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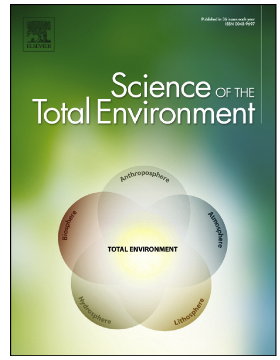

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Sensitivity Analysis of the Pesticide Water Calculator model for Applications in the Pampa Region of Argentina.

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Abstract

Despite the widespread use of pesticides in the Pampa region of Argentina, mathematical models are rarely employed to predict pesticide fate due to the lack of regionally tested models and the absence of readily available databases to run such models. The objective of the current study was to perform a sensitivity analysis of the Pesticide in Water Calculator (PWC) model for the Pampa Region of Argentina. The sensitivity analysis was performed while simulating applications of 2,4-D (mobile, low Kd) and glyphosate (soil-binding, high Kd) in five localities of the Pampa region: Anguil, Paraná, Marcos Juárez, Pergamino and Tres Arroyos. The sensitivity of the various parameters involved in PWC modelling was evaluated though a two-steps sensitivity analysis which included a first screening of less sensitive parameters with Morris method, followed by a fully global sensitivity analysis of the remaining parameters using Sobol method. When ran under soil and climate conditions typical of the Pampa region of Argentina, PWC was most sensitive to 25% of the parameters evaluated. The sensitive parameters identified depended mainly on the nature of the pesticide molecule being modelled; the location and endpoint considered having much less influence on the sensitivity results. Sensitive parameters belonged to two main grand categories: (i) degradation rates of the pesticide in soil and water, and (ii) parameters descriptive of soil binding, runoff and erosion. The sensitivity analysis of the model PWC performed in the current study represents a crucial first step towards the development and expansion of probabilistic pesticide risk assessment in Argentina, and provides important parameterization criteria that will help obtaining more certain modelling results from PWC in Argentina and elsewhere.

Keywords

Risk Assessment – Agriculture – Contamination – Agrochemicals – PWC – Water Quality

1. Introduction

The Pampa region of Argentina is characterized by fertile deep soils and temperate climate that have favored the establishment of a thriving farming economy (Barros et al. 2014). Extensive agriculture is largely predominant in the region, and most of the land is dedicated to pesticide-dependent genetically-modified soybean, corn and wheat crops. When sprayed on crops, a fraction of applied pesticides may reach surface and/or groundwater through runoff, drainage or drift, potentially altering aquatic ecosystems health and drinking water quality (Schäfer et al., 2011). A number of recent studies have, indeed, revealed the presence of a variety of pesticide residues in fish, surface waters, groundwater, sediments, soils and rainwater of the Pampa region (Peruzzo et al., 2008, Aparicio et al., 2013, Bonansea et al., 2013, De Gerónimo et al., 2014, Lupi et al., 2015, Hunt et al., 2016, Ronco et al., 2016, Etchegoyen et al., 2017, Pérez et al., 2017, MacLoughlin et al., 2017, Primost et al., 2017, Brodeur et al., 2017, Castro Berman et al., 2018, Alonso et al., 2018).

Mathematical models are now widely used in many countries to predict the transport and fate of pesticides in the environment (Teklu et al. 2015, Gagnon et al. 2016, Ouyang et al. 2017, Hartz et al. 2017, Bach et al 2017, Xie et al. 2018, Rumschlag et al., 2019). Modelling represents an attractive alternative to environmental monitoring, which is expensive and time-consuming, and may sometimes be imprecise, as results depend on sampling frequency, and spatial and temporal variability (Bundschuh et al., 2014; Nsibande et al., 2015; Lorenz et al., 2017). In contrast, mathematical models are fast, versatile and cost effective and allow to: (i) explore the potential range of aquatic concentrations of several pesticide molecules before they are actually applied to crops and (ii) assess how climate, soil and crop growth conditions in different geographic locations influence the fate of pesticides

(Blenkinsop et al., 2008; Nolan et al., 2008, Bach et al. 2016). Nevertheless, in spite of widespread intensive pesticide use, mathematical models are rarely employed to predict pesticide fate in the Pampa region of Argentina. Part of this situation is due to the lack of regionally tested or developed fate models and the absence of readily available databases to run such models. This state of affairs precludes the development of probabilistic environmental risk assessment at the regional and national levels, since results from mathematical fate models are essential for conducting such high tier risk assessment (Rousseau et al., 2012; Gagnon et al., 2016).

Globally, a number of models have been developed to model the fate of pesticides in surface and ground waters. Models adopted for regulatory purposes in the European Union include: (i) runoff estimations with PRZM (Carsel et al., 1984), (ii) drainage estimations with MACRO (Larsbo and Jarvis 2003) and (iii) pesticide presence in surface water with TOXSWA (Adriaanse 1996). For their part, both the United States and Canada actually rely on the Pesticide in Water Calculator (PWC) for aquatic pesticide risk assessment. PWC is a flexible software that models pesticide fate in the environment using locally relevant characteristics of climate, soil, hydrology, and crop management. PWC user interface allows performing simulations with data from pre-loaded scenarios or sites selected and parameterized by the user. The water bodies modelled by PWC may be ponds, reservoirs or even custom size waterbodies, and may include, or not, fluctuations in water levels throughout the simulation period. Output values are made available in terms of regulatory formats accepted by the USEPA as average pesticide concentrations in surface water over the entire simulation, the peak and the 1-, 4-, 21-, 60- and 90-days average pesticide concentrations. Sediment and benthos pesticide concentrations are also calculated by PWC, as well as the fate of metabolites from parent molecules (Young 2016).

According to best practice guidelines for implementation and use of pesticide fate models (USEPA, 2009), it is essential to perform a sensitivity analysis of fate models before using them, in order to obtain a quantitative evaluation of the model's uncertainty. A sensitivity analysis is defined as "the study of how the uncertainty in the output of a model (numerical or otherwise) can be apportioned to different sources of uncertainty in the input of this model" (Saltelli, 2004). The identification of the most influential/sensitive parameters of a mathematical model represents a first step towards the reduction of overall model uncertainties. In addition, setting the values of non-influential parameters can decrease computational time without reducing the performance of the model (Gan et al., 2014).

Several methods exist to perform a model-based sensitivity analysis (Pianosi et al., 2016). The selection of the appropriate method depends on the information expected from the analysis, the number of model variables and the available computational power (Saltelli et al., 2008, Saltelli et al. 2019). The simplier types of analysis are the so-called local sensitivity analysis, which involve keeping all parameters at nominal values while varying one parameter at a time within the associated maximum and minimum value range, and observing the effect on the output variables. This process is repeated sequentially for all parameters. Comparatively, global sensitivity analyses, are most-advanced sensitivity methods, which require the simultaneous variation of several parameters to allow the exhaustive exploration of the multidimensional parameter space (Pianosi et al., 2016, Sarrazin et al., 2016). However, because they involves sampling methods such as the Monte-Carlo method, the computational requirements and complexity of global sensitivity analyses is generally high, especially when models include numerous parameters (Saltelli 2019). For futher readings about sensitivity analysis methodologies across disciplines Saltelli et al. (2017, 2019).

