Application of PEARL to study the effect of organic matter on bioavailability of soil applied herbicides in the top soil layer

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Summary

Within-field variation of soil properties leads to differences in efficacy of soil applied herbicides. Taking into account local circumstances when applying input reduces costs and prevents unnecessary spilling to the environment, while still ensuring good yield. This study explores how the complex model PEARL can be used to study the bioavailability of the active substances isoxaflutole and dimethenamid-P in response to varying degrees of soil organic matter. The system at study was pre-emergence application of these herbicides in forage maize on a sandy soil. The model was run and for organic matter contents ranging from 1% to 7% for 20 consecutive meteorological years. Output of the top 10 cm showed that concentration in the liquid phase was highest in the top few centimetres of the soil and steeply declined with depth. This is favourable for weeds as germination is highest in the top few centimetres of the soil. Within a month, the fast transforming isoxaflutole vanished from the top of the soil. The concentration of its metabolite DKN diminishes within the growing season of maize. The model output showed that dimethenamid-P stays was still present at low concentrations at the end of the growing season. The relation between %OM on the concentration in the liquid phase on specific days after application (t=0, 4, 7, 14, 21, 28) of individual years was further examined. Concentration decreased exponentially for all substances with increasing %OM. A general model could be fitted to the data. Year specific models could also be fitted to the data and the parameters of the year specific curves often differed significantly from one another. The relation between organic matter, weather and herbicide concentration needs further investigation in order to develop decision support rules. Possibilities of developing such rules based on the model results are discussed.

Keywords

Precision agriculture, herbicide, soil, organic matter, maize, weather, soil moisture, efficacy, bioavailability, Freundlich sorption

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Introduction

Soil plays a major role in the fate and behaviour of pesticides (Helling et al., 1971). The extent to which a specific active ingredient partitions between the solid and aqueous phase of the soil impacts its behaviour in the soil in terms of persistence, transportation and efficacy (Wauchope et al., 2002). Of the soil components, soil organic matter, is the main determinant of sorption of pesticides to the soil (Wauchope et al., 2002) (Farenhorst, 2006). Besides attributes of the agro environment, physico-chemical characteristics of herbicides affect behaviour of the herbicide after application (Carter, 2000).

Pre emergence herbicides are applied to the bare soil after sowing and before emergence of the crop. They kill germinating weeds in the top soil layer. The amount of herbicide available for effectively controlling weeds is strongly depended on the degree of sorption to the soil. Less herbicide is available for uptake if it is sorbed by clay or soil organic content of the soil (Williams et al., 2001). The efficacy of a specific herbicide is thus determined by soil factors such as organic matter (Blumhorst et al., 1990;Peter &Weber, 1985;Williams et al., 2001).

Arable fields show within-field variation of soil properties such as texture and organic matter content (see a.o. (Cambardella et al., 1994;Heijting et al., 2011)). The practice of precision farming takes this variation into account when applying crop management activities such as fertilization and spraying. When adjusting input of soil applied herbicides to local needs, the financial and environmental spillage is minimized, while still ensuring good control of weeds. An increasing amount of data on within-field soil variation becomes available. To adjust herbicide dosage to local circumstances, not only data on field variability are needed but also knowledge and insight in processes affecting the herbicide efficacy.

In the present study we will examine the effect of organic matter content on the bioavailability of two soil applied herbicides using the pesticide leaching model Pearl. Pesticide leaching models are used to assess environmental risks of pesticide application and these are commonly employed as part of the registration process of plant protection products in the EU (Carter, 2000) (Boesten, 2000;Farenhorst, 2006). For registration of pesticides a lot of data is asked by national authorities. As it is not economically feasible to measure all required data models are applied to assess leaching potential of pesticides (Boesten, 2000). Pesticide models showed that leaching of pesticides is very sensitive to input parameters describing pesticide sorption to the soil and transformation rates of the pesticide (Boesten &Van der Linden, 1991). Sensitivity analysis of four pesticide leaching models showed that parameters related to sorption and degradation affected prediction of pesticide loss largest (Dubus et al., 2003).

We regard the concentration of the active ingredient in the liquid phase (at equilibrium) as the bioavailability as it is available for uptake and control of weeds. We will focus on two soil applied herbicides based on the active substances isoxaflutole and dimethenamid-P. They are both registered for use a.o. pre-emergence application in forage maize in the Netherlands. In Northern Europe, maize is cropped as silage maize and is either cropped continuously or in a crop rotation (Vasileiadis et al., 2011). In the Netherlands silage maize is grown on 240,000 ha of land (CBS, 2011) whereby weed control relies heavily on herbicides (van Schooten et al., 2010).

Isoxaflutole is a so called-pro-herbicide. It is rapidly hydrolysed to its metabolite diketonitrileisoxaflutole (DKN) (Pallett et al., 1998), both in the soil and in the plant (Mitra et al., 2000). DKN is subsequently transformed to its inactive benzoic acid derivative. DKN and isoxaflutole are phytotoxic. They inhibit the an enzyme of the carotenoid biosynthesis and symptoms on susceptible plants are bleaching (Pallett et al., 1998). Dimethenamid-P is a chloroacetamid herbicide; it inhibits the fatty acid synthesis. Both isoxaflutole, DKN and dimethenamid-P control annual grasses and broad leaved weeds.

(Mitra et al., 2003) established that persistence and mobility of isoxaflutole was highly correlated with organic matter of the soil, and not with texture. Sorption of isoxaflutole (Mitra et al., 2001), its metabolite DKN (Mitra et al., 1999) and dimethenamid-P to organic matter could be described with the Freundlich equation.

