Preferential flow modelling of chlorpyrifos leaching in two arid soils of irrigated agricultural production areas in Argentine Patagonia

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Abstract

An analysis was made of the transport and fate of the organophosphate pesticide chlorpyrifos in productive soils from the Alto Valle of the Río Negro in Argentine Patagonia. The climate of the region is arid, so traditional fruit production is under flood irrigation. The soils in the floodplain are predominantly Aridisols with textures ranging from sandy loam to clay loam.

The calibration was performed with water table data and chlorpyrifos concentration in the soil horizons. Field experiments made with Brilliant Blue FCF at the profile scale enabled the parametrisation of the dual-permeability model MACRO. The model calibration was evaluated by a comparison of observed and simulated data and statistics.

The simulation of the groundwater table depth was satisfactory and the chlorpyrifos leaching revealed a different pattern in the two soil types studied . The sandy loam texture soil produced more percolation of irrigation water, but the clay loam soil produced greater leaching of chlorpyrifos under similar application conditions, presumably due to preferential flow under non-equilibrium conditions.

Productive management alternatives to reduce leaching into the underlying unconfined aquifer were simulated. Among these, the incorporation of organic matter was the best alternative.

Keywords: MACRO model; macropore; pesticide; solute transport; organophosphate; water quality

1. Introduction

Groundwater contamination by pesticides is a widespread problem in areas with agricultural production. The vulnerability is greater in shallow unconfined aquifers due to the proximity of the water table to the surface. In these situations, the soil and the conditions of production determine the leaching of pesticides to the aquifer.

Pesticide leaching in the subsurface occurs through flow in the soil matrix and also through preferential pathways that enable the rapid entry of undegraded solutes (Jarvis, 1995). The existence of preferential flow through macropores and soil heterogeneities has long been recognised (Beven and German, 2013; Jarvis et al., 2016) and has been studied at different scales (Allaire et al., 2009; Hendrickx and Flury, 2001; Köhne et al., 2009a, 2009b). Several authors have focused on preferential flow related to soil type; for example, Gerke (2006) did so with structured soils, Katterer et al. (2001) with humic gleysol, Perillo et al. (1999) with soils of glacial origin, Wang et al. (2009) with sandy soils. Stagnitti (2002) examined the approaches to preferential flow modelling and proposed a multi-domain model. Gerke (2006), Köhne et al. (2009a, 2009b), Merdun (2005) and Šimůnek et al. (2003) focused their examination on preferential flow models.

Field dye tracing tests are one of the techniques that enable preferential flow characterisation; they have the advantage of being low cost, but are laborious and destructive (Allaire et al., 2009). Many have conducted specific trials on soils using colourimetry, such as Allaire et al. (2009), Flury et al. (1994), Flury and Wai (2003), Kramers et al. (2009), Steenhuis et al. (1997) and Wang et al. (2009). The influence of irrigation conditions and soil moisture on preferential flow were investigated by Perillo et al. (1999) by using dyes in sandy loam soils of agricultural use. They found that under flood irrigation conditions, the preferential movement of the dye is deep, independent of the initial soil water content and preexisting vegetation. The irrigation method has a strong effect on the transport of pesticides, with flood irrigation being more favourable to preferential flow than sprinkler irrigation (Perillo et al., 1999). This has been confirmed for the movement of water and conservative solutes, but cannot be generalised to non-conservative solutes (Flury, 1996; Jarvis, 2007).

Modelling the leaching of pesticides at the soil profile scale allows us to understand the dynamics of transport in irrigated areas and evaluate the impact of agricultural practices on groundwater quality. The dual-permeability model MACRO is a physically based model of water and solute transport in macroporous soil (Jarvis, 1994; Jarvis and Larsbo, 2012; Larsbo and Jarvis, 2003) that can better reproduce pesticide breakthrough curves than simple porosity models (Bergström and Jarvis, 1994). Some examples of MACRO performance analysis in relation to simple porosity models can be found in Kuzmanovski et al. (2015), who compare it with the PRZM (Pesticide Root Zone Model), or in Giannouli and Antonopoulos (2015), who contrast it with the PEARL model or Köhne et al. (2009a, 2009b) who carried out a review of models simulating pesticide transport in structured soils subject to preferential flow. The modelling of micropores and macropores requires a greater number of parameters, so the sensitivity analysis helps parametrise the model. Beulke et al. (2002) made a guide to estimate the parameters for MACRO while Jarvis and Larsbo (2012) analyzed the main parameters in preferential flow transport in structured soils. Other authors, such as Dubus and Brown (2002), Dubus et al. (2003) and Trucano et al. (2006) analysed the sensitivity of MACRO results to the most important parameters.

The presence of pesticides in the unconfined aquifer of the Alto Valle of the Río Negro due to the application of organophosphates for the cultivation of fruit trees was indicated by Loewy et al. (2006). They found azinphos-methyl in groundwater samples during 1995-1998 period ranging from 0.22 to 7.66 $\mu g \cdot L^{-1}$. Some advances in the preferential modelling of azinphos-methyl leaching with MACRO were presented by Dufilho et al. (2011).

In this paper, we present the results of chlorpyrifos transport modelling with MACRO 5.2 by preferential pathway in two types of dominant soils: sandy loam and clay loam. Subsequently, agricultural management alternatives to reduce the leaching of chlorpyrifos to the unconfined aquifer are simulated using the calibrated model.

2. Material and methods

2.1. Study area

The study area is located in the alluvial plain of the Neuquén river near the confluence with the Limay river, where they form the Río Negro river, in the northwest of Argentine Patagonia (Fig. 1). The terrain is comprised of plateaus and valleys, covered by natural arbustive steppe vegetation, with native arid environment species (Movia et al., 1982) adapted to mean annual precipitations of 180 mm. The mean annual temperature is 13.4 °C, with a mean thermal amplitude of 14 °C and an annual potential evapotranspiration of 950 mm (Galeazzi and Lutz, 2006).

The Neuquén river has a mean annual flow of 308 $m^3 \cdot s^{-1}$ and provides irrigation water of about 70,000 ha via the irrigation system of the Alto Valle of the Río Negro (Fig. 1), where an average of approximately 1,200,000 t of pears and apples are produced annually (FUNBAPA, 2010).

The traditional irrigation system is via flood irrigation, with total water applied ranging from 80–120 mm on average every 10–14 days. The overall efficiency of the irrigation system in the region has been estimated to be 50–60% (Peri, 2004), with percolation losses estimated to be close to 30–40%. The aquifer recharge in the study area due to these excess has been estimated at approximately 500 mm annually (Dufilho et al., 2011). This causes the elevation of the water table, which is located at a depth of between 1–3 m, bringing it close to the surface during the irrigation period, and then descending through drainage until it reaches equilibrium.