In the present study, the software Pesticide in Water Calculator v.1.52 (PWC) was used to model pesticide fate in water bodies of the Pampa region. The selection of PWC as the modelling software was based on a number of characteristics: (i) PWC is freely available online, (ii) it is versatile and allows the introduction of a large number of locally - or regionally- specific parameter values, (iii) it is widely used for North American pesticide regulation and registration. Although studies using PWC have previously been published in the literature (Xie et al. 2018, Hatz et al 2019, Rumschlag et al., 2019), we are not aware that any sensitivity analysis has previously been performed for PWC, for either input values from the Pampa region or elsewhere. In this context, the objective of the current study was to perform a model-based sensitivity analysis of PWC for the Pampa Region of Argentina. The sensitivity analysis was performed while simulating applications of 2,4-D and glyphosate in five (5) localities of the Pampa region. 2,4-D and glyphosate were selected as model pesticides because they have two extreme and opposite ways of behaving within the environment. Glyphosate and its metabolite AMPA bind strongly to topsoil particles and therefore reach waterways, ponds and lakes through water erosion events (Todorovic et al., 2014, Bento et al., 2018, Bento et al., 2019). For its part, 2,4-D is a highly mobile herbicide presenting potential of runoff to aquatic habitats (Canada 2016). Similarly, the five localities selected represented the largest possible ranges of variability in climate, soil and slope conditions found within the Pampa region (Moscatelli et al. 1991, Barros et al. 2014). The sensitivity analysis was carried out for output values of average surface water concentration over 4 and 60 days to illustrate acute and chronic toxicity scenarios for a surface water body, respectively. The methodological approach consisted in two steps: (i) detecting and eliminating from the analysis the less sensitive variables using the Morris method for sensitivity analysis, and (ii) comparing the sensitivity indices of the remaining parameters using the Sobol global sensitivity analysis.

2. Methodology

2.1. Study area

The Pampa region is a vast herbaceous flat plain of about 500,000 km^2 that covers most of central Argentina and is located between south latitudes 31 and 39 and west longitudes 57 and 65 (Fig. 1). The Pampa is characterized by flat or slightly undulated landscapes and native vegetation composed of small shrubs and grasses. The temperate climate and deep fertile soils have favored the establishment of a prosperous agricultural economy. Over the last 40 years, the region has experienced an accelerated process of agricultural intensification, where activities changed from a mixture of livestock and grain production to extensive soybean monoculture (Paruelo et al., 2005). During this period, the cultivated area doubled from 14 to 31 million hectares (MAGyP, 2015).

The climate of the Pampa region of Argentina is temperate humid, without a dry season and with a very hot summer (Hall et al., 1992). 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). The western limit of the region is marked by the 600 mm isoline of rainfall that constitutes the natural limit of rainfed agriculture. Most of cultivated soils belong to the order of the Mollisols, which were developed from wind sediments of the Pleistocene era (Moscatelli, 1991). In the central zone, soils belong mainly to the great group of the Argiudolls (Panigatti, 2010), while the Haplustolls are abundant in the western limit.

Haplustolls are soils that have sandy granulometry, low organic matter content in the upper soil (1-3%), and low clay content (Moscatelli, 1991, Satorre, 2011).

2.2. PWC Model PWC is a graphic user interface that links the output of two sub-models: (i) the "Pesticide Root Zone Model version 5 (PRZM 5)" and (ii) the "Variable Volume Water Body Model (VVWM)" (Burns, 2004; Fry et al., 2014). PRZM 5 is a one-dimensional and dynamic compartmental model that is used to simulate the movement of chemicals in unsaturated soil systems within and immediately below the plant root zone (Carsel et al., 1984). The hydrologic component for calculating runoff and water erosion in PRZM 5 is based on the curve number technique (NRCS, 1986) and the Universal Soil Loss Equation (Williams 1975, Young and Fry, 2014). For its part, VVWM is designed to model the transport and fate of chemical substances in a water body. 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 and the fate of chemical substances in aquatic ecosystems (Burns, 2004). Mass balance equations used in PWC assume that all materials in water and sediment are at thermodynamic equilibrium. The inflow of dissolved pesticides or drift is delivered to the water compartment, and sorbed pesticides are delivered to both water and sediment. Pesticides are removed from the water body via sediment burial, volatilization, and degradation (Rumschlag et al., 2019). Additional background information on PWC can be obtained from Young (2016).

2.3. Parametrization

To simulate the environmental fate of a sprayed pesticide and ensuing concentrations in surface water, PWC requires four major categories of input parameters (Table 1): (i) the mode and date of the pesticide application and the physicochemical characteristics of the applied pesticide, (ii) local/regional characteristics of climate, soil, and crop phenology and (iii) the limnological characteristics and dimensions of the receiving water body, (iv) water erosion and runoff processes. In total, excluding the weather file and soil horizon data, 38 parameters need to be characterized before performing a simulation with PWC (Table 1). Range of values used in the current study for each of these parameters are described in Table 1 to 5 of the Supplementary Material.

2.3.1. Parameters describing the physicochemical characteristics of the pesticide and application modes and dates.

As mentioned above, glyphosate and 2,4-D, two pesticides with contrasting soil adsorption coefficient (*kd*) were used for sensitivity analysis to insure that the variation in pesticide behavior was maximized. The ranges of plausible values of pesticide physicochemical parameters used in the current study are described in Supplementary Material Table 1 for both 2,4-D and glyphosate. These ranges were defined according to the information found in the literature. Seven main databases were consulted: (i) Pesticide Properties Database (PPDB) (Lewis et al., 2016), (ii) Toxnet - Hazardous Substances Data Bank (HSDB) (National Library of Medicine, 2018), (iii) European Union (European Commission, 2001, 2002), (iv) Department of Pesticide Regulation of the State of California (Schuette, 1998; Walters, 1999), (v) Network of Extension Toxicology (Cornell University) (Hotchkiss et al., 1989), (vi) Reports of the Food and Agriculture Organization (FAO / WHO, 1998) and (vii) EPA Evaluation Records (USEPA, 1999). Only parent compounds were considered in the analysis, even though PWC allows to simulate the fate of metabolites.