The aim of this study is to determine the effect of varying amounts of organic matter in the soil on the concentration in the soil water of pre-emergence applied soil herbicides isoxaflutole and dimethenamid-P in maize using the model pesticide fate model Pearl. In the Netherlands maize is grown mostly on sandy soil. For running the model, the soil type Hn21 (gleyic podzol with low loam content) was chosen as it is the most dominant sandy soil type.

Materials and methods

General information on Pearl

PEARL is an acronym of *Pesticide Emission Assessment at Regional and Local Scales*. PEARL is a one-dimensional model and comprises two parts: a soil water model SWAP (Soil, Water, Atmosphere and Plant) and PEARL to determine the pesticide fate. An overview of processes considered in PEARL is provided in Figure 1.

In this study the pesticide fate model PEARL (version 4.4.4) was used with the aim to study the effect of within-field variation in organic matter content on the bioavailability of soil applied herbicides.



Figure 1 Overview of processes included in the PEARL model. (Source: (Tiktak et al., 2002) and <u>http://www.pearl.pesticidemodels.eu/pdf/pearlman.pdf)</u>

Germination and subsequent emergence of annual weed species in the surface layer of the soil was studied by (Grundy et al., 2003). Some differences between species were present but overall germination and subsequent emergence of the weeds took place within the top few cm. In the study by (Benvenuti et al., 2001) germination of weeds was found till a greater depth. Therefore, in the present study, it was decided in to look at the bioavailability of the herbicides in the 0-5 cm layer of the soil and at 2.5 cm as most germination of weeds take place around that depth (Grundy et al., 2003). To run the model PEARL, the entire soil column had to be regarded.

A theoretical field was created using the same soil and the same crop, which was maize. Therefore, several calculations were done modifying only the organic matter content (OM) in the first 10 cm of the soil profile. The range of organic matter content varied between 1 and 7%. Steps of 1.0% were used, and then calculations with 1%, 2%, 3%, 4%, 5%, 6%, 7% organic matter content in the first 10 cm were performed for the three compounds.

In order to perform the calculations PEARL requires different input parameters. The input parameters used for this exercise are described in the paragraphs below.

Soil section

Soil data such as texture, pH, bulk density and organic matter content were the ones for soil Hn21, a Veldpodzol soil (Table 1).

Layer n	Horizon code	Depth (cm)	OM (%)	Clay (%)	Silt (%)	Sand (%)	рН-КСІ	pH-H2O	Bulk density (kg m-3)
1	1Ap	0-25	5.4	3	10	87	4.8	5.6	1.375
2	1Bhe	25-40	2.2	3	8	89	4.5	5.4	1.576
3	1BCe	40-60	1.0	3	8	89	4.5	5.4	1.633
4	1Cg	60-120	0.3	3	6	91	4.7	5.5	1.672

Table 1. Hn21 Veldpodzol soil characteristics.

The pH-H2O values were not available, and then were calculated as follows (FOCUS, 2009):

pH-H2O = 0.820 pH-KCl + 1.69.

The van Genuchten parameters were calculated using the software developed by Wösten et al. (2001). The values used for running PEARL are shown in Table 2.

	Theta	Theta				Saturated	
Layer n	Saturatio n (m3.m- 3)	Residual (m3.m-3)	(cm-1)	Alpha Wet (cm-1)	n (-)	conductivity (m.d-1)	і (-)
1	0.50	0.01	0.0198	0.0396	1.482	0.3228	0.032
2	0.46	0.01	0.0208	0.0416	1.658	0.416	0.081
3	0.45	0.01	0.0206	0.0412	1.89	0.4807	0.112
4	0.43	0.01	0.0198	0.0396	2.258	0.7283	0.133

Table 2. van Genuchten parameters.

Dispersion is used to describe the width of the peak in chromatographic flow with the higher the dispersion the broader the peak. However, since flow in soils is not perfectly chromatographic, currently dispersion is used as a pragmatic approach to lumping the field variability of all processes that affect solute transport. Since the interest was focused on the first 10 cm, the dispersion length was set to 2.5 cm.

Weather and irrigation

Data on rainfall, minimum and maximum temperature, and evapotranspiration are required for the whole simulated period in order to perform calculations with PEARL. These meteo data were taken from the database present within GeoPEARL. The variability of weather conditions across the Netherlands is represented in GeoPEARL by climate districts, published by the Royal Dutch Meteorological Institute (Tiktak et al., 2003). Fourteen meteo districts with time series of 20 years are present in GeoPEARL (Fig. 2). The meteo distric of 'Winterswijk' was chosen because it is in the area in which a lot of silage maize is grown on the Hn21 soil type. The evapotranspiration (ET) values in GeoPEARL are calculated according to Makkink equation. As in PEARL the Penman equation is used, the GeoPEARL values were converted. No irrigation was considered for this exercise.



Figure 2. Meteo districts in GeoPEARL.

Compound section

The properties of the substances are given in Table 3.

