Pesticide fate modeling in conservation tillage: simulating the effect of mulch and cover crop on S-metolachlor leaching

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ABSTRACT

Conservation tillage practices mainly based on cover crops and no-tillage with accumulation of crop residues at the soil surface (mulch) modify the environmental fate of pesticides. However, only few pesticide fate models are able to consider mulch of crop residues as well as the effect of intermediate cover crops. Thus, the objective was to develop an approach to model the effects of crop residues left at the soil surface and cover crops on the fate of pesticides. This approach consisted in (1) considering the crop residues as a soil layer with specific physical, hydrodynamic and pesticide-reactivity properties close to that of a high organic content soil layer, and (2) introducing a correction factor of the potential evapotranspiration, estimated through a calibration step, to take into account the reduction of soil evaporation by the presence of a mulch. This approach was developed using MACRO as support pesticide model. To assess the model performances, we used the data from a field experiment designed in an irrigated maize monoculture under conservation tillage. Soil water content, water percolates, soil temperature and S-metolachlor herbicide concentrations in the leachate at 1 m depth were measured during two years. The approach chosen to simulate the mulch effects allowed MACRO to make acceptable predictions of the observed water percolation, soil temperature and to a less extent herbicide leaching. However, it showed a poor performance to simulate the soil water content. Results are discussed in terms of further modeling options to better assess the environmental risks of pesticides under conservation tillage. This approach remains to be tested against various soils, crops, pesticides and types of mulch.

Keywords:

26 Pesticide fate model

27 MACRO

28 Crop residue

29 Cover crop

30 Field experiment

31 Pesticide

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34 **1. Introduction**

35 Conservation tillage systems are mainly characterized by no-tillage,
36 accumulation of harvested crop residues as mulch on the soil surface as well as presence
37 of cover crops during the fallow period. These cropping systems are interesting
38 alternatives to conventional systems having many benefits on the soil protection and
39 crop productivity (Hartwig and Ammon, 2002; Thierfelder et al., 2013; Trail et al.,
40 2016).

41 Crop residues left at the soil surface allow reduction of surface runoff and soil
42 erosion (Prosdocimi et al., 2016), regulation of the soil surface temperature (Alletto et
43 al., 2011), capture of rainfall water (Iqbal et al., 2013), increase in soil water content by
44 reducing the evaporation from the soil surface (Dahiya et al., 2007), control of weeds
45 (Martins et al., 2016), and increase in the total organic matter content in the top soil
46 (Castellanos-Navarrete et al., 2012). Cover crops are efficient to reduce nitrate leaching
47 and increase carbon sequestration (Plaza-Bonilla et al., 2016, 2017; Tribouillois et al.,
48 2016) contributing to preserve the groundwater quality and to reduce the impact on the
49 net global warming potential, respectively (Yagioka et al., 2015).

The fate of pesticides in soil under conservation tillage systems is different from their fate under conventional system (Alletto et al., 2010). Some studies have shown that no-till enhances pesticide adsorption on soil because of the increase in organic carbon (OC) content but also that the adsorption varies with the nature and/or the degree of decomposition of the crop residues (Alletto et al., 2013; Aslam et al., 2013; Cassigneul et al., 2015). The presence of a mulch can result in increase in pesticide volatilization (Whang et al., 1993) and increase in pesticide persistence because of a decrease of its bioavailability to degrading microorganisms (Cassigneul et al., 2016). However, opposite effects have also been observed. For example, Gan et al. (2003) showed that the degradation rates of the dicamba and 2,4-D herbicides in mulched soils were enhanced because of the increase in soil OC content and in the abundance of microbial degrading population. Regarding volatilization, Bedos et al. (2017) noted a modification of its dynamics and Weber et al. (2006) observed that crop residues helped to maintain high soil humidity, which decreased soil temperature and consequently the volatilization of metolachlor. Concerning cover crops, field studies have evidenced a reduction of pesticide leaching, which was mostly due to modifications of the soil water balance (Alletto et al., 2012).

Models able to take into account the combined effects of crop residues and cover crops on water balance, soil temperature and pesticide fate would be useful tools to assess the environmental impacts of these rising conservation tillage practices. However, very few models are available (Mottes et al., 2014). To simulate the soil water dynamic under a mulch of crop residues using the Hydrus 1-D model (Simunek et al., 2005), Singh et al. (2011) replaced the crop residue layer by a hydraulically equivalent soil layer, and Dahiya et al. (2007) optimized the potential evaporation rate to take into account the effect of crop residues on the soil water and temperature regimes. However,

no pesticide was considered in their studies. Recently, Lammoglia et al. (2017) combined STICS (a crop model able to simulate various agricultural practices, Brisson et al., 2009) and MACRO (a pesticide fate model, Larsbo and Jarvis, 2003) to simulate pesticide leaching under different cropping systems. The performance of the resulting STICS-MACRO model was found to be acceptable but it was not tested under mulch conditions. The approach developed by Queyrel et al. (2016) consisted to implement a pesticide-module to STICS, leading to the STICS-Pest model. STICS-Pest was found to be as efficient as other capacity pesticide fate models to predict pesticide leaching in some contexts, however, the main limitation of STICS-Pest is its inability to describe water dynamics in presence of preferential flows or a fluctuating shallow water table because the description of water dynamic is based on a capacity approach. Ghirardello et al. (2010) developed SoilPlus to simulate the fate of non-ionized organic chemicals in the air-litter-soil system. The main features of the model are the double-layered air compartment interacting dynamically with multilayered litter and soil compartments, with seasonal dissolved organic carbon fluxes. However, the water balance is based on a capacity approach. The RZWQM model considers plant residues (as layer of crop residues or other plant materials immediately overlying the surface of the soil) and their effects on pesticides fate (Wauchope et al., 2004). However, none of the four models, PELMO, PRZM, PEARL and MACRO, used for risk assessment for European pesticide registration (FOCUS, 2000) allows to simulate mulch effects.

