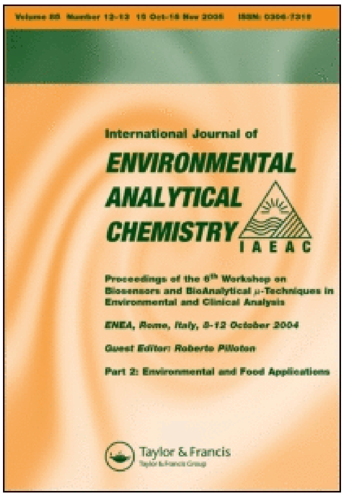

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FIELD STUDY ON MOBILITY AND PERSISTENCE OF LINURON AND MONOLINURON IN AGRICULTURAL SOIL

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A field site equipped with suction cup lysimeters was installed at Treviglio (BG) to assess the migration capacity of the herbicides linuron and monolinuron from topsoil to groundwater and to verify the appearance of their relevant transformation products in soil and water samples. A constant hydraulic head was applied in order to develop water saturation conditions in the upper layers. KCl was used as a tracer to evaluate water infiltration velocity through the vertical soil profile. The constant hydraulic head accelerated infiltration rates, while herbicide concentrations reached maximum contamination because soil adsorption capacity was underdeveloped. The results indicated two main processes of pesticide transport: firstly transport due mainly to water infiltration through macropores; secondly the transport driven by matrix flow. Linuron was found to be the most mobile herbicide, while chloroanilines were found to be the major transformation products of the herbicides considered.

Keywords: Linuron; monolinuron; matrix flow; preferential flow; suction cup lysimeter; vadose zone

INTRODUCTION

The risk of groundwater contamination from agricultural herbicide use is ultimately determined by the relative rates of percolation and degradation within the soil profile, as well as by factors controlling these processes, such as climate, soil properties, microbial activity and chemical properties of the herbicides. Groundwater contamination is less likely to occur if the degradation rates of parent compounds and their metabolites exceed their percolation rates through the soil profile[1]. The task of accurately predicting pesticide movement in soil can be

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complicated by ***macropore*** or ***preferential flow*** herbicide transport, a term which describes several physical non-equilibrium flow processes [2]. In fine textured soils, large and discontinuous macropores caused by soil shrinkage cracks, earthworm channels or root holes act as preferential flow pathways and can cause rapid movement of chemicals through the unsaturated zone [3,4]. Preferential flow is not confined solely to heavy clay soils, although they represent the worst case. From dye trace experiments conducted at fourteen sites, Flury *et al.*[5] concluded that preferential flow was to be expected in most Swiss agricultural soils.

The phenomenon is critical for herbicide leaching and groundwater contamination, since significant amounts of herbicide may bypass the active topsoil layer [3,4,6]. The variable nature of these fissures and microchannels, in both size and length, makes it difficult to quantify and predict their contribution to groundwater contamination.

Quantitative field evaluation studies on the extent of preferential movement are quite scarce in literature. The use of lysimeters equipped with suction cups is considered the most adequate and appropriate modality of investigating herbicide leaching behaviour in field experiments[7].

The application of ^{14}C labelled herbicides to large undisturbed soil cores (monoliths) exposed to outdoor conditions may give information about the fate of the substances in question, as well as allowing all kinds of preferential flow [6] to be identified. Nevertheless, it has to be considered that there are some differences between the natural field situation and the lysimeter studies[7]. The monolith wall, for example, may prevent lateral dispersion and confine water and solutes within the defined soil core, while the operation related to the sampling may create cracks or macropores within the core. However, in several countries lysimeter studies form a substantial part of the pesticide registration procedure [7].

In this study the leaching and mobility capacity of an inorganic tracer (chloride ion) and of the herbicides linuron and monolinuron were studied under saturated water flow conditions in a field site equipped with suction lysimeters and tensiometers. The experimental field was located in a cereal crop tillage area where the underground profile permeability features were particularly favourable to herbicide migration toward the groundwater body. The vulnerability to groundwater contamination was enhanced by the existence of a shallow water table.

The temporal evolution of herbicide concentrations in the leachates collected from the installed suction cups was studied in order to allow the description of the breakthrough curves at different depths. Herbicide degradation was monitored by analysing their main transformation products (TPs), urea and aniline derivatives both in leachates and in the groundwater samples.

MATERIALS AND METHODS

Experimental site description and geo-pedological analyses

The experimental site is located in the eastern part of Lombardy plain in Treviglio (BG) near the Adda river. It pertains to the fundamental level of the Po plain with a deep substratum of sandy or gravel-sandy type occurring below a depth of 120–140 cm. The topsoil and the subsoil horizons are characterised by a loam texture class with 40–45% of silt and 10–20% of clay contents (Table I). Sand content increases with depth, so that below 2 m the amount of silt and clay is negligible. Soil pH values are similar at all the horizons analysed, while the organic carbon content is characterised by a decreasing trend from 2.7 % in the topsoil samples to 0.02 % in the deepest layers (Table I). An analogous decreasing trend is also observed for chloride content and cationic exchangeable capacity (CEC).

The water table level was monitored weekly, giving a minimum value of 5.85 m at the beginning of September and a maximum of 8.83 m in May. During the herbicide experiment (July-August) the aquifer level measured about 6 m.

