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Modelling herbicide treatment impact on groundwater quality in a central Italy area

Daniela BUSINELLI*, Enrico TOMBESI, Marco TREVISAN

Dipartimento di Scienze Agro-Ambientali e della Produzione Vegetale, Sezione di Chimica Agraria, Università degli Studi di Perugia, Borgo XX Giugno, 72-06121 Perugia, Italy

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Abstract – A simulation study, using the MACRO-DB pesticide leaching model, was carried out to determine the impact of different weed control strategies on groundwater quality in a Central Italy area (Umbria) where the drinking water wells for the city of Perugia are located. The simulations considered nine representative soil profiles and two different crop rotations. Weather conditions were those of ten years. Thirty herbicides and twenty-two weed control strategies were tested for their groundwater concentrations. Two maps reporting the risk of groundwater contamination were made from simulations of the two crop rotations applying the strategy with the least groundwater pollution risk for each crop. As even the less polluting strategy in the four-crop rotation exceeds the EU Directive 414/91 limit for drinking water, only the three-crop rotation is recommended. The present findings testify that crop selection is an effective way to minimise groundwater pollution risk.

groundwater / pollution / simulation model / herbicide / soil type

Résumé – Simulation de l'impact de plusieurs traitements herbicides sur la qualité des eaux souterraines dans une zone de l'Italie centrale. Sur la base du modèle MACRO-DB pour la prévision du lessivage des produits phytosanitaires le long des profils du sol, on a effectué une simulation en vue de déterminer l'impact environnemental provoqué par différentes stratégies de désherbage sur les eaux de nappe dans une zone de l'Italie centrale (Ombrie) où se trouvent les puits pour l'approvisionnement en eau de la ville de Pérouse. Les simulations ont pris en considération neuf profils de sol représentatifs de la zone examinée et deux assolements différents. Les conditions climatiques prises en considération sont celles couvrant dix années. On a calculé au niveau de la nappe les concentrations de trente herbicides et vingt-deux stratégies de désherbage. On a réalisé deux cartes qui reportent le risque de contamination, en simulant deux rotations culturales et en appliquant à chaque culture la stratégie comportant le plus bas risque de pollution de la nappe. Étant donné que la stratégie la moins polluante dans la rotation prévoyant quatre cultures dépasse encore la limite prévue par la Directive EU 414/91 pour les eaux potables, il s'impose de préférer l'assolement à trois cultures, la sélection culturale s'avérant être une méthode valable pour réduire le risque de pollution des eaux de nappe.

nappe / pollution / modèle prévisionnel / herbicide / type de sol

1. INTRODUCTION

Application of pesticides on agricultural land has contributed to non-point contamination of groundwater

resources. Concern has been expressed as to pesticides spreading into the environment, especially to areas where groundwater is the major source of irrigation or drinking water. An assessment of the potential health

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* Correspondence and reprints
agrochim@unipg.it

and environmental risks posed by groundwater contamination is needed to improve the decision-making processes [20]. An estimation of these risks may be made through extensive monitoring programmes of groundwaters and wells, focused on determining whether a given agricultural chemical has appeared in drinking water wells in a certain region [16]. Generally, this approach is costly and time-consuming; a viable alternative may therefore be to use a fast and cheap method such as a validated model able to predict potential pesticide movement to groundwater through the evaluation of pesticide Predicted Environmental Concentrations in groundwater (PEC_{gw}). FOCUS (FORum for the Coordination of pesticide fate models and their Use), a European commission established in 1993 to provide guidance to member states and industries on the appropriate role of modelling in the EU registration processes, recommend four out of the numerous pesticide leaching models available: MACRO, PELMO, PESTLA and PRZM [4, 5]. Of these, MACRO is the most widely used model for highly structured heavy soils since it considers preferential flow [3, 11–14]. As the soils in this study were heavy-textured and consequently heavy-structured, MACRO was used for the simulations.

