Lysimeter experiments with metolachlor in Tor Mancina (Italy)

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Abstract

The paper describes one of the four datasets used to test pesticide leaching models within the Working Group Modelling of the EC European Program COST Action 66 'Fate of Pesticides in the Soil and the Environment'. The Tor Mancina dataset is the result of a 3-year lysimeter experiment carried out near Rome (Italy) on a clay-loam calcareous fluvisol, which aimed to asses the risk of groundwater contamination from some herbicides commonly used in the Mediterranean area.

Parameters available for modelling are water percolation, bromide leaching, and the occurrence of metolachlor residues in leachates. All parameters refer to two irrigation treatments to evaluate the effect of different water supplies (398 and 548 mm).

The total amount of percolated water was equal to 660 mm as an average for both the treatments, with a total rainfall of 2432 mm. The average concentration of metolachlor in the leachate was $0.008 \div 0.012 \, \mu g \, l^{-1}$, and maximum concentration $1.63 \div 22.9 \, \mu g \, l^{-1}$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The increased concern over pesticides in surface and ground waters has required the evaluation of their mobility as a basis of risk analysis. Lysimeters offer good possibilities to conduct such tests, because they constitute closed systems, with the control of water leaching through the soil (Bergström, 1990; Hance and Führ, 1992). More recently the EC

Directive 91/414 (European Community, 1991) concerning the marketing of plant protection products, and the following EC Directive 95/36, have stressed the use of lysimeters as an essential tool for water risk assessment.

In the Mediterranean area only a few lysimeter studies on pesticides have been carried out in recent years (Marucchini et al., 1992; Businelli et al., 1993). The results presented in this paper concern a 3-year lysimeter experiment set up in Italy in 1993, aiming to evaluate the risk of groundwater contamination by some herbicides commonly used in the Mediterranean area (Capri et al., 1994a, 1995; Francaviglia et al., 1996). The objectives included the development of a lysimeter protocol to be adopted in the Mediterranean pedo-climatic environment, the evaluation of some simulation models to predict the fate of agro-chemicals (both pesticides and fertilisers), and the study of the possible occurrence of by-pass flows through soil cracks. The paper deals with the monitoring of water percolation, bromide and metolachlor leaching, and refers to a period of 3 years (27 May 1993–4 June 1996).

2. Materials and methods

2.1. Lysimeter description

The lysimeter installation is situated in central Italy, about 30 km north of Rome (42°03′N, 12°36′E, 50 m a.s.l.). The system is made up of 30 cylindrical lysimeters of reinforced concrete, with an internal diameter of 1.6 m. Lysimeters are buried, and were filled in 1987 with sieved soil coming from the topsoil layer of the Tiber Valley; therefore they can be considered gravity drained repacked lysimeters.

The bottom of each lysimeter is connected with PVC tubes to an underground laboratory, where data-loggers record lysimetric and climatic data. The water table depth in the lysimeters can be modified by means of a system of communicating vase; as an alternative, lysimeters can be used as free draining systems where the volume of water discharged is collected and recorded through tipping rain-gauges.

Only four free draining lysimeters 1.5 m deep were used in the experiment to limit the cost of the research. Each of them contained 1 m of a clay loam calcareous fluvisol over a gravel bed 0.5 m deep. Chemical soil data (Table 1), showed slight differences among lysimeters and soil layers, due to weathering, leaching, and cropping conditions during the previous years.

2.2. Crop rotation

The study was planned for a 3-year period, with a crop rotation soybean, bread wheat, maize, broad bean, fresh bean and wheat (Table 2). This rotation has allowed the study of the mobility of herbicides in different seasons, and for a long period of time.

2.3. Application of the chemicals

Dualin SP (metolachlor 40%, linuron 10%) was applied in pre-emergence on 27 May 1993 on soybean, and on 2 June 1995 on French bean. Formulated product was applied on

Table 1
Soil characterisation of the four lysimeters (mean ± standard deviation)[a]