The experimental plot

The experimental plot (20 m^2 area, a circular area 5 m in diameter) was laterally confined with a high density polythene sheet and equipped with Teflon (T) and/or ceramic (C) suction cup (0.5 L of capacity) pressure-vacuum lysimeters (Timco, U.S.A.). In the experiment the following lysimeters were installed: C30, T30, C60, T60, C80, T80, C90, T110 and C180. The first letter indicates the material type of the suction cups and the number the depth (cm) at which they were installed. All the Teflon lysimeters captured low water sample volumes during this experiment because of the low hydrophilicity of the Teflon with respect to ceramic material and, in particular, the T60 lysimeter did not allow for sufficient water sample suction in the lysimeter cup in order to be able to describe any breakthrough curves.

A borehole 13 cm in diameter was excavated for the installation of each suction cup lysimeter. A slurry of fine silica flour mixed with distilled water was poured into each borehole in order to establish a continuum between the lysimeter and the surrounding soil. The lysimeter body was centrally located within the borehole diameter and the silica slurry poured round the annular area of the unit. A bentonite seal was installed next, followed by a tamped backfield. A Millipore vacuum pump was used to establish a 15 kPa pressure in the cup lysimeter and allowed the collection of water samples. At the same depths as the lysimeters, manometer type tensiometers were also installed. A ceramic cup connected to a 2 mm plastic tube and a mercury manometer formed the tensiometers. In the present investigation the tensiometers were used to verify if the saturation condition of the different soil horizons was maintained throughout the experiments.

A 15 m depth well was excavated 2 m downstream from the experimental plot and a 10 cm PVC tube bored from 3 to 15 m was pushed into the borehole in order to collect surface groundwater samples. The groundwater samples were collected using a submergible electric pump (7.6 cm e.d. JS4/08; GEO-Impianti, Italy).

Tracer and herbicide application

Potassium chloride salt (at a concentration of 1.5 g/L for chloride ion) was used as a tracer to study the mobility of non-reactive compounds transported downward by water flow. The commercial ARESIN (Hoechst Schering AgrEvo, Germany; powder formulate) and SIOLCID SC products (SIAPA, Italy; aqueous suspension formulate) containing monolinuron (41.5 %) and linuron (37.6%) respectively was used in the experiment for the herbicide application. Linuron and monolinuron are pre-emergence herbicides, used at 1.5–7 kg active ingredient/ha for the control of weeds in maize, sunflower, and potato crops. The herbicide applied concentrations were: 31.7 mg/L for monolinuron and 29.3 mg/L for linuron. 600L of solutions containing salt and herbicides was applied in about 1 hour using a water reservoir and a PVC tube irrigation system installed on the experimental plot. The applied irrigation system, i.e. the herbicide application by soil submersion, is a commonly used agricultural practice in Italy.

During this experiment, conducted in 1998, a constant hydraulic head (3 cm max.), corresponding to 30–60 mm/day of rain, was established over the soil surface in order to reach saturation conditions. These features may actually occur in April-May period in the Lombardy region. The experimental condition was adopted in order to simulate the worst weather condition and the highest vulnerability risk for the aquifer. For water distribution, the experimental plot was equipped with a tube net for dripping water throughout the plot in a homogeneous mode. The water saturation condition in the top soil was controlled by the 30 cm tensiometer values (a tensiometer value of zero is equivalent to the water saturation condition) and therefore the amount of water added per day to the plot varied from 600 L/day to 1,200 L/day) according to the water content in the top soil horizon.

TABLE I Chemico-physical characteristics of Treviglio soil samples

	Undisturbed samples								*Disturbed samples*		
Horizons	Apl	Ap2/1	Ap2/2	BA	Btl	Bt2/1	Bt2/2	BCt	CB	C1	C2
Depth of sample (cm)	0–10	10–28	28–42	42–52	52–70	70–88	88–106	106–120	150	200	480
Org.Carb.(%)	27	1.3	1.1	0.6	0.6	0.4	0.3	0.2	0.3	0.1	0.0
Cl- (mg/kg)	15	12	12	12	12	9	9	8	14	9	n.d.
Gross sand	24	21	24	21	19	15	15	35	50	69	75
Fine sand	19	24	15	14	17	17	17	13	12	9	6
Gross silt	13	16	14	14	11	13	14	11	5	5	5
Fine silt	35	29	33	34	32	29	26	20	13	10	9
Clay	10	11	14	18	22	26	27	22	21	6	6
Texture class	loam	loam	loam	loam	loam	loam	clay loam	loam	clay sandy loam	sandy loam	sandy loam
pH	8.0	8.0	8.0	8.0	7.9	7.9	7.9	8.0	8.4	n.d.	n.d.
CEC (meq/100g)	20	16	14	13	13	12	11	10	7	3,91	4,14

TABLE II Recovery experiments of phenylureas and their main TPs with Lichrolut EN and water samples

Samples (vol.)	*Conc. (µg/L)*	*MFU*		*MCA*		*DFU*		*DMU*		*DCA*		*MON*		*LIN*	
		Mean	*CV (%)*	*Mean*	*CV (%)*	*Mean*	*CV (%)*	*Mean*	*CV (%)*	*Mean*	*CV (%)*	*Mean*	*CV (%)*	*Mean*	*CV (%)*
MilliQ (0.1 L)	10	95	2	47	19	93	2	93	1	69	13	89	2	87	3
Lysimeter sample (0.1L)	10	94	6	63	19	90	13	82	21	79	24	84	18	82	17
Sup. aquifer (0.1L)	10	92	8	68	20	89	11	96	4	81	8	78	10	92	9
Sup. aquifer (1L)	5	78	6	53	18	83	9	82	7	83	5	83	14	80	9
Deep aquifer (2 L)	0.5	106	6	71	18	107	8	106	3	94	10	109	14	113	5
Deep aquifer (2L)	0.1	108	8	66	11	114	6	115	5	76	27	109	8	108	11