The objective of this study was to compare different weed control strategies to identify those with a minimum pollution impact on groundwater in an area where the drinking water wells for the city of Perugia are located [8]. Model simulations were performed considering nine representative soil profiles and two different crop rotations.

2. MATERIALS AND METHODS

2.1. Area

The area is located near Petrignano di Assisi (Umbria, Italy), altitude 195 to 435 m above sea level, latitude 43°05' N, about 33 km², and generally cultivated with winter cereals rotated with maize, sunflower and sugar beet.

The Petrignano area has a mean annual temperature of 13.6 °C and a mean total annual rainfall of 934 mm, with an increase in autumn and a decrease in summer [9].

2.2. MACRO-DB model

The MACRO-DB [15] is a decision-support tool for predicting pesticide fate and mobility in soils. It consists of soil, pesticide, climate and crop databases linked to parameter estimation routines and a simulation model

(MACRO, Version 4.1). MACRO [11] is a physically-based, one-dimensional, numerical model of water flow and reactive solute transport in field soils. The model can calculate coupled unsaturated-saturated water flow in cropped soil, including the location and extent of perched water tables, and also the saturated flow to field drainage systems. The model accounts for macropore flow with the soil porosity divided into two flow domains (macropores and micropores) each characterised by a flow rate and solute concentration. Richards' equation and the convection-dispersion equation are used to model soil water flow and solute transport in the soil micropores. A simplified capacitance-type approach is used to calculate fluxes in the macropores. Exchange between the flow domains is calculated using approximate, physically-based expressions based on an effective aggregate half-width. Additional model assumptions include first-order kinetics for degradation, together with an instantaneous sorption equilibrium and a Freundlich sorption isotherm. Soil sorption parameters required in MACRO-DB are calculated automatically by combining chosen soil properties with compound properties.

As concerns irrigation, the model automatically irrigates when the soil water deficit in the root zone exceeds the critical water deficit specified before the simulation. The applied amount of water is 90% of the deficit. The critical deficit should be interpreted as the soil water deficit in the root zone which will cause unacceptable yield losses: in the model, the soil water deficit is calculated as the difference between field capacity (water content at 50 cm tension) and the current water content, summed over the root depth. In this study, the critical deficit was assumed to be 100 mm.

The simulation was performed using experimentally determined soil, climate and crop data, and hard-coded pesticide data from the model [18].

2.3. Soils

The Petrignano area contains the following soil sub-groups: Typic Hapludalfs, Typic, Fluventic and Calcixerollic Xerochrepts, Typic Xerorthents and Typic Xerofluvents [19]. The inputs required by the MACRO-DB model include the number and type of horizons of the soil profiles, soil texture, soil structure, pH, organic C and bulk density. The parameter values used in this application as shown in Tables I and II were taken from Giovannotti and Calandra [9].

Table I. Petrignano soil inputs for the MACRO-DB model.

Typic Hapludalfs (48)*			Typic and Calcixerollic Xerochrepts (40)*			Fluventic Xerochrepts (5)*			Typic Xerorthents (4)*			Typic Xerofluvents (3)*		
No.	Horizon	Depth (cm)	No.	Horizon	Depth (cm)	No.	Horizon	Depth (cm)	No.	Horizon	Depth (cm)	No.	Horizon	Depth (cm)
1 (5)**	Ap	50	11 (8)**	Ap	40	7 (1)**	Ap	70	30 (4)**	Ap	45	31 (3)**	Ap	50
	AB	25		Bw	45		Bw	50		Cr	15		Cr	200
	Bt	60		Ck	265		Ck	280						
12 (40)**	Ap	40	19 (32)**	Ap	60	23 (4)**	Ap	50						
	Bt	35		Bw	60		Bw	50						
	Ck	275		Cr	230		Cr	160						
25 (3)**	Ap	60												
	Bt	60												
	Ck	230												

* Percentage area of soil subgroup in total cultivated area (29.16 km²).** Percentage area of soil series in total cultivated area (29.16 km²).**Table II.** Petrignano soil inputs for the MACRO-DB model.