Soil layer (cm)	0–25	25–50	50–75	75–100
pH	7.7 (0.08)	7.7 (0.04)	7.7 (0.02)	7.7 (0.02)
Organic C (%)	1.21 (0.26)	1.00 (0.12)	0.98 (0.18)	0.95 (0.27)
Sand (%)	19 (1)			
Silt (%)	53 (1)			
Clay (%)	28 (2)			
Mineral density (kg l^{-1})	1.37 (0.01)			
CEC (meq 100 g^{-1})	17 (1)	17 (1)	16 (1)	16 (<1)
Saturated hydraulic conductivity (mm h^{-1})	12 (5)			
Water content (g g^{-1} d.s.)				
0.33 bar	0.31 (0.01)			
−2 bar	0.26 (0.01)			
−15 bar	0.24 (0.01)			

[a] Parameters reported for a single layer were measured in 1987 during the packment of lysimeters.

the soil surface using a small sprayer distributing 800 l ha^{-1}, in the maximum amount per hectare as reported on the label, and crop management (including nitrogen fertilisation) followed the good agricultural practice of the region. The application rate of metolachlor was 1.2 kg ha^{-1}. Bromide, as sodium or calcium bromide, was applied in pre-emergence on 27 May 1993, 11 July 1994, and 20 June 1995, at a rate of 100 kg ha^{-1} with a water solution.

2.4. Climatic data

Meteorological data were measured from a climatic station close to the lysimetric installation, and equipped with a datalogger CR7 from Campbell Scientific. The following data were collected on a daily basis: maximum/minimum air temperature (°C), rainfall (mm), pan evaporation (mm), solar radiation (cal cm^{-2} per day), maximum, minimum and average relative humidity (0–1), and wind speed (m s^{-1}).

Table 2
Type and date of crop management[a]

Crop	Management			
	SBP	L	S	H
Soybean	24/05/93	24/05/93	27/05/93	12/10/93
Wheat	9/12/93	9/12/93	13/12/93	24/06/94
Maize	4/07/94	4/07/94	5/07/94	2/12/94
Broad bean	Sod seeding		17/12/94	21/04/95
French bean	Sod seeding		20/06/95	28/09/95
Wheat	Sod seeding		11/12/95	20/06/96

[a] SBP = seed bed preparation; H = harvest; S = sowing; L = soil tillage using the spade. Maximum depth reached in soil management is 20 cm.

2.5. Irrigation treatments and water sampling

Two watering treatments using a small sprinkler system were followed (two lysimeter each) to simulate typical water inputs in Central Italy during the whole period: a normal case (IRR1 = 398 mm), and a worst case condition (IRR2 = 548 mm). Lysimeters 12 and 14 followed the IRR1 treatment, lysimeters 11 and 13 the IRR2. The irrigation amounts per day ranged from 30 to 60 mm as a maximum.

A total of 64 samples was collected for each lysimeter. Drainage water was collected in glass bottles every week, or after a heavy rainfall. Each sample of water was analysed to detect the occurrence of all the active ingredients applied until that moment.

2.6. Herbicide analyses

Water samples were firstly added with 10% of methilic alcohol to inhibit microbial growth; then they were filtered with GF/A pre-filters to separate sediment from water, extracted with Empore Disk[®], and stored in a freezer at $-5°C$. Pre-filters were extracted with 50 ml of acetone, Empore Disks with 20 ml of ethyl-acetate. Analyses of herbicides were performed at UCSC-Piacenza, by GLC-ECD on water samples of 2 l (when it was possible). The quantification limit was <0.1 $\mu g\,l^{-1}$. Results of Linuron, the other component of Dualin, are available elsewhere (Francaviglia et al., 1996).

2.7. Bromide analyses

Bromide in the leachates was quantified using a Dionex 4500 I ion chromatograph equipped with an anion micro membrane suppressor to chemically suppress background through H_2SO_4 0.025 N. The used column was a Ion Pack AS4A, composed of a 15 μ polystyrene/divinyl benzene substrate agglomerated with an anion exchange latex. The mobile phase eluent was 1.8 mmol l^{-1} Na_2CO_3: 1.7 mmol l^{-1} $NaHCO_3$ solution at a rate of 2 ml min^{-1}. Bromide detection was performed by conductivity. Retention time was approximately 5 min. The standard solutions used were Anion Multi-elements Standard I by Merck.

2.8. Laboratory half-life measurements

The half-life of the herbicides was measured following the protocol described in Capri et al. (1994b) and reported in laboratory degradation studies of the cost 66 ring test (Suett, 1996).

Freshly-collected soil samples from each lysimeter at 20 cm depth were sieved at 0.5 cm mesh and stored for 2 weeks in the dark in loosely-closed containers at 3°C until herbicide treatment. Prior to the herbicide treatment water was applied to bring the soil to a moisture content at about 10% (dry weight).

