume, pesticides loss via surface runoff is normally considered more important than losses via soil erosion, (Duus Børgesen et al., 2015). The dominance of runoff pathways over erosion is highlighted by the fact that SCUs selected for intermediate Kd pesticides share more similarities with the SCUs selected for low Kd pesticides rather than high Kd pesticides, in terms of soil characteristics such as HSG, erodibility factor, and clay, silt and sand contents.

CONCLUSION

In conclusion, a statistically-based approach was employed to identify SCUs that may be used as realistic worst-case scenarios for the modeling of pesticide PECs in the Pampa region of Argentina. Results obtained demonstrated that the SCU selected for a specific modeling exercise should depend on the Kd of the pesticide evaluated and whether short term or long term pesticide fate modeling and exposure assessment is required. Four of the most regionally representative SCUs were specifically identified for modeling the fate of pesticides with low, high and intermediate values of Kd. Fate modeling of pesticides with an intermediate Kd requires the use of a different SCU for short-term versus long-term pesticide modeling, whereas this distinction is not necessary in the case of pesticides with both low and high Kd. The current definition of realistic worst-case soil-climate scenarios represents a crucial step towards better pesticide fate modeling and risk assessment in the highly agricultural in the Pampa region of Argentina.

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Figure Captions:

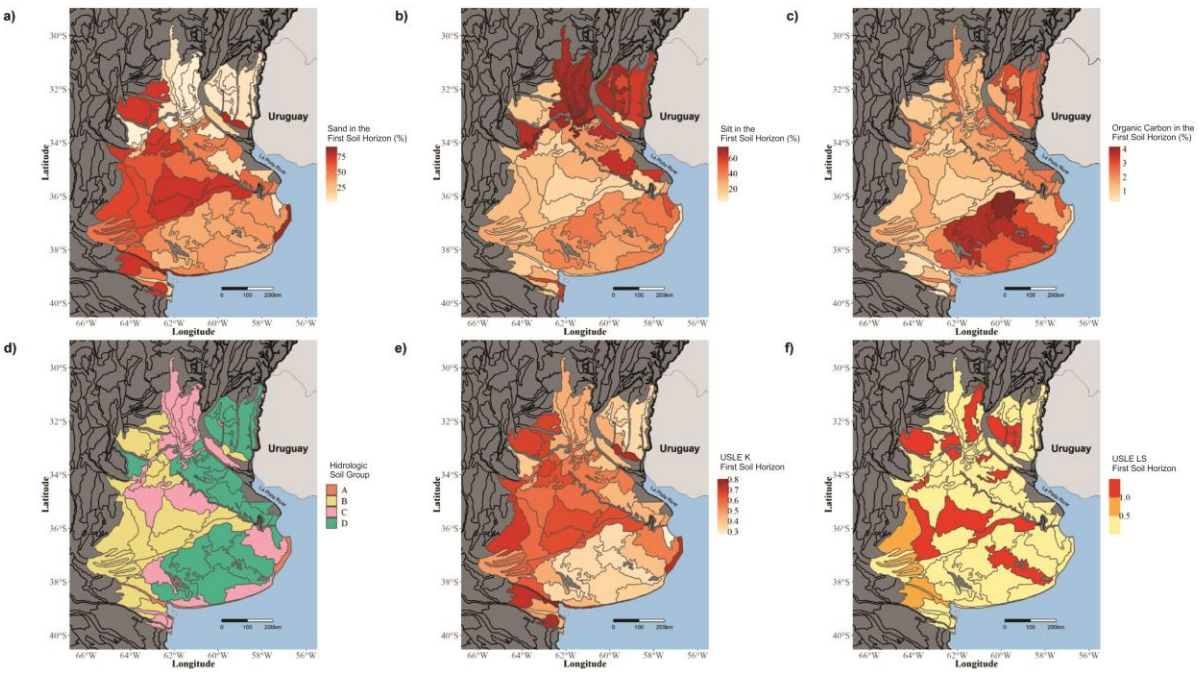

Figure 1. Percent a) sand b) silt and c) organic carbon of the first soil horizon, d) hydrological group, e) erodibility factor (K) and f) topographic factor (LS) of the Universal Soil Loss Equation for the 77 SCUs considered in the study.