No.		Sand (%)	Silt (%)	Clay (%)	Structure			Bulk density (g·cm ⁻³)	Organic C (%)	pH
					Class	Development	Form			
1	Ap	26	39	35	medium	strong	blocky	1.21	1.10	7.7
	AB	29	39	32	medium	strong	blocky	1.50	0.46	8.1
	Bt	17	40	43	structureless	structureless	structureless	1.56	0.27	8.0
12	Ap	32	42	26	fine	strong	blocky	1.35	0.78	7.7
	Bt	12	44	44	medium	strong	blocky	1.53	0.35	7.9
	Ck	25	50	25	structureless	structureless	structureless	1.63	0.01	8.2
25	Ap	30	45	25	fine	moderate	blocky	1.47	1.16	7.5
	Bt	16	42	42	coarse	strong	prismatic	1.55	0.46	7.4
	Ck	29	48	23	structureless	structureless	structureless	1.59	0.31	8.0
11	Ap	9	49	42	fine	strong	blocky	1.31	1.10	8.0
	Bw	4	47	49	medium	strong	blocky	1.47	1.10	7.8
	Ck	20	48	32	structureless	structureless	structureless	1.62	0.01	8.2
19	Ap	26	42	32	medium	strong	blocky	1.52	0.93	8.0
	Bw	23	42	35	medium	strong	blocky	1.54	0.49	8.2
	Cr	28	47	25	structureless	structureless	structureless	1.66	0.01	8.1
7	Ap	18	50	32	fine	moderate	blocky	1.56	0.62	8.1
	Bw	22	42	36	medium	moderate	prismatic	1.71	0.20	8.2
	Ck	8	62	30	structureless	structureless	structureless	1.60	0.01	8.2
23	Ap	31	44	25	medium	moderate	blocky	1.36	1.09	8.0
	Bw	16	54	30	fine	weak	blocky	1.53	0.58	8.1
	Cr	40	42	18	structureless	structureless	structureless	1.61	0.52	8.1
30	Ap	15	47	38	medium	strong	blocky	1.29	1.11	7.9
	Cr	3	50	47	structureless	structureless	structureless	1.65	0.01	8.2
31	Ap	44	37	19	fine	moderate	blocky	1.49	1.07	8.0
	Cr	56	29	15	fine	weak	blocky	1.60	0.49	8.1

2.4. Crops

The crops chosen for this simulation were winter wheat, maize, sugar beet and sunflower, being the most widespread crops in the Petriano area. Crop inputs requested by the MACRO-DB model include data on emergence and harvest, the maximum leaf area index and maximum root depth. The values for each crop are reported in Table III.

2.5. Herbicides

The simulated herbicide strategies for winter wheat, sugar beet, maize and sunflower were those commonly used in Italy [10]: some of the products were used only

in pre-emergence and others only in post-emergence. The name, dose rates and application date of the herbicides belonging to each strategy are reported in Tables IV, V, VI and VII. A further simulation for maize was performed by adding atrazine in pre-emergence and the results were used as a reference for risk. Pesticide properties for the simulations were taken from the PETE database, which is included in the MACRO-DB model [15, 18]. Characteristics of the herbicides used in different crops are reported in Table VIII.

2.6. Weather data

The weather dataset included total daily rainfall (mm), together with the variables needed to calculate daily

Table III. Crop inputs for the MACRO-DB model.

Crop	Day of emergence	Day of m.area/r. depth.*	Day of harvest	Maximum root depth	Maximum leaf area index (LAI)
	dd/mm	dd/mm	dd/mm	m	
maize	14/05	30/07	04/10	1	5
sugar beet	31/03	29/06	19/09	0.8	5
sunflower	09/04	19/06	09/09	1	5
winter wheat	19/12	09/05	30/06	1	7

* Day of maximum leaf area and/or maximum root depth.

Table IV. Winter wheat herbicide application rates for different strategies and concentrations in the leachate at groundwater level.