An aqueous solution of the liquid formulation of herbicide (Dualin SP), kept separate, was applied to the soil (about 1 kg) to give a concentration of 10 mg of active ingredient per kilogram dry soil. Soil was then mixed thoroughly, and transferred as two sub-samples of 500 g each into loosely closed glass containers.

The containers were then stored for 3 months in an incubator in the dark. Trials with 23% soil moisture (± 3%) were incubated at 10, 20 and 30°C (± 1°C). Trials with 5 and 37% soil moisture were also incubated at 20°C. 50 g samples were collected at 0, 1, 4, 7, 14, 28, 60 and 90 days from treatment to measure the herbicide residue and soil moisture.

Half-lives (HF), i.e. the time required for any pesticide to undergo dissipation and/or degradation to half its initial concentration, were derived from a first-order kinetic model defined by the relations

$$\frac{dC}{dt} = -kC \tag{1}$$

$$HF = \frac{\ln 2}{k} \tag{2}$$

where dC/dt is the time derivative of the concentration, and k is the first-order reaction rate constant.

The effect of temperature on degradation were expressed using the Arrhenius equation

$$\log\left(\frac{H_1}{H_2}\right) = \left(\frac{dE}{2.303}\right) R\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3}$$

where H_1/H_2 is the rate between the half-lives at temperatures T_1 and T_2 (the absolute temperatures where the half-lives 1 and 2 were calculated), dE is the activation energy and R is the gas constant.

The fit of the Arrhenius equation was derived by linear regression of the logarithm of the half-life against the reciprocal of the absolute temperature. The constant for temperature effects at 23% soil moisture was 29.77 ($r^2 = 0.94$).

The effects of moisture were analysed by means of the empirical equation developed by Walker (Walker, 1974)

$$H = AM^{-b} \tag{4}$$

where H is the half-life, A the intercept of the regression line measuring the degradation/moisture dependence and M is the soil moisture content.

The fit of this empirical equation was determined by linear regression analysis of the logarithm of the half-life against the logarithm of soil moisture at 10 and 30°C. The constant for soil moisture effect was 0.46 ($r^2 = 0.98$).

2.9. Sorption measurements

The sorption constant K_d was measured only at one concentration point using a concentration close to the maximum application rate in soil as reported by Cleveland (1996). The 106 OECD method was followed (OECD, 1993). Soil was air dried and sieved to 2 mm and re-equilibrated with approximately its weight of water before starting the trial. In either case the dry weight content of soil was determined. The adsorption test was carried out in triplicate using 1 : 1 w/v soil : solution ratio (25 g–25 ml) approximately. 1 mg l^{-1} of calcium chloride 0.01 M solution of each pesticide was used and the experiment was run at 25 ± 2°C. Glass containers (250 ml) were used which adsorb negligible amounts of active ingredient. Blank tests performed using three soils

Table 3
K_d values for metolachlor ($\pm$standard deviation)

Soil layer depths (cm)	K_d (ml g^{-1})
0–25	2.05 ± 0.18
25–50	2.21 ± 0.35
50–75	1.90 ± 0.05
75–100	1.95 ± 0.22

with only calcium chloride 0.01 M solution indicated no analytical interference. Agitation, performed for 24 h, is obtained using agitator apparatus IKA Labortecnik Hs 501 Digital (150 counts min^{-1}). During each test a blank with chemical solution with no soil was used to check possible losses of active ingredient, and also for the correction of the initial concentration. After shaking, samples are centrifugated and a solution aliquot was drawn for HPLC analysis. HPLC conditions are RP-18 column, eluent water : acetonitrile (1 : 1), flow 1.5 ml min^{-1} 214 nm.

K_d values (Table 3) are calculated following the 106 OECD method

$$K_d = \left(\frac{X/m}{C_e}\right) \tag{5}$$

where K_d = sorption constant; $X = (G - C_e)V_0$; m = mass of the soil dry weight (g); G = herbicide blank solution (μg ml^{-1}); C_e = herbicide concentration in the aqueous phase after the adsorption test (μg ml^{-1}) and V_0 = volume of the aqueous phase before the adsorption test. Then

$$K_{OC} = K_d \left(\frac{100}{O_C}\right) \tag{6}$$

2.10. Metolachlor residues in the soil

Soil cores were collected on 9 July 1996, using a hand operating auger at 0–25; 25–50; 50–75 and 75–100 cm depth. Four replicates for each lysimeter were mixed, sieved through a 5 mm mesh and frozen at $-20°$C until analysis. Soil sampling was carried out after the plant harvesting when the lysimeter experiment was over.