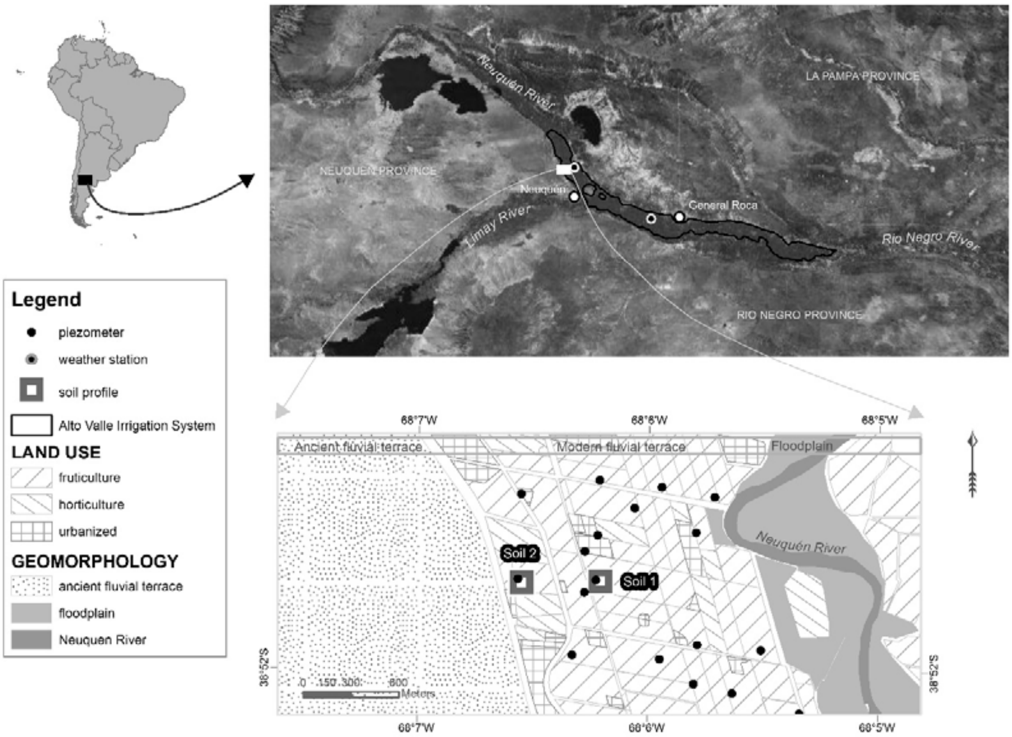

Figure 1. Location of the study area in the Patagonian region and the Alto Valle of the Río Negro irrigation system. Current land uses in the alluvial plain of Neuquén river.

The unconfined aquifer is formed by a package of coarse heterogeneous sediments with a maximum thickness of 25 m, on which Aridisol and Entisol soil orders are formed (US Soil Taxonomy classification) to varying degrees of development (Irisarri, 2006), or Fluvisols (FAO classification). The Aridisols represent 68% of the irrigated area in the Neuquén and Río Negro valleys, and the Entisols 32% (Peri, 2004). They are moderately deep soils of sandy loam, sandy, and clay types; they are rich in bases, low in organic matter, and of a moderately alkaline pH.

For pest control, 8–12 applications of pesticides are made annually, mainly organophosphates (Cichón and Garrido, 2012). One of these is chlorpyrifos, which belongs to Class II (moderately hazardous) according to the classification of pesticides by hazard (WHO, 2010). The carpocapsa *Cydia pomonella* (L) is the pest which has most impact on the production of pears and apples in the region. Applications are mainly concentrated in the first two months of the productive season (October and November). The pesticide is applied to the fruit trees at high pressure, dissolved in varying concentrations according to the brand. The total amount of pesticides applied per year in the regional fruit production is 12.9 kg·ha^{-1}, with azinphos-methyl, carbaryl and chlorpyrifos accounting for 70% (Libiquima-Citaac, 2016).

2.2. Field data

Based on soil information (Irisarri, 2006), two sites with the same fruit production system were selected, but with different species (apples and pears) and different types of dominant soil (Fig. 1).

The soil properties were obtained from soil pits made near the existing piezometers. In each horizon, soil thickness and structure were characterised (according to FAO classification) and samples were taken to determine texture (clay, silt and sand content), organic carbon content (OC) and bulk density (Table 1).

Soil 1 is loam to sandy loam, whereas soil 2 is finer with a higher clay content and clay loam texture in the upper two horizons. Both soils have a low OC content. In 1000 ha of the irrigated valley of the Rio Negro, 43% of the surface area is occupied by coarse-textured soil (similar to soil 1), whereas fine-textured soil (similar to soil 2) occupies 25%, and other types of textures 32% (INTA, 2008). These proportions are expected to be similar in the alluvial plain of the Neuquén river.

The physical and hydraulic properties of the soils were determined from the water retention curve obtained from representative samples in each soil horizon. The water content was determined for the pressure points 5, 10, 30, 100, 500 and 1500 kPa (Fig. 2) in the pressure plate. Soil 2 had a higher water content for low and high pressures because its texture was finer than that of soil 1.

Soil 1 Horizon	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Soil texture	OC (%)	Bulk density ($t \cdot m^{-3}$)
A	0 – 20	19.4	38.9	41.7	Loam	2.16	1.27
B	20 – 40	17.0	29.2	53.8	Sandy loam	0.46	1.69
C1	40 – 70	14.6	31.6	53.8	Sandy loam	0.31	1.41
C2	70 – 100+	14.6	46.1	39.3	Loam	0.4	1.27

Soil 2 Horizon	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Soil texture	OC (%)	Bulk density ($t \cdot m^{-3}$)
A	0 – 15	36.4	34.1	29.5	Clay loam	2.03	1.20
B	15 – 32	26.7	48.6	24.7	Clay loam	0.39	1.26
C1	32 – 70	14.6	58.3	27.1	Silt loam	0.28	1.21
C2	70 – 90+	19.4	63.2	17.4	Silt loam	0.41	1.04

Table 1. Physical and chemical properties of soils.

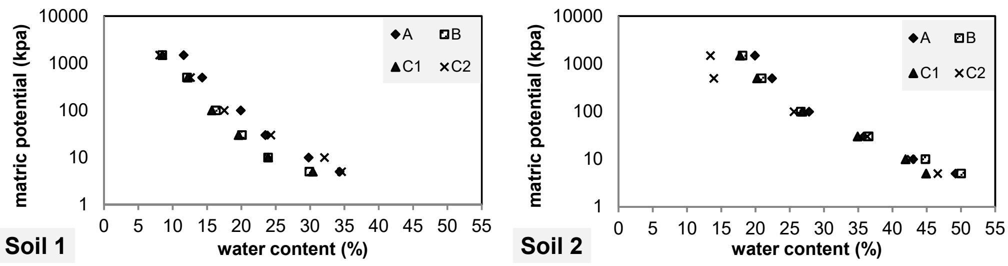

Figure 2. Water retention curve in A, B, C1 and C2 horizons of soil 1 and soil 2.

One of the methods indicated for the study of preferential flow by Allaire et al. (2009) is direct observation and the qualification of structures at the profile scale. This usually involves measuring the number and shape of macropores capable of producing preferential flow. The field experiments were performed with the dye tracer FD&C Blue N°1 (Brilliant Blue FCF), applying water depth similar to that used in production irrigation, to describe the preferential flow mechanisms present in the A and B soil horizons. A 100 mm sheet of water with blue dye at 20 $mg \cdot L^{-1}$ was added to the soil surface with a cylinder of 20 cm diameter allowing infiltration down to the lower horizons of the soil under irrigation conditions (Fig. 3). The time elapsed until complete infiltration was measured. A vertical cross-section of the soil profile was obtained for each soil type by excavation. The structure of the cross-section was described visually, characterising the macropores (length, diameter), cracks, roots, fauna, concretions, etc. These structures, together with the textural heterogeneities within and between the soil horizons, are preferential paths for the movement of water and solutes, which move faster than in the micropores of the soil matrix structures. High resolution photographs were taken and the procedure was then repeated in vertical layers approximately 2–3 cm parallel to the exposed surface. These tests were repeated at the site for observations in horizontal layers, but the observations did not provide any more information regarding the preferential pathways.

These photographs were digitally analysed using the Principal Component Analysis technique (Fig. 3 lower) and information, such as length, number and area occupied by macropores, was obtained in order to determine some parameters of the model, like the effective diffusion pathlength. Additionally, the importance of the preferential flow in relation to the flow in the soil matrix, the exchange length between macropores and the matrix, and the dispersivity of the medium were estimated. A homogeneous flow is observed in the A horizon of soil 1, whereas the B horizon presents fingering type preferential flow and a narrow zone of interaction between macro- and micropores around small roots and conduits. Preferential flow is produced in the contact of the two layers due to the discontinuity and heterogeneity of the medium, which corresponds to channelled flow. In soil 2, the A horizon presents a marked preferential flow due to the structures and cracks. Below this, the clay loam texture of the B horizon, although with a lower clay content than the A horizon, demonstrates less preferential flow and an exchange zone of 1–3 mm in width between the matrix and the macropores. Considering that the test was carried out under similar irrigation conditions, the greater depth of advance in the clay soil must be due to the existence of preferential paths in the first 15 cm of soil.