A ground application of pesticide was simulated once a year for thirty consecutive years. The amount of pesticide applied on each occasion was kept constant at 1.037 and 2.16 kg/ha for 2,4-D and glyphosate respectively. These doses correspond to maximum, approved application rates for soybean in Argentina. Spray efficiency and drift were arbitrarily set at 0.99 and 0.001, respectively. Pesticide application dates were selected to occur in a period of 7 to 15 days before soybean emergence. The exact dates of this application period vary in every locality as soybean emergence date depends on latitude. Namely, application dates were selected among the worst possible cases (in terms of surface water contamination), defined as a date immediately prior to the occurrence of a rainfall event greater than 3 mm within the period considered for each location and year simulated. If during a year it did not rain more than 3 mm during the considered range of possible dates, the application date corresponded to the soybean emergency date for the corresponding location.

2.3.2. Parameters describing local/regional characteristics of climate, soil, and crop phenology

Although it may make sense for some parameters to be varied independently within their possible range as previously described for the physicochemical characteristics, it makes little sense to use this approach when parameters are tied one to another such as when describing the different horizons of a soil type or linking weather data to soil types within a specific region. For this reason, instead of varying each soil and climate input data independently, we chose to vary these parameters altogether to examine the impact of variation in soil and climate data on the model output. This was achieved by running the model in five distinct and, as different as possible, locations considering the normal range of variability existing within the Pampa region. Selected localities include: Anguil (La Pampa Province), Paraná (Entre Ríos Province), Marcos Juárez (Córdoba Province), Pergamino (Buenos Aires Province) and Tres Arroyos (Buenos Aires Province) (Fig. 1, Table 2). These locations were selected because they cover the whole range of latitudes and longitudes included in the Pampa Region and exhibit a range of soil and climate characteristics that cover most of the variability expected within this region. Three of the localities, Paraná, Pergamino, and Marcos Juárez are located in the north and, although they present similar temperatures and rainfalls, they differ in terms of their hydrologic soil group, and their slopes. The locality of Tres Arroyos is located to the south of the region and exhibits the lowest temperatures, whereas Anguil, located at the western limit of rainfed agriculture, has sandy soils and low rainfalls (Fig. 1, Table 2).

To standardize the analysis, it was decided that a fallow application of pesticide preceding a soybean crop would be modelled in all locations. Although the same crop was modelled in all locations, the phenology of the soybean crop was varied according to the conditions existing in each locality. General information regarding the phenology characteristics and weather stations that were used in each location are described in Table 2 and Supplementary Material Table 2. Climate data were thoroughly checked for quality and consistency as part of a recently published study (D'Andrea et al. 2019). Data describing soil profile characteristics are described for each location in Supplementary Material Table 3, while the range of values used for all other location-specific parameters, including hydrologic variables, are given in Supplementary Material Tables 4 and 5.

2.3.3. Parameters describing the limnological characteristics and dimensions of the receiving water body

The goal of the current study was to identify the parameters which are most sensitive amongst the high number of parameters that are needed to run PWC. Because it is clear that the size of the water body is a sensitive parameter that will modify the final water concentration of the pesticide, this parameter was set to a constant in the current study so that the sensitivity of the other parameters could be better determined. The decision to use a constant and unique size for the water body was also motivated by the fact that very little quantitative information is available regarding the ranges of water body sizes existing in the different localities. Input data used in the section "Watershed and water body dimensions" of PWC were: (i) area of treated field, 290000 m^2 (29 ha); (ii) fraction of the field cropped, 1; (iii) surface area of water body, 8000 m^2 (0.8 ha); and (iv) initial and final depths, 1.5 m. These values correspond to a well-studied water body located in the locality of Paraná. For their part, limnologic parameters were varied according to the ranges of values found in the literature regarding Pampean lakes and ponds. Values used can be found in Supplementary Material Table 4.

2.4. Construction of weather files for PWC

An R package named PWCfilegenerator v0.1.0 (D'Andrea and Brodeur, 2019) was designed to facilitate the construction of weather files in an input file format needed to run PWC. The package is freely available from a GitHub repository: https://github.com/flor14/PWCfilegenerator.

2.5. Global sensitivity analysis

Given the large number of parameters involved in PWC simulations, the sensitivity of the various parameters was evaluated simultaneously though a global sensitivity analysis executed in two consecutive steps: (i) the less computationally demanding Morris method was used to identify a first subset of the least sensitive parameters, and (ii) the more complex Sobol method was applied to compare their sensitivity of the remaining parameters and identify the most sensitive parameters in each location/pesticide combination modelled.

2.5.1. Morris method

The Morris method (Morris, 1991) is a global sensitivity analysis technique that allows the least sensitive parameters to be identified within a mathematical model by using threshold sensitivity values (Sarrazin et al., 2016). Its computational requirements are lower than that of most other global methods and it is considered one of the simplest global sensitivity analysis techniques available because it discretizes the parameter space to allow a "once at a time" (OAT) design to be applied a certain number of times (Iooss and Lemaître, 2014). Each repetition is called "a trajectory", and the optimal number of trajectories for an analysis is normally considered to be between 4 and 10 (Saltelli, 2004, 2008). When a model presents a large number of input values, the Morris method is used to allow a preliminary analysis and thereby identify least sensitive parameters (Morris, 1991). The method is based on systematic sampling of the multidimensional space defined by the possible values of the parameters to generate a random set of OAT experiments (Pianosi et al. 2016). Two measures of sensitivity are calculated: μ, which characterizes the influence of a given parameter on the output, and σ that is used to quantify the interaction the parameter with other factors (Saltelli, 2004). In the current study, 10 trajectories were performed for each location/pesticide combination. The definition of the sampling trajectories and the calculations of the μ and σ estimators of sensitivity were performed using SimLab 2.2 (Tarantola, 2005). The ranges of values used for the different parameters required by PWC are described in Supplementary Material Tables 1 to 5, and sections 2.3.1 and 2.3.3 . In cases where values could not be found in the literature for the Pampa region, the widest possible range reported was used in the analysis. SENSAN software was used to automate the sensitivity analysis (Doherty, 1994). A sensitivity threshold was established where a variation in the output was considered significant if it exceeded 1 μg/L. Therefore, all input parameters that resulted in a variation of more than 1 μg/L in the output, were considered sufficiently sensitive to be further examined and included in the second part of the sensitivity analysis which used Sobol method.

2.5.2 Sobol method

As mentioned above, the subset of parameters which exceeded the sensitivity threshold in the Morris method was included in the second part of the sensitivity analysis. Here, Sobol's method (Sobol, 1993) was used to quantify the amount of variation in the model output contributed by each input parameter (Song et al., 2015). These quantities, whether generated by a single parameter or by the interaction of two or more parameters, are expressed as sensitivity indices. The use of the Monte Carlo analysis as a sampling method for this analysis implies a high level of computational complexity. The Sobol method returns two types of indices: (i) a first-order index or main effects index that measures the direct contribution of an individual input factor to the variance of the model output, and (ii) an index of total order or index of total effects that measures the general contribution of an input factor, considering its direct effect and its interactions with all other factors (Pianosi et al., 2016).