Therefore, the objective of this work was to use MACRO to model the effects of crop residues left at the soil surface and cover crops on the fate of pesticides. The strategy was (1) to consider crop residues as a soil layer having its own hydraulic properties (following the approach of Singh et al., 2011), and pesticide adsorption and degradation coefficients, and (2) to use a correction factor in the calculation of the

potential evapotranspiration to consider the effect of the crop residues on the water balance and consequently on solute movement (following the approach of Dahiya et al., 2007). This work was based on a field experiment monitoring the leaching of the S-metolachlor herbicide in a conservation tillage irrigated maize monoculture cropping system (with cover crops and both maize and cover crop-residue mulch).

2. Materials and methods

2.1. Model description

MACRO is a process-based, one-dimensional, dual-porosity model which considers preferential flows by dividing the soil pore space into micropore and macropore domains characterized by different flow rates and solute concentrations (Larsbo and Jarvis, 2003). The boundary between the two domains is defined by a soil water pressure head close to saturation, and its associated water content and hydraulic conductivity. Soil water flow and solute transport in the micropores are described by the Richards' equation and the convection-dispersion equation, respectively. For the macropore domain, water flow is gravity driven and solute transport is assumed to be solely convective. Exchange between the two domains is calculated according to physically based expressions using an effective aggregate half-width. Degradation of pesticides follows first-order kinetic and solute sorption is described using the Freundlich isotherm. The model simulates degradation and sorption processes in both micro- and macropore domains. The effect of soil moisture content and soil temperature on the pesticide degradation rate is also taken into account. Soil temperatures are calculated from air temperatures using the heat conductivity equation. A detailed description of the model can be found in Larsbo and Jarvis (2003). For this work we

used a development version of the MACRO model provided by the MACRO developers, aiming at replacing the official release MACRO 5.2 in the future.

2.2. Field experiment

Experimental data came from a field-scale leaching study conducted in Toulouse area (Southwest of France). A conservation tillage maize monoculture cropping system was designed in an experimental plot of 12 m x 60 m. According to IUSS WRB (2007), the soil is a Stagnic Luvisol with clay-loam texture (Table 1).

The cropping system comprised a maize monoculture (2011 and 2012) and a mixture of oat, phacelia and vetch as intermediate cover crops (2010-2011, 2011-2012 and 2012-2013). Residues were left at the soil surface after maize harvest and after cover crop destruction by the glyphosate herbicide. At the end of 2010, the first cover crop was sown after a conventional tillage with a mouldboard plow (25-28 cm depth) while a reduced tillage with a working depth ≤ 10 cm was carried out before sowing the cover crop in 2011 and 2012. A direct seeding into crop residues was systematically done for the maize crop. The resulting crops succession along with the crops development dates are listed in Table 2. Sprinkler irrigation was applied in summer during the maize growing season in events that ranged from 25 to 40 mm reaching a total water amount of 220 mm in 2011, and 255 mm in 2012 (Fig. 1).

S-metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl) acetamide] is a selective herbicide used for pre- or post-emergence weed control in crops such as maize, sorghum or soybean. The whole surface of the plot was sprayed once with S-metolachlor at 1.52 kg a.i./ha as Calibra (Syngenta) formulation on 3 May 2012 (post-emergence) (49 days after the cover crop destruction and thus after the occurrence of a mulch on the soil). Two percent of the S-metolachlor applied rate

was assumed to be intercepted by the growing maize (Marín-Benito et al., 2014). Prior to the experimentation set up in 2011, the herbicide had never been applied over the experimental plot.

Climatic data were collected with a meteorological station located at the field site. Soil water content and temperature were monitored with TDR probes and temperature sensors, respectively, installed at 0.2, 0.5 and 1 m depth. Water flows were monitored using one tension plate lysimeter with a fixed tension of -100 hPa installed at 1 m depth in the middle of the experimental plot. Leachates were periodically sampled and kept at 4°C until S-metolachlor analyses. The analyses were done by the Laboratoire Départemental d'Analyses de la Drôme (Valence, France) accredited by COFRAC (French Committee of Accreditation). The limit of quantification and the limit of detection were 0.02 and 0.007 $\mu\text{g L}^{-1}$, respectively.

2.3. Model parameterization to take into account the effect of crop residues and cover crops on the fate of pesticide

2.3.1. Representation of a mulch layer in MACRO and model parameterization

MACRO was parameterized with all available site-specific data. Parameters that were not measured were either estimated by pedotransfer functions, taken from the literature or set to default values according to the model users manual.