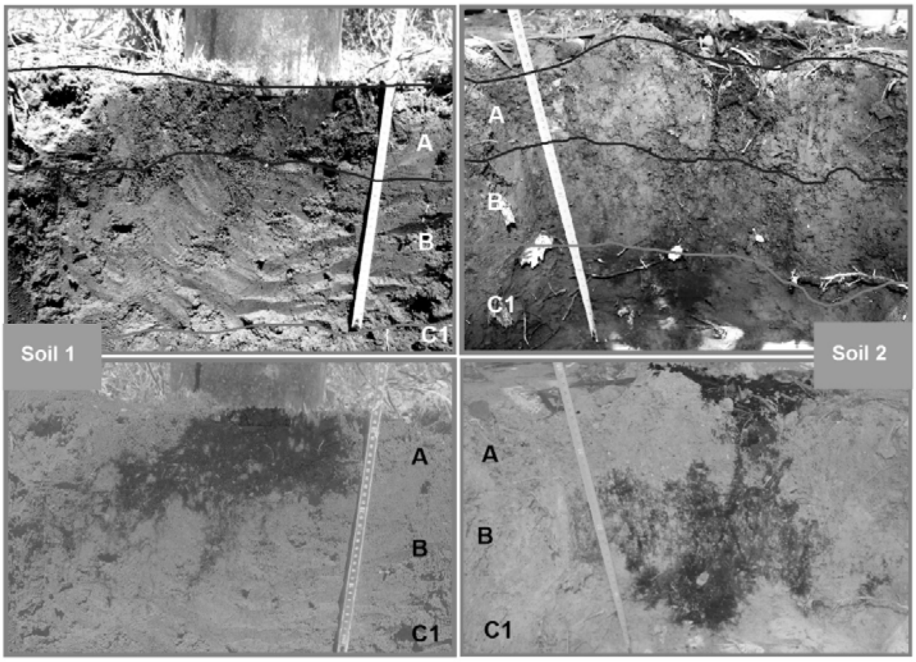

Figure 3. Field experiments with Brilliant Blue FCF in soils 1 and 2 (upper). Profile image done with Principal Component Analysis technique (lower).

Concerning the agricultural production conditions, the Irrigation Consortium of Colonia Centenario (Neuquén Province) provided monthly irrigation and water table depth measurements from 1 January 2008 to 31 March 2014. The depth of the water table from two piezometers near the studied soils was used to adjust the calibration of the water flow in the model. The growers also provided information regarding the application of pesticides.

The concentrations of chlorpyrifos in each soil horizon were determined in samples obtained with a hand auger. Analyses were carried out in LIBIQUIMA at the National University of Comahue, using solid-phase extraction (SPE), quantification by gas-chromatography with nitrogen-phosphorus detection, and confirmation by gas chromatography-mass spectrometer (GC-MS). The limit of detection of chlorpyrifos in soils was 0.400 $\mu g \cdot kg^{-1}$ and the limit of quantitation was 1.600 $\mu g \cdot kg^{-1}$. A total of 48 samples (20 from soil 1 and 28 from soil 2) from between 2008 and 2014 were analysed. The highest concentration occurred in the A horizon (60.48 $\mu g \cdot kg^{-1}$ in soil 1 and 31.33 $\mu g \cdot kg^{-1}$ in soil 2). In the B horizon, it decreased to 5.28 $\mu g \cdot kg^{-1}$ in soil 1 and to 0.400 $\mu g \cdot kg^{-1}$ in soil 2. It was not detected in horizons C1 and C2 in the 14 samples collected.

The daily meteorological data required by the MACRO model, precipitation and minimum and maximum air temperature were obtained from the Agrometeorological Station of the Faculty of Agrarian Sciences (FCA) at the National University of Comahue, located about 4 km to the north of the study site (Fig. 1) and the INTA Alto Valle station (located about 30 km to the east).

2.3. Model parametrisation

MACRO is a dual-permeability model of water flow and reactive solute transport in a soil profile. The soil porosity is divided into two domains, micropores and macropores. Water and solute exchange are calculated using approximate first-order expressions based on an effective diffusion path length. The vertical water flow through the micropores in the unsaturated zone is calculated using the Richards' equation and a modified form of the van Genuchten function is used to describe the water retention function. Through the macropores, the vertical flow is calculated by the Darcy's equation assuming a unit hydraulic gradient. Solute transport in the micropores is calculated by the advection-dispersion equation while in the macropores is only advective transport. To describe pesticide sorption a Freundlich isotherm is used, and first-order kinetics is assumed for degradation. The water balance includes precipitation, evapotranspiration, deep seepage and fluxes to drains. The solute balance includes advective-dispersive transport, sorption, biodegradation, plant uptake and canopy interception. The model has been described in detail by Jarvis (1994) and Larsbo and Jarvis (2003).

The implementation of MACRO 5.2 (Jarvis and Stenemo, 2001) in the profile of both soils was made by using a water table in the profile as a bottom boundary condition for water flow, in other words, the outflow to groundwater is controlled by the height of the water table above the base of the profile. Therefore, soil 1 was considered down to 2 m depth and soil 2 down to 2.50 m, in order to include the oscillation of the water table depth observed with the piezometers. The unconfined aquifer is located at the base of the profile, with a regional hydraulic gradient estimated at 0.001 obtained from the piezometer readings in the study area (Fig. 1).

For the numerical resolution of the transport equation, the soil profile was divided into 60 layers with an average thickness of 0.033 m for soil type 1, and 0.0416 m for soil type 2. To minimize numerical errors, the discretization of the upper layers of the A soil horizon was smaller as suggested by van Dam (2000) and in all cases the thickness of the layers was less than 5 cm as indicated by Larsbo (2005) for clay soils.

The parameters of the model were estimated through the method of trial and error using field and laboratory measurements and bibliographic values. In some cases, the initial value was calibrated. Table 2 shows the calibrated hydraulic parameters, and Table 3 indicates the calibrated transport parameters.

The shape parameters (α and n) of the soil moisture function of van Genuchten, the water contents in the wilting point at 15,000 cm of tension and the saturated water content of micropores were determined from the characteristic curve of each soil horizon (Fig. 2) using the RETC program (van Genuchten et al., 2009). The porosity values were calibrated within the values obtained from the soil samples, considering that MACRO macroporosity is given by the difference between the saturated water content and the tension defining the macropore-micropore boundary. It is known that in soils with macropores, hydraulic conductivity increases very rapidly with small changes in tension as it approaches saturation (Clottier and Smetten, 1990; Jarvis and Messing, 1995; Larsbo and Jarvis, 2003). Therefore, the separation between the micropore and macropore regions, which the user must define as a break point in the water retention curve, can generate large variations in the values of hydraulic conductivity and in the solute leached.

Parameter	Description	Unit	Horizon	Soil 1	Soil 2
ALPHA	alpha of van Genuchten function	$1 \cdot cm^{-1}$	A	0.070	0.018
			B	0.050	0.010
			C1	0.050	0.008
			C2	0.010	0.007
ASCALE	Effective diffusion pathlength	mm	A	20	20
			B	10	30
			C1	10	10
			C2	10	10
CTEN	Boundary soil water tension	cm	A	18	40
			B	18	25
			C1	25	12
			C2	25	15
KSATMIN	Saturated hydraulic conductivity	$mm \cdot h^{-1}$	A	120.12	53.50
			B	80.14	67.41
			C1	80.04	115.87
			C2	79.96	15.26
KSM	Boundary hydraulic conductivity	$mm \cdot h^{-1}$	A	4	4
			B	1	3
			C1	2	6
			C2	3	4
TPORV	Saturated water content	%	A	48.89	52.78
			B	42.22	51.09
			C1	44.12	52.90
			C2	44.12	42.53
WILT	Wilting point	%	A	6	16
			B	4	15
			C1	4	12
			C2	4	9
XMPOR	Boundary soil water content	%	A	43.34	48.67
			B	37.01	48.18
			C1	40.11	48.93

Parameter	Description	Unit	Horizon	Soil 1	Soil 2
			C2	40.11	40.91
ZM	Tortuosity factor micropores	-	All	0.5	0.5
ZN	Pore size distribution factor for macropores	-	All	4	2

Table 2. Calibrated hydraulic parameters of MACRO for soil 1 and soil 2.