Table 3. Properties of the substances.

		isoxaflutole	DKN metabolite of isoxaflutole	dimethenamid-P
Crop		maize	-	maize
% crop interception at application times	source/ comments	-	-	-
Molar mass (g/mol)	value	359.5	359	275.8
	source/ comments	European Commission, 2003a; CTGB database (accessed on 8Nov2011)	Ramanarayanan et al., 2005	European Commission, 2003b
DegT50 at 20°C, pF = 2 in top soil (d)	value	0.9	8.7	23
	source/ comments	CTGB database (accessed on 8Nov2011);European Commission, 2003a	CTGB database (accessed on 8Nov2011)	European Commission, 2003b
Maximum occurrence factor (-)	value	-	0.95	-
	source/ comments	-	PPDB database (accessed on 8Nov2011)	-
Water solubility (mg/L) at 20°C	value	6.2	325	1450
	source/ comments	European Commission, 2003a; CTGB database (accessed on 8Nov2011)	(Ramanarayanan et al., 2005)	European Commission, 2003b
Saturated vapour pressure (Pa)	value	1 x 10 ⁻⁶ Pa at 20 °C	-	2.5 x 10 ⁻³ Pa at 25°C
	source/ comments	European Commission, 2003a; CTGB database (accessed on 8Nov2011)	-	European Commission, 2003b
<i>К_{ом}</i> (L/kg) for soil	value	65	63	132
	source/ comments	CTGB database (accessed on 8Nov2011);European Commission, 2003a	CTGB database (accessed on 8Nov2011)	European Commission, 2003b
Freundlich exponent (-) for soil	value	0.95	0.94	0.9 (mean)
	source/ comments	European Commission, 2003a	CTGB database (accessed on 8Nov2011)	European Commission, 2003b

Other parameters required by the model were chosen as follows:

- E_a for degradation in soil: 65.4 kJ/mol (EFSA, 2007)
- Factor *B* describing moisture dependency of degradation: 0.7 (FOCUS, 2000)
- Depth dependency of degradation as proposed by FOCUS (2000)
- Uptake factor for plants: 0.5 (FOCUS, 2000)

- Molar enthalpy of vaporisation: 95 kJ/mol (FOCUS, 2000)
- Molar enthalpy of dissolution: 27 kJ/mol (FOCUS, 2000)
- Molar enthalpy of sorption: 0 (FOCUS, 2000)
- Reference diffusion coefficient in water: 0.43 ×10⁻⁴ m²/d (FOCUS, 2000)
- Reference diffusion coefficient in air: 0.43 m²/d (FOCUS, 2000)
- Reference moisture content for degradation: assume optimal conditions (pF = 2)

Management section

For both parent compounds one application every year was simulated. The pesticide was applied pre-emergence on the 5th of May of each year. The dosages applied were according to recommendations on the Dutch label. For isoxaflutole the dosage was 0.0997 kg a.i./ha, for dimethenamid-P was 1.008 kg a.i./ha. No tillage was simulated.

Crop section

The input parameters for the crop were taken from the Hamburg maize scenario described by the FOCUS groundwater working group (FOCUS 2000, 2009). It was chosen as the Hamburg scenario because was the most relevant one.

Output

The aim of this exercise was to study how %OM effects the bioavailability of herbicides in the top layer of the soil. The amount of a.i. in liquid phase is available for killing weeds, therefore the relevant output was the concentration in the liquid phase.

In PEARL, soil properties are specified as a function of soil horizons. A soil horizon is assumed to have uniform chemical and physical properties. Soil horizons are divided into numerical soil layers. Soil layers are represented by nodal points, which are situated in the centre of these layers (Fig. 3).



Figure 3. Vertical discretization of the soil in PEARL (Tiktak et al., 2000).

In this study a compartment thickness of 5 mm in the top 10 cm was chosen. The depth of the output was set at 2.5, 5, 7 and 10 cm. The model can calculate the concentration at the different depths and also the average concentration over a certain depth.

The PEARL model runs for 26 years, with the first six years for warming up of the model. Only the last 20 years are considered as model output. The time-domain for the old Dutch standard scenario is 01-Jan-1980 until 31-Dec-2000.

As an example, the input file of isoxaflutole for PEARL is provided in Appendix I. The runs were done in the command line version of PEARL which offered to run batches of runs differing only in organic matter content of the top soil layer. The fate of the herbicides for the range of 1-7 % organic matter were run with steps of 1 %. The files provided in the Appendices are those of organic matter content of 3%.

Sorption to soil organic matter

Sometime after application of the pesticide, an equilibrium is established between pesticide in the liquid phase (C_L ; kg/m3) and the amount sorbed to the solid phase (X_{eq} ; kg/kg). Sorption of pesticides to the soil is done with the Freundlich equation (see also Pearl manual) :

$$X_{eq=} K_{F,eq^*} C_{L,R} (C_L / C_{L,R})^N$$

 $C_{L,R}$ is the reference concentration in the liquid phase. *N* is the Freundlich exponent and has a default value of 0.9.

It is recommended in the manual of Pearl to determine both Freundlich parameters $K_{F,eq}$ and N in a slurry experiment following OECD guideline 106. The Freundlich coefficient at the equilibrium ($K_{F,eq}$; m³kg¹) can be calculated from the coefficient of equilibrium sorption on

organic matter ($K_{om,eq}$, m³/kg) and the mass content of organic matter ($m_{om; kg/kg}$) amount of organic matter in the soil:

 $K_{F,eq} = m_{om} K_{om,eq}$

Statistical analysis

The relation between concentration at a specific moments since application and organic matter content of the soil was statistically analysed for each compound and moment separately. Initial inspection of the data showed that an exponential model could fit the data. Concentrations per year at t=0 (day of application), t=4, 7, 14, 21 and 28 days after application for the different %OM were analysed using nonlinear regression fitting the exponential curve; $y=a+b^*r^X$.