Chemical analysis of water samples

Cl^- and K^+ concentrations were determined using a portable cuvette kit (Dr Lange, Germany); at the beginning of the experiment the Cl^- and K^+concentrations of the lysimeter samples and of the water used for the irrigation system were lower than the detection limit of the kits, 5 and 8 mg/L, respectively; Cl^- level in the groundwater sample collected by the surface well was close to 18 mg/l, while no potassium was detected. The Cl^-in the topsoil (Table I) was determined as 15 mg/g, while no potassium was detected.

The analyses of linuron (LIN), monolinuron (MON) and their TPs were conducted by concentrating water samples (a sample volume different in agreement at the expetcted concentrations) on 200 mg Lichrolut EN column (Merck, Germany). The TPs considered were: for linuron 1-(3,4-dichlorophenyl)-3-methylurea (DMU), 1-(3,4-dichlorophenyl)urea (DFU) and 3,4-dichloroaniline (DCA) and for monolinuron 1-(4-chlorophenyl)urea (MFU) and 4-chloroaniline (MCA). Alltech (USA) supplied the pure chemicals for quantitative herbicide analysis.

The analyses were conducted in HPLC Diode-Array 1050 (Hewlett Packard, USA) equipped with an automatic sampler and Lichrospher™ 5100 C18 column (HPLC Technology, Great Britain; 25 cm × 4.6 mm). The mobile phases were: t=0 min. water: acetonitrile 60:40 v/v; t=20 min. water: acetonitrile 25:75 v/v.

For quantitative analysis the external standard method involving a calibration curve obtained at a wavelength of 250 nm with 5 concentrations ranging from 0.25 to 10 mg/L was used.

In this condition the detection limits for 1 L water samples were 0.06 μg/L for DFU, DMU, LIN, MFU and MON and 0.1 μg/L for MCA and DCA.

Chemical analysis of soil samples

The soil was sampled by pushing a 120 cm iron tube (i.d. 5 cm) into the Treviglio soil profile. Soil sample cores were collected 1, 9, 28, 73 and 137 days after herbicide application and cut up in laboratory into seven sub-samples following the different soil horizons.

After collection, all soil samples were frozen in sealed dark glass bottles and stored at-20°C. For the determination of pesticide content the soil sample was defrosted and dehydrated under air conditions and laboratory temperature (20–22°C) for 96 hours. The water content of the air dried soil samples was determined by treating 10 g of soil in a stove at 105 °C for 24 h. The dry sample was sieved using a 2 mm sieve.

The extraction procedure was performed according to Guzzella *et al.* [8]. An amount of 10–50 g of air-dried sifted soil sample was treated with pesticide-free grade methanol (150 mL) in a Soxhlet extraction apparatus for 8 hours. The extract was then evaporated in Rotavapor in a water bath under light negative pressure conditions and at 40–45°C. The extract was then filtered on 0.45 μM membrane and evaporated in light N_2 flux to 0.1 mL. MilliQ water was added to make the methanol-water mixture obtained up to 1 mL in volume and the extract was analysed as for the water samples. In this condition the detection limits for 50 g soil samples were: 0.6 μg/kg for DFU, DMU, LIN, MFU and MON and 1 μg/kg for MCA and DCA.

RESULTS

Recovery experiment

MilliQ water, uncontaminated leachate water, surface and deep groundwater was used for the experiments. The results are shown in Table II as the mean of three different replicates. The phenylurea compounds and their TPs were recovered with yields of 80% and approaching 100% for deep groundwater samples.

The variation coefficients (VC) were 5% lower for MilliQ samples while for the other samples considered they were higher, especially for lysimeter samples (VC between 6 and 24%); in this case the matrix interference due to the high organic carbon content of the samples may have influenced the recovery efficiency results.

TABLE III Recovery experiments of phenylureas and their main TPs with Lichrolut EN and soil samples

Sample	*Surficial soil (0–30 cm)*				*Deep soil (60–80 cm)*			
Amount added (μg/kg)	*10*		*50*		*10*		*50*	
	Mean	CV	Mean	CV	Mean	CV	Mean	CV
MFU	64	15	75	12	60	39	49	18
MCA	44	48	22	10	46	24	53	25
DFU	47	12	73	23	70	40	45	24
DMU	72	14	73	17	73	17	76	7
DCA	33	19	37	31	36	65	88	7
MON	66	9	54	3	46	17	53	8
LIN	65	32	48	16	49	24	48	12

Chloroaniline metabolites showed significant lower recoveries than the urea derivatives with a minimum observed value of 47% for MCA while higher CV values were determined for this compounds, with a maximum value of 27% for DCA.

Other recovery experiments were undertaken with soil samples collected at Treviglio in an uncontaminated area at two different depths: 0–30 and 60–80 cm. The means of three replicates with the amount added (10 and 50 µg/kg) are reported in Table III. The mean recoveries of parental compounds and of urea derivatives are quite good (> 50%) while those of chloroanilines are the worst (values generally between 20 and 50%) as was found for the water samples.