Strategy	Herbicide	Application method		each pesticide y.m.c.* µg/l	Leachate total pesticide y.m.c. in each strategy** µg/l
		application rate kg/ha	application date (Julian day number)		
W1	Diflufenican	0.150	353	0.0003	0.276
	Isoproturon	0.750	353	0.2755	
W2	Diflufenican	0.188	353	0.0004	0.550
	Isoproturon	1.500	353	0.5492	
W3	Fenoxaprop-ethyl	0.100	18	0.0000	0.038
	Metsulfuron-methyl	0.004	18	0.0384	
W4	Isoproturon	1.000	18	0.4388	1.144
	Mecoprop-p	0.250	18	0.7056	
W5	Fluroxypyr	0.200	18	0.7348	2.040
	MCPA	0.800	18	1.3050	
W6	Bifenox	0.300	18	0.0000	0.492
	Ioxynil	0.090	18	0.0528	
W7	Isoproturon	1.000	18	0.4388	0.792
	Amidosulfuron	0.015	88	0.1264	
	Mecoprop-p	0.260	88	0.6402	
	Metsulfuron-methyl	0.004	88	0.0257	

* Yearly mean herbicide concentration in the leachate for each pesticide.

** Yearly mean herbicide concentration in the leachate for the sum of herbicides used in each strategy.

Table V. Sugar beet herbicide application rates for different strategies and concentrations in the leachate at groundwater level.

Strategy	Herbicide	Application method		each pesticide y.m.c.* µg/l	Leachate total pesticide y.m.c. in each strategy** µg/l		
		application rate kg/ha	application date (Julian day number)				
S1	Chloridazon	1.256	90	3.9689	3.991		
	Metolachlor	0.404	90	0.0223			
S2	Chloridazon	1.256	90	3.9689	4.308		
	Metamitron	0.150	90	0.3388			
S3	Ethofumesate	0.600	90	0.6118	2.844		
	Lenacil	0.240	90	2.2323			
S4	Ethofumesate	0.090	116	0.0935	2.462		
	Ethofumesate	0.090	132	0.1184			
	Phenmedipham	0.040	116	0.0007			
	Phenmedipham	0.040	132	0.0012			
	Metamitron	0.350	116	1.0834			
	Metamitron	0.350	132	1.0854			
	Triflusalufuron	0.020	116	0.0383			
	Triflusalufuron	0.020	132	0.0413			
	S5	Phenmedipham	0.315	116		0.0047	2.262
		Phenmedipham	0.315	132		0.0086	
Metamitron		0.150	90	0.3388			
Metamitron		0.350	116	1.0834			
Metamitron		0.350	132	1.0854			
Triflusalufuron		0.020	116	0.0383			
Triflusalufuron		0.020	132	0.0413			
S6	Clopyralid	0.084	132	0.2024	0.972		
	Phenmedipham	0.186	132	0.0051			
	Fluazifop-buthyl	0.094	132	0.7646			

* Yearly mean herbicide concentration in the leachate for each pesticide.

** Yearly mean herbicide concentration in the leachate for the sum of herbicides used in each strategy.

Table VI. Maize herbicide application rates for different strategies and concentrations in the leachate at groundwater level.

Strategy	Herbicide	Application method		each pesticide y.m.c.* µg/l	Leachate total pesticide y.m.c. in each strategy** µg/l
		application rate kg/ha	application date (Julian day number)		
M1	Atrazine	2.000	134	3.6367	3.637
M2	Metholachlor	1.360	134	0.0771	0.080
	Pendimethalin	0.713	134	0.0029	
M3	Metholachlor	1.500	134	0.0849	0.813
	Terbuthylazine	0.750	134	0.7276	
M4	Dimethenamid	1.200	134	1.8176	1.818
M5	Nicosulfuron	0.021	166	0.0310	0.252
	Nicosulfuron	0.042	152	0.2209	
M6	Dicamba	0.212	158	0.0047	0.005
	Rimsulfuron	0.015	158	0.0005	

* Yearly mean herbicide concentration in the leachate for each pesticide.

