Comparing PELMO and MACRO results with herbicide percolation measurements in three sites of the lower Padana Plane

L. Nencini[1], A. Bertacchini[2], V. Caffarelli[1], C. Calzolari[3], N. Laruccia[4], F. Mazzini[5], M. Morelli[6], M.R. Rapagnani[1], R. Rossi[5], C. Scotti[2], F.Ungaro[3]

1) ENEA – Sezione Sicurezza Alimentare Sanitaria e Ambientale – via Anguillarese 301 – 00060 Roma; 2) I.TER – Progettazione Ecologica del Territorio - via Brugnoli 11 – 40122 Bologna; 3) Istituto di Ricerca per la Protezione Idrogeologica (CNR) – p.le delle Cascine 15 – 50144 Firenze; 4) Servizio Geologico, Sismico e dei Suoli - Regione Emilia-Romagna – vle Silvani 4/3 – 40122 Bologna; 5) Servizio Fitosanitario – Regione Emilia-Romagna – via Saliceto 81 – 40129 Bologna; 6) Laboratorio Analisi Chimiche ARPA - Via Bologna, 534 - Chiesuol del Fosso (Ferrara)

Research funded by Centro Ricerche Produzioni Vegetali – via Vicinale Monticino – Diegaro di Cesena (FC)

Introduction

The Rural Development Plan of the Emilia-Romagna Region, ensuing EC Regulation 1257/99, defines the objectives for Integrated Production Plans in the Region. Particularly, it is stated that crop protection shall be carried out only by choosing, among equivalent pesticides, those that minimize the risk for human health and environment. In the above framework, and also on the basis of the EC Directive 414/91 concerning the placing of plant protection products on the market, in 2002 the Region has started the updating of its Integrated Production Plans, and is currently reclassifying all the relevant pesticides, according to their toxicological and ecotoxicological characteristics. In this context the PELMO model was applied to more than 100 chemicals and metabolites currently employed on two important crops of the Region (pear and sugar beet), to assess the potential movement to groundwater across the nine most widespread soil tipologies. However, an important feature of the Region is that many agricultural areas are endowed with fine texture, low matric conductivity soils where preferential flow is important. In these cases the MACRO model is probably to be preferred, in order to evaluate the role of solute transport through macropores.

The aim of the present work is to evaluate the perfomance of MACRO in predicting the percolation of two commonly employed herbicides through three soils with distinct features: a fine textured soil with high content of swelling clay, a sandy soil and an intermediate case. The results were compared to soil core concentration measurements carried out in 2004 in three maize cropped fields. The relevant hydrological properties were deduced from laboratory measurements on soil specimens; no calibration of the parameteres was attempted. Simulations were performed also with PELMO, for purpose of comparison.

Emilia-Romagna stretches over the lower Padana Plane and is bounded by the Po river (north) and the Appennini mountains (south)

Experimental fields, crops, soils and hydrological properties

The experiment was carried out on three maize cultivated fields, belonging to farms with soil features and management practices representative of widespread scenarios of the region (see Tables 1 and 2). Soil preparation was carried out on the previous autumn by ploughing, clod breaking and harrowing. Crop growth stages are reported on Table 3. Threefold specimens of the principal horizons were collected in all soils and analyzed to obtain the hydrological parameters necessary to the simulation. Two pedotransfer functions (PTFs) were also considered, mainly for purpose of comparison: the in-built Macro5.0 PTF and a specific PTF worked out on the soils of the Emilia-Romagna Region (SINA). The measured water characteristic functions and the PTF predictions are consistent in most cases (*see* Fig. 1). Other notable features of the soils are the bimodal pore size distibution of the sandy soil (C.U.M.) and the large cracks, over two meters deep, which form during summer in the clayey soil (Il Raccolto), providing a direct access to the water table.

Location	Soil type	Site management
Farm: **C.U.M.** Province of Ferrara	sandy soil typical of sand deposits of the coastal plain	Lateral irrigation flow from ditches raises the water table during crop growth up to 40 cm below surface
Farm: **Zeccardi** Province of Bologna	medium textured soil typical of the levee, generally located along the principal rivers	Drains at 1 m depth, 30 m apart; ditches 2 m deep. No irrigation. Water table oscillating between 140 cm in winter and >200 cm in summer
Farm: **Il Raccolto** Province of Bologna	fine textured soil with high content in swelling clay, typical of interfluvial basins	Lateral ditches. No irrigation. Water table always below bottom of soil profile.