The initial values of the saturated hydraulic conductivity of the micropores were obtained with pedotransfer functions in the Soil Water Characteristics (SWC) program by Saxton et al. (1986), which requires the clay, sand, OC and gravel content (Table 1). A range of values was obtained for the different samples of each type of soil in the area and then the value was adjusted by calibration.

Parameter	Description	Unit	Horizon	Soil 1	Soil 2
DEGMAL - DEGMIL	Degradation rates macropores and micropores liquid phase	d^{-1}	A	0.0270	0.0390
			B	0.0230	0.0140
			C1	0.0150	0.0120
			C2	0.0050	0.0070
DEGMAS - DEGMIS	Degradation rates macropores and micropores solid phase	d^{-1}	A	0.0138	0.0190
			B	0.0100	0.0090
			C1	0.0080	0.0090
			C2	0.0020	0.0040
FRAC_KIN	Fraction of sorption sites for kinetic sorpcion	-	A	0.8	0.8
FRACMAC	Fraction sorption sites in macropores	-	A	0.02	0.02
ZKD	Sorption coefficient	$ml\cdot g^{-1}$	A	90.34	162.4
			B	74 75	31.2
			C1	72.24	22.4
			C2	72.24	32.8

Table 3. Calibrated solute transport parameters for soil 1 and soil 2.

The total saturated hydraulic conductivity was estimated by the value of the final infiltration rate determined in field tests. The values obtained in the study area by CIL (1988) and Storti (2008) were also used.

The tortuosity factor in micropores takes a value of 0.5 in the Mualem model to estimate the hydraulic conductivity. The tortuosity factor in macropores takes a value of 2 in bimodal soils like clays and coarse sand, while it is 4 in sandy loam. Giannouli and Antonopoulos

(2015) used a value of 4 in loam soil, this being the value suggested by Beulke et al. (2002). In FOCUS (2015), loam soils were calibrated at 3–4, and clay loam at 2–4; FOCUS (2000) sets a value of 3 for depths between 0–60 cm, and 2 for deeper layers.

The effective diffusion pathlength was calibrated according to the values presented in the literature, along with observations of the size of the aggregates in the soil profiles. Values may be between 5–150 mm, they frequently decrease with depth in loam soils and increase in fine and clay soils. Beulke et al. (2002) indicated values of 10 mm in poorly structured soils, 20 mm in medium and 30 mm in well-structured soils, whereas Alaoui et al. (2003) gave values of 6 mm in sandy loam and Giannouli and Antonopoulos (2015) 6 mm in loam soil. At higher values, the exchange of solutes between macropores and micropores decreases and preferential becomes stronger. In the FOrum for the Co-ordination of the pesticide fate model and their USe (FOCUS, 2015), horizons with the same texture were calibrated with different values, e.g., the clay loam horizon was given a value of 20–100 mm in the same profile, and the value was calibrated at 55 mm for loam, sandy loam and clay loam.

Regarding the solute transport parameters, the sorption distribution coefficient (K_d) was estimated from the sorption constant (K_{oc}) and the OC of the soil. The K_{oc} values used are the averages for chlorpyrifos provided by the Pesticide Properties DataBase of the University of Hertfordshire (PPDB, 2016), from 2,785 to 31,000 ml·g^{-1}.

The sorption processes are controlled by the fraction of sorption sites in the macropores and kinetic sorption. They were set according to FOCUS (2015). The exponent of the Freundlich isotherm was set at 1.

The degradation rate coefficient parameters for the solid phase (in the macropores and micropores) and for the liquid phase (in the macropores and micropores), were estimated from the half-life of chlorpyrifos in soils, ranging from 11–141 days (PPDB, 2016) in laboratory measurements. The degradation for the horizons up to 1 m was calculated as a function of the degradation ratio suggested in FOCUS (2000). A degradation rate of 0.03 was used below 1 m depth. Micropores and macropores were considered with the same properties.

For apple and pear cultivation, a root depth of 1 m was given and the fruit parameters in FOCUS (2015) were used. Solar radiation data, vapour pressure, wind speed and air temperature were used to estimate potential evapotranspiration by the Penman Monteith method with MACRO. The estimated potential evapotranspiration values for apple and pear trees in the region by Galeazzi and Lutz (2006) were used to adjust the calibration of the crop parameters.

Regarding the irrigation parameters, the applied irrigation water was determined by estimating the volume of water delivered by the Irrigation Consortium and the productive area; water depth measurements were also performed during irrigation. The sheet of water varied between 84–112 mm, made in 12–14 irrigations during the season, which begins on 1 August and ends on 1 May each year. Chlorpyrifos was applied as a spray at doses between 0.41 to 1.5 $kg \cdot ha^{-1}$ of active product depending on the season. The interception of the pesticide spray was 10% at the beginning of the fumigation season and 30% at the end. The intercepted pesticide in the canopy is degraded. The irrigation efficiency values in the valley estimated by FACA (2004) and by Peri (2004) were used to verify the hydrological balance and percolation to the aquifer estimated by MACRO.

The initial water content in the soil profile is considered to be in equilibrium with the natural drainage. Although the soil water content is important for the transport of pesticides, in this study where the pesticide is applied during a period of irrigation, the profile is expected to be wet and without significant variations.

The initial soil temperature is defined as being in equilibrium with the local meteorological conditions at 15 °C.

At the beginning of the simulation, the concentration of the pesticide in each soil horizon is equal to the average value determined in 2008. In soil 1, the values were 1.8 mg·m^{-3} in A horizon, 0.4 in B horizon and 0.04 in C horizon. In soil 2, they were 0.5 mg·m^{-3} in A horizon, 0.14 in B and 0.01 in C.

Rainwater and irrigation water do not contain pesticides and the concentration of solute in the aquifer is zero.

2.4. Sensitivity analysis

Sensitive parameters for chlorpyrifos leaching were carried out with the maximum absolute ratio of variation (MAROV) by Dubus et al. (2003). A total of 38 parameters relating to the flow and transport of pesticides in the soil were modified in the model. There were no changes related to vegetation because its influence in the transport of pesticides is minor. The variation of the parameters was performed using a range of values measured in the field and found in the literature.

The influence of the 40% variation in the amount of applied irrigation water was included in this analysis as there is uncertainty in the measurement of this factor. This occurs because the irrigation water is delivered to the plot of land according to the duration and height of the sluice gate opening. In this way, the volume of water delivered is not precisely measured and varies from one plot to another.

The applied dose of pesticide was also analysed because of the uncertainty in determining some application dates and doses. The dose in the irrigation sheet was modified by 30%

through the parameter concentration of the substance in the irrigation water on the application dates modelled.

The sensitivity analysis determined the most influential parameters in the leaching of chlorpyrifos in both soils. For the parameters that the model was least sensitive to, the values suggested by FOCUS (2015) and the authors cited above were used.

2.5. Model evaluation

The evaluation of the performance of the model was performed by making a visual comparison of the simulated and measured graphs of water level depth and total chlorpyrifos concentration in the soil profile. In addition, the root mean square error (RMSE) defined in Anderson and Woessner (1992) and Loague and Green's coefficient of residual mass (CRM) and model efficiency (EF) were used (Loague and Green, 1991). Model efficiency is significant when the time series are continuous and when the measured and simulated data are on the same time scale (Reichenberger, 2005). In our case, the observed data on water level depth are on a monthly scale and the data on chlorpyrifos concentrations are on a longer time scale. Therefore, it is expected that the EF statistic will not be useful for the comparison with the daily simulated series. In these cases, the choice of other criteria to measure deviations is valid.

2.6. Proposed agricultural practices to reduce chlorpyrifos leaching

Reducing pesticide leaching to the aquifer is possible with the implementation of appropriate agricultural practices. Although improving the efficiency of the irrigation system and reducing the amount of applied irrigation water is, a priori, the best environmental alternative, it is not possible to implement it under the current flood irrigation production system. Therefore, only methods that rely on cultural practices that can feasibly be implemented under the current productive conditions in the Alto Valle of the Río Negro are proposed.