The mulch layer was considered as a porous medium analogous to a 100%-sand soil layer of 5 cm-thickness at the top of the soil (physical description) having hydrodynamic properties corresponding to a high organic soil layer (hydrodynamic description) (Wösten et al., 1999) (Table 1).

The depth of the 1-D soil profile was set to 2 m and split into four horizons of different thicknesses (Table 1). Van Genuchten's soil-water retention parameters (θ_s , α

and n) and the tortuosity factor in micropores (ZM) were calculated using the pedotransfer functions reported by Wösten et al. (1999), while the residual soil water content parameter (θ_r) was set to 0.01. The soil water content at wilting point was estimated from the water retention curves (θ_{WP} , $pF=4.2$) and the saturated hydraulic conductivity values (K_{sat}) from tension infiltrometer measurements made for the soil profile (0-100 cm) (Table 1).

The soil characteristics of the macropore domain were chosen as follows: the boundary soil water pressure head between micro and macropores was set to default values ($CTEN=10$ cm), and the water content corresponding to this boundary soil water pressure head (θ_b) was calculated from the water retention curves (Table 1). The pore size distribution index in the macropores (ZN) was determined following the recommendations of Beulke et al. (2002). On the other hand, the boundary hydraulic conductivity (K_b) in the soil profile, and the parameter which controls the exchange of both water and solute between the micropore and macropore flows ($ASCALE$) were estimated with the pedotransfer functions included in MACRO 5.2 (Moeys et al., 2012). Given the lack of data in the literature for these macropore domain parameters corresponding to crop residues, similar values were used for the mulch layer than for the first soil horizon (Table 1).

Topsoil and mulch S-metolachlor sorption (K_d) and degradation (DT_{50}) parameters were obtained from laboratory experiments on soil, oat and vetch residues (after 56 days of decomposition) and/or on soil+oat and vetch residues (Table 3). The K_d values for deeper soil layers were estimated assuming this coefficient was proportional to OC content (Marín-Benito et al., 2014) while the variation of DT_{50} with depth was calculated according to the recommendations of FOCUS (2000) (Table 3).

Daily solar radiation, air temperature, relative humidity, wind speed, rainfall and reference evapotranspiration used for the simulations were measured using the meteorological station aforementioned.

2.3.2. Modelling the effect of the mulch layer and cover crops on the water balance

Crop residues have a direct effect on heat and water transfer in the soil profile and they indirectly reduce the soil evaporation (Khaledian et al., 2012). Under frequent rainfall or irrigation events, the crop residues evaporate the stored water (Findeling, 2001) and thus decrease the temperature at the soil surface creating a micro-climate around the mulch with reduced global climatic demand. To represent this micro-climate, we introduced an empirical correction factor (k_m) to decrease the potential evapotranspiration (ETP) for periods when crop residues were present, modifying the global climatic demand (Khaledian et al., 2012). The ETP in the presence of mulch (ETP_m) was thus calculated by applying a crop factor (k_c) and the correction factor (k_m) to the reference evapotranspiration data (ET_0) as indicated in equation [1]:

$$ETP_m = (ET_0 \times k_c) \times k_m \quad [\text{Eq. 1}]$$

The k_c values were taken from FOCUS (2000) for maize and cover crops (considered as winter cereals), and the k_m values were determined according to a two-step parameterization as follows.

In the first step (Step 1), two k_m values (non-optimized k_m values) were fixed, one for each cropping period: the cover crop growth and the maize growth under cover crop mulch (CC residues) (Fig. 2). We assumed: (1) no reduction in evaporation ($k_m=1$ in Eq. 1) during the growth of the cover crop, (2) a constant reduction in evaporation ($k_m<1$ in Eq. 1) after the destruction of the cover crop (5 April 2011 and 15 March 2012) and during the maize seasons until the emergence date of the new cover crop cycle (20

October 2011 and 7 October 2012) due to the presence of CC residues. We assigned a value of 0.84 to k_m based on the study of Khaledian et al. (2012).

In the second step (Step 2), k_m values were optimized by calibration for each crop, maize and cover crop, by fitting the simulated water percolated volumes to the measured ones. This calibration step allowed to consider the effects of different crop development stages, amounts of irrigation and thus of water stored in the crop residues, year period, amount of crop residues and/or degree of mulch decomposition, among others, that participate to the reduction of the global climatic demand caused by the crop residues (Abu-Awwad, 1999; Alletto et al., 2011; Chen et al., 2007; Lascano and Baumhardt, 1996; Li et al., 2008). Therefore, different k_m values were estimated for the total simulation period (Fig. 2). For maize, a lower value of k_m was assigned to the first part of its growing period than to the second part in order to account for the effect of decomposition of CC residues on mulch thickness. For cover crops, k_m remained equal to 1 (Fig. 2).

2.3.3. Crop parameterization

Crop parameters that were not measured, such as LAI, root depth and root distribution at the different development stages (emergence, flowering and harvest dates) were taken from Marín-Benito et al. (2014) for maize and from the FOCUS Châteaudun scenario (FOCUS, 2000) for cover crops (oat with phacelia and vetch crops) considered as winter cereals (see 2.2, Table 2). Indeed, the emergence and harvest dates observed in the experimental site for winter cereals and the climatic conditions (rain and temperature) were similar to those of Châteaudun scenario allowing assumption of similar crop development.