With *y*=concentration in mg/l, *a* is asymptote, *b* is a parameter indicating intersection with Y-axis (*x*=0) and *r* relative decline, and *x* the %OM. The analysis was applied using Genstat (14th edition) to fit a general model to the relation between %OM and the concentration of each substance at a specific time after application. Next, the model was fitted to the data of the individual years and the presence of a significant effect of year on the value of parameters *b* and *r* was analysed using accumulated ANOVA.

Results

The concentration of the compounds throughout the 20 years of the model run are presented in Fig. 4, 5 and 6. The varying percentages of OM of the soil are indicated by different lines. Increasing %OM strongly decreases the concentration of all three compounds in the liquid phase.

For isoxaflutole concentrations calculated for the 2.5 cm node (Fig. 4A) showed larger fluctuations between years than the average concentration of the top 5 cm of the soil (Fig. 4B). Isoxaflutole has a very short half-life and has a very low water solubility compared to the other two compounds of this study. This average concentration of the top 5 cm is averaged over the top 10 layers of each 5mm thickness. The difference between Fig 4A and 4B indicates that between the of the soil column and 2.5 cm depth weather strongly affects fate of the herbicide but overall is not so strongly affected by year.



Fig. 4AB. Concentration of isoxaflutole during 20 years at the 2.5 cm node (Fig 4A) and averaged over the top 5 cm layer of the soil (Fig. 4B)

For the metabolite DKN (Fig 5AB) and dimethenamid-P (Fig. 6AB) year has less effect on the concentration. Dimethenamid-P showed highest concentrations overall. Its application rate was tenfold of isoxaflutole, it also has a much higher water solubility (1450 compared to 6.2 and 325 of isoxaflutole and DKN resp.) and a slower degradation rate and higher K_{om} value than the other two compounds.





Fig. 5AB. Concentration of DKN during 20 years at the 2.5 cm node (Fig 5A) and averaged over the top 5 cm layer of the soil (Fig. 5B)



Fig. 6B

Fig. 6AB. Concentration of DIMP during 20 years at the 2.5 cm node (Fig 5A) and averaged over the top 5 cm layer of the soil (Fig. 5B)

Differences between the course of the concentrations at the 2.5 cm node are illustrated at 2%OM in Fig 7ABC. Each of the three substances showed their own profile in time. The short half-life of isoxaflutole is clearly reflected in Fig 7A as it disappears within 2 weeks. T=0 is days of application. The concentration of Dimethenamid-P is higher and decreases slower. It has the longest half-life and highest Kom value. In Fig 8ABC the course of the concentrations averaged over the top 5 cm of the soil since time of application is presented and shows less variation than the concentration of the three studied compounds at 2.5 cm (Fig 7). DKN concentration reaches its peak a few days after application as the compound is not present yet at time of application. It only appears after transformation of isoxaflutole to DKN.



Fig 7. Concentration at 2.5 cm and 2%OM in days since day of application at 2.5 cm depth for isoxaflutole (A), DKN (B) and DIMP (C). The data of all years is presented as the 5 and 95 percentile and the median.



Fig 8. Concentration at 2.5 cm and 2%OM in days since day of application in top 5 cm of the soil for isoxaflutole (A), DKN (B) and DIMP (C). The data of all years is presented as the 5 and 95 percentile and the median.

The amount of compound calculated for the four nodes 2.5 cm, 5cm, 7 cm and 10 cm depth at different moments since application for one year (year 1) are presented in Figure 9-11. The amount of herbicide decreases quickly with depth.



Figure 9. Concentration of isoxaflutole with depth at 7 days after application.



Figure 10. Concentration of metabolite DKN with depth at 7 days after application.



Figure 11. Concentration of Dimethenamid-P with depth at 7 days after application.

Isoxaflutole and %OM

For isoxaflutole the concentration at 2.5 cm (Fig 11) and the average concentration in the top 5cm (Fig.12) both showed a relation with organic matter at specific days after application. Both concentrations fitted the exponential model significantly. We will further focus on the

model fitting the top 5 cm and the mode fitting of 2.5 cm is not shown for the three compunds. Table 4 provides data on the general model fitting the data at specific times since application. If year specific models were fitted, the parameters describing these curves differed significantly between years. If the details were considered (which year differed from which other year) no immediate years emerged that stood out among the other years in their effect on the concentration. This needs further inquiry.



Fig 11 A-F. Concentration of isoxaflutole at 2.5 cm as a function of %OM at different times since application: t=0 (A), t=4 (B), t=7 (C), t=14 (D), t=21(E) and t=28 (F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.



Fig 12 A-F. Average concentration of isoxaflutole in the top 5 cm of the soil as a function of %OM at different times since application: t=0 (A), t=4 (B), t=7 (C), t=14 (D), t=21(E) and t=28 (F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.

Days since application	b	r	а
0	0.20848*	0.4857*	0.020881
4	0.4921*	0.05976*	0.00619
7	0.02384	0.4978	0.002518
14	0.003127	0.512	0.000341

Table 4 Values of parameter b and r of fitted curves at t = 4, 7 and 14 days after application for isoxaflutole averaged in the top 5 cm of the soil. * indicate that a year of application had a significant effect on the parameter.

DKN and %OM

Concentrations in the liquid phase declined steeply with increasing organic matter content both at 2.5 cm and in the top 5 cm (Fig 13-14). At 2.5 cm and 1% OM the variation between years was largest. The relation between %OM and concentration was relatively similar for t=4 to two weeks after application (Table 5). Parameters describing the shape of the curve differed significantly, but less strong than for the concentration at 2.5 cm (not shown here).In Fig. 15 the fitted general model and the data of the 20 years is presented for t=7d.