Soil samples were analysed after extraction with acetone and dichlormethane (Del Re et al., 1991). Recoveries were $90 \pm 5\%$ and quantification limit 0.01 mg kg^{-1}. Soil data reported in Table 4 are not corrected for the recovery.

3. Results

3.1. Water percolation

The cumulated percolation of water has been equal to 660 mm for both treatments, despite the different irrigation inputs (IRR1 $-$ IRR2 $= 150$ mm). This situation is surely due to the intense losses by evapotranspiration during spring and summer.

Table 4
Metolachlor residues (mg kg^{-1} dry soil)[a]

Depth	Lysimeters			
	11	12	13	14
0–25	0.020	0.017	ND	0.014
25–50	ND	ND	ND	ND
50–75	ND	ND	ND	ND
75–100	ND	ND	ND	ND

[a] ND = not detected. Sampling date: July 1996.

Water percolation varied sharply during the experiment. The Tor Mancina environment shows the typical climatic conditions of the Mediterranean area, in which annual rainfall varies widely from one year to another (often by a factor 2 or greater). The intensity of rainfall can be very high, e.g. more than 100 mm per day have been reported. The occurrence of these events is particularly higher on the Mediterranean coast. Local flash floods frequently result under these weather conditions, and in the same way dry periods may occur for a long time. As a consequence, outdoor lysimeters are either completely dry or are filled up of water.

Water percolation was particularly high during the first 8 months of the experiment, and about 60% of water leached from the beginning of the experiment until the end of January 1994, due to the heavy rainfall in the autumn of 1993. In that period the deviation of actual rainfall from the average values have been close to 100% (Fig. 1).
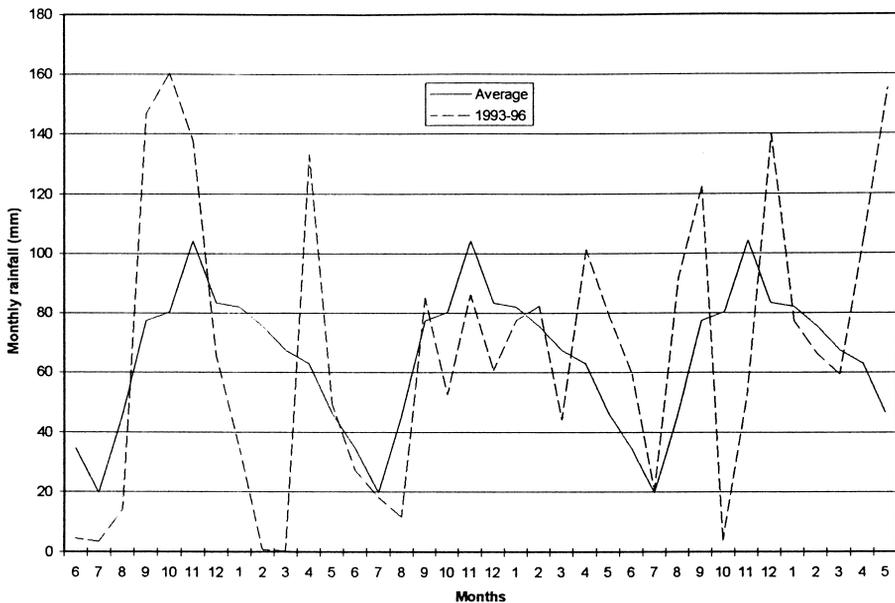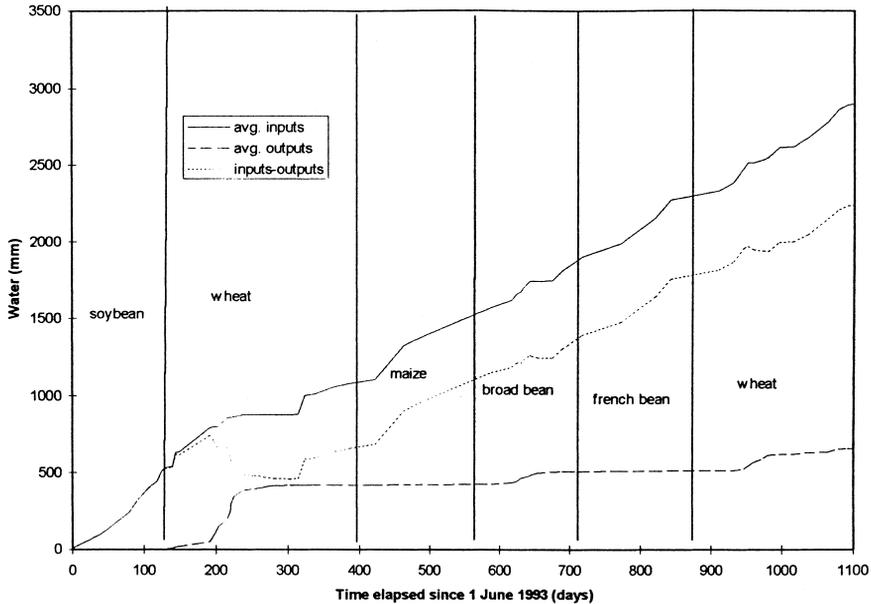