One of these is the time of pesticide application (Alternative 1). Leaching can be very sensitive to the application pattern, especially at the time of application in relation to the prevailing climate (Alaoui et al. 2003; Gish et al. 2004; Jarvis, 2007; Jarvis and Stenemo, 2001). In arid zones, precipitation is not such an important factor, but irrigation is. In a flood irrigation system, the day before irrigation is a priori the most unfavourable time to spray because the degradation of the product is in its initial phase. The lowest risk condition would be the application of the pesticide 3–4 days after irrigation, which is only possible—from the operational point of view—in some soils where the spraying machine can travel without problems. To represent this alternative, the spraying dates have been changed in the model but not the doses applied (i.e., 2000 $L{\cdot}ha^{-1}$ doses with an average concentration of 350 g of active product per 1000 L of water).

Another possible practice is to incorporate organic matter into the soil (Alternative 2). Through agricultural work, straw or manure can be incorporated into the soil to a depth of 20–30 cm, the decomposition of which generates humus that increases the adsorption capacity of the soil and increases the distribution coefficient of the pesticide (Johnson et al., 1997), so that more will be retained in the A and B horizons, allowing the pesticide to degrade. Besien et al. (1997) obtained good modelling results using field samples in the laboratory where buried straw and animal manure were incorporated in clay soil. This aggregate was modelled by doubling the OC in the A and B soil horizons and modifying the K_d parameter. In practice, the incorporation of organic matter up to 30–40 cm depth introduces other physical, chemical and biological modifications in the soil, including the following: a decrease in bulk density, an increase in macroporosity (and biopores), increased water holding capacity and soil porosity. It also improves ion exchange and promotes the development of microorganisms that contribute to the degradation of substances. Although Besien et al. (1997) indicated that the diffusion pathlength and the tortuosity factor in macropores decreased, they have not been modified in our simulation.

Finally, a scenario is presented that features the simultaneous implementation of both agricultural practices (Alternative 3).

3. Results and discussion

The total water balance of the simulated period (2,282 days) is indicated in Table 4. The entries were due to precipitation of 173.7 mm·yr^{-1} on average and irrigation of 1,374 mm·yr^{-1} in soil 1 and 1,350 mm·yr^{-1} in soil 2. There was no runoff and the canopy water storage of 42 mm was similar for both crops. The estimate of potential evapotranspiration is 970 mm·yr^{-1} or 2.68 mm·d^{-1}, a value similar to the 2.58 mm·d^{-1} estimated by Galeazzi and Lutz (2006).

	Unit	Soil 1	Soil 2
Accumulated Rainfall	mm	173.8	173.8
Accumulated Irrigation	mm	1374.4	1350.1
Accumulated Infiltration	mm	1506.3	1481.8
Accumulated Runoff	mm	0.0	0.0
Actual Accumulated Evapotranspiration	mm	893.9	970.3
Potential Accumulated Evapotranspiration	mm	970.3	970.3
Accumulated Percolation	mm	650.6	550.1
Total water storage (profile)	mm	110.9	154.5
Change in water content (micro + macropores profile)	mm	+ 4.6	+ 5.2

Table 4. Annual water balance of the simulated period (2,282 days).

Throughout the simulated period, the water storage in the profile remained in equilibrium, although it increased by 4.05% in soil 1 and 3.36% in soil 2 compared to the initial storage on 1 January 2008.

Therefore, the mean annual percolation of water was 650 mm in soil 1, and 550 mm in soil 2. Although the irrigation applied in sandy soil is 2% higher than in clayey soil, percolation represents 47.3% and 40.7% of the annual amount of applied irrigation water for soils 1 and 2 respectively. Using the definition of the efficiency of application as the percentage of water delivered to the plot that is used by the plant, an average of 35% was established in irrigated areas according to the FACA study (2004), and Peri (2004) indicated an efficiency of land use of between 60–70%. Therefore, the sites studied would have a plot irrigation efficiency halfway between the two studies, approximately 52.7% in soil 1 and 59.3% in soil 2.

In relation to the pesticide balance, the simulation was calculated with a solute mass balance error of less than 0.01% in both soils and is presented for the whole period in Table 5. Of the total amount applied, an annual average of 3.19 kg·ha^{-1} in soil 1 and 2.74 kg·ha^{-1} in soil 2, soil degradation consumed 94.6% in soil 1 and 83.3% in soil 2, while the total storage variation in the profile was 1.36% and 0.74%, for soils 1 and 2 respectively. The storage and subsequent degradation in the soil was significant, functioning as a barrier to the passage of solutes to the aquifer. The degradation in the vegetation was very low in soil 1, at 0.45%, and 13.7% in soil 2. Leaching to the aquifer was 1.25.10^{-5} % and 1.3.10^{-3} % in soil 1 and soil 2, respectively.

Component	Unit	Soil 1	Soil 2
Accumulated Fumigation	mg·m^{-2}	319.3	273.8
Accumulated Degradation (soil)	mg·m^{-2}	301.9	228.2
Accumulated Degradation (canopy)	mg·m^{-2}	1.4	37.6
Solute transferred to groundwater	mg·m^{-2}	3.9.10^{-5}	3.6.10^{-3}
Change in stored solute (micro + macropores profile)	mg·m^{-2}	+4.3	+2.0

Table 5. Annual solute balance of the simulated period (2,282 days)

3.1. Simulation of groundwater table depth

Figure 4 presents the simulated groundwater table depth together with the values measured for soil 1 and soil 2. The model correctly reproduces the trend of the observed values, with a variation pattern that exhibits peaks due to flood irrigation during the irrigation period and then decreases through natural drainage until recovering its state of equilibrium in the subsoil in the period without irrigation. In soil 1, the model overpredicts some high depths and underestimates some low depths. The same thing occurs for soil 2 but less noticeably. However, the root mean square error (RMSE) for soil 1 is 0.39 and for soil 2 is 0.34. The depth of the water table is controlled by a drainage system designed to keep the water below the root depth of the fruit trees. Therefore, the levels observed do not exceed 2.5 m deep.

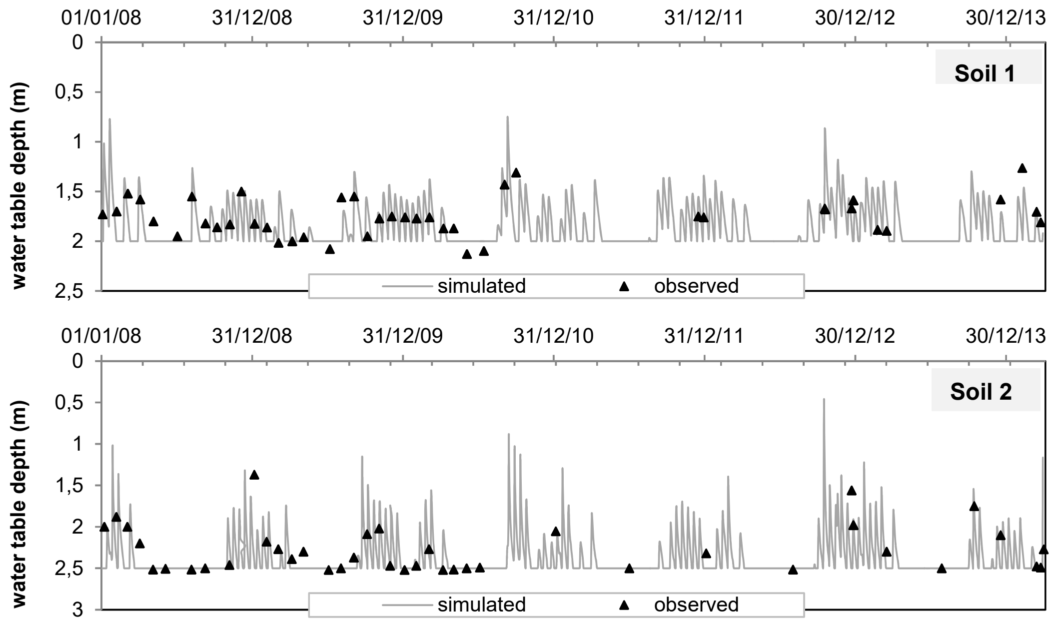

Figure 4. Comparison of measured water table depth with those simulated in soil 1 and soil 2.