Fig 13 A-F. Concentration of DKN at 2.5 cm as a function of %OM at different times since application: t=0 (A), t=4 (B), t=7 (C), t=14 (D), t=21(E) and t=28 (F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.



Fig 14 A-F. Average concentration of DKN in top 5 cm as a function of %OM at different times since application: t=0 (A), t=4 (B), t=7 (C), t=14 (D), t=21(E) and t=28 (F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.

Days since application	b	r	а
0	0.05296*	0.4717*	0.004649
4	0.15427	0.4859	0.01489
7	0.15957	0.4929	0.015904
14	0.12898	0.5066	0.013429

Table 5 Values of parameter b and r of fitted curves at t= 4, 7 and 14 days after application for DKN averaged in the top 5 cm of the soil. * indicate that a year of application had a significant effect on the parameter.



*Fig.*15 *Fitted general model to DKN concentration at t=7 days after application for 20 years.*

Dimethenamid-P and %OM

For dimethenamid-P a similar relation between concentration and OM% was found at the various times since application both at 2.5 cm (Fig 16) and in the top 5 cm of the soil (Fig. 17). Variation at the 1.5 cm node was larger than in the top 5 cm of the soil. In both cases spread at 1% OM showed greatest variation between years.



Fig 16 A-F. Concentration of DKN at 2.5 cm as a function of %OM at different times since application: t=0 d(A), t=4 d(B), t=7 (C), t=14 d(D), t=21 d(E) and t=28 d(F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.



Fig 17 A-F. Average concentration of DKN in the top 5 cm as a function of %OM at different times since application: t=0 d(A), t=4 d (B), t=7 (C), t=14 d(D), t=21 d(E) and t=28 d (F). Each black cross represents the value of 1 year and the red dot indicates the mean of all years.

The exponential model fitted the curve well and the general model was highly significant (P<0.001). Year of model run had a significant effect on the parameters of the exponential curve. The parameters for the general model at the examined times after application are provided in table 6.

Days since application	b	r	а
0	1.9780*	0.45682	0.16135
4	1.6499*	0.4625	0.14349
7	1.4982*	0.4647	0.13335
14	1.2704*	0.4710*	0.11562

Table 6 Values of parameter b and r of fitted curves at t=4, 7 and 14 days after application for DKN averaged in the top 5 cm of the soil. * indicate that a year of application had a significant effect on the parameter.



Fig. 18 Fitted general model to DIMP concentration at t=7 days after application for 20 years.

Discussion

The effect of varying organic matter contents on the concentration of isoxaflutole, the metabolite of isoxaflutole and dimethenamid-P was studied with the pesticide fate model Pearl. When the top 5 cm of the soil were considered, the model provided relatively little fluctuation between years. If however the concentration at 2.5 cm depth, where most weeds have been found to germinate (Grundy et al., 2003), some differences between the years were present. For isoxaflutole, the maximum attained concentration was fluctuating largely at 2.5 cm.

Concentration and %OM

The relation between the concentration of the compounds at a specific moment in time after application and the organic matter content was described by an exponential decrease. The general model was highly significant. At 1 %OM the fluctuations showed greatest variation between the data of individual years. The concentration appears inversely related to OM% for all three compounds. This is most likely caused to the calculation of the concentration in the liquid phase in Pearl as this concentration is inversely related to organic matter content. The curve of the exponentially fitted curve became less steep with increasing time. In the field, it will not be the concentration at one time that determines the efficacy and this needs to be established in a field experiment. (Tielen, 2010) established the efficacy of isoxaflutole and dimethenamid-P in soils of varying OM content in a greenhouse experiment. Biomass reduction (ED90) was determined and related to organic matter content. For both examined compounds, a linear relation was present between the ED90 and the %OM.

It is important to note that the model was currently run for one set of parameters for each compound and changing the values of for example DT50 or Kom value will affect the output. This was found by (Boesten &Van der Linden, 1991) in a study on leaching of pesticides using Pearl. Nevertheless, in the study presented here the compounds exhibited the same relation between concentration and %OM. Still, the effect of varying parameters on the model output needs to be further investigated. For example, (Vasilakoglou et al., 2001) found other values for the Freundlich coefficient of dimethenamid-P. The DT50 values of isoxaflutole was approximately two weeks instead of less than a day (Rouchaud et al., 2002). In addition, the pH independent calculation of the Freundlich sorption was used whereas in some studies a pH effect was found on this process (Mitra et al., 1999;Rice et al., 2004). In a study by (Sims et al., 2009) the transformation rate of isoxaflutole to its metabolite DKN was influenced by OM%. The complex model Pearl takes into account all possible processes related to hydrology and pesticide fate and gives an indication of field performance. It is important to determine the effect of varying sorption related parameters on the established relation with soil organic matter.

Weather

The 20 years used in the model runs differed in precipitation and temperature in the month following the application. Weather and soil moisture is known to affect herbicide performance

(leBaron, 1970). The physico-chemical properties of the three compounds differed and this was reflected in the model output. The results of this study showed that concentrations of isoxaflutole, with its short half-life, declined rapidly after application. Within three weeks it was practically all transformed to its metabolite DKN. Dimethenamid-P, with the highest half-life of the three, showed slowest decline in time after application.

The effect of specific weather characteristics on the fate of the herbicides in this study need to be further investigated. Insight can help to optimize the time of application. In particular, the effect of temperature and precipitation in the few days since application on the concentration. (Michael et al., 1996) used both climatic records and a hydrological model to look for more environmentally safer windows in forestry. (Van Alphen &Stoorvogel, 2002) combined a model, weather information and information on local conditions of soil of a farm in the Netherlands to find out which of 19 pesticides leached highest. Soil variability affected within-field pesticide leaching and high risk areas were identified in which herbicides leaching was high.