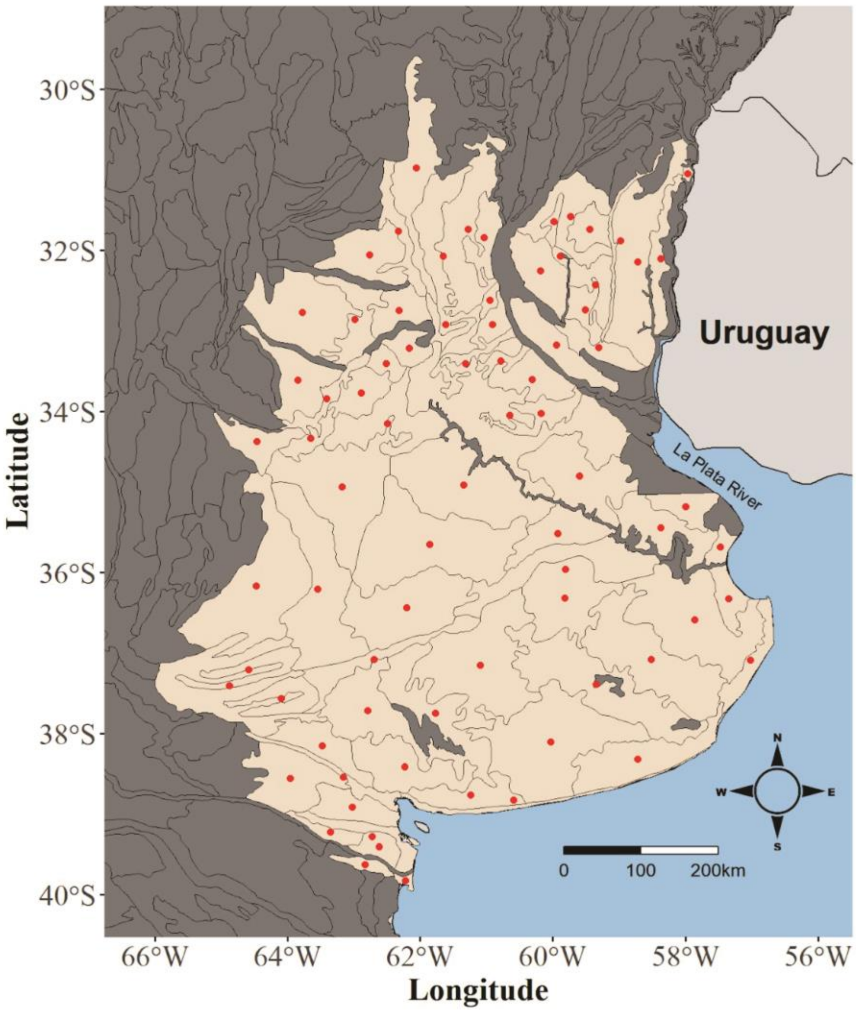

Figure 2. Location in the Pampa region of the 77 cartographic units considered in the current study. The red dots indicate the position of the centroids for which a spatial interpolation of climate data was performed.