Fig. 1. Average and actual (1993–1996) rainfall.

Fig. 2. Water balance during the experiment under the given crop rotation. Average inputs = total rainfall + irrigations; Average outputs = measured total water percolation; inputs − outputs = actual evapo-transpiration measured from the balance.

A tentative water balance is reported in Fig. 2. Average inputs (rainfall and irrigation) have been equal to 2892 mm, and the difference between inputs and outputs, which should represent a gross estimation of evapotranspiration, is 2231 mm. So, during the experiment, about 77% of inputs have been used by the crops. In some winter and spring periods, in particular during December 1993 and February 1994, the soil was oversaturated, so that after each rainfall nearly the same amount of water percolated from the lysimeters. During the summer months, there was no leaching, and all water inputs from rainfall and irrigation were used for evapotranspiration.

Many Mediterranean soils have a clay-loam texture and a particular soil moisture regimen typical of arid climates, so can be very often characterised by by-pass flows due to macropores and cracks, often sub-superficial. Preferential flows through the lysimeters have occurred, since some soil cracks have often developed, both in summer and in winter months. A deeper discussion on the evidence of preferential flows is reported in Sections 3.2 and 3.3.

3.2. Bromide leaching

In parallel with the water percolation, no differences were found between the leaching of bromide from the two treatments: the leaching of IRR1 ('normal case') was 116.9, and that of IRR2 ('worst case') 114.7 kg ha^{-1}. However, the recovery of bromide resulted higher in the lysimeters following the IRR1 treatment (Fig. 3). Since bromide is repelled
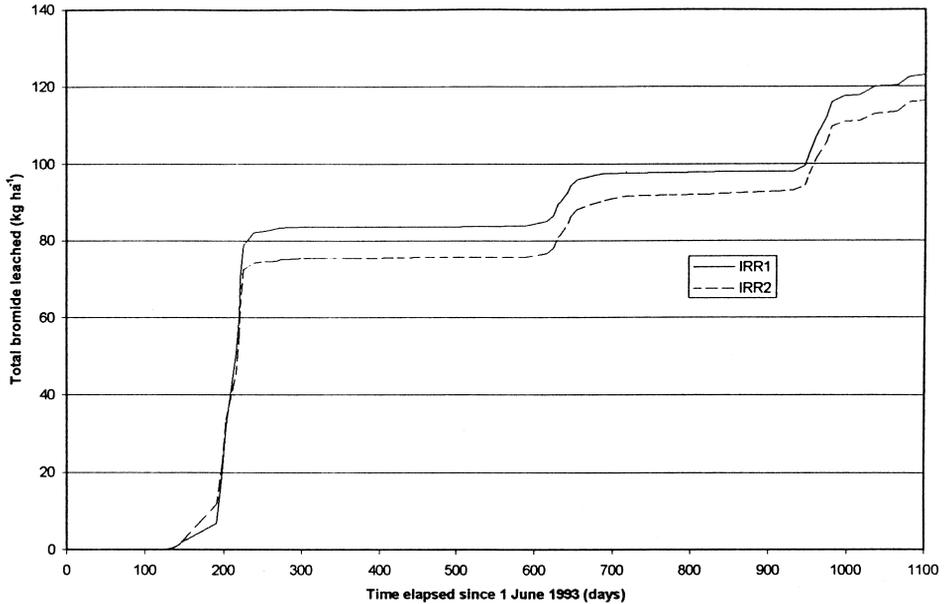
Fig. 3. Leaching of bromide of the two treatments.