Table 1 – Description of the experimental soils

	C.U.M.	Zeccardi	Il Raccolto
Sowing	10/4	30/3	31/3
Emergence	26/4	10/4	10/4
Maximum leaf area	5/8	15/7	28/7
Harvest	7/10	20/9	23/8

Table 3 – Dates of the principal growth stages; year 2004.

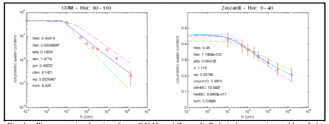

Fig. 1 – Water retention function, farms C.U.M. and Zeccardi. Red circles: experiment; blue: fit by Brooks & Corey or Van Genuchten models; dashed green: PTF SINA; dashed magenta: PTF Macro5.0

	Hor.	depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	O.M. (%)	Bulk density. (kg/L)	Structure	Strength	Shape	Ksat (cm/h)
C.U.M	1	0-40	90	10	0	7.8	0.8	1.40	none	weak	granular	35
	2	40-60	90	10	0	8	0.3	1.40	none	weak	granular	35
	3	60-110	90	10	0	8.4	0.2	1.40	none	weak	granular	35
	4	110-135	90	10	0	8.5	0.2	1.40	none	weak	granular	35
Zaccardi	1	0-40	20	54	26	8.0	1.7	1.25	medium	moderate	blocky	1
	2	40-55	20	54	26	8.2	1.2	1.25	medium	moderate	blocky	1
	3	55-90	30	47	23	8.3	1.2	1.40	medium	weak	blocky	1
	4	90-120	10	66	24	8.3	0.6	1,45	medium	weak	blocky	1
	5	120-150	10	59	31	8.4	0.6	1.45	medium	moderate	blocky	0.01
	6	150-190	5	61	34	8.4	0.7	1.45	medium	moderate	blocky	0.1
Il Raccolto	1	0-30	5	53	42	8.1	2.2	1.38	medium	moderate	blocky	0.1
	2	30-50	5	53	42	8.0	2.1	1.38	medium	moderate	blocky	0.1
	3	50-95	5	50	45	8.0	1.5	1.47	medium	strong	blocky	0.01
	4	95-135	25	52	23	8.0	0.9	1.36	medium	weak	blocky	1
	5	135-170	10	43	47	7.8	0.8	1.46	medium	strong	blocky	0.01

Table 2 – Soil horizons

Meteorological data

Meteorological data for the quadrants where the farms are located were provided by the Regional Meteorological Service. The potential evapotranspiration was obtained by means of the Hargreeves expression:

$$ETp = 0.0023\frac{R}{2.456}\left(\frac{T_{max}+T_{min}}{2}+17.8\right)\cdot(T_{max}-T_{min})^{0.5}\ ;$$

where $R(\theta,t)$ is the astronomical radiation at the relevant latitude and date. In the period April to October 2004 the daily precipitation intensities were detected also at the experiment sites. As evident in Fig. 2, the evapotranspiration rate overwhelms precipitation over most of the maize growing period.

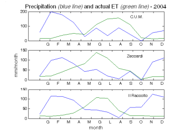

Fig 2 – Monthly precipitation and actual ET

Macro: simulation of irrigation and water table oscillation

C.U.M.: during summer, irrigation is made possible by seepage from lateral ditches, by opening the locks upstream to raise the water table up to 40 cm below soil surface. This feature was simulated applying the 4.3b version of Macro, that allows to define an ascending flow from the soil bottom during the proper period (CHAPAR -> BGRAD<0) (Fig. 3a). Zeccardi: in this case the water table level is controlled by drains, 1 m deep 30 m apart, and lateral ditches 2 m deep. When these features were inserted into Macro 5.0, and adopting the maximun allowed value for BGRAD, the resulting water table was rather higher than the level measured during the period relevant to the experiment (Fig. 3b). Hence we preferred to carry out the simulation using a unitary gradient condition at soil bottom. Il Raccolto: the water table is always below the soil bottom, hence the simulation was carried out with Macro 5.0 and a unitary gradient at soil bottom.

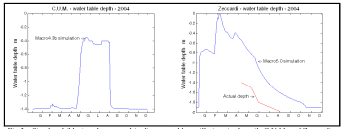

Fig 3 – Simulated (blue) and measured (red) water table oscillations in the soils C.U.M. and Zeccardi