The importance in general of weather conditions for pre-emergence of soil herbicides is underlined by (van Schooten et al., 2010). They discourage this type of application as early application requires higher dosages and unfavourable weather circumstances can diminish efficacy. Further study on weather conditions with the help of Pearl can provide insight in favourable moments for application.

On the label of Merlin (isoxaflutole) moist soil conditions are recommended for effective control of weeds. Thus application should be geared to weather conditions. Isoxaflutole is known to exhibit a so-called recharge behaviour. Isoxaflutole is hydrophobic and sorbed to the soil under dry conditions. (Taylor-Lovell et al., 2000) suggested that under such conditions, the compound will stay unavailable and almost stable until moist conditions occur and it is transformed to DKN. This delayed effect can cause crop injury (Inoue et al., 2009). It can even cause crop injury in the following year (Felix &Doohan, 2005) and organic matter content is suspected to play a role in this. The decrease in concentration in the top soil layer of isoxaflutole and DKN is in accordance with findings of (Rouchaud et al., 2002). In their study both substances disappeared entirely in the 0-10 cm surface layer.

Implications for practice and recommendations for further research

The relation between organic matter content and concentration in the liquid phase was established for specific days since day of application. As mentioned above, the parameters describing the relation changed. For isoxaflutole this decline was fastest and for dimethenamid slowest. It is important to examine if and at what time frame exactly the concentration is most crucial for efficacy in the field. Varying sensitivities of weed species has been reported in various studies for isoxaflutole (Knezevic et al., 1998) (Tielen, 2010) (Bhowmik et al., 1999) and dimethenamid-P (Tielen, 2010). Thus depending on the weed species composition of a field, tank mixes may be needed. Also, the relation between concentration in the liquid phase and field rate needs to be established. The relation between %OM and concentration can be further examined in a field study to check its field validity. Soil moisture content, precipitation and exact organic matter content need to be determined.

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APPENDIX I

*	
* Scenario (CLC
*	
200.0	DT50Ref_PX (d)
1000.0	KomEql_PX (L.kg-1)
1000.0	KomEqlMax_PX (L.kg-1)
*	
* Section 1:	Control section
*	

FOCUSPEARL	CallingProgram
1.1.1	CallingProgramVersion
6	InitYears
01-Jan-1901	TimStart
31-Dec-1926	TimEnd
0.001	ThetaTol (m3.m-3)
Day	OptDelTimPrn
1	DelTimPrn (d)
No	RepeatHydrology
OnLine	OptHyd
ISO1	SwapID
0.0001	FacPrecisionPrl (-)
0.00001	DelTimMinPrl (d)
1E-5	DelTimSwaMin (d)
0.2	DelTimSwaMax (d)
Yes	PrintCumulatives
1.0	GWLTol (m)
30	MaxItSwa
3	MaxBackTrSwa
No	OptHysteresis

0.2	PreHeaWetDryMin (cm)
Yes	OptScreen
All	OptSys
Yes	OptPersistency
No	OptSnow
No	OptNoResVert
None	OptAux
No	OptDisLay
*	
* Section 2:	Soil section

*_____

Hn21 SoilTypeID

NL Location

table SoilProfile

ThiHor NumLay

(m)

- 0.10 20
- 0.15 6

0.15 6

0.20 8

0.60 12

end_table

* Boundary pressure head - controls runoff

0.0 Hb (cm) Boundary pressure head

table horizon SoilProperties

Nr	FraSanc	l FraSilt	: FraCla	y CntOr	n	pН
	(kg.kg-1) (kg.kg-	1) (kg.kg	g-1) (kg.	kg-1)	(-)
1	0.87	0.10	0.03	0.01	5.6	
2	0.87	0.10	0.03	0.054	5.6	
3	0.89	0.08	0.03	0.022	5.4	

4	0.89	0.08	0.03	0.01	5.4			
5	0.91	0.06	0.03	0.003	5.5			
end_	end_table							
table	e horizon	VanGenu	chtenPar					
Nr	ThetaSa	t Theta	Res Alp	haDry	AlphaWet	n KS	at l	
	(m3.m-3)) (m3.n	n-3) (cr	m-1)	(cm-1) ((m.d	-1) (-)	
1	0.50	0.01	0.0198	0.039	6 1.482	0.3228	0.032	
2	0.50	0.01	0.0198	0.039	6 1.482	0.3228	0.032	
3	0.46	0.01	0.0208	0.041	.6 1.658	0.416	0.081	
4	0.45	0.01	0.0206	0.041	.2 1.89	0.4807	0.112	
5	0.43	0.01	0.0198	0.039	6 2.258	0.7283	0.133	
end_	_table							
Inpu	ıt Op	tRho						
table	e horizon	Rho	(kg	.m-3)				
1	1375.2							
2	1375.2							
3	1575.9							
4	1632.7							
5	1671.8							
end_	_table							
end_	_table							
end_ 0.00	_table	ZPndMa>	« (m	1)				
end_ 0.00 0.00	_table 02 01	ZPndMa> RstSurRi	د (m unOff (د) 1)				
end_ 0.00 0.00 0.01	_table 02 01	ZPndMax RstSurRi ThiAirBou	د (m unOff (د اLay (m	1) 3)				

* Soil evaporation parameters

Boesten	OptSolEvp	
1.0	FacEvpSol	(-)
0.79	CofRedEvp	(cm1/2)
0.01	PrcMinEvp	(m.d-1)