from negatively charged soil particles, and can move easily through the macropores and the soil cracks were the flow of water is more rapid, these results suggest the possible occurrence of by-pass flows. The drier the soil is (e.g. IRR1 treatment in this experiment), the higher the flow of water and sediments through the soil cracks will be. Some uncertainties and the difficulties met in reaching a total mass balance could be ascribed to the detection limit (1 mg l^{-1}) as well as to crop uptakes (Jemison et al., 1994).

3.3. Metolachlor leaching

The herbicide was detected in the leachates mainly for a short period of 10–20 days, and 111–123 days after the first treatment in 1993; some water samples collected in the period October 1993–February 1995 showed metolachlor residues, with concentrations ranging from 0.09 to 0.5 µg l^{-1}. No residues were detected after the second application of 1995, except one sample in January 1996 with a concentration of 0.06 µg l^{-1}. Recoveries ranged from 0.052 to 0.077 g ha^{-1}, the average concentration in the leachate was 0.008 ÷ 0.012 µg l^{-1}, and maximum concentration 1.63 ÷ 22.9 µg l^{-1} (Table 5).

Although the average concentration in the leachates during the experiment does not exceed 0.1 µg l^{-1} (EU 80/778 Directive for drinking waters), some peak-values higher than the EU drinking water limit in the leachates are detected.

The rapid disappearance of metolachlor can be explained by the fact that its measured half-life in the typical field conditions of the environment (temperature 20°C; soil moisture 23%) is 22 days (Table 6). Considering its low Koc (200 ml g^{-1}), and high solubility (530 mg l^{-1}), metolachlor can also be readily transported towards the deeper

Table 5
Results obtained for metolachlor leaching

	IRR1 treatment		IRR2 treatment	
	Lys 12	Lys 14	Lys 11	Lys 13
Total percolated amount of water (mm)	635.11	685.61	675.08	646.38
Average concentration in the leachate ($\mu g\,l^{-1}$)	0.012	0.008	0.012	0.009
Highest concentration in the leachate ($\mu g\,l^{-1}$)	2.12	1.89	22.87	1.63
Time spent to reach the highest concentration (days)	133	133	122	133
Time spent to reach the bottom of lysimeters (days)	122	133	111	63
Total residues in water (μg)	76749	51786	77713	58275

Table 6
Herbicide half-lives (duplicate ± 5%) in laboratory conditions

Temperature (°C)	Soil moisture (%)	Half-life (days)	r^2
10	23	28.4	0.92
20	5	40.1	0.85
20	23	22.0	0.96
20	37	15.3	0.90
30	23	12.2	0.94

soil layer. The leaching of the herbicide occurred when the soil was cracked, and water samples were rich in sediment, again confirming the occurrence of by-pass flows.

4. Conclusions

Lysimeter studies in Mediterranean conditions should mainly consider the environmental peculiarities they should represent, and the climate in particular. Since high temperatures and variable rainfall clearly make easier pesticide degradation, which makes them harmless to the soil and the groundwater, a study protocol should include an actual situation representative of the typical pedoclimatic scenarios.

Due to the high rates of evapotranspiration, the supply of high amounts of water in the Mediterranean environment does not represent a real worst case condition, and in fact this situation has never occurred in our data set at least.

The results of the experiment suggest the possible occurrence of by-pass flows due to soil cracks occurring during dry periods, in parallel with the presence of small amounts of pesticide residues in the leachates. As a consequence, also a herbicide with a low half life, e.g. metolachlor, could show some risk for groundwater.

The data derived from particular pedoclimatic combinations occurring as an exception and in small areas are not representative of the actual situation of the Mediterranean area, meaning that the effects of strongly unfavourable climatic and pedologic conditions

can also be considered only to assess the potential risk of a given pesticide/soil combination. To develop a standard of evaluation, data from an actual situation should be preferred.

The dataset represents an effective base for model application. A future improvement for the testing of pesticides could be the application of a mobile but more persistent than metolachlor substances, in parallel with the monitoring of the soil moisture regimen.

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