Tensiometer behaviour and water regime

The measurements of the water regime were performed throughout the experiment. The matrix potential values showed that the water saturation of the topsoil horizon was already reached one hour after the herbicide application and was maintained without interruption during the first 3 days. On the following days a slight variation of the matrix potential occurred, probably because a quasi-constant hydraulic water head was applied to the experimental plot. The observed variations in the matrix potential were generally limited to the topsoil and less evident in soil horizons deeper than 30 cm.

Chloride and potassium concentrations

Chloride was used in both experiments as water tracer because this ion is not retained by the soil. Furthermore, the chloride concentrations measured in the top soil and lysimeter leachate samples before the beginning of the experiment were so low (18 mg/L for chloride and < 8 mg/L for potassium) with respect to the applied amount (1.5 g/L), that all likelihood of any artefact can be excluded.

The application of chloride ion to detect water transport is widely used in similar transport experiments [9]. Bromide salt was applied in some studies [10] as an alternative to chloride salt, but the use of chloride is often preferred in field experiments because it is more difficult to analyse bromide and to undertake measurements in the field.

In this experiment, the chloride transport to 30 and 80 cm (C30, T30, C80 and T80) (Figure 1) may have been influenced by preferential water flow, as is confirmed by the short time necessary for reaching the maximum peak concentration (4 – 6 hours) and by the high concentrations detected in the water samples (up to 65% of the initial Cl^- concentration). In the other lysimeters diffusive flow

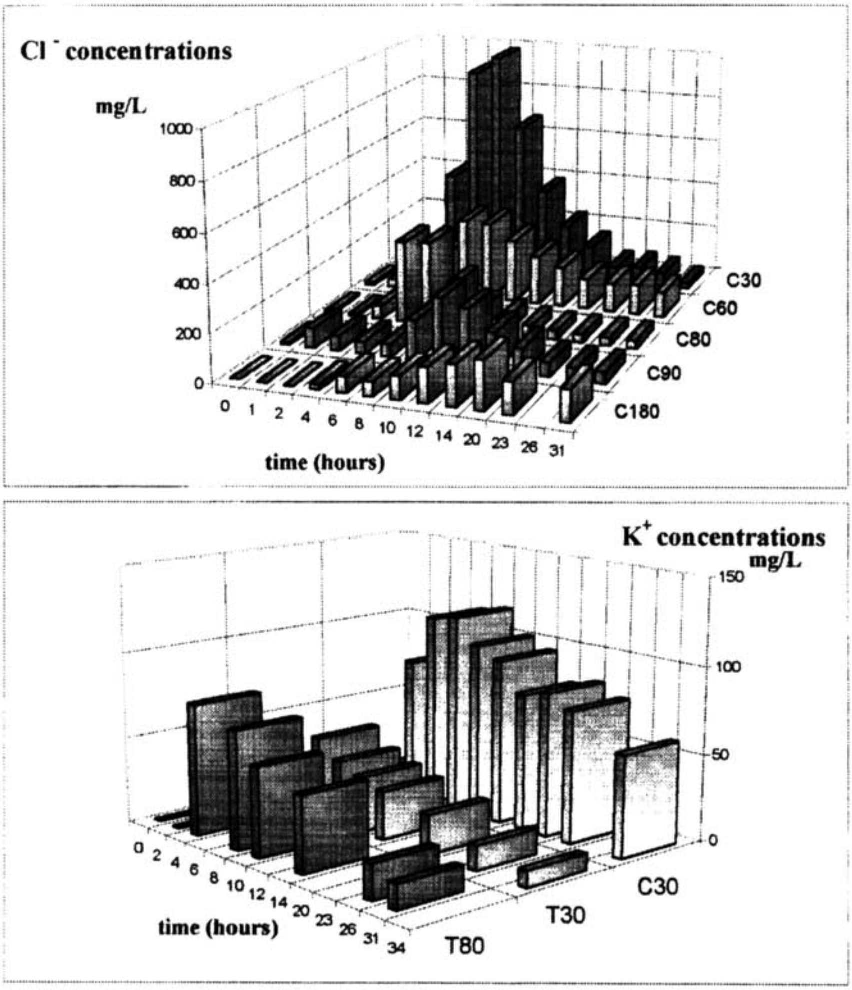


FIGURE 1 Chloride and potassium trend in the first days of the experiment in some lysimeters

appears to prevail, as is shown by a decreasing concentration trend with increasing soil depth (Figure 1) and by the longer time taken to reach the maximum concentration peak (20 hours to reach 110 cm). The lysimeters located at the same depth (for example, 30 and 80 cm) showed different chloride breakthrough curve behaviours (Figure 1) depending on the different transport mechanisms, preferential or matrix flow, and spatial heterogeneity in the soil profile.