** Yearly mean herbicide concentration in the leachate for the sum of herbicides used in each strategy.

Table VII. Sunflower herbicide application rates for different strategies and concentrations in the leachate at groundwater level.

Strategy	Herbicide	Application method		each pesticide y.m.c.* µg/l	Leachate total pesticide y.m.c. in each strategy** µg/l
		application rate kg/ha	application date (Julian day number)		
SF1	Metobromuron	0.626	99	2.6375	2.837
	Metolachlor	1.212	99	0.1992	
SF2	Oxyfluorfen	0.240	99	0.0002	0.0002
SF3	Metobromuron	0.672	99	2.8240	2.827
	Pendimethalin	1.071	99	0.0035	

* Yearly mean herbicide concentration in the leachate for each pesticide.

** Yearly mean herbicide concentration in the leachate for the sum of herbicides used in each strategy.

Table VIII. Herbicide characteristics.

Name	Crop*	log Kow	pKa	Water solubility (mg/l)	Vapour pressure (Pa, 25 °C)	t ^{1/2} (days, 20 °C)
Amidosulfuron	W	1.60	3.58	9 (20 °C)	2.2 × 10 ⁻⁵	45
Atrazine	M	2.34	1.70	30 (20°C)	4.0 × 10 ⁻⁵	44
Bifenox	W	4.50	–	0.35 (20 °C)	3.2 × 10 ⁻⁴ (30 °C)	7
Chloridazon	S	1.19	–	340 (20 °C)	1.0 × 10 ⁻⁶ (20 °C)	21
Clopyralid	S	1.10	2.30	1000 (20 °C)	1.6 × 10 ⁻³	49
Dicamba	M	3.10	1.87	6500 (20 °C)	4.5 × 10 ⁻³	14
Diflufenican	W	4.90	–	0.05 (20 °C)	7.0 × 10 ⁻⁵ (30 °C)	120
Dimethenamid	M	2.15	–	1200 (25 °C)	3.7 × 10 ⁻²	30
Ethofumesate	S	2.70	–	50 (25 °C)	6.5 × 10 ⁻⁵	35
Fenoxaprop-ethyl	W	4.12	–	0.9 (25 °C)	1.9 × 10 ⁻⁸ (20 °C)	2
Fluozifop-buthyl	S	3.18	3.22	1 (20 °C)	5.5 × 10 ⁻⁵ (20 °C)	40
Fluroxypyr	W	-0.20	2.90	0.9 (20 °C)	1.4 × 10 ⁻⁵	7
Ioxynil	W	3.40	4.80	50 (25 °C)	<1.0 × 10 ⁻³ (20 °C)	6
Isoproturon	W	2.24	–	55 (20 °C)	3.3 × 10 ⁻⁶ (20 °C)	29
Lenacil	S	1.90	–	6 (25 °C)	2.7 × 10 ⁻⁷ (20 °C)	8
MCPA	W	2.70	3.10	825 (23 °C)	2.0 × 10 ⁻⁴ (21 °C)	5
Mecoprop-p	W	3.20	3.18	620 (20 °C)	3.1 × 10 ⁻⁴ (20 °C)	4
Metamitron	S	0.83	–	1700 (20 °C)	8.6 × 10 ⁻⁸ (20 °C)	12
Metobromuron	SF	2.41	–	330 (20 °C)	4.0 × 10 ⁻⁴ (20 °C)	30
Metolachlor	S	3.48	–	530 (20 °C)	1.7 × 10 ⁻³ (20 °C)	30
	M					
	SF					
Metsulfuron-methyl	W	1.64	3.64	9500 (20 °C) (pH 7)	3.3 × 10 ⁻¹⁰	60
Nicosulfuron	M	1.50	4.60	18000 (28 °C) (pH 7)	1.6 × 10 ⁻¹³	20
Oxyfluorfen	SF	4.70	–	0.1 (20 °C)	2.7 × 10 ⁻⁵	35
Pendimethalin	M	5.18	–	0.3 (20 °C)	4.0 × 10 ⁻³	90
Pendimethalin	SF	5.18	–	0.3 (20 °C)	4.0 × 10 ⁻³	90
Phenmedipham	S	3.60	–	6 (20 °C)	1.3 × 10 ⁻⁹	21
Rimsulfuron	M	2.00	4.60	7300 (25 °C) (pH 7)	1.5 × 10 ⁻⁶	2
Terbuthylazine	M	3.04	2.00	8.5 (20 °C)	1.5 × 10 ⁻⁴ (20 °C)	60
Triflusalufuron-methyl	S	7.00	4.40	110 (25 °C)	1.3 × 10 ⁻⁵ (20 °C)	4