2.3.4. Simulation conditions

To minimize the impact of the initial conditions on the results, and given that temperature and soil moisture measurements were not available at the beginning of the experiment along the soil profile, a warm up period of 3 months previous to the first crop period was used to initialize the simulations (Marín-Benito et al., 2014). Hydrostatic pressure equilibrium was thus initially considered in the soil profile. A constant hydraulic gradient equal to 1 was assumed for the bottom boundary condition since the groundwater level was always below 2 m depth during the simulation period. Simulations were run from 10 July 2010 to 31 December 2012.

2.4. Evaluation of model performance

The performance of MACRO was assessed using three statistical indices: the modelling efficiency (EF), the coefficient of residual mass (CRM), and the Pearson correlation coefficient (r) (Smith et al., 1996). These indices were calculated according to the following equations:

$$EF = 1 - [\sum_{i=1}^n (S_i - O_i)^2 / \sum_{i=1}^n (O_i - O_m)^2] \quad [\text{Eq. 2}]$$

$$CRM = (\sum_{i=1}^n O_i - \sum_{i=1}^n S_i) / \sum_{i=1}^n O_i \quad [\text{Eq. 3}]$$

$$r = \sum_{i=1}^n (O_i - O_m) \times (S_i - S_m) / [\sum_{i=1}^n (O_i - O_m)^2]^{1/2} \times [\sum_{i=1}^n (S_i - S_m)^2]^{1/2} \quad [\text{Eq. 4}]$$

where O_i and S_i are the observed and simulated values, respectively, O_m and S_m are the mean observed and simulated values respectively, and n is the number of sampling dates. The optimum value of EF and r is +1, and that of CRM is zero. If $CRM > 0$, then there is an underestimation of observed values, and an overestimation if $CRM < 0$.

3. Results

3.1. Modelling soil temperature

Because pesticide degradation rate depends on temperature, correct simulation of the soil temperature along the soil profile is critical. MACRO simulated very well the soil temperature (Fig. 3): $EF > 0.90$, $r > 0.89$, and CRM ranged from 0 to 0.01 (Table 4), without any modification of parameterization regarding the potential effects of crop residues on soil temperature.

3.2. Modelling soil water content

When no k_m factor was considered for ETP calculation, the soil water content was generally overestimated by the model at the three different depths during the second cover crop cycle (CC-2) and during the non-irrigated period of the second maize crop cycle (Maize-2) (until 20 June 2012) (Fig. 4). Then, the soil water content along the soil profile was underestimated from the irrigated period of Maize-2 to the emergence of the third cover crops (CC-3) at the end of October 2012 when MACRO overestimated again the soil water content (Fig. 4). The underestimation simulated during the irrigated period of Maize-2 was mainly observed at 0.2 m depth and it disappeared with depth suggesting a decrease in the effect of the crop residues on soil moisture at lower depths (Fig. 4) (Bussière and Cellier, 1994).

When the fixed k_m value of 0.84 (Khaledian et al., 2012) was used for each maize cycle (Step 1) to account for the crop residues effect on evapotranspiration during the maize growth, the simulation of soil water content at the different soil depths was partially improved (Fig. 4). When considering the whole cropping period of Maize-2, a significant increase in EF was obtained for the soil water content at 0.2 m depth ($EF=0.21$) but not at 0.5 and 1 m depth (Table 4). Similarly, when only considering the

irrigated period of Maize-2 season after 20 June of 2012, simulation of soil water content at 0.2 m was improved compared to the simulation without k_m (Table 4, higher EF and lower CRM). The r values increased for both the whole period and the irrigated period of Maize-2 at the different soil depths after the application of the fixed k_m value (Table 4).

Calibrating the ETP correction factor for each growing period (Step 2) improved the modelling of soil water content after the 20 June of 2012, but it remained poor when considering the whole cropping period ($EF < 0$, $r < 0.53$) (Fig. 4, Table 4). However, the measured soil water content was only slightly overestimated as indicated by the negative CRM values close to 0 ($-0.07 < CRM < -0.04$). The low EF values were strongly conditioned firstly by the noisy measured data and secondly by the large overestimation of soil water content simulated before 20 May 2012 (Fig. 4). The three statistical indices were therefore improved ($-0.20 < EF < 0.21$, $-0.03 < CRM < 0.03$, $0.58 < r < 0.61$) when they were calculated for the second cropping period, from 20 June 2012 (beginning of the irrigated period of Maize-2) to the end of simulation (Table 4).

3.3. Modelling water percolation

Without modifying the ETP by the k_m factor, MACRO underestimated the volume of water measured in the lysimeter, except on 17 December 2012 when it was overestimated (Fig. 5a). The total observed volume of water leachates (181 mm) was underestimated by 34%.

Step 1 led to a slight improvement in the simulation of the percolated volumes when looking at the cumulative percolation over the whole period (Fig. 5b), with EF of 0.33 compared to 0.01 without ETP correction (Table 4). However, simulated volumes

were strongly lower than the observed ones during Maize-1 period, especially from the first important leaching event on 19 September 2011 (Fig. 5a). During the CC-2 period, the percolated volumes were underestimated in the same way as in the absence of ETP correction while during the second irrigated Maize-2 season, simulations were slightly improved with the k_m correction. However, for the CC-3 period after Maize-2 period, the model largely overestimated the percolation volumes in fall 2012 (events between October and December) (Fig. 5a).