When performing Sobol's analysis, it is necessary to assign a specific distribution to all input parameters. In the present study, most parameters were described by a uniform distribution, with the exception of the universal soil loss equation (USLE) soil conservation practice factor (*usle p*), the USLE soil erodibility factor (*usle k*), the photolysis parameter (*dfac*), and the lowest depth at which erosion interacts with the soil (*edepth*). A triangular distribution was assumed for these parameters because a most probable value could be determined for the Pampa region within the considered data range (Supplementary Material Tables 3 and 5). The parameter *ireg* representing the location of NRCS 24-hour hyetograph was sampled among the three possible values with equal probability (Supplementary

Material Table 5). The ranges of values used for the different parameters are described in Supplementary Material Tables 1 to 5 and sections 2.3.1 and 2.3.3. Ranges of input parameter values used were the same for both Morris and Sobol methods. The sample size selected to ensure the convergence of the indices was established at 11,776 for each pesticide/locality combination in order to obtain stable indices of main and total effects (Pianosi et al., 2016). The generation of samples and calculations of main and total effects were carried out using SimLab 2.2. (Tarantola, 2005). The SENSAN software was used to automate Sobol's sensitivity analysis (Doherty, 1994).

3. Results

3.1 Sensitivity Analysis Part A: Morris Method

The results of the first part of the sensitivity analysis, carried out with Morris method, are presented in Fig. 2, 3 and 4 for 4-d average concentration outputs, and in Supplementary Materials Fig. 1, 2 and 3 for 60-d average concentration outputs. This first part of the sensitivity analysis, identified that 14 of the 38 parameters evaluated presented a sensitivity value lower than the set threshold (μ<1 µg/L) when considering all pesticide/locations combinations. These 14 parameters are considered to have a very low influence on the output of the model because they exhibit sensitivity values between 10 to more than 100 times lower than the remaining other 24 parameters. For this 14 less sensitive parameters (μ < 1 µg/L), the values of σ never exceeded 1 µg/L, indicating that these parameters do not interact significantly with others. On the other hand, of the 24 more sensitive parameters, 17 are sensitive in simulations realized with both glyphosate and 2,4-D. These parameters include: (i) the curve number (*cna*), (ii) the amount of runoff that interacts with the soil (*rseff*), (iii) the universal equation of soil loss (USLE) in particular the topographic factor (*usle ls*), (iv) soil conservation practice factor USLE (*usle p*), (v) USLE coverage management factor (*usle c*), (vi) hydrolysis (*hidrohl*) of the pesticide, (vii) the average life of the pesticide in the water column, (*wchl*), (viii) the soil adsorption coefficient to the soil (*kd*), (ix) the half-life of the pesticide in the benthos, (*bdhl*), (x) the mass transfer coefficient for exchanges between the benthos and the water column (*mxc*), (xi) the organic fraction of solids in suspension in the water column (*wcfoc*), (xii) the depth of water extraction for evaporation in the soil (*evapod*), (xiii) retention of water by the leaves of the canopy of the crop (*choldup*), (xiv) the half-life of the pesticide in the soil (*soilhl*), (xv) the exponential decrease in the interaction of runoff as a function of depth in the soil (*rdecli*), (xvi) the concentration of suspended solids in the water column (*wcss*) and (xvii) the correction factor for biodegradation based on the actual temperature (*Q10*).

Two parameters were sensitive only when simulated with 2,4-D: (xviii) the greater depth at which the runoff interacts with the soil (*rdepth*) and (xix) the pan evaporation coefficient (pfac). On the other hand, four parameters were sensitive only when glyphosate was used in the model: (xx) the organic carbon concentration in the water column (*wcdoc*), (xxi) the root depth of the crop (*rootd*), (xxii) the hydraulic terrain slope (*slope*), (xxiii) the Manning coefficient before cultivation (*mna*) and (xxiv) the location of the 24-hour hyetograph (*ireg*). These 24 parameters for which the PWC model proved to be sensitive in one or more opportunities were selected to go through further analysis using Sobol's method.

3.2 Sensitivity Analysis Part B: Sobol method

The results of the secong part of the sensitivity analysis, carried out with Sobol method, are presented in Fig. 5 for 4-d average concentration outputs, and in Supplementary Materials Fig. 4 for 60-d average concentration outputs. Sobol sensitivity analysis demonstrated that PWC is most sensitive to 9 different input parameters when ran under climate and soil conditions characteristic of the Pampa Region. The most sensitive parameters identified depended greatly on the nature of the pesticide molecule being modelled; the location and endpoint considered having much less influence on the sensitivity results. When both 2,4-D and glyphosate were modelled, the following four parameters were identified as sensitive, as they presented the highest μ and σ values: (i) half-life of the pesticide in soil (*soilhl*), (ii) the soil adsorption coefficient (*kd*), (iii) half-life of the pesticide in the water column, (*wchl*), and (iv) the value of curve number (*cna*). In the case of 2,4-D, two more input parameters were sensitive: (v) the amount of runoff that interacts with the soil (*rseff*), and (vi) the hydrolysis half-life (*hidrohl*) of the pesticide. In contrast, five different input parameters specifically appeared as sensitive when glyphosate was modelled: (vii) the topographic factor (*usle ls*), (viii) the USLE crop management factor (*usle c*), and (ix) the fraction of solids in suspension in the water column (*wcfoc*).

Specific characteristics of the locality modelled had less influence on the identity of the parameters identified as sensitive than the pesticide molecule that was used in the model. Indeed, when modelling 2,4-D, very similar results were obtained in four out of five sites; the locality of Tres Arroyos being the only exception where the soil adsorption coefficient (*kd*) explained almost all of the variability. Similarly, when glyphosate was modelled, the same input parameters were highlighted as sensitive irrespectively of the locality being modelled, the only difference residing in the order in which these parameters were ranked. Finally, using 4d or 60d average concentration as an endpoint had little influence on the results of the sensitivity analysis, except for the half-life of the pesticide in the water column (*wchl*), whose sensitivity increased when considering 60d instead of 4d average concentrations for both pesticides modelled.

4. Discussion

The two-step sensitivity analysis performed in the current study revealed that, when used with soil and climate conditions representative of the Pampa Region, PWC was most sensitive to about 25% of the parameters evaluated. Considering all possible combinations of localities, and pesticides tested, PWC exhibited a significant sensitivity to 9 input parameters in one or more simulations. Highlighted sensitive parameters belong to two main grand categories: (i) degradation rates of the pesticide in soil and water (*soilhl*, *wchl, hidrohl*), and (ii) parameters descriptive of soil binding, runoff and erosion (*kd, cna usle ls*, *usle c, rseff*). The aforementioned parameters should therefore be carefully parameterized when performing PWC modelling, since, the variability in the value entered for these parameters can be directly translated into a variability in the output of the model. Four of the above mentioned parameters were identified as sensitive in all simulations carried out: the half-life of the pesticide in the water column (*wchl*), the soil adsorption coefficient (*kd*), the half-life of the pesticide in the soil (*soilhl*), and the curve number value (*cna*). It is therefore recommended to always have solid specific information regarding these parameters when modelling pesticide fate with PWC, especially in the Pampa region, but probably elsewhere too.