The potassium cation showed a similar chloride trend but a significant adsorption to the soil matrix was observed, as is shown by the lower concentrations

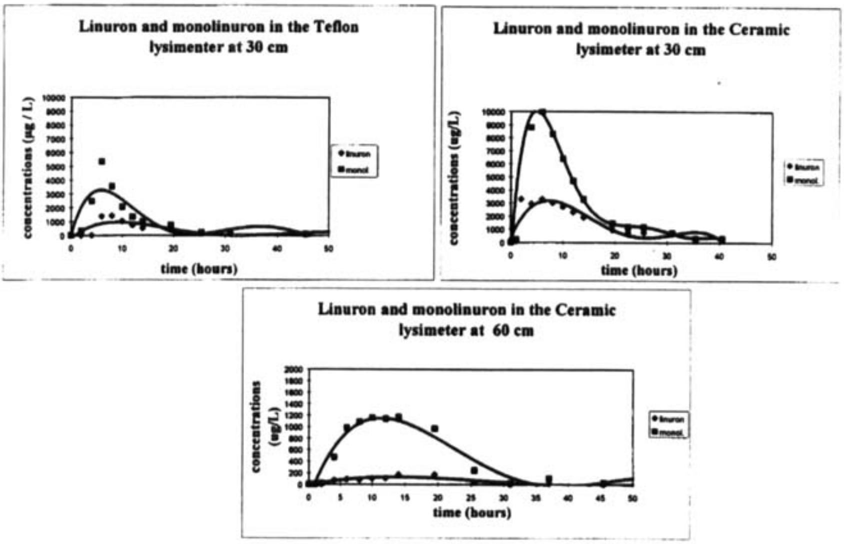


FIGURE 2 Herbicide breakthrough curves in lysimeters at 30 and 60 cm

(Figure 1). The potassium transport to T80 lysimeter seemed to be influenced by preferential water flow since it was detected in measurable amounts at 80 cm of depth, while it was absent in other lysimeters installed at the same depth (C80); different transport behaviours for lysimeters located at the same depth were displayed also by potassium.

No chloride or potassium concentration increase was measured in the water table after tracer application.

Herbicide breakthrough curves

In the experiment the herbicides tested were found to be partially retained by the soil, as is shown by the attenuated and delayed response in terms of leachate concentrations (Figures 2 and 3). The phenomenon is particularly evident for linuron, which is characterised by the highest value of K_{oc}(0.41–0.86 m^3/kg) and the lowest solubility (81 mg/L) in respect to monolinuron (0.18–0.5 m^3/kg of K_{oc} and 735 mg/L of solubility) [11]. The herbicide breakthrough curves (obtained from the curve trend by means of the interpolation of a 5° polynomial equation) of the lysimeters installed at 30 and 80 cm of depth showed a pattern similar to Cl^- (Figures 2 and 3). The lysimeters are characterised by very high herbicide concentrations compared with those measured in the other lysimeters and the time taken to reach peak concentration is equal to that of chloride, demonstrating that the herbicides were not adsorbed by the soil (Figure 4). The concentration curves showed very sharp peaks and the herbicide values increased and decreased in only a few hours, showing that preferential transport prevailed over matrix flow, i.e. the herbicides moved mainly via macropore transport with low interaction with the soil.

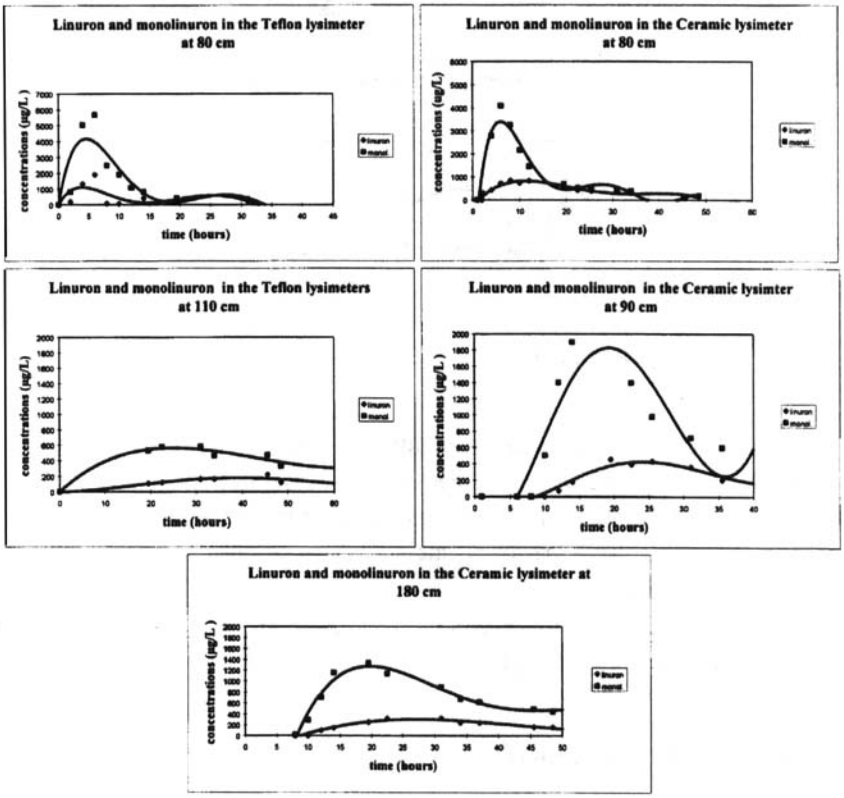
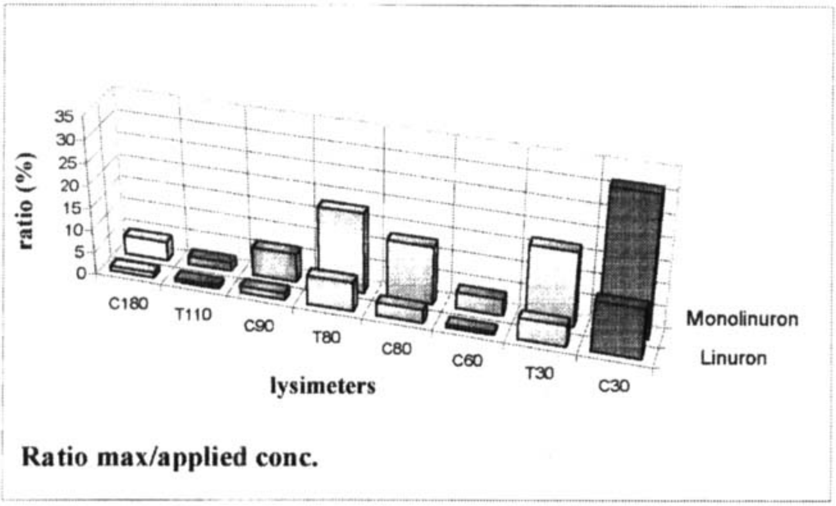