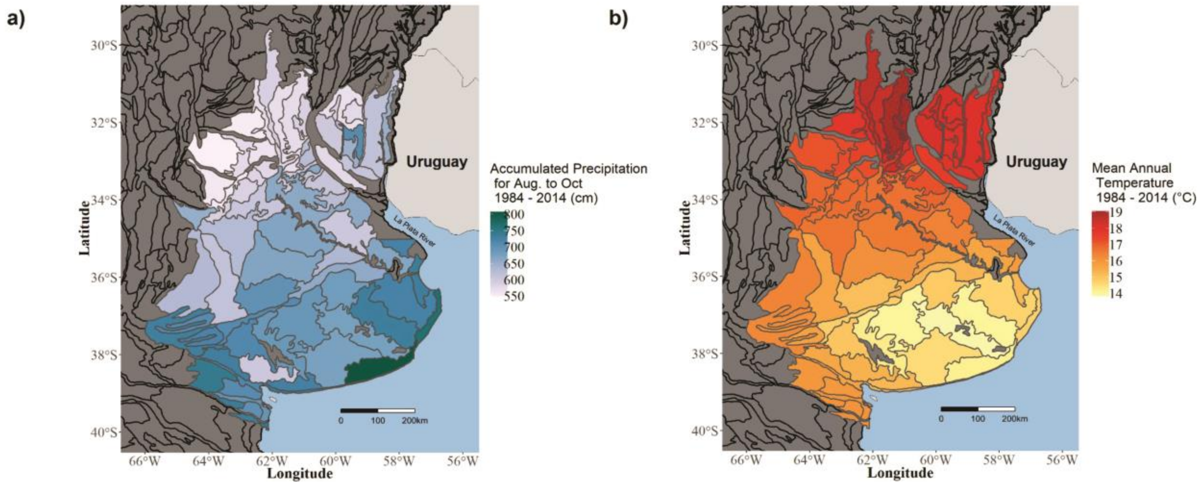

Figure 3. a) Accumulated precipitation in 30 years for the months of August to October in 30 years (cm) and b) mean annual temperature in 30 years (^{o}C) of the 77 SCUs considered in the study.