* M = Maize

S = Sugar beet

SF = Sunflower

W = Winter wheat

potential evapotranspiration using the Penman-Monteith equation [17], i.e. solar radiation, daily minimum and maximum air temperatures, wind speed and vapour pressure. Weather data was provided by the Umbria Region Datasets [1] and refers to the Petriignano/Assisi area for the period 1 January 1995 to 31 December 1998. This 4-year dataset was replicated twice and the first two years added again in order to obtain a 10-year dataset. Daily minimum and maximum temperatures and total rainfall trends in the 4-year period have been reported elsewhere [3].

2.7 Output

Average yearly concentrations in the leachate were obtained by simulating the weeding strategy on each of the nine soil profiles and then by calculating the weighted mean of the values obtained for each herbicide in each strategy, using the percentage value of each soil on the total cultivated area as a coefficient. As the herbicide concentrations in the leachate did not correspond to those in the groundwater since dilution by water coming from the uncultivated hilly areas is to be considered, all concentrations were multiplied by 0.38 because it was previously calculated [2] that the water coming from the surrounding hilly areas would amount to 62%. The model shell ranked ten mean annual concentrations from lowest to highest with a warm-up period of three years for which simulation data was not considered. The warm-up period is the estimated period of time after which the model produces outputs that are not affected by the window effect. The window effect is caused by the initial discontinuity (i.e. no applied pesticides, no rains, etc. in the years before the beginning of the simulation) in time-dependent input data (applied pesticides, meteorological data), thus the initial state of the system is unrealistic. As suggested by FOCUS [6], the 80th percentile weather values were used to evaluate the herbicide concentrations in the leachate because they could be considered more realistic than the worst case (100th percentile). Microsoft Excel software was used to compute the 80th percentile formula, which in a seven dataset gives the weighted mean of the 5th and 6th data of the ordered set ($80th = 0.8 * 6th + 0.2 * 5th$) as the 80th percentile. In order to evaluate the influence of crop weeding strategies on leaching, two crop rotations, one with four (winter wheat-sugar beet-maize-sunflower) and the other with three (winter wheat-maize-sunflower) crops were considered. In this case, supposing that all the crops were sown every year each in one quarter or in one third of the Petriignano area, the weighted mean of the herbicide concentrations at groundwater level for each

crop was calculated using the percentage of cultivated area for each crop considered as a coefficient.

3. RESULTS AND DISCUSSION

The mean concentrations for each herbicide and for the sum of herbicides used in each strategy in the leachate at groundwater level, calculated as described in Section 2.7 above, are reported in Tables IV, V, VI and VII.

According to the increase of environmental risk of leachate concentration values at groundwater level in the simulated conditions, the herbicides used in the weed control of winter wheat (Tab. IV) can be classified as follows: Bifenox = Fenoxaprop-ethyl \leq Diflufenican < Metsulfuron-methyl < Ioxynil < Amidosulfuron < Isoproturon < Mecoprop-p \leq Fluroxipyr \leq MCPA. The first five herbicides show PEC_{gw} values lower than 0.1 $\mu\text{g/l}$ [7]. For Fenoxaprop-ethyl and Ioxynil this behaviour is due to its low application rate, a high K_{ow} and low t_{1/2} values, for Bifenox to its low application rate and high K_{ow}, for Diflufenican to its high K_{ow} and low solubility and for Metsulfuron-methyl to its low application rate. The PEC_{gw} values higher than 0.1 $\mu\text{g/l}$ for Amidosulfuron are due to its low K_{ow} and high t_{1/2}, for Fluroxipyr to its very low K_{ow}, for Isoproturon to its high application rate, for Mecoprop-p to its high water solubility and for MCPA to its high water solubility and high application rate. The increase in pollution risk with the strategies can be ranked as follows: W3 < W1 < W6 < W2 < W7 < W4 < W5. According to EC regulations [7], where the maximum allowed concentration in groundwater for the sum of herbicides is 0.5 $\mu\text{g/l}$, only the first two strategies could be used to avoid pollution risks.