The information obtained from the above-described sensitivity analysis of PWC is also crucial to promote and help develop the use of pesticide fate modelling for environmental risk assessment in the Pampa region. Indeed, by knowing which parameters are most critical when modelling pesticide fate with PWC, it is possible to orient research efforts towards the generation of regionally and/or locally-specific field and experimental values describing the parameters highlighted as most sensitive. For example, given the demonstrated constant large sensitivity of PWC to soil adsorption coefficient (*kd*), particular attention should be placed on determining locally-specific Pampean *kd* values for most used pesticides in the region; especially considering how largely *kd* values can vary based on soil characteristics such as pH and organic or clay contents (Wauchope et al., 2002, Okada et al., 2016, De Gerónimo et al. 2018). The sensitivity analysis performed in the current study demonstrated that guided efforts to obtain more precise soil- or locally-specific data on degradation rates, soil-binding capacity, or erosion or runoff descriptive factors, should reduce the uncertainty of pesticide fate modelling and risk assessment in the Pampa Region and elsewhere.

The sensitivity analysis performed also demonstrated that the nature of the pesticide modelled has a greater influence on model output than locality or type of output considered (ie. 4d or 60d average concentrations). In the present study, the two modelled pesticides, glyphosate and 2,4-D were selected because of their opposite behavior in the environment: whereas glyphosate tends to bind strongly to soil particles, 2,4-D, because of it lower *kd*, is mainly dissolved and thus transported by runoff. This difference in the physicochemisty and resulting environmental behavior of the two pesticide molecules was critical for determining which input parameters of PWC were most sensitive in each simulation. Indeed, because of the tight binding of glyphosate with soil particles, water erosion specific parameters of the USLE equation such as *usle ls*, *usle p* and *usle c* were identified as most sensitive in simulations with this pesticide, whereas for the most water-soluble pesticide 2,4-D, the most sensitive parameters corresponded to runoff-associated parameters such as the curve number (*cna*) or efficiency of runoff interaction with soil (*rseff*). Likewise, the greater sensitivity of the parameter hydrolysis (*hidrohl*) in simulations with 2,4-D rather than with glyphosate, is probably related to the fact that PWC's algorithm considers *hidrohl* only in dissolved molecular species (Fry et al., 2014).

In view of above-mentioned observations, anticipating the environmental behavior of the molecule to be modelled may help define which model parameters are the most strategic to carefully parametrize and refine in order to obtain simulation outputs as precise as possible. Similarly, it can logically be deduced that all efforts at reducing water erosion in agricultural lands would be efficient at reducing surface water contamination of soil-binding pesticide molecules. Furthermore, although the sensitivity of PWC to most parameters was similar when comparing 4d- and 60d-average concentrations, the exception to this rule was the pesticide half-life in water (*wchl*), which presented a greater sensitivity when considering the longer (60d) average pesticide concentration. In PWC, *wchl* models the degradation of the pesticide from the moment it reaches the water body. It is therefore logical for the sensitivity of PWC to *wchl* to become more important as longer periods are considered.

Finally, it has to be clarified that, the calculated surface water concentrations, and the whole simulation exercise performed in the current study were realized for model evaluation purposes only, and may not be used for further interpretations regarding pesticides water contamination. Indeed, although many parameter values used were realistic, our focus was to select parameter ranges that allowed an effective sensitivity analysis of PWC, not to reproduce a field reality. Likewise, the fact that little differences in parameters sensitivity were observed when varying the simulated locality, only means that similar parameters are sensitive in most sites, regardless of soil or climate specification, not that all locations are equivalent in terms of pesticide concentrations that could reach surface water bodies. In fact, results obtained, which show that parameters descriptive of soil binding, runoff and water erosion are amongst the most sensitive of PWC, are an indication that site differences surely exist within the Pampa Region in terms of pesticide fate to surface water. These results also mean that the next step in the path to using PWC in the Pampa Region will be to define and compare Pampean exposure scenarios.

5. Conclusion

The current study describes a two-steps sensitivity analysis which includes a first screening of less sensitive parameters with the Morris method, followed by a fully global sensitivity analysis of the remaining parameters using Sobol's method. Results obtained show that, when used in soil and climate conditions characteristic of the Pampa Region, the model PWC is most sensitive to about 25% of the parameters evaluated. Parameters identified as most sensitive belong to two main categories: (i) degradation rates of the pesticide in soil and water and (ii) parameters descriptive of soil binding, runoff and erosion. More specifically, the following 9 parameters were detected as sensitive in one or more simulations: (i) pesticide half-life in soil (*soilhl*), (ii) soil adsorption coefficient (*kd*), (iii) pesticide half-life in water column, (*wchl*), (iv) curve number (*cna*), (v) runoff soil interaction (*rseff*), (vi) pesticide hydrolysis half-life (*hidrohl*), (vii) the USLE factors (*usle ls*), (viii) *usle c*, and (ix) solids in suspension in water column (*wcfoc*). The sensitivity analysis of the model PWC performed in the current study is a crucial first step towards (i) parametrize more efficiently PWC, reducing uncertainty in the results; (ii) facilitate the elaboration of pesticide exposure scenarios for pesticide fate modelling in the Pampa region and (iii) use PWC to estimate environmental concentrations values needed to perform aquatic pesticide risk assessment in the Pampa region of Argentina.

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Table 1. Abbreviations of the parameters used by PWC and the process they describe.