FIGURE 3 Herbicide breakthrough curves in lysimeters at 80, 90, 110 and 180 cm

Conversely, in the other lysimeters (C60, C90 and T110) the breakthrough curves were characterised by a typically large-base curve with a progressive slow attenuation of the peaks over time, probably due to a prevailing matrix flow. This phenomenon is particularly evident in the T110 lysimeter where the time taken by the herbicide to reach the maximum concentration value differs significantly from that of chloride; besides, the observed concentrations are very low compared with the amount of herbicide applied.



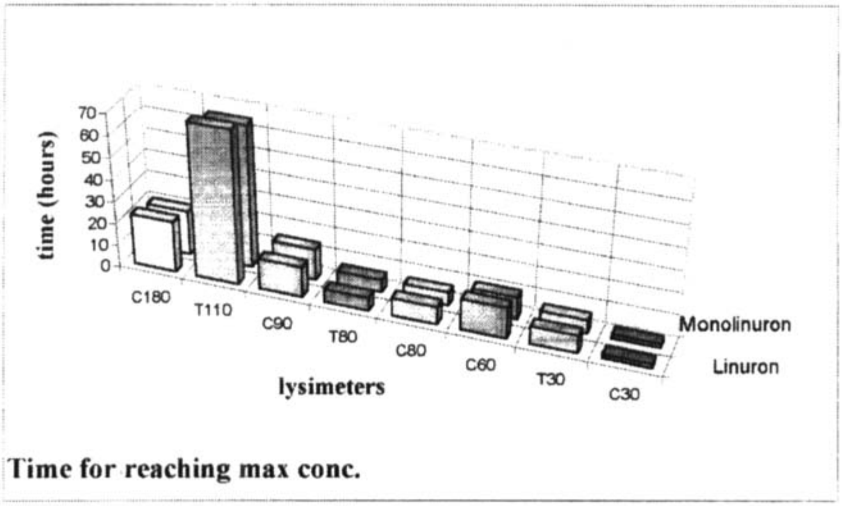


FIGURE 4 Time taken to reach the maximum concentration and ratio of maximum to applied concentrations of herbicides in the experiment

The herbicide concentrations measured in the C180 lysimeter are quite high with regard to its depth and the breakthrough curve were probably influenced by the preferential flow of the upper soil horizons.

No differences in herbicide recovery were noted between the Teflon (T) and ceramic (C) cups. Different transport mechanisms rather than the cup material could perhaps explain differences in the herbicide behaviour at the same depth (for example 30 and 80 cm).

No herbicide and TP peak concentrations were observed in the groundwater, probably because the elevated water dilution of the soil leachate in the superficial aquifer did not allow a detectable herbicide concentration of the groundwater samples to be reached.

Transformation product analysis in lysimeter samples

Urea herbicides gradually decompose over a medium period, usually no more than 2–3 months[11]; the steps and the rate of decomposition depend on the stability of the molecule and of the medium [12]. The herbicides applied to the soil surface are physicochemically decomposed by UV and by the acid and alkaline compounds of the soil, while soil micro-organisms undergo biological degradation. Microbial degradation proceeds stepwise to aryl ureas, which are decomposed into aryl amines (11). The microbial degradation of monolinuron and linuron follows a similar path: LIN⇒ DMU⇒ DFU⇒ DCA, while MON⇒ MMU⇒ MFU⇒ MCA. In both cases the aniline derivatives formed are the end products of microbial degradation (12).

In this experiment (Figure 5), the presence of the transformation products of linuron and monolinuron, with the exception of MMU (1-(4-chlorophenyl)-methylurea), which was not commercially available, was monitored in water samples collected from lysimeters located at depths of 30 and 80 cm.