Tables V, VI and VII report the herbicides and strategies for the weed control of sugar beet, maize and sunflower, respectively. They can be ranked, in increasing order of pollution risk, as follows:

- herbicides used in sugar beet: Phenmedipham < Metolachlor < Triflusaluron < Ethofumesate < Clopyralid < Fluazifop-butyl < Metamitron < Lenacil < Chloridazon, and strategies: S6 < S5 < S4 < S3 < S1 < S2. This is mainly due to the K_{ow} values of the single pesticides. The PEC_{gw} of the first three herbicides applied separately is lower than 0.1 $\mu\text{g/l}$, but in all strategies (i.e. combination of pesticides) the total herbicide concentration is higher than 0.5 $\mu\text{g/l}$.
- herbicides used in maize: Rimsulfuron < Pendimethalin < Dicamba < Metolachlor < Nicosulfuron < Terbutylazine < Dimethenamid < Atrazine, and strategies: M6 < M2 < M5 < M3 < M4 < M1. The PEC_{gw} values are lower than 0.1 $\mu\text{g/l}$ for

the first five herbicides. This behaviour, for Rimsulfuron, is mainly due to its soil sorption capability, fast degradability and very low application rate, for Pendimethalin to its high soil sorption capability while for Dicamba to its fast degradability together with the low application rate. On the other hand, the PEC_{gw} values higher than 0.1 µg/l for Atrazine and Terbutylazine are due to their low degradability and low soil sorption capability while for Diphenamid to its low soil sorption capability and high water solubility. Only the first three strategies gave PEC_{gw} values lower than 0.5 µg/l.

- herbicides used in sunflower: Oxyfluorfen < Pendimethalin < Metolachlor < Metobromuron, and strategies: SF2 < SF1 = SF3. The PEC_{gw} values lower than 0.1 µg/l for Oxyfluorfen and Pendimethalin are due to their high soil retention capability and low water solubility. The PEC_{gw} values higher than 0.1 µg/l for Metolachlor and Metobromuron are mainly due to their high water solubility. The first two herbicides and only the second strategy gave PEC_{gw} values lower than 0.1 and 0.5 µg/l, respectively. The ambivalent place of Metolachlor, whose PEC_{gw} is lower than 0.1 µg/l when used as a weed killer in sugar beet and maize,

but is higher than 0.1 µg/l when used in sunflower, is due to its higher application rate in sunflower than in sugar beet and to the different application day and consequently different weather conditions from that of maize.

To evaluate the influence of soil type on leaching, a crop rotation with the four crops considered (winter wheat-sugar beet-maize-sunflower) was simulated. The map in Figure 1a illustrates the sum of all the herbicide concentrations for the best strategy for each crop (W3, S6, M6, SF2). Table IX, where the correlation between the herbicide concentrations at groundwater level and some soil characteristics is reported, shows that leaching is negatively correlated to organic carbon, the soil depth of the first two layers and bulk density of the first layer. The most susceptible soil profiles for leaching are numbers 11, 12, 19 and 30 while the least are numbers 23, 25 and 31.

Using a similar assumption, the map in Figure 1b illustrates the sum of the herbicide concentrations for the three-crop rotation, i.e. without sugar beet. As can be seen, the environmental impact of herbicides is reduced in this rotation, testifying that crop selection is one possible way to reduce the risk of groundwater pollution.