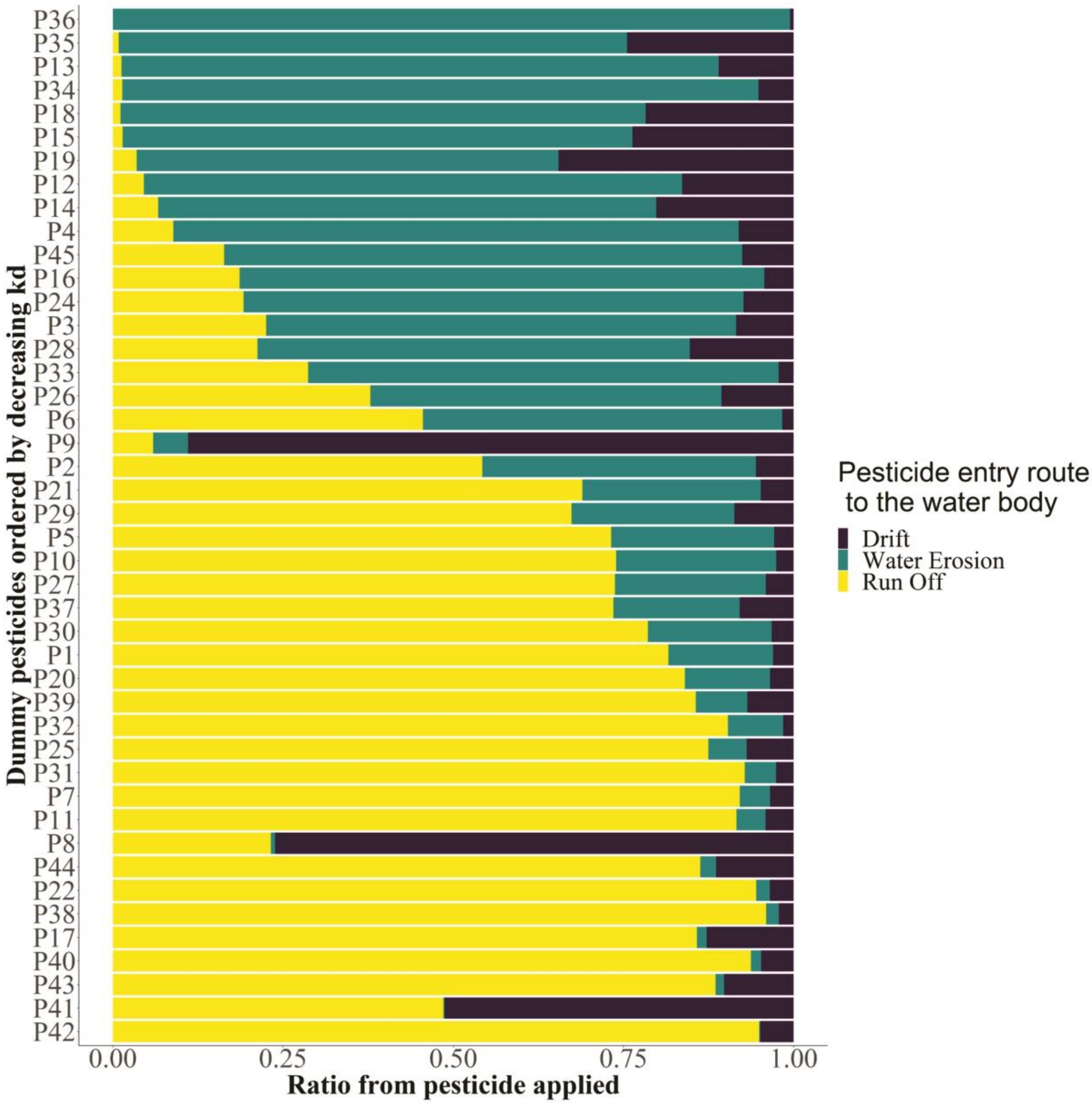

Figure 4. The ratio of total pesticide applied that reaches the water body by surface runoff, water erosion, and drift. The 45 dummy pesticides are ordered by decreasing Kd, with dummies higher on the y-axis having a larger Kd.