Abbreviation	Definition	Process Described
bbiomass	Benthic Biomass (g/cm2).	Water Body Physical Parameters
bdhl	Benthic Metabolism half-life (day)	Pesticide
cheight	Canopy Height (cm)	Growth Descriptors
choldup	Canopy Holdup (cm)	Growth Descriptors
ccover	Canopy Cover (%):	Growth Descriptors
cna	Curve Number (before and after crop)	Run Off/Erosion
cnb	Curve Number (during crop)	Run Off/Erosion
chlor	chlorophyll concentration, effects photolysis attenuation only.	Water Body Physical Parameters
cropfrac	Cropped Area Fraction	Water Body Dimensions
dfac	DFAC: photolysis parameter as defined in VVWM documentation	Water Body Physical Parameters
edepth	E-Depth (cm): The lowest depth at which erosion interacts with the soil.	Distribution of Eroded Soils
evapod	Evaporation Depth (cm)	Hydro Factors
foliarhl	Foliar half-life (day)	Pesticide
hidrohl	Hydrolysis half-life (day)	Pesticide
ireg	Location of NRCS 24-hour hyetograph.	Run Off
kd	Sorption Coefficient (mL/g)	Pesticide
mna	Manning coefficient before and after cropping	Run Off/Erosion
mnb	Manning coefficient when cropping	Run Off/Erosion
mxc	Mass Xfer Coefficient: Mass transfer coefficient for exchange between benthic and water column (m/s).	Water Body Physical Parameters
pfac	Pan Factor	Hydro Factors
phohl	Aqueous Photolysis Half-life (days)	Pesticide
Q10	Q10 factor: increase in the degradation rate every 10 ° C	Pesticide
rdecli	R-Decline (cm): The exponential decline of runoff interaction as a function of depth.	Distribution of Runoff in Surface
rdepth	R-Depth (cm): The lowest depth at which runoff interacts with the soil.	Distribution of Runoff in Surface
rseff	The amount of runoff that interacts with the soil.	Distribution of Runoff in Surface
slope	Slope of the hydraulic flow path	Run Off
soilhl	Soil half-life (day)	Pesticide
solubility	Solubility (mg/L)	Pesticide
usle c	Universal soil loss cover management factor	Run Off/Erosion
usle ls	Universal soil loss equation topographic factor	Run Off/Erosion
usle p	Universal soil loss equation practice factor	Run Off/Erosion
vappres	Vapor Pressure (torr)	Pesticide
wcbiomass	Water Column Biomass: biomass concentration in water column (mg/L).	Water Body Physical Parameters
wcdoc	Water Column DOC: Dissolved Organic Carbon content in water column.	Water Body Physical Parameters
wcfoc	Water Column foc: Organic Carbon fraction on suspended solids in water column	Water Body Physical Parameters
wchl	Water Column Metabolism half-life (day)	Pesticide
wcss	Water Column SS: suspended solid concentration in water body.	Water Body Physical Parameters

Table 2. Source of the climatic data used in the five localities included in the sensitivity analysis.

	Anguil	Marcos Juárez	Paraná	Pergamino	Tres Arroyos	Reference
Latitude (˚E)	-36.50	-32.70	-31.78	-33.93	-38.33	
Longitude (˚N)	-63.98	-62.15	-60.48	-60.55	-60.25	
Elevation (meters above sea level)	165	114	78	65	115	
Hydrologic Soil Group (HSG)	B	C	D	D	D	Godagnone et al. (2014)
Great Group of Soil	Entic Haplustolls	Typic Argiudolls	Vertic Argiudolls	Typic Argiudolls	Typic Argiudolls	
Climate Data	WMO station 87624	WMO station 87467	WMO station 87374	WMO station 87484.	WMO station 87688	INTA(2018) / SMN
Average Precipitation (mm)	721	881	1080	1003	787	
Average Temperature	7.9	11.6	13.5	10.5	7.6	
Climatic zone *	A	B	B	C	A	Diaz and Mormeneo, 2002

WMO = World Meteorological Organization, INTA = Instituto Nacional de Tecnología Agropecuaria, SMN = Servicio Meteorológico Nacional.

FIGURE LEGENDS

Figure 1. Geographic locations within the Pampa of the five localities used in the present study.

Figure 2. Results of PWC model sensitivity analysis performed using Morris Method in each of the five Pampa localities. The test pesticide was 2,4-D and the output used was the upper 90^{th} ranked annual 4d average water concentrations.

Figure 3. Results of PWC model sensitivity analysis performed using Morris Method in each of the five Pampa localities. The test pesticide was glyphosate and the output used was the upper 90^{th} ranked annual 4d average water concentrations.

Figure 4. Overview of sensitivity values (μ) obtained using Morris Method when modelling the fate of either 2,4-D or glyphosate in each of the five Pampa localities. Results obtained when using the upper 90^{th} ranked annual 4d average water concentrations are presented.

Figure 5 Results of PWC model sensitivity analysis performed using Sobol Method in each of the five Pampa localities. Test pesticide was (a) 2,4-D and (b) glyphosate forthe upper 90^{th} ranked annual 4d average water concentration.

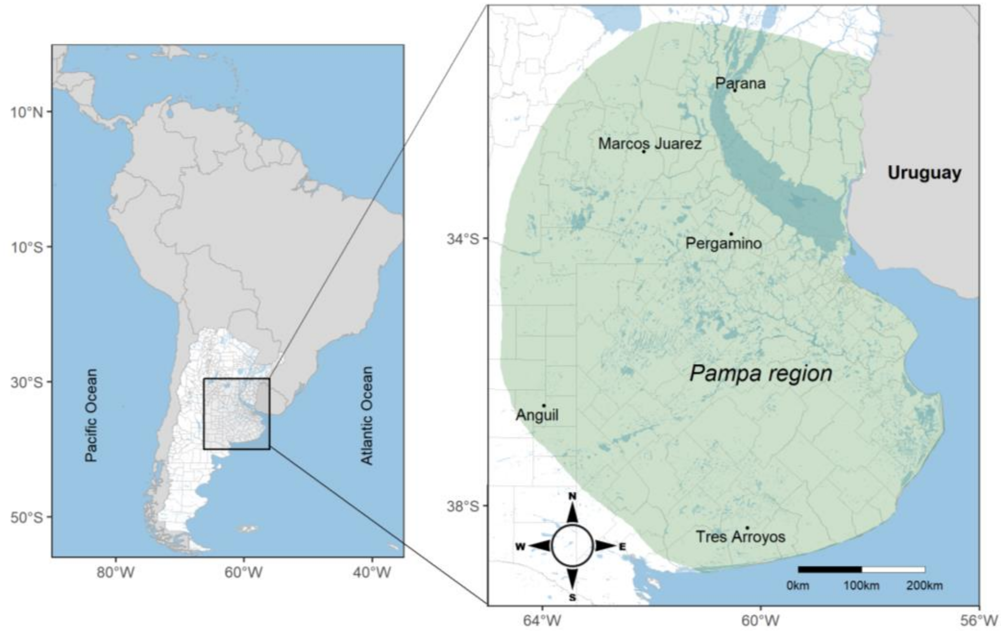

Figure 1. Geographic locations within the Pampa of the five localities modelled in the present study.