The efficiency of the model is good in both soils according to the CRM and RMSE statistics (Table 6), which give values close to zero, whereas the negative values of EF, far from 1, indicate a poor fit. As already mentioned, the measured and simulated data are at a different time scale, so the EF statistic is not especially useful (Reichenberger, 2005).

	CRM		EF		RMSE	
	Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2
Water table depth	-0.03	-0.09	-0.163	0.160	0.267	0.233

Table 6. Evaluation of the performance of the model to simulate water table depth. Coefficient of residual mass (CRM), modelling efficiency (EF), root mean square error (RMSE).

3.2. Concentration of chlorpyrifos in the soil profile

Measured and simulated storage of chlorpyrifos in the soil are presented in Figures 5 and 6. Only the upper horizons, A and B, are included, since the detected and simulated concentrations in the lower horizons are smaller than the level of detection throughout the simulated period.

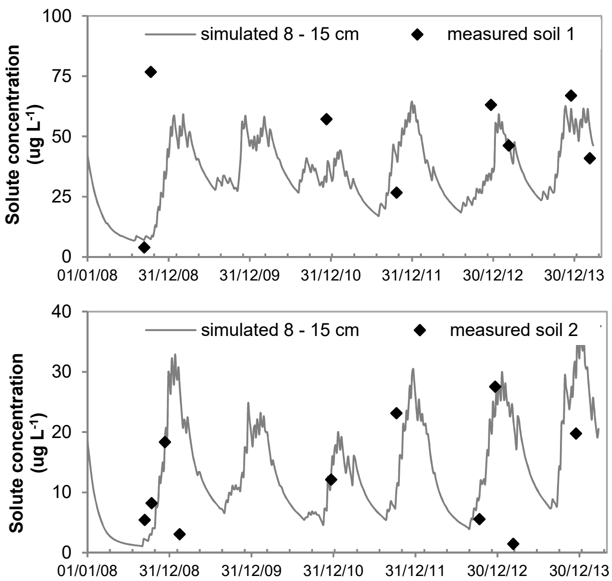

Figure 5. Comparison of measured chlorpyrifos concentration with those simulated by MACRO-Horizon A in soil 1 and soil 2.

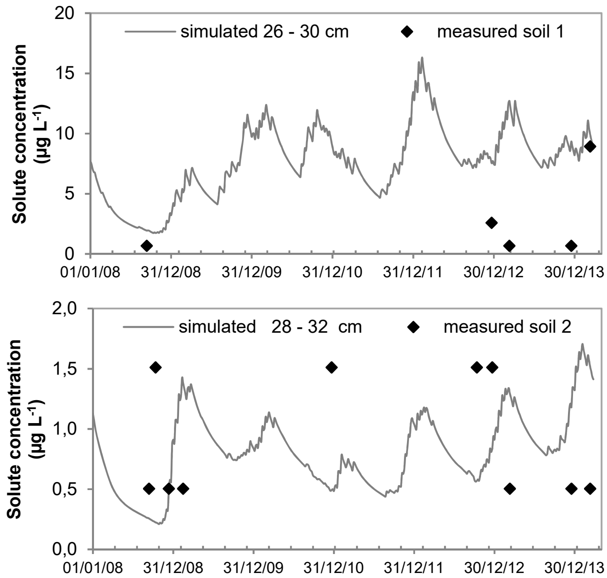

Figure 6. Comparison of measured chlorpyrifos concentration with those simulated by MACRO. Horizon B in soil 1 and soil 2.

The simulation of the concentrations in the profile remains within the range of observed values, reproducing the periods of chlorpyrifos application. However, the negative EF value in all cases indicates a poor fit (Table 7). In the case of the A horizon of soil 1, the positive CRM is due to an overestimation of the model, whereas there is an underestimation in the A horizon of soil 2. For the B horizon, the low concentrations and the low amount of samples make it difficult to analyse the efficiency, although the deviations are acceptable.

	CRM		**EF**		**RMSE**	
	Soil 1	**Soil 2**	**Soil 1**	**Soil 2**	**Soil 1**	**Soil 2**
Horizon A	0.140	-0.320	-0.517	-0.229	27.367	12.186
Horizon B	-3.921	-0.114	-3.459	-1.822	6.746	0.829

Horizon A: measured and simulated values between 8 and 15 cm depth in both soils. Horizon B: measured and simulated values between 26 and 30 cm in soil 1 and 28 and 32 cm in soil 2.

Table 7. Evaluation of the performance of the model to simulate concentrations in horizons A and B of soils 1 and 2.

The RMSE indicates larger errors in the predictions of concentrations in the A horizon of both soils, although it is necessary to remember how sensitive this statistic is to the outliers.

The simulated A horizon reproduces the variations of concentrations observed in soil profile 1 (sandy loam) (Fig. 5). For soil 2 (clay loam), a better concordance between simulated and observed values is observed. The tendency to increase the observed and simulated concentrations towards the end of the simulated period in both soils would reflect the replacement of azinphos-methyl pesticide with chlorpyrifos (Dufilho, 2016).

The concentrations in the A horizon of the sandy soil (soil 1) are higher than those of the clay soil (soil 2), due to the predominance of dispersive transport in the sandy medium (Peclet number is 7) and advective transport in macropores of fine-structured soils. It is also influenced by the lower rate of degradation used in sandy soils.

In the B horizon, the observed values are below the values simulated by the model for soil 1. In soil 2, the measured values are within the instrumental limits. In both soils, the simulated and observed concentrations are lower than in the A horizon.

Both the observed and simulated concentrations are lower in the clayey soil 2, in both the A and B horizons. This can be observed in Figure 7, which represents the simulated concentrations in the soil profile after the application of chlorpyrifos. The concentration at the upper edge of the A horizon at these dates is much higher than the values observed at between 8–15 cm depth due to the initial adsorption of chlorpyrifos.

Figure 7 presents the variation in the concentrations according to depth and the variation of the concentration of solutes in the upper horizons. The concentrations from 1 m and below remain constant due to the low rate of degradation at this depth. The concentration profile also reflects the change to silt loam in the texture of soil 2.

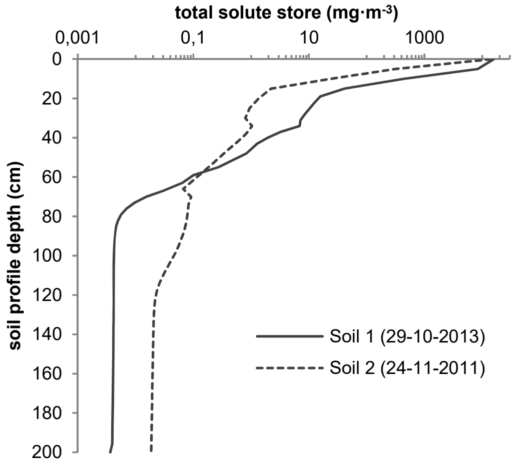

Figure 7. Chlorpyrifos concentration in the soil profile after pesticide application (application date in parenthesis).

3.3. Solute loss to groundwater

The results of the simulation of leaching to the aquifer are presented in Figure 8 for the two soils studied, indicating the accumulated mass of chlorpyrifos leached to the aquifer and the accumulated mass leached by micropores at the bottom of the profile. It also shows the date of application and the dose used.