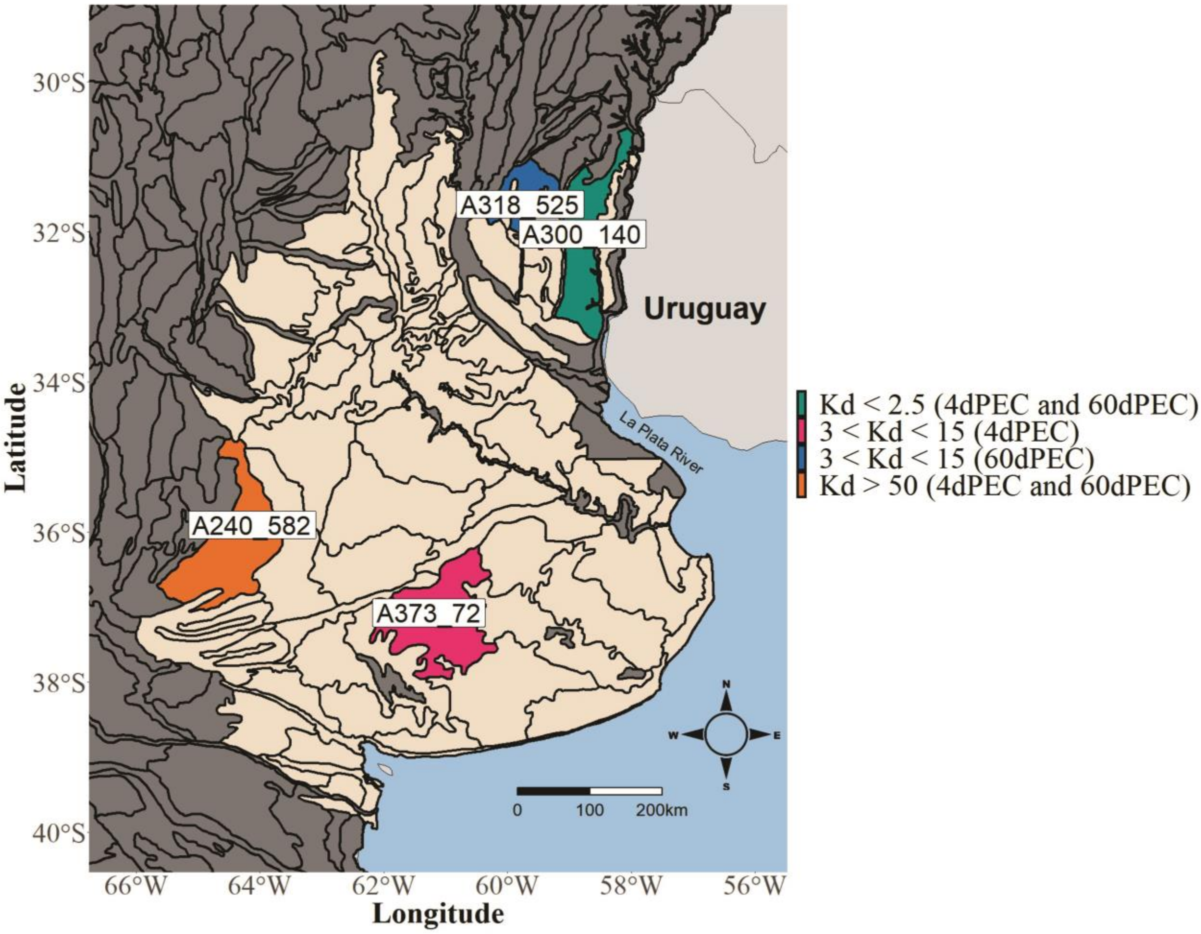

Figure 5. SCUs selected for worst case scenarios modeling of PECs in the Pampa region of Argentina. The SCU selected for a specific modeling exercise should depend on the Kd of the pesticide evaluated and whether short term or long term pesticide fate modeling and risk assessment is required.

Table Captions:

Table 1. SCUs with highest selection frequency based on the Kd of the dummy pesticide. K is the soil erodibility factor of the Universal Soil Loss Equation (USLE). HSG = Hydrologic Soil Group. SCUs in bold correspond to those selected as regional scenarios for each category.

Soil-Climate Units	Location	Soil Type	Organic Carbon (%)	Clay (%)	Silt (%)	Sand (%)	HSG	USLE K	Slope (%)	Selection Frequency (%)
4d PEC										
Kd < 2.5										
A300_140	North East	Typic Hapludert	2.72	33.6	60.5	5.9	D	0.33	0 - 2	78.6
A329_577	North East	Aquic Argiudol	1.55	27.6	67.9	4.5	D	0.46	2 - 5	64.2
3 < Kd < 15										
A373_72	Center South	Typic Natraquoll	3.76	25.2	41.9	32.9	D	0.33	0 - 2	72.7
A269_50	Center North	Typic Argiudol	1.42	27.9	70.2	1.2	C	0.46	0 - 2	63.6
Kd > 50										
A240_582	Center West	Entic Haplustoll	0.9	9.4	22.2	68.4	B	0.70	2 - 5	77.8
A311_231	South West	Typic Ustorthents	0.52	8.87	15.51	75.62	B	0.73	2 - 5	77.8
60d PEC										
Kd < 2.5										
A329_49	North East	Aquic Argiudol	1.55	27.6	67.9	4.5	D	0.46	2 - 5	57.1
A371_492	Center East	Typic Natraqualfs	1.92	23.7	29.9	46.4	D	0.50	0 - 2	50
A329_577	North East	Aquic Argiudol	1.55	27.6	67.9	4.5	D	0.46	2 - 5	42.9
A300_140	North East	Typic Hapludert	2.72	33.6	60.5	5.9	D	0.33	0 - 2	42.9
3 < Kd < 15										
A318_525	North East	Vertic Argiudol	3.07	25.5	69.9	4.9	D	0.38	0 - 2	72.8
A371_492	Center East	Typic Natraqualfs	1.92	23.7	29.9	46.4	D	0.50	0 - 2	63.6
A354_360	Center	Typic Arguidol	1.7	20.1	33.1	46.8	D	0.55	0 - 2	63.6
Kd > 50										
A240_582	Center West	Entic Haplustoll	0.9	9.4	22.2	68.4	B	0.70	2 - 5	88.9
A293_584	South West	Entic Haplustoll	1.68	11.2	21.3	67.68	B	0.60	2 - 5	50