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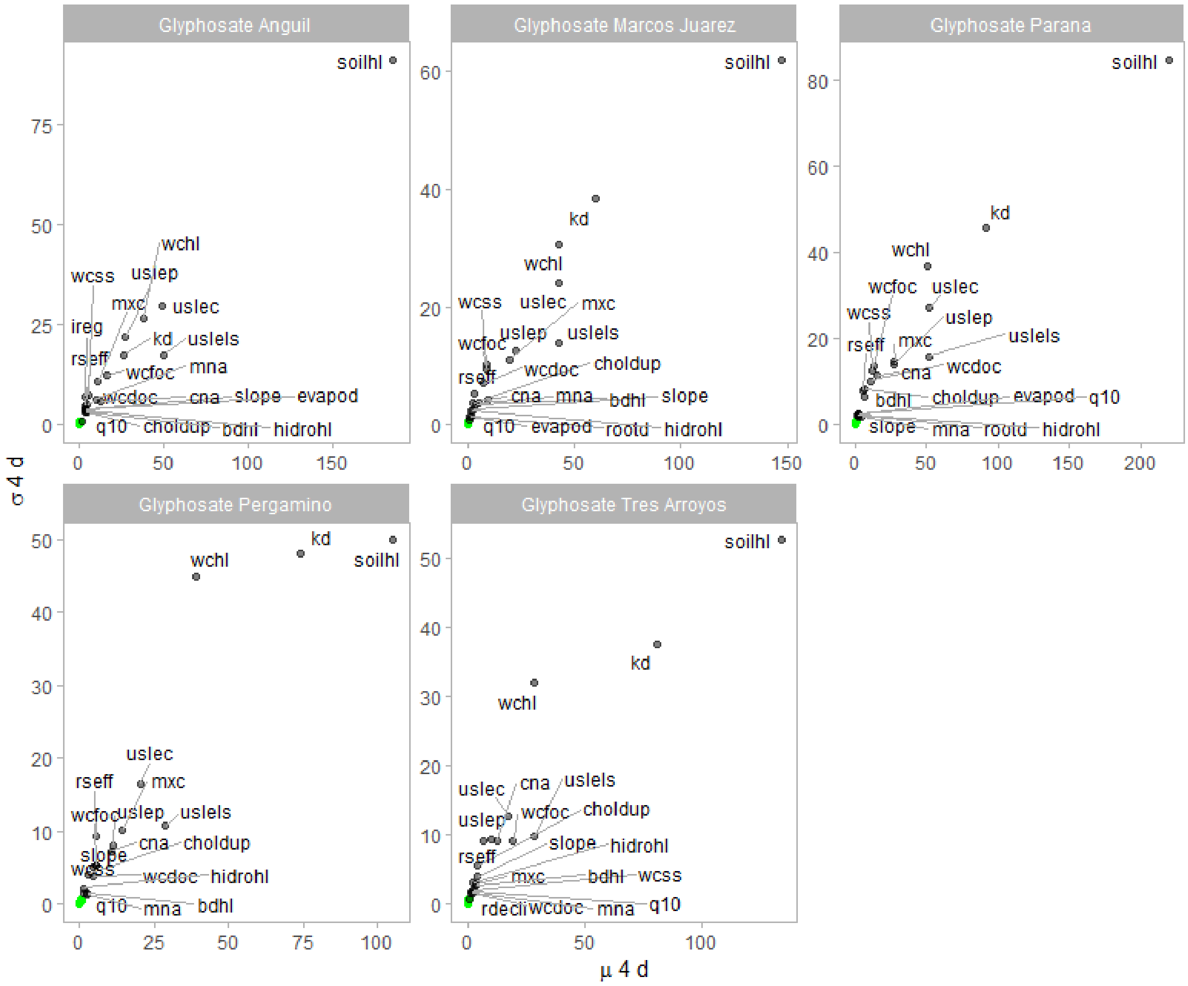
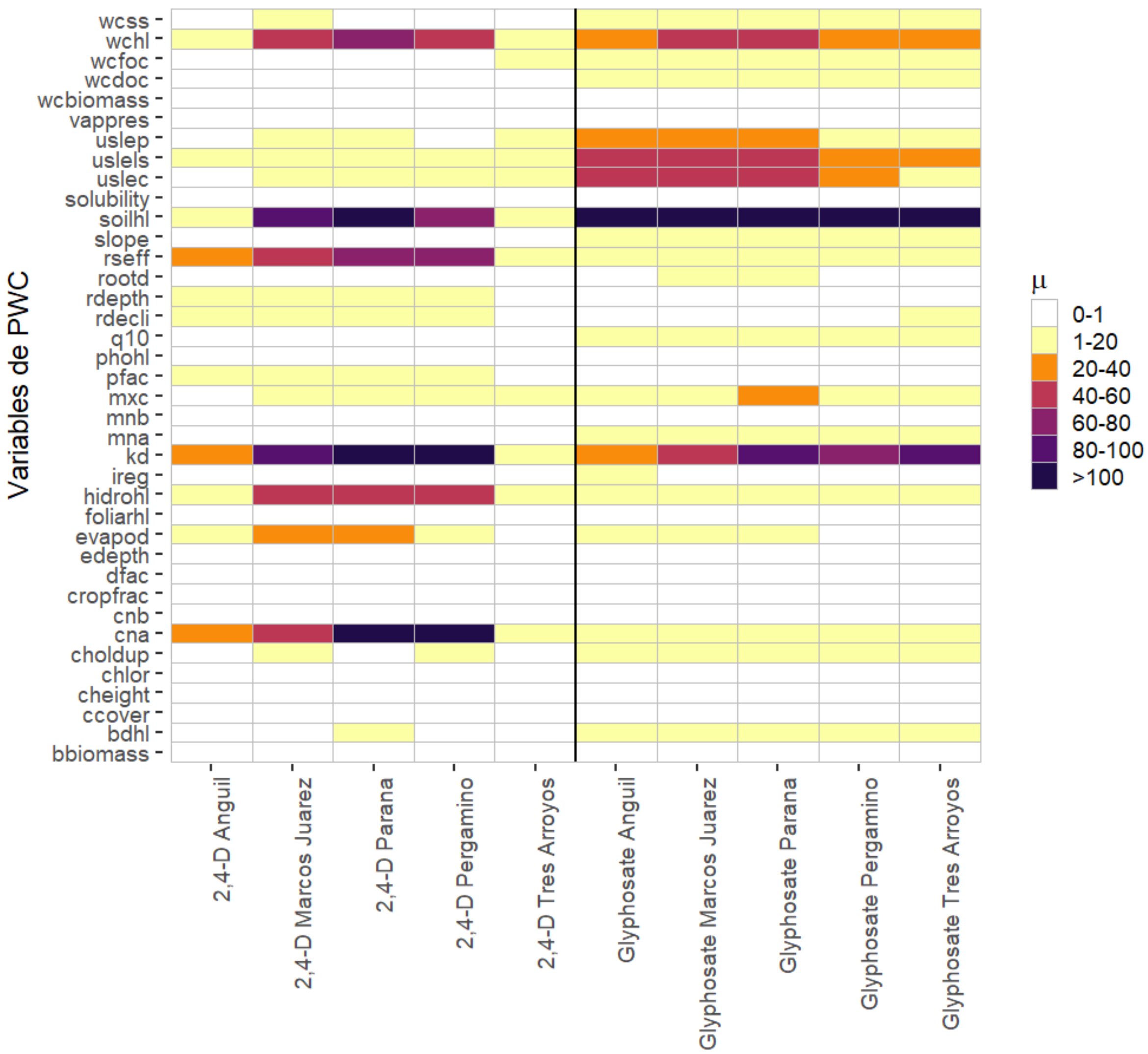


Figure 3. Results of PWC model sensitivity analysis performed using Morris Method in each of the five Pampa localities. The test pesticide was glyphosate and the output used was the upper 90th ranked annual 4d average water concentrations.