After Step 2, MACRO simulated satisfactorily not only the total amount of water leachates but also the individual leaching events (Fig. 5a, Table 4). The main discrepancies between observations and simulations occurred during three periods: (1) 22 June - 25 July 2011, (2) 15 November 2011 - 16 January 2012, and (3) 8 August - 29 October 2012, when no leachate volume was collected in the lysimeter while MACRO simulated some water percolation (Fig. 5a).

3.5. Modelling *S-metolachlor* leaching

On 22 May 2012, 19 days after its application, *S-metolachlor* was detected in the leachate at $7.1 \mu\text{g L}^{-1}$ (Table 5). The high cumulated rainfall from 4 to 22 May 2012 (79.2 mm, Fig. 1) together with the high solubility in water of this herbicide could explain this quick leaching. Since 22 May 2012, the herbicide concentration in the water leachate decreased progressively until $0.08 \mu\text{g L}^{-1}$ on 17 December 2012 (last event of measured leachate) (Table 5).

Because of the poor simulation of water flow without ETP correction, MACRO was not able to model *S-metolachlor* transport at 1 m depth ($\text{EF} < 0$) (Table 4). Except for the latest drainage period, *S-metolachlor* concentrations and flows were largely underestimated (Table 5).

Step 1 did not improve the overall simulation of solute concentration and flow (Tables 4 and 5). Concentrations were underestimated in the two first leaching periods and then were largely overestimated especially for the two latest leaching periods which occurred during the CC-3 season. Conversely, water flows were underestimated during the two first events while they were overestimated during the three last ones (Table 5).

When using various k_m values (Step 2), MACRO modelling of the herbicide concentrations and flows was improved ($EF=0.47$ and 0.19 respectively, $CRM=-0.38$ and -0.42 respectively, $r=0.82$ and 0.65 respectively) (Tables 4 and 5). The negative CRM value shows that the model tends to overestimate the herbicide concentrations and flows, but it is mainly due to the marked overestimation of S-metolachlor concentration and flow measured in the 6-17 December 2012 period when MACRO overestimated the herbicide concentrations by factor of 53 and 285, respectively (Table 5). Contrary to the observations, the simulated S-metolachlor concentrations did not show a clear trend. MACRO underestimated the herbicide concentrations in the 26 April – 22 May 2012 period, but they were generally overestimated (23 May – 17 December 2012). However, it has to be underlined that, most of the time, simulated and measured concentrations were in the same order of magnitude (Table 5).

4. Discussion

4.1. Accounting for the effects of mulch of crop residues on water and pesticide flows

Without correction of evapotranspiration, MACRO was not able to simulate the variations of soil water content measured in the soil profile when both a mulch of crop residues and a cover crop were introduced in the maize monoculture. Surprisingly, soil temperature simulations were quite good without any correction probably because the model simulated only small differences of temperature ($<1^{\circ}\text{C}$) at the time scale and

depths considered when the mulch layer was or not included in the soil profile (data not shown). Using different k_m values had no effect on soil temperature simulation (Fig. 3).

In the second series of simulations, we first only considered (Step 1) the effect of the crop residues mulch on the evapotranspiration during the maize growing season, because the presence of crop residues on soil surface is known to decrease ETP (Findeling et al., 2001; Khaledian et al., 2009). No ETP modification was done during the cover crop growing season. In these conditions, the simulations of soil water content and percolation volumes were improved, for instance that of the soil water content at 0.2 m depth, which was under the direct influence of the crop residues. However, we were not able to satisfactorily simulate the dynamic of water percolation neither the S-metolachlor flow during the whole period. Consequently, in a second step (Step 2), we optimized the ETP correction choosing two k_m values for each maize cropping period (Fig. 2). We assumed that the reduction of the ETP depends on the mulch layer thickness and coverage and on the decomposition of crop residues (Findeling et al., 2007; Khaledian et al., 2009). Two different k_m paired values had to be defined for 2011 (Maize-1) and 2012 (Maize-2). In 2011, an optimized $k_m=0.77$ was used from the first cover crop destruction (5 April 2011) to the beginning of the irrigation period of the Maize-1 (18 May 2011). In 2012, a $k_m=0.39$ was used from the second cover crop destruction (15 March 2012) to the beginning of the irrigation period of the Maize-2 (20 June 2012). This low k_m value was half the value used for the analogous period in 2011 ($k_m=0.77$). This is consistent with the higher amount of crop residues on the soil surface after the cover crop destruction in 2012 (5.3 ± 0.9 t dry matter ha⁻¹, more than 50% of soil surface was covered by the crop residues) than in 2011 (1.0 ± 0.4 t dry matter ha⁻¹, 25-35% of soil surface was covered by the crop residues) and with the findings of Khaledian et al. (2009). In our study, the high percentage of soil surface covered by the

crop residues in 2012 could have partially inhibited the development of the maize, as evidenced by the lower maize grain yield obtained in 2012 (7.5 t ha^{-1}) than in 2011 (10.0 t ha^{-1}), which could explain the decrease in the ETP. Some authors have also observed a decrease in the emergence rate or a delay in the development of the main crop in presence of a mulch layer, which reduced the yield compared to conventional tillage (Chen et al., 2007; Khaledian et al., 2012, 2009).