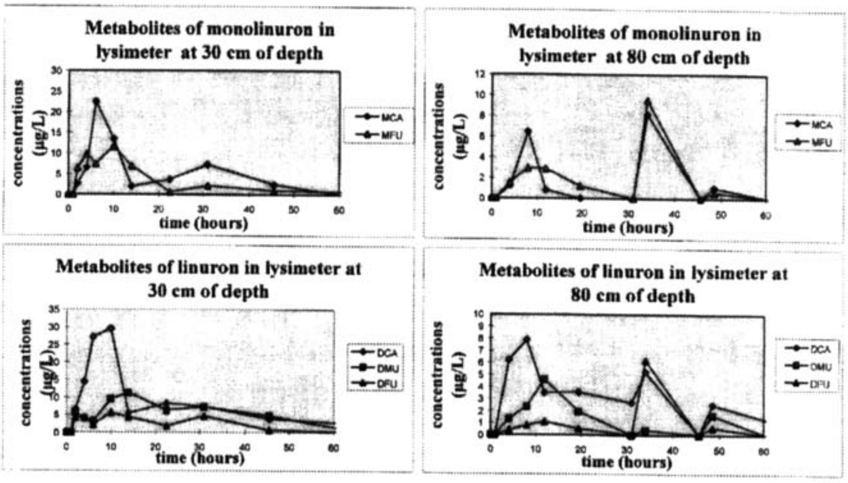


FIGURE 5 Transformation product concentrations in C30 and C80 lysimeters

All the tested TPs were determined in the lysimeter samples only a few hours after herbicide application, since these compounds are present in commercial products applied in quantities varying from 0.1 to 0.3% in respect to the parental compounds. The TPs trend showed in Figure 5 replicates the linuron and monolinuron breakthrough curves with an observed concentration peak 10 hours after herbicide application. This first TP peak value is to be attributed to metabolite transport. A second concentration peak of TPs was also observed 40 hours after herbicide application. This peak may be due to herbicide degradation processes; in fact, the peak is more evident for the 80 cm lysimeter, where the TPs accumulated by leaching from the upper soil horizons.

Herbicide concentration in soil profile

The results of the seven soil core profiles are reported in Figure 6. The first core sampled the first 30 cm of depth, because it represents the initial soil contamination, since it was collected during the first day after herbicide application. The results show that after 73 days the soil contamination was evidently reduced to less than 30 µg/kg for both herbicides, although linuron seemed to be retained by the top soil layer for longer than the monolinuron: its concentrations were higher than those of monolinuron seven days after application. Monolinuron seemed, on the contrary, a more strongly leaching herbicide; in fact, the monolinuron contamination affected deeper soil layers (10–60 cm soil samples).

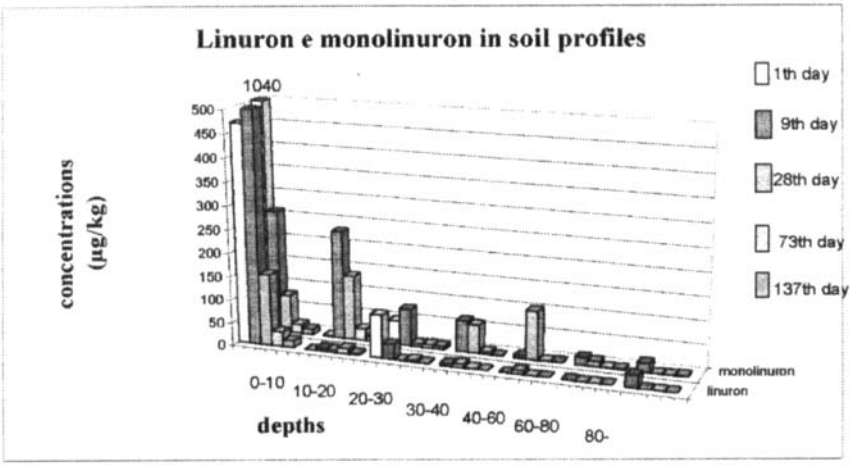


FIGURE 6 Herbicide concentrations in the different soil profiles

These observations are in agreement with the herbicide's physico-chemical characteristics. Matolcsy [12] confirmed that linuron and monolinuron have the same stability, although the latter is strongly adsorbed on the soil.

DISCUSSION AND CONCLUSIONS

In the present experiment, the lysimeters installed at depths of 30 and 80 cm showed similar breakthrough curves both for Cl^- and herbicides. The leaching of herbicides in the lysimeter samples started at the same time as chloride leaching, without displaying any chromatographic time delay. The occurrence of preferential flows may explain the increased herbicide mobility.

Conversely, the lysimeter and soil sample results showed that monolinuron is a more strongly leaching herbicide than linuron. Considering the environmental properties of these herbicides, the results obtained appear to be consistent with expectations. Monolinuron is much more mobile than linuron, because of its low K_{oc} and high solubility [11]; it is poorly adsorbed on soil and very soluble in water, thus it can be readily transported towards the deeper soil layers.

The low mobility of linuron was confirmed by other experiments in literature. Francaviglia *et al.* [10] demonstrated in similar lysimeter experiments that linuron is much less mobile than metolachlor; in fact, the presence of linuron was determined only in two lysimeters and at low concentrations. Vollner *et al.*[13] studied monolinuron behaviour with respect to diuron and terbuthylazine. Monolinuron was found to be more mobile than the other two herbicides.

Furthermore, by comparing these results with those of a previous similar experiment conducted in 1996/97 [14, 15] with metolachlor and terbuthylazine, linuron and monolinuron breakthrough curves were found to be similar to those determined for terbuthylazine and metolachlor, respectively. Terbuthylazine, as linuron in the present experiment, proved a less leaching compound than metolachlor.