Table horizon LenDisLiq (m)

1 0.025

2 0.025		
3 0.025		
4 0.025		
5 0.025		
end_table		
MillingtonQu	uirk OptCofDifRel	
2	ExpDifLiqMilNom (-)	
0.6667	ExpDifLiqMilDen (-)	
2	ExpDifGasMilNom (-)	
0.6667	ExpDifGasMilDen (-)	
*		
* Section 2a: Macropore section		
*		
No	OptMacropore	
*		
* Section 3: Weather and irrigation section		
*		

WINT-M	MeteoStation
Daily	OptMetInp
No	OptRainfallEvents
Input	OptEvp
1.0	FacPrc (-)
0.0	DifTem (C)
1.0	FacEvp (-)
9.4	TemLboSta (C)
No	OptIrr
No	IrrigationScheme
Laminar	OptTraRes

*_____

* Section 4a: Lower boundary flux *_____ FreeDrain OptLbo ZGrwLevSta (cm) -150 CLC LowerBoundaryFile *_____ * Section 4b: Drainage/infiltration section *_____ OptDra No No OptSurDra 0 NumDraLev *_____ * Section 5: Compound section *_____ iso SubstanceName table compounds iso met1 end_table EqlDom_Input OptDT50_iso EqlDom_Input OptDT50_met1 359.5 MolMas_iso (g.mol-1) 359.32 MolMas_met1 (g.mol-1) table FraPrtDau (mol.mol-1) 0.95 iso -> met1

end_table

OptimumConditions OptCntLiqTraRef_iso

0.9 DT50Ref_iso (d)

20.0 TemRefTra_iso (C)

0.7	ExpLiqTra_iso (-)	
1.0	CntLiqTraRef_iso (kg.kg-1)	
65.4	MolEntTra_iso (kJ.mol-1)	
OptimumCor	nditions OptCntLiqTraRef_met1	
8.7	DT50Ref_met1 (d)	
20.0	TemRefTra_met1 (C)	
0.7	ExpLiqTra_met1 (-)	
1.0	CntLiqTraRef_met1 (kg.kg-1)	
65.4	MolEntTra_met1 (kJ.mol-1)	
table horizor	n FacZTra (-)	
hor iso met1		
1 1.0 1.0		
2 1.0 1.0		
3 0.5 0.5		
4 0.5 0.5		
5 0.3 0.3		
end_table		
table horizor	n FacZSor (-)	
hor iso met1		
1 -99 -99		
2 -99 -99		
3 -99 -99		
4 -99 -99		
5 -99 -99		
end_table		
0.0	MolEntSor_iso (kJ.mol-1)	
20.0	TemRefSor_iso (C)	
pH-independent OptCofFre_iso		
65.0	KomEql_iso (L.kg-1)	
65.0	KomEqlMax_iso (L.kg-1)	
1.0	ConLiqRef_iso (mg.L-1)	
0.95	ExpFre_iso (-)	
0.0	MolEntSor_met1 (kJ.mol-1)	
20.0	TemRefSor_met1 (C)	

63.0	KomEql_met1 (L.kg-1)
63.0	KomEqlMax_met1 (L.kg-1)
1.0	ConLiqRef_met1 (mg.L-1)
0.9	ExpFre_met1 (-)
1E-6	PreVapRef_iso (Pa)
20.0	TemRefVap_iso (C)
6.2	SlbWatRef_iso (mg.L-1)
20.0	TemRefSlb_iso (C)
27.0	MolEntSlb_iso (kJ.mol-1)
95.0	MolEntVap_iso (kJ.mol-1)
0.000	PreVapRef_met1 (Pa)
20.0	TemRefVap_met1 (C)
325.0	SlbWatRef_met1 (mg.L-1)
20.0	TemRefSlb_met1 (C)
27.0	MolEntSlb_met1 (kJ.mol-1)
95.0	MolEntVap_met1 (kJ.mol-1)
0.0	CofDesRat_iso (d-1)
0.0	FacSorNeqEql_iso (-)
0.0	CofDesRat_met1 (d-1)
0.0	FacSorNeqEql_met1 (-)
0.5	FacUpt_iso (-)
0.5	FacUpt_met1 (-)
0.01	ThiAirBouLay (m)
Lumped	OptDspCrp_iso
1000000.0	DT50DspCrp_iso (d)
1000000.0	DT50PenCrp_iso (d)
1000000.0	DT50VolCrp_iso (d)
1000000.0	DT50TraCrp_iso (d)
0.0001	FacWasCrp_iso (m-1)
Lumped	OptDspCrp_met1
1000000.0	DT50DspCrp_met1 (d)
1000000.0	DT50PenCrp_met1 (d)
1000000.0	DT50VolCrp_met1 (d)

1000000.0	DT50TraCrp_met1	(d)
-----------	-----------------	-----

0.0001 FacWasCrp_met1 (m-1)

20.0 TemRefDif_iso (C)

4.3E-5 CofDifWatRef_iso (m2.d-1)

0.43 CofDifAirRef_iso (m2.d-1)

20.0 TemRefDif_met1 (C)

4.3E-5 CofDifWatRef_met1 (m2.d-1)

0.43 CofDifAirRef_met1 (m2.d-1)

*_____

* Section 6: Management section

*_____

FOCUS_EXAMPLE ApplicationScheme

1.0	ZTgt (m)	
1	DelTimEvt (a)	
table A	opplications	
01-Em	g-01 AppSolSur 0.099	
end_ta	ble	
table T	ïllageDates	
end_table		
table ir	nterpolate CntSysEql (mg.kg-1)	
0.0	0.0	
50.0	0.0	
end_ta	ble	
table interpolate CntSysNeq (mg.kg-1)		
0.0	0.0	
50.0	0.0	
end_table		
No DepositionScheme		
table	FlmDep (kg.ha-1.d-1)	
end_ta	ble	
0.2	ZTil (m)	