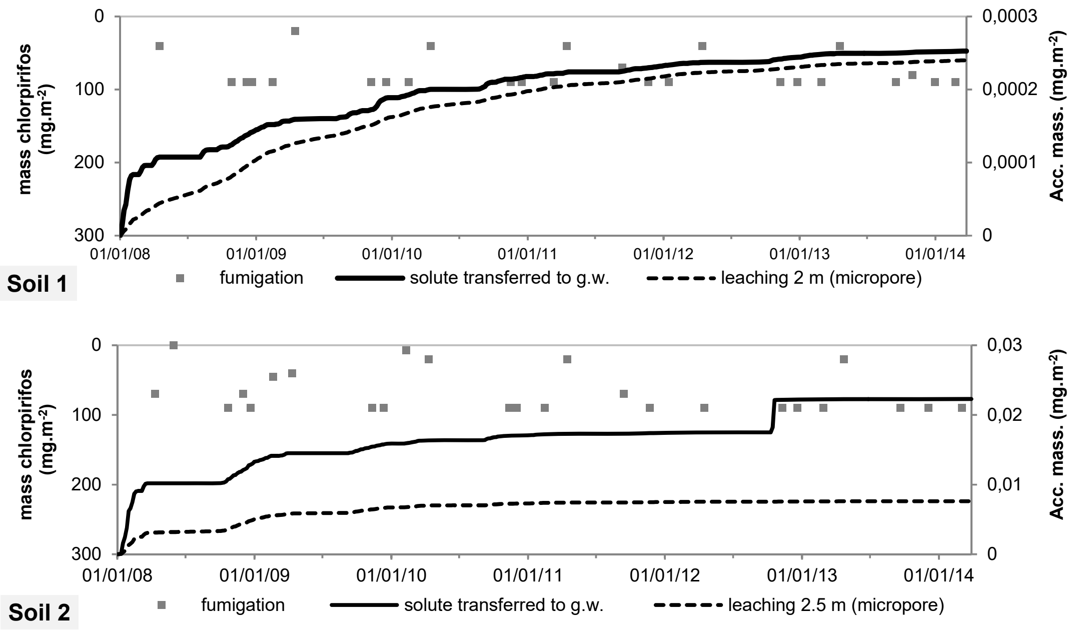

Figure 8. Accumulated chlorpyrifos leaching to the aquifer at the bottom of the profile and leaching by micropores. Pesticide application dates and concentration are indicated.

In soil 1, the total leaching is $2.53.10^{-4}$ mg·m^{-2}, whereas it is greater in soil 2, being $2.23.10^{-2}$ mg·m^{-2}. The decrease in the leaching rate from the second simulated month may be due to the initial conditions of solute concentrations in the soil. The influence of the initial conditions was also indicated by Dubus et al. (2003) through sensitivity analysis in sandy loam and clay loam soils. This effect of the initial conditions in the simulation in the first two months was approximately $7.7.10^{-5}$ mg·m^{-2} in soil 1 and $7.5.10^{-3}$ mg·m^{-2} in soil 2. Therefore, the total accumulated leaching, excluding the first 2 months, could be estimated at $1.76.10^{-4}$ mg·m^{-2} and $1.47.10^{-2}$ mg·m^{-2}. These values represent an average leaching of 0.28 mg·ha^{-1} during each simulated year for the production of apples in soil type 1 (sandy loam), while for the production of pears in soil type 2 (clay loam) it was 23.51 mg·ha^{-1} each year.

In soil 1, the curve of solute transferred to groundwater reflects the relationship with pesticide applications and responds to processes of homogeneous flow in the micropores and macropores of the soil, with the medium saturated hydraulic conductivity of a loam to sandy loam soil. In the case of the clay soil (soil 2), there is a leap in the accumulated leaching to the aquifer at the end of the year 2012, which corresponds to the flow of solute in macropores. It is also observed that, at the end of the simulation, the rate of leaching of chlorpyrifos decreases. A priori, the cause of this may be due to a combination of degradation in the vegetation and soil, leaving little excess available for leaching.

There is more solute leaching in soil 2 than in soil 1, although in the degradation rate and the K_d parameter are higher in the A horizon of soil 2 than in soil 1 (Table 3). This occurs mainly because the solutes are not retained in the A and B horizons due to the preferential flow (Table 2).

In synthesis, although the percolation of water to the aquifer is significant, it is not reflected in the leaching of solutes. The process exists, but degradation and adsorption play an important role in its attenuation. This is in agreement with the very low leaching potential index GUS (Gustafson, 1989) for chlorpyrifos (PPDB, 2016). However, according to the results obtained, the measured values of chlorpyrifos (maximum 1.2 $\mu g \cdot L^{-1}$) in the unconfined aquifer of the study area may be explained by the preferential leaching of solutes through the macropores in the soil.

In sandy soils, leaching is mainly caused by flow of water through pores, whereas in clay soils, the sharp increases associated with pesticide application reflect an element of preferential flow. This difference is reflected at 1 m depth, where the leaching mass that reaches the aquifer will be similar to that which crosses this section, due to the decrease in degradation at depth. In sandy soil (soil 1), the percolation of water by macropores at 1 m is less than in clay soil (soil 2) (Fig. 9). While the maximum velocities are similar, the number of events the macropores are active is greater in the clay soil. The leaching of solutes in macropores is directly correlated with the percolation in macropores.

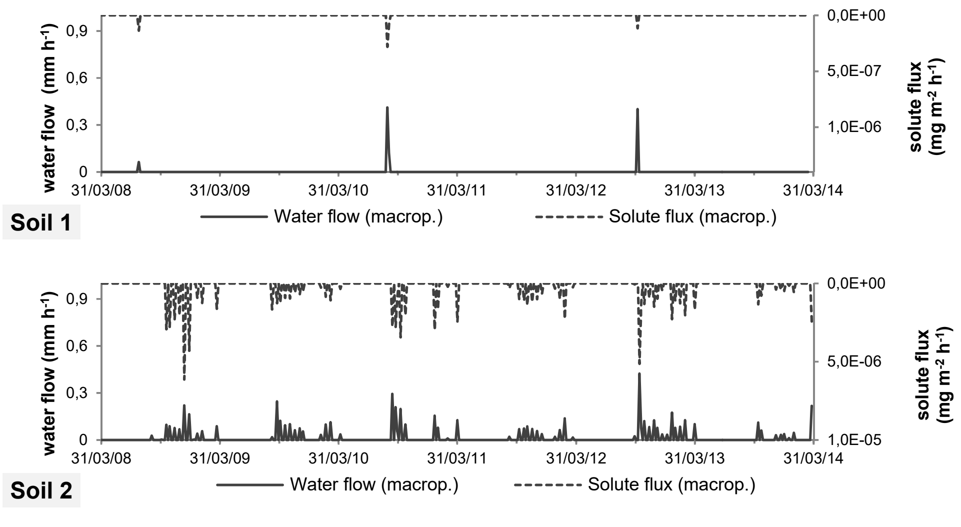

Figure 9. Water flow and solute flux in macropores at 1 m depth in soil 1 and soil 2.

3.4. Sensitivity of the leaching to the calibrated parameters

According to Dubus et al. (2003) a parameter with a MAROV value of <10 indicates that the model is not sensitive. In this sense, leaching in both soils (Fig. 10) is sensitive to calibrated hydraulic parameters (Table 2) and less so to calibrated chemical parameters (Table 3).

In relation to the aspects of the productive system, the analysis indicates that one aspect that is of vital importance in both soils is the amount of irrigation water applied, due to the sensitivity that the model exhibited with respect to the solute leaching to the aquifer. However, in the case of chlorpyrifos in soil 1, the index indicates that a modification of 1 mm in the amount of irrigation water applied produces a 540-fold increase in the leaching of chlorpyrifos, which seems exaggerated and may be due to the small amount of total solute leached to the aquifer (Fig. 8). Regarding the concentration of the substance in the irrigation water, the model was not very sensitive when increasing the dose applied by 30% because the chlorpyrifos leaching was 3.10^{-4} mg·m^{-2} for soil 1 and $2.4.10^{-2}$ mg·m^{-2} for soil 2, with a MAROV value of 4.10^{-4} and $2.1.10^{-1}$, respectively.