For the two irrigation periods, from the starting of the irrigation to the emergence date of the following cover crops, we used $k_m=0.80$ and $k_m=0.92$ in 2011 and 2012 respectively (Fig. 2). During the Maize-2 season, the strong change of k_m from 0.39 to 0.92 might be explained by the effect of mulch decomposition and by the climatic conditions. The average air temperature recorded for this period was lower in 2011 (19.7°C) than in 2012 (21.7°C), and the amount of rain plus irrigation was lower in 2011 (3.0 mm d^{-1}) than in 2012 (3.3 mm d^{-1}). This supports the different corresponding k_m values ($k_m=0.80$ in 2011 and $k_m=0.92$ in 2012). In a study carried out in maize fields under different water management practices, Liu et al. (2010) also observed that the experiment with supplementary irrigation showed the highest cumulative real evapotranspiration (ETR).

During the two maize crop cycles, the optimized k_m values accounting for the crop residues effects on water balances considerably increased the quality of the simulation for both water and pesticide flow (Table 4). Step 2 involved a total decrease in ETR of 17% compared to the simulation that considered no k_m value to determine the ETP_m . This percentage is within the experimental rate observed by Khaledian et al. (2012).

4.2. Accounting for the effects of cover crop growth on water and pesticide flows

The introduction of cover crops can considerably reduce water drainage and pesticide flow in maize cropping systems (Alletto et al., 2012). When optimizing the k_m values for the cover crop growing season, k_m was systematically kept to 1 which means that no ETP modification was necessary to simulate soil water content. Indeed, in the field, the cover crop grows in the presence of the maize crop residues during winter when evapotranspiration remains low. Consequently the effect of crop residues on ETP is negligible as was observed for CC-1 and CC-2.

However, for CC-3, both the soil water content and especially the water percolation were overestimated (Fig. 4, Table 5) leading to strong overestimation of the pesticide flow by MACRO. A higher ETP than that simulated would have been required for this period. Though a decrease in the ETP due to the presence of a mulch layer on the soil surface was frequently reported (Findeling, 2001; Khaledian et al., 2009), the opposite effect has been also observed (Shen et al., 2012). However, we chose to keep k_m equal to 1 rather than using $k_m > 1$ during the CC-3 period because evapotranspiration is usually low in winter period, as mentioned above. The discrepancies between observed and simulated data could also be related to progressive changes in soil hydraulic properties due to the adoption of conservation techniques and reduction of tillage in 2010. Such changes have been widely described in the literature (Green et al., 2003; Strudley et al., 2008) however they were not considered in our simulations.

As a summary, our results showed that to simulate the effect of the crop residues and cover crops on water balance and pesticide fate with MACRO, the introduction of a correction factor for the ETP, which is the key determining factor, can be done according to the following rules: (1) $k_m < 1$ and decreases when the amount of crop residues on soil surface and the surface cover increase, and (2) k_m depends on the degree of crop residue decomposition.

5. Conclusions

Accounting for the combined effect of crop residue mulch and cover crops is critical to correctly simulate water balance and pesticide fate in conservation tillage systems. We tentatively used the MACRO model to simulate S-metolachlor herbicide leaching in an irrigated maize monoculture with intermediate cover crops.

The effect of the crop residues on both water and solute movements was simulated considering the mulch as a high organic soil layer with its own hydraulic properties, and pesticide adsorption and degradation coefficients, while the effect of the crop residues on the water balance was taken into account by applying a correction factor (k_m) to the ETP. Adjusting this empiric correction factor through a calibration exercise and according to observable criteria such as mulch thickness, soil coverage and plant residue decomposition improved the results of the simulations. The used parameterization allowed acceptable prediction of the field observations of water percolation and herbicide leaching although the performance of MACRO to simulate the soil water content was poorer. Though the possible effects of crop residues on soil temperature were not considered, the model predicted well the observed temperatures. This parameterization remains however limited to this case study and cannot be proposed for a predictive use of the model. Therefore, this approach needs to be tested against other soil-chemicals-crops-mulch combinations to be able to use the model as predictive tool.

Considering the importance of conservation tillage in today agricultural practices and the current limits pointed out by our study, despite the approach was developed following an “ideal path” (Lahtinen et al., 2017), there is a need to improve pesticide fate models used for risk assessment for pesticide registration at the European level in

such cropping systems. A first option would be to include in MACRO a module allowing to parameterize different k_m values according to the above-mentioned criteria and also to the type of crop residues. Another possibility would be to develop in such models, a specific module able to simulate the different processes occurring within the mulch layer and at the soil interface, and to account for different retroactions between mulch decomposition, water balance and pesticide fate and transport.

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Figure captions

Fig. 1. Measured rainfall and irrigation in Toulouse (Southwest France) experimental site from 10 July 2010 to 31 December 2012.

Fig. 2. Values of the ETP correction factor k_m used for the different cropping periods, with fixed correction (non-optimized) during the maize season or with a variable correction adjusted (optimized) for each maize cycle.

Fig. 3. Observed and simulated (without the application of the ETP correction factor k_m , and with non-optimized and optimized k_m values) soil temperature at 0.2, 0.5 and 1 m depth.