Treatments. Soil sampling and analysis

Terbuthylazine (N^2-*tert*-Buthyl-6-chloro-N^4-ethyl-1,3,5-triazine-2,4-diamine – henceforth referred to as **TBA**) and **s-Metolachlor** (2-chloro-6-ethyl-*N*-(2-methoxy-1-methylethyl)aceto-*o*-toluidide) – **sMet**) are two herbicides widely employed in maize cultivation. **Desethylterbuthylazine** (**DTBA**) is known to be TBA's most important metabolite. The chemodynamic parameters adopted for the simulation are reported in Table 3. According to the Groundwater Ubiquity Score (*GUS* – last column in Table 3), TBA and DTBA can be classified as probable leachers and sMet as a possible leacher. A single treatment was carried out on all soils with Primagran Gold 4 L/ha, corresponding to 0.75 kg/ha of TBA and 1.25 kg/ha of sMet. The application was done before maize emergence in two cases (C.U.M. and Zeccardi) and one month after emergence in the third (Il Raccolto). Samples were collected at five depths and five dates (six in one case) in the period from one day to one year after the application. In order to avoid cross contamination, the sampling of the first two layers (0-5 and 5-15 cm) was done by digging to the desired depths. Each one of the deeper samples was extacted by a carefully cleaned hand auger and had its upper surface scraped off. Five replicates of each sample were taken and then mixed together. Preparation for GCMS or LCMS analysis was carried out in the following way: weighing of 100 g; extraction with 200 ml of a mixture of n-hexane, acetone and dichloromethane 1:1:1; 30' ultrasonic bath; filtration; vaccum concentration to dryness; dissolution with 5 ml of acetone. All soils were also analysed before the application to check that no residues of the three molecules were left from previous years.

		TBA					DTBA					sMet				
C.U.M.	*(cm)*	0-5	5-15	15-45	45-60	60-100	0-5	5-15	15-45	45-60	60-100	0-5	5-15	15-45	45-60	60-100
	15/4	0.685					0.022					0.598				
	5/5	0.436	0.184	0.066			0.064	0.022	0.011			0.266	0.249	0.076		
	16/6	0.268	0.056	0.035			0.179	0.034	0.012			0.210	0.045	0.012		
	27/9	0.155	0.032	0.012	0	0	0.010	0.011	0	0	0	0.010	0	0	0	0
	6/4	0	0	0.005	0.004	0.001	0	0	0.002	0.004	0.001	0	0	0	0	0
Zeccardi	*(cm)*	0.-5	5-15	15-40	40-60	60-100	0.-5	5-15	15-40	40-60	60-100	0.-5	5-15	15-40	40-60	60-100
	31/3	0.580					0.022					0.44				
	27/4	0.363	0.144				0.113	0.023				0.419	0.132			
	20/5	0.207	0.153	0.094	0.059		0.124	0.059	0.059	0.024		0.321	0.188	0.130	0.071	
	16/6	0.230	0.071	0.070	0.035		0.218	0.047	0.023	0.012		0.344	0.130	0.035	0.012	
	24/9	0.077	0.080	0.034	0.034	0	0.044	0.034	0.014	0.014	0	0.077	0.057	0.023	0.045	0
	15/3	0.016	0.019	0.012	0	0.002	0.006	0.006	0.006	0	0.002	0.007	0.011	0.004	0	0
Il Raccolto	*(cm)*	0-5	5-15	15-30	30-60	60-100	0-5	5-15	15-30	30-60	60-100	0-5	5-15	15-30	30-60	60-100
	11/5	0.587					0.022					0.509				
	31/5	0.392	0.037				0.257	0.012				0.559	0.075			
	16/7	0.236	0.095	0.106			0.135	0.024	0.035			0.472	0.142	0.177		
	28/9	0.086	0.024	0.024	0.024	0	0.049	0	0	0	0	0.232	0.012	0.012	0.012	0
	16/3	0.010	0.020	0.037	0.005	0.003	0.004	0.008	0.007	0.003	0	0.010	0.010	0.012	0.004	0.004

Table 5 – Measured concentrations (mg/kg). Raws: sampling dates; columns: soil layers

	DT50 (days)	*K_{oc} (L/Kg)*	*GUS*
TBA	101	212	3.35
DTBA	57	69	3.79
sMet	17.4	201.5	2.08

Table 4 – Chemodynamic parameters.
$GUS = \log_{10}(DT50) \times (4 - \log_{10}(K_{oc}))$

Macro: soil moisture and water fluxes

The matric potential variation in the three soil profiles are reported in Fig 4; the difference between the irrigated soil (C.U.M.) and the two non irrigated soils is striking. In Fig 5 Macro results are compared to the moisture profiles measured in the soil cores. Fig. 6 shows the overall water fluxes computed for the three soils; macropore flow is important in both the silty loam and the silty clay soil. The huge runoff over the lowest permeability soil (Il Raccolto) is probably an overestimation, in view of the perfect flatness of the fields in the area and of the high air humidity for long periods of the year. However the percolation results should not be greatly affected, since most of the predicted runoff events fall outside the experiment period.