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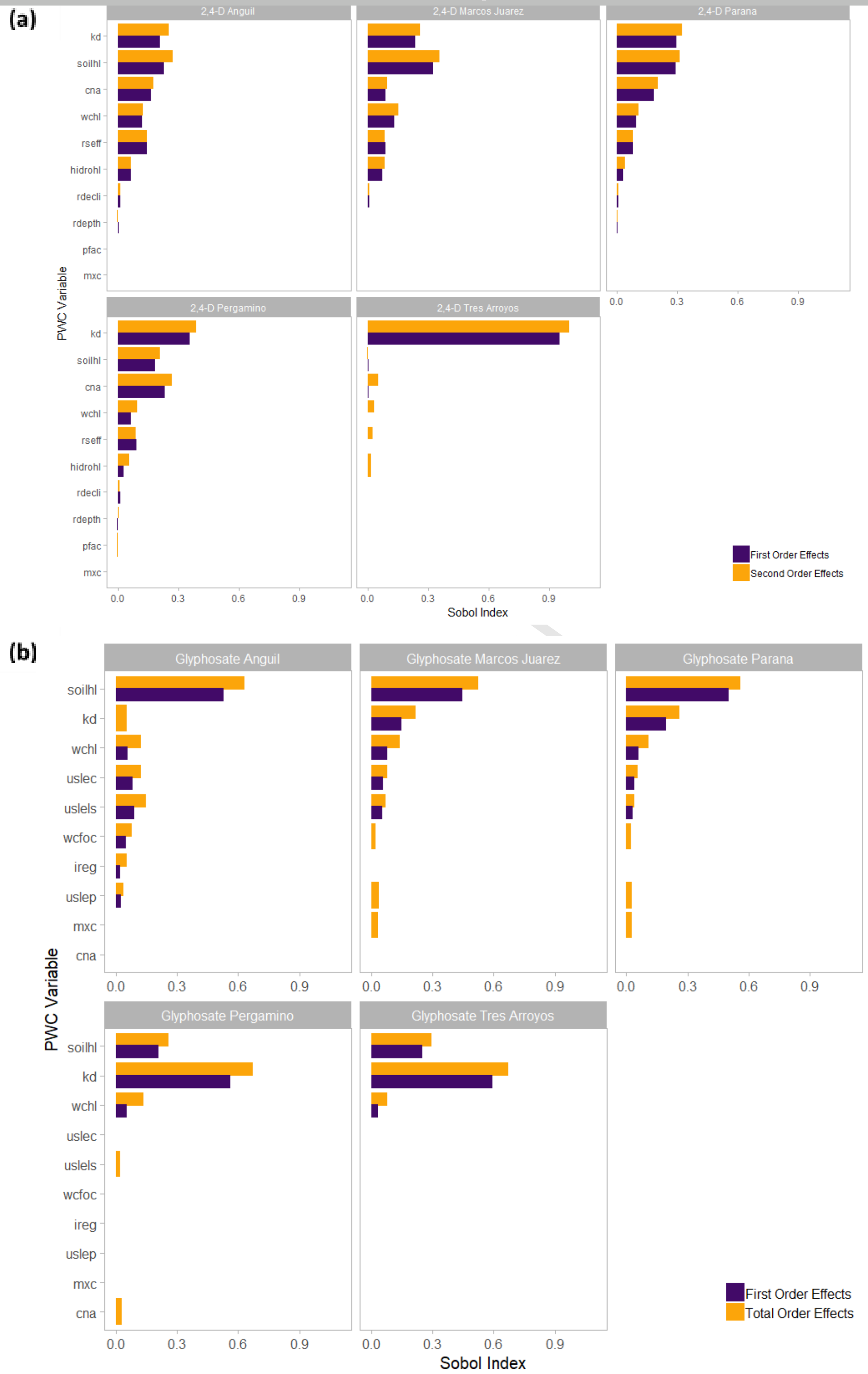
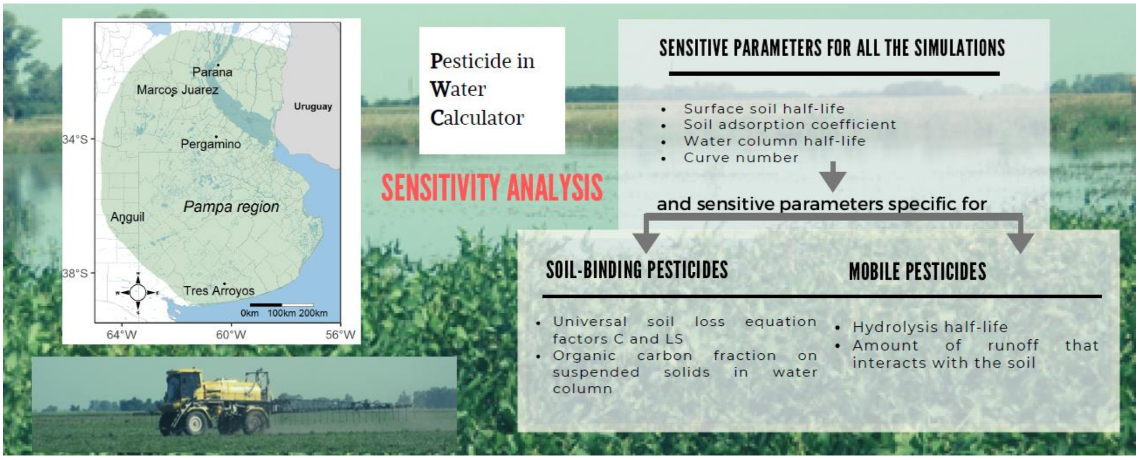


Figure 5. Results of PWC model sensitivity analysis performed using Sobol Method in each of the five Pampa localities. Test pesticide was (a) 2,4-D and (b) glyphosate for the upper 90th ranked annual 4d average water concentration.



Graphical abstract

Highlights

- A sensitivity analysis was performed for PWC for the Pampa region of Argentina.
- PWC was most sensitive to 25% of the parameters evaluated.
- Soil adsorption coefficient and water and soil half-lives are sensitive parameters.
- Sensitive parameters depended on the nature of the pesticide modelled.