*_____

* Section 7: Crop section

*_____

HAMB-MAIZ	E CropCalendar
Yes	RepeatCrops
Fixed	OptLenCrp
table Crops	
05-May	20-Sep MAIZE1
end_table	
table CrpPa	r_MAIZE1
0.0 0.0	1.05 0.0 0.0
0.62 4.2	1.05 1.0 0.0
0.628 4.2	1.1 1.0 0.0
0.781 4.2	1.1 1.0 0.0
0.788 4.2	0.83 1.0 0.0
1.0 4.2	0.83 1.0 0.0
end_table	
table RootD	ensity_MAIZE1
0.0 1.0	
1.0 1.0	
end_table	
-15.0	HLim1_MAIZE1 (cm)
-30.0	HLim2_MAIZE1 (cm)
-325.0	HLim3U_MAIZE1 (cm)
-600.0	HLim3L_MAIZE1 (cm)
-8000.0	HLim4_MAIZE1 (cm)
70.0	RstEvpCrp_MAIZE1 (s.m-1)
0.39	CofExtDif_MAIZE1 (-)
1.0	CofExtDir_MAIZE1 (-)
0.0001	CofIntCrp_MAIZE1 (cm)
0.0	TemSumSta_MAIZE1 (C)
0.0	TemSumEmgAnt_MAIZE1 (C)
0.0	TemSumAntMat_MAIZE1 (C)

0.2 ZTensiometer_MAIZE1 (m)

-100.0 PreHeaIrrSta_MAIZE1 (cm)

15.0 IrgThreshold_MAIZE1 (mm)

*_____

* Section 8: Output control

*_____

table VerticalProfiles

end_table

No	OptDelOutFiles
Yes	SoilReport

0.05 ThiLayPer (m)

Yes LeachingReport

No DrainageReport

No AirReport

80 TargetPercentile (%)

Years DateFormat

G12.4 RealFormat

table OutputDepths (m)

0.025

0.05

0.07

0.10

0.15

end_table

No	print_AmaHarCrp
No	print_AmaWasCrp
No	print_AmaTraCrp
No	print_AmaAppCrp
Yes	print_AmaAppSol
No	print_AmaCrp
No	print_AmaDra_1

No	print_AmaDra_2
No	print_AmaDra_3
No	print_AmaDra_4
No	print_AmaDra_5
No	print_AmaDraPro
Yes	print_AmaEqlTgt
Yes	print_AmaEqlPro
No	print_AmaEqlTil
Yes	print_AmaErrPro
Yes	print_AmaForPro
No	print_AmaHarCrp
Yes	print_AmaNeqTgt
Yes	print_AmaNeqPro
No	print_AmaNeqTil
Yes	print_AmaSysTgt
Yes	print_AmaSysPro
No	print_AmaSysTil
Yes	print_AmaTraPro
Yes	print_AmaUptPro
No	print_AmaDspCrp
No	print_AmaWasCrp
No	print_ConGas
Yes	print_ConLiq
Yes	print_ConLiqLbo
Yes	print_ConLiqSatAvg
Yes	print_ConSys
No	print_ConSysEqI
No	print_ConSysNeq
Yes	print_CntSysPer
Yes	print_ConLiqPer
No	print_DelTimPrl
Yes	print_Eps
Yes	print_FacCrpEvp
No	print_FlmDepCrp

No	print_FlmGas
No	print_FlmGasVol
No	print_FlmLiq
Yes	print_FlmLiqInfSys
Yes	print_FlmLiqLbo
No	print_FlmSys
No	print_FlvLiq
No	print_FlvLiqInf
No	print_FlvLiqGrwSur
No	print_FlvLiqDra_3
No	print_FlvLiqDra_4
No	print_FlvLiqDra_5
Yes	print_FlvLiqEvpIntIrr
Yes	print_FlvLiqEvpIntPrc
Yes	print_FlvLiqEvpSol
Yes	print_FlvLiqEvpSolPot
No	print_FlvLiqIrr
Yes	print_FlvLiqLbo
No	print_FlvLiqGrw
Yes	print_FlvLiqTrp
Yes	print_FlvLiqTrpPot
No	print_FraCovCrp
Yes	print_GrwLev
No	print_LAI
No	print_PreHea
Yes	print_Theta
No	print_StoCap
No	print_VvrLiqDra
No	print_VvrLiqUpt
No	print_ZRoot
No	print_FlvLiqDra_1
No	print_FlvLiqDra_2
Yes	print_FlvLiqPrc
Yes	print_Tem

No	print_ConLiqDra_2
No	print_ConLiqDra_3
No	print_ConLiqDra_4
No	print_ConLiqDra_5
No	print_ConLiqDra
No	print_ZPnd
No	print_AvoLiqSol
No	print_AvoLiqErr
No	print_RstAer
No	print_RstBou
No	print_VelWnd
No	print_RstAirLam
No	print_VelFriLcl
No	print_TemAir
Yes	print_AmaRunOff
Yes	print_AmaErrMic

print_ConLiqDra_1

No

*_____

* End of PEARL input file

*_____

*** New ***

No OptPaddy

- Constant OptPnd
- No print_AmaRunOff
- No print_AmaErrMic