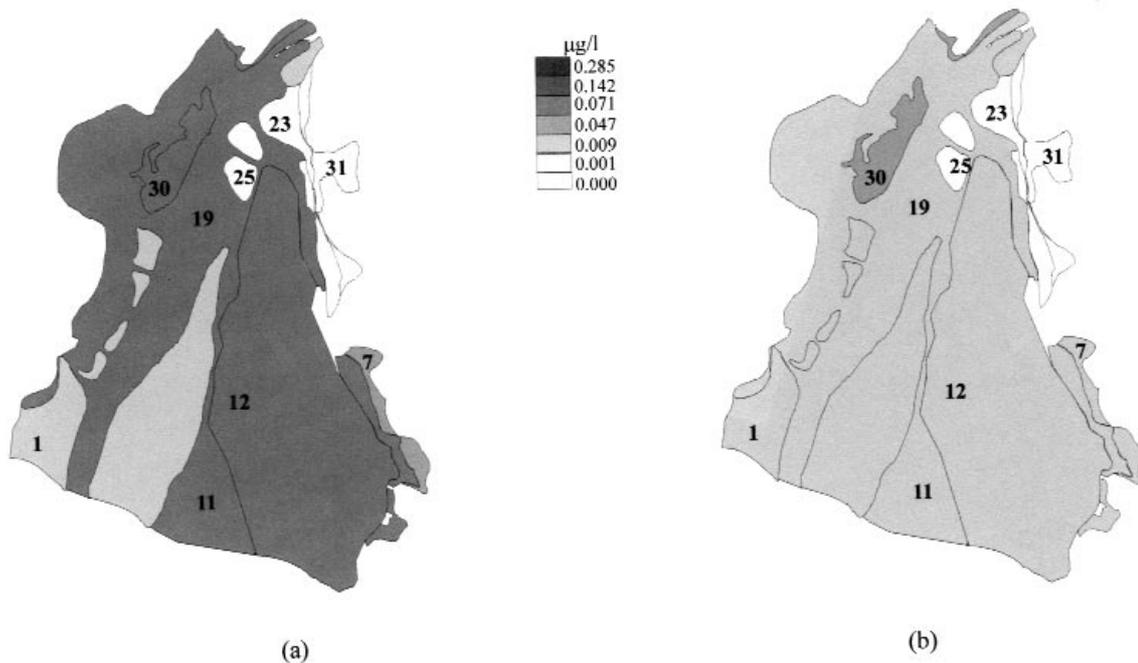


Figure 1. Environmental risk maps showing the yearly mean herbicide concentration (µg/l) in groundwater using the best herbicide strategies for two crop rotations: (a) winter wheat, sugar beet, maize and sunflower and (b) winter wheat, maize and sunflower. The numbers indicate the locations of the collected samples within each soil type area.

Table IX. Correlation and t-test probability between herbicide concentrations at groundwater level and some selected soil characteristics.

Soil characteristic	Correlation	Probability
Total depth	-0.047	8.45×10^{-5}
Depth of layer 2	-0.515	0.011
Depth of layer 1	-0.362	3.07×10^{-7}
Bulk density of layer 2	0.070	5.78×10^{-9}
Bulk density of layer 1	-0.220	2.98×10^{-9}
Organic carbon of layer 2	-0.215	0.083
Organic carbon of layer 1	-0.386	4.51×10^{-7}

4. CONCLUSIONS

The research indicates that many of the herbicides studied, which have a high mobility and/or low degradability and require high application doses, have PEC_{gw} values higher than 0.1 µg/l. Obviously, the simulated strategies where these herbicides were included have a high risk of groundwater pollution. Soil type does not seem to influence herbicide leaching which mainly depends on the soil depth of the first two layers, the bulk density of the first layer and soil organic carbon content. A particular environmental hazard was found with the strategies simulated for sugar beet. The present findings suggest that the risk of groundwater pollution may be mitigated by a careful crop rotation selection. Moreover, the method described could be used to select new strategies inducing low herbicide leaching through soils.

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