Fig. 4. Observed and simulated (without the application of the ETP correction factor k_m , and with non-optimized and optimized k_m values) soil water content at 0.2, 0.5 and 1 m depth.

Fig. 5. Observed and simulated (without the application of the ETP correction factor k_m , and with non-optimized and optimized k_m values) water percolation per period (a) and cumulated (b) at 1 m depth.

Table 1. Soil and mulch physicochemical and hydraulic characteristics.

	Depth (m)	0-0.05	0.05-0.15	0.15-0.35	0.35-0.65	0.65-2.05 ^a
Characteristic						
Clay (%)		0.00 ^b	39.8	40.1	45.8	51.5
Silt (%)		0.00 ^b	47.2	45.3	42.2	38.2
Sand (%)		100 ^b	13.0	14.6	12.0	10.3
OC (%)		42.8 ^c	1.40	1.16	0.88	0.60
pH (0.01 M CaCl ₂)		6.2 ^d	7.2	7.4	7.8	8.3
Bulk density (g cm ⁻³)		0.12 ^e	1.48	1.41	1.54	1.63
θ_r (m ³ m ⁻³) ^f		0.01	0.01	0.01	0.01	0.01
θ_s (m ³ m ⁻³) ^g		0.766 ^h	0.420	0.445	0.385	0.382
α (cm ⁻¹) ^g		0.013 ^h	0.022	0.026	0.018	0.014
n (-) ^g		1.204 ^h	1.111	1.121	1.072	1.058
K _{sat} (mm h ⁻¹)		3.3 ^h	98.7	126.0	44.2	14.5
CTEN (cm) ^f		10	10	10	10	10
K _b (mm h ⁻¹) ⁱ		0.289	0.289	0.303	0.229	0.179
θ_b (m ³ m ⁻³) ^j		0.756	0.413	0.435	0.381	0.379
ASCALE (mm) ⁱ		1	1	50	150	150
ZN (-) ^k		3	3	3	2	2
ZM (-) ^g		0.400 ^h	-4.321	-3.947	-4.548	-4.830
θ_{WP} (m ³ m ⁻³) ^j		0.268	0.220	0.216	0.277	0.287

Note: The parameters without exponent correspond to measured parameters

^a Physicochemical and hydraulic characteristics measured or estimated for the horizon 0.65-1.05 m and also used to parameterize the horizon 1.05-2.05 m

^b Mulch layer was parameterized as a virtual sandy soil layer

^c From Cassigneul et al. (2016)

^d From Rampoldi et al. (2011)

^e From Garnier et al. (2004) for wheat residues

^f Default value

^g Estimated by HYPRES pedotransfer functions (Wösten et al., 1999)

^h From Wösten et al. (1999) for an organic soil

ⁱ Estimated using the pedotransfer functions included in MACRO 5.2

^j Calculated from the water retention curves

^k Estimated from Beulke et al. (2002)

Table 2. Input parameters for crop development.

Crop	Date	Crop development	LAI (m ² m ⁻²) ^b	Root depth (m) ^b	Root distribution ^{b,c}
Cover crops (CC-1)	14/10/2010	Emergence	0.01	0.01	
	04/04/2011	Flowering	1.51	0.37	0.67
	05/04/2011	Harvest ^a	1.51	0.37	
Maize (Maize-1)	05/05/2011	Emergence	0.01	0.01	
	20/07/2011	Flowering	3.29	0.80	0.60
	07/10/2011	Harvest	3.29	0.80	
Cover crops (CC-2)	20/10/2011	Emergence	0.01	0.01	
	14/03/2012	Flowering	0.94	0.19	0.67
	15/03/2012	Harvest ^a	0.94	0.19	
Maize (Maize-2)	28/04/2012	Emergence	0.01	0.01	
	17/07/2012	Flowering	3.29	0.80	0.60
	21/09/2012	Harvest	3.29	0.80	
Cover crops (CC-3)	08/10/2012	Emergence	0.01	0.01	
	24/04/2013	Flowering	3.40	0.56	0.67
	25/04/2013	Harvest ^a	3.40	0.56	

^a The cover crops (oat+phacelia+vetch) destruction date was considered as harvest date.

^b From FOCUS (2000) for cover crops (considered as winter cereals) in Châteaudun scenario, and from Marín-Benito et al. (2014) for maize crop.

^c Fraction of root density in the uppermost 25% of the root depth.

Table 3. Sorption coefficients (K_d) and half-lives (DT_{50}) of S-metolachlor in the mulch and in the soil profile.

Depth (m)	S-metolachlor	
	K_d (cm ³ g ⁻¹)	DT_{50} (d)
0-0.05 (mulch)	25.45 ^a	61.5 ^b
0.05-0.15	1.9 ^c	57 ^{d,e}
0.15-0.35	1.58	57
0.35-0.65	1.2	105
0.65-1.05	0.482	169
1.05-2.05	0.482	n.d. ^f

^a Estimated from $K_{d \text{ soil}}=1.9 \text{ L kg}^{-1}$ and $K_{d \text{ mulch}}=49 \text{ L kg}^{-1}$ and taking into account that 50% of the soil surface was covered by mulch after harvest.

^b Estimated from $DT_{50 \text{ soil}}=57 \text{ d}$ and $DT_{50 \text{ soil+mulch}}=66 \text{ d}$ and taking into account that 50% of the soil surface was covered by mulch after harvest.