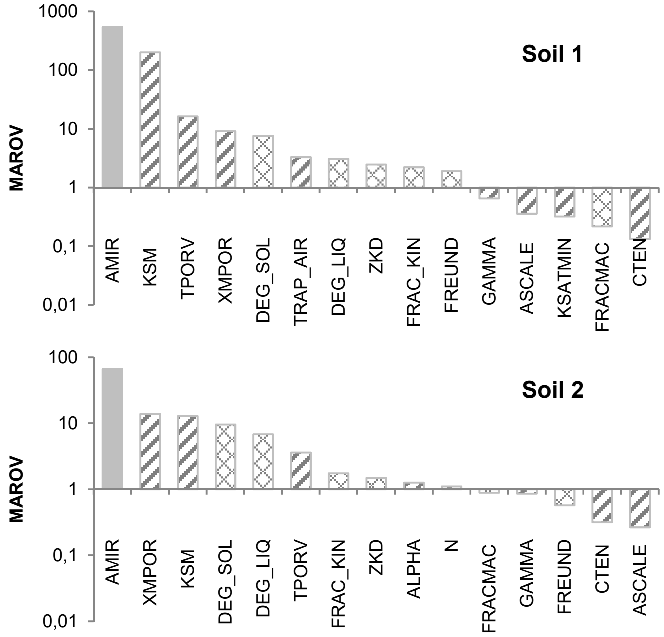

Figure 10. *MAROV* index for the most sensitive parameters to chlorpyrifos leaching for soil 1 and soil 2. Filled column: irrigation parameters, inclined lines: hydrodynamic parameters, and diamond pattern: pesticide transport parameters. AMIR: irrigation amount (mm), DEG_SOL = (DEGMAS + DEGMIS), DEG_LIQ = (DEGMAL + DEGMIL), TRAP_AIR: trapped air content (%), FREUND: Freundlich exponent (-), GAMMA: bulk density (g·cm^{-3}), N: *n* of van Genuchten function.

In both soils, the saturated hydraulic conductivity of the micropores (KSM) and the porosity (TPORV and XMPOR) are the most sensitive parameters and, therefore, those that contribute most uncertainty to the prediction of leaching. The study by Larsbo (2005), in a loam soil and a clay soil, indicated the sensitivity of the model to these parameters and also the influence of KSM on solute concentrations in the profile.

The water tension (CTEN) in the soil that marks the macropore-micropore boundary is not very sensitive and was calibrated according to the values suggested by Beulke et al. (2002), depending on the weighted clay content of the soil structure.

The effective diffusion pathlength (ASCALE) is not very sensitive in either soil and was calibrated according to bibliography values together with observations on the size of the aggregates in the soil profiles.

The chemical parameters that are most sensitive to the leaching of chlorpyrifos are the degradation rate (DEG) and the sorption distribution coefficient (ZKD). The higher sensitivity of the DEG in clayey soil contrasts with the analyses carried out by Dubus and Brown (2002), who indicated a greater sensitivity of degradation in coarse-textured soils (similar to soil 1).

FRAC_KIN and FRACMAC are among the 15 most sensitive parameters. However, they are poorly analysed in other publications and were adjusted by calibration.

3.5. Management alternatives to reduce leaching

In order to standardise the results, the alternatives were compared with a situation that would represent the worst scenario. In clay soil (soil 2) the greatest leaching occurs when spraying occurs 1 day before flood irrigation, whereas in sandy soil (soil 1), the highest leaching to the aquifer occurs under the current management conditions.

The amount of leaching to the aquifer under the three simulated alternatives are presented in Table 8 in annual values per hectare. In Figure 11, the percentages of change are presented with respect to the most unfavourable scenario.

In the three simulated alternatives, clay loam soil (soil 2) responds most positively, decreasing the leaching of chlorpyrifos by up to 44%.

Soil	Unit	Worst-case scenario	Alternative 1	Alternative 2	Alternative 3
sandy (soil 1)	$mg \cdot ha^{-1}$	0.2815	0.2820	0.2228	0.2820

Soil	Unit	Worst-case scenario	Alternative 1	Alternative 2	Alternative 3
clay (soil 2)	mg·ha^{-1}	33.34	30.41	19.29	18.71

Alternative 1: pesticide application timing, Alternative 2: organic matter incorporation, Alternative 3: pesticide application timing and organic matter incorporation.

Table 8. Annual chlorpyrifos leaching to the aquifer in the simulated alternatives.

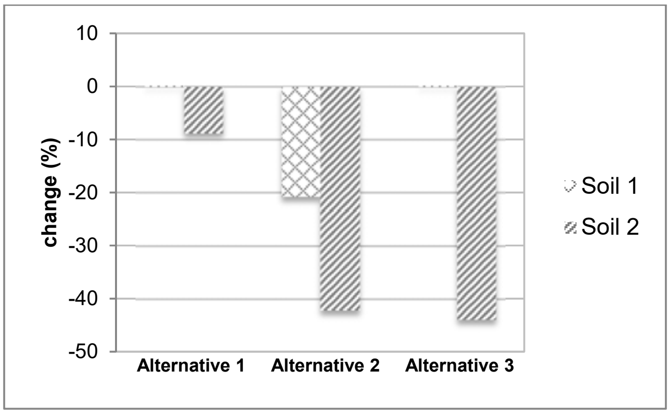

Figure 11. Impact of simulated alternatives in the pesticide leaching to the aquifer, in relation to the worst-case scenario.

In the sandy loam soil (soil 1), the addition of organic matter decreases leaching by 21%, whereas increasing the spraying interval to 10 days after irrigation (alternative 1) does not produce significant changes, at least under the low leaching conditions simulated. Furthermore, the management of time and the incorporation of organic matter do not produce the expected effects.

In the case of clay soil, increasing the interval between irrigation and pesticide application reduces the leaching. The incorporation of organic matter increases the retention time and the degradation of the pesticide in the soil. Although the reduction of leaching to the aquifer was verified, the application of this alternative will entail investigating the influence of the condition of the organic matter has on the soil adsorption capacity and on degradation due to microbiological activity. The combination of the timing of the application of the pesticide and the incorporation of organic matter produces an improvement inferior to the sum of the individual alternatives. Therefore, the incorporation of organic matter is the most effective alternative.

4. Conclusions

The observations with in situ colourimetric tests revealed the preferential flow that occurs in the upper horizons of both types of soils. In addition to the flow in biopores common to both soils, fingerings predominate in the sandy loam horizon, and flow through cracks and inter-aggregates predominate in clay loam. The results indicate that the field experiments with dye are a suitable instrument to be used in the field to determine the type and magnitude of preferential flow in these types of soils.

As expected, the percolation of water to the aquifer is significant and similar in both sandy loam and clay loam soils. The excesses of irrigation that reach the aquifer are higher in the sandy loam soil (47%) than in the clay loam soils (41%). However, the leaching of chlorpyrifos is greater in the clay loam soil. Chlorpyrifos reaches the aquifer through macropores and micropores, but transport by preferential routes is greater in the clay loam soil than in the sandy loam soil.

If we consider that there are about 70,000 ha of irrigated terrain in the Alto Valle of the Río Negro, and assuming that 43% of this terrain is coarse-textured soil (similar to soil 1) and 25% is fine-textured soil (similar to soil 2), it was possible to estimate the total annual amount of chlorpyrifos that reaches the groundwaters. Using MACRO, the mean annual leaching of 0.28 and 23.51 $mg \cdot ha^{-1}$ for soils 1 and 2 respectively were obtained. Therefore we could expect that the total amount of chlorpyrifos that reaches the groundwaters is two orders of magnitude higher in clay soils (411 $g \cdot yr^{-1}$ for soil 2 and 8 $g \cdot yr^{-1}$ for soil 1) although they represent only a quarter of the irrigated area of the valley, which shows the importance of preferential flow in the area.

The distribution of the pesticides in the profile reveals the positive effect of the A and B horizons in the attenuation of the leaching. Simulated management measures aim to enhance this effect. Of the agricultural practices that are feasible under current conditions, the incorporation of organic matter is the most efficient in reducing the leaching of chlorpyrifos to the aquifer in both soil types.

Acknowledgments

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