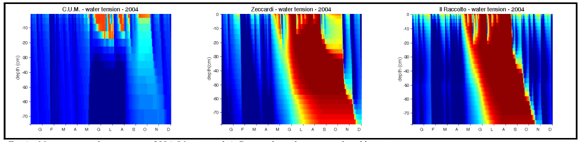

Fig 4 – Matric potential variations in 2004 (Macro results). Deep red = wilting point; deep blue = micropore saturation.

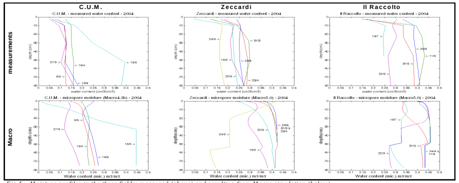

Fig 5 – Moisture profiles in the three fields: measured (above) and resulting from Macro simulation (below)

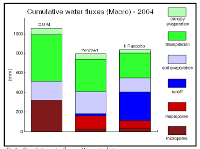

Fig 6 – Cumulative water fluxes – Macro simulation

7. Results and conclusion

The experimental and simulation results for the three chemicals are summarized in Figs. 7-9. Each figure shows the concentration profiles of the three fields, at all sampling dates. In all cases the first sampling was done the day after the treatment. Watching the figures it can be observed that:

- *Pelmo and Macro* results are generally consistent with each other;

- *concentration 24 h after application:* only the surface layer (0-5 cm) was sampled. In all cases TBA and sMet concentrations are remarkably lower than predicted by the models, suggesting that the chemicals penetrated deeper than 5 cm during the application;

- *C.U.M.; TBA and sMet:* with the exception of the first sampling date, the agreement between measures and simulations is satisfactory;

- *Zeccardi and Il Raccolto; mobility of TBA and sMet:* in these fields the percolation seems to be faster than predicted by the models. As an example it can be noted that 51 days after treatment both chemicals had reached the 40-60 cm layer of the Zeccardi soil, whereas according to the models no percolation should have occurred beyond the first 15 cm;

- *Zeccardi and Il Raccolto; persistence of TBA and sMet:* while the TBA disappearance rate was consistent with its half life (101 d), sMet showed a surprising persistence in the two fine textured soils (Zeccardi and Il Raccolto), if compared to its short half life (17.4 d). In fact sMet was detected in these soils even on the last sampling date, one year after the treatment;

- *DTBA:* all the experimental results shown in Fig 9 are ramarkably different from what expected on the basis of the TBA and DTBA degradation rates, and seem to indicate a bimodal accumulation kinetics for this metabolite. In fact a period when the formation was faster than predictable, lasting until June or July, is followed by a drop to lower than expected concentrations (samples of September 04 and March 05).

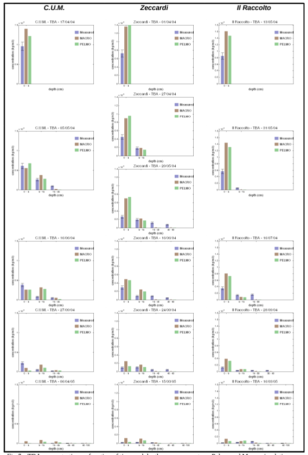

Fig 7 – TBA concentration as function of time and depth: measurements vs Pelmo and Macro simulations

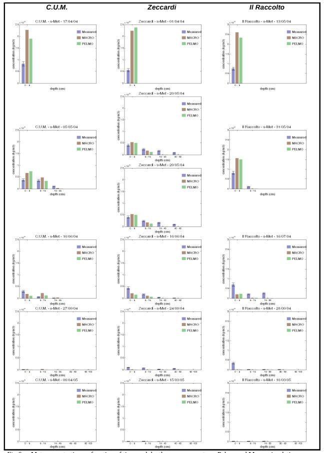

Fig 8 – sMet concentration as function of time and depth: measurements vs Pelmo and Macro simulations

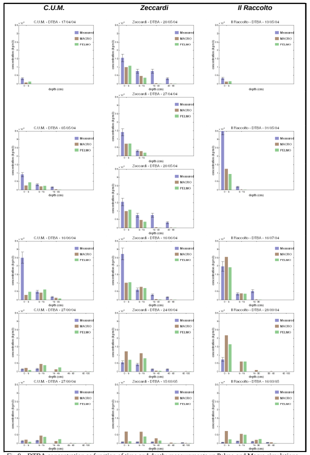

Fig 9 – DTBA concentration as function of time and depth: measurements vs Pelmo and Macro simulations