^c From laboratory experiments. Values for deeper soil layers were estimated assuming sorption coefficients are proportional to organic carbon content.

^d From laboratory experiments with the same field soil.

^e Variation of the degradation rate k ($k \text{ (d}^{-1}) = \ln(2) / DT_{50}$) with depth: k for 0.05–0.35 m, $k \times 0.5$ for 0.35–0.65 m, $k \times 0.3$ for 0.65–1.05 m, $k = 0$ for >1.0 m (FOCUS, 2000).

^f n.d.= no degradation.

Table 4. Modelling efficiency (EF), coefficient of residual mass (CRM) and sample coefficient correlation (r) of MACRO for the soil water content (θ) and temperature (T) at 0.2, 0.5 and 1 m depth, and for the percolation and solute leaching at 1 m depth (with and without considering the ETP correction factor k_m).

Output	EF			CRM			r		
	0.2 m	0.5 m	1 m	0.2 m	0.5 m	1 m	0.2 m	0.5 m	1 m
Without k_m values									
θ (whole period)	-0.55	-0.24	-0.18	0.07	-0.02	-0.02	0.19	0.26	0.20
θ (since 20/06/2012)	-2.05	-0.84	-0.15	0.14	0.02	0.01	0.55	0.35	0.30
T (whole period)	0.91	0.95	0.94	0.01	0.00	0.00	0.90	0.98	0.97
Percolation	-	-	0.39	-	-	0.29	-	-	0.64
Cumulative percolation	-	-	0.01	-	-	0.81	-	-	0.91
Solute concentration	-	-	-0.62	-	-	0.83	-	-	0.14
Solute flow	-	-	-0.62	-	-	0.88	-	-	0.19
With non-optimized k_m values (step 1)									
θ (whole period)	0.21	-0.33	-0.44	-0.01	-0.06	-0.05	0.50	0.61	0.61
θ (since 20/06/2012)	0.03	-0.31	-0.19	0.03	-0.03	-0.03	0.49	0.52	0.48
T (whole period)	0.91	0.95	0.94	0.01	0.00	0.00	0.90	0.98	0.97
Percolation	-	-	0.27	-	-	0.25	-	-	0.61
Cumulative percolation	-	-	0.33	-	-	0.54	-	-	0.89
Solute concentration	-	-	-1.24	-	-	0.06	-	-	0.64
Solute flow	-	-	-1.14	-	-	0.19	-	-	0.59
With optimized k_m values (step 2)									
θ (whole period)	-0.20	-0.67	-0.62	-0.04	-0.07	-0.06	0.23	0.44	0.53
θ (since 20/06/2012)	0.21	-0.20	-0.03	0.03	-0.03	-0.03	0.58	0.58	0.61
T (whole period)	0.91	0.95	0.94	0.01	0.00	0.00	0.90	0.98	0.97
Percolation	-	-	0.65	-	-	-0.08	-	-	0.83
Cumulative percolation	-	-	0.96	-	-	0.01	-	-	0.99
Solute concentration	-	-	0.47	-	-	-0.38	-	-	0.82
Solute flow	-	-	0.19	-	-	-0.42	-	-	0.65

Table 5. Observed and simulated mean concentrations and cumulative flows of S-metolachlor in the leachates collected at 1m depth.

Period	Mean concentrations ($\mu\text{g L}^{-1}$)				Cumulative flows ($\mu\text{g m}^{-2}$)			
	Observed	MACRO			Observed	MACRO		
		Without	With non-	With		Without	With non-	With
		k_m	optimized	optimized		k_m	optimized	optimized
			k_m	k_m		k_m	k_m	k_m
			(step 1)	(step 2)			(step 1)	(step 2)
Maize-2								
26/04 - 22/05/2012	7.10	0.04	0.46	5.14	172.8	0.166	3.083	160.1
23/05 - 12/06/2012	5.20	0.74	2.68	6.48	193.5	14.48	61.94	189.5
17/07 - 07/08/2012	2.30	0.00	4.83	4.80	61.49	0.000	97.25	98.18
CC-3								
30/10 - 05/12/2012	0.64	0.25	1.42	1.17	12.04	2.720	50.38	39.22
06/12 - 17/12/2012	0.08	1.13	4.96	4.24	0.430	29.87	143.9	122.6

Fig. 1. Measured rainfall and irrigation in Toulouse (Southwest France) experimental site from 10 July 2010 to 31 December 2012.

Fig. 2. Values of the evapotranspiration correction factor k_m used for the different cropping periods, with fixed correction (non-optimized) during the maize season or with a variable correction adjusted (optimized) for each maize cycle.

Fig. 3. Observed and simulated (without the application of the evapotranspiration correction factor k_m , and with non-optimized and optimized k_m values) soil temperature at 0.2, 0.5 and 1 m depth.

Fig. 4. Observed and simulated (without the application of the evapotranspiration correction factor k_m , and with non-optimized and optimized k_m values) soil water content at 0.2, 0.5 and 1 m depth.

Fig. 5. Observed and simulated (without the application of the evapotranspiration correction factor k_m , and with non-optimized and optimized k_m values) water percolation per period (a) and cumulated (b) at 1 m depth.