To summarize the observed results, the herbicide concentrations determined in the top soil samples (0–10 cm) were elaborated as an exponential curve (Figure 7) by considering the entire experimental time (the first curve) and the last part of the experiment, from the 20th day to the end (the second curve). In the first curve, leaching prevailed over biodegradation because of the applied water saturation flow condition. In the second curve, due to the interruption on water addition and to the high temperature measured in July and August, biodegradation prevailed over leaching.

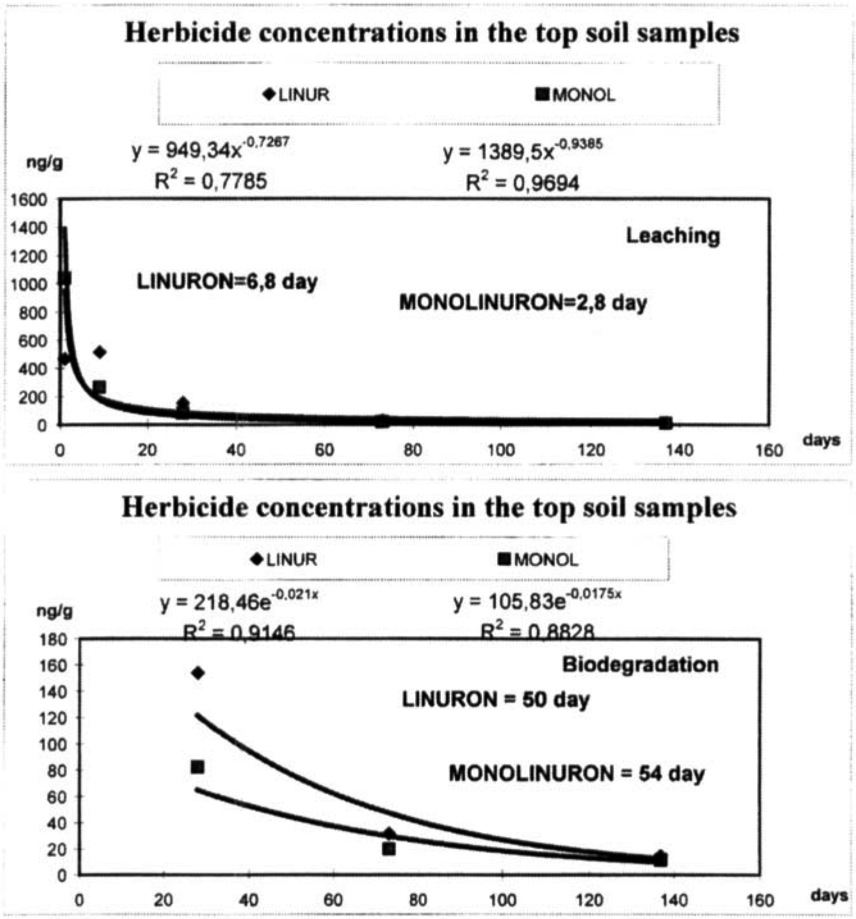


FIGURE 7 Leaching time value calculated on the basis of herbicide concentrations in the top soil samples in different experimental periods

The elaboration of the first curve allowed the calculation of a new proposed Aquifer Vulnerability Index: the Leaching Time (LT) (6.8 days for linuron and 2.8 days for monolinuron), i.e. the time necessary for a half-quantity reduction of the herbicide concentrations in the topsoil. Our hypothesis is that LT represents an indicative value of the herbicide mobility in field experiment in the worst weather condition (30–60 mm/day of rain). The higher the LT value, the lower the herbicide risk for the aquifer. The LT elaboration for the tested herbicides confirmed the greater mobility of monolinuron compared with linuron. The LT of linuron was actually the highest value among those actually elaborated [16], while the LT of monolinuron was equal to that of metolachlor (metolachlor = 2.8; alachlor = 3.5; terbuthylazine = 3.9).

Moreover, the LT values proved to be a first order function of the herbicide water solubility ($R^2 = 0{,}9267$) as shown in Figure 8. It should thus be possible in future to calculate LT values when only the water solubility of herbicides is known.

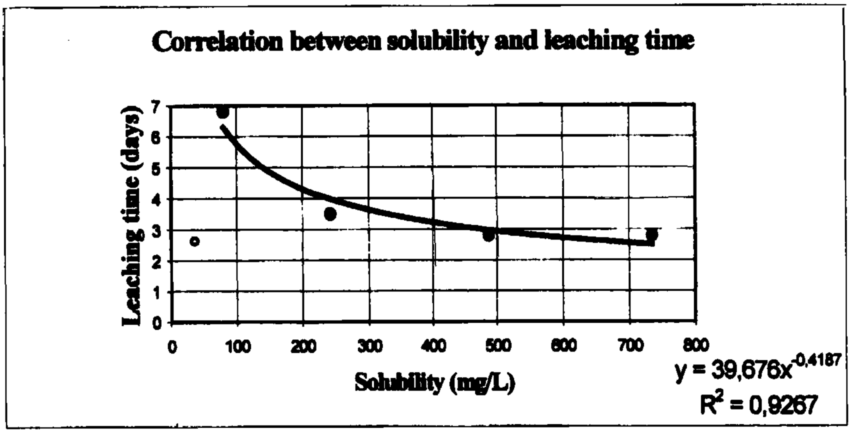


FIGURE 8 Correlation existing between herbicide solubility and leaching time calculated on the basis of our experiments

Among the LT values considered, that of terbuthylazine (empty dot) is located outside the curve (Figure 8); this may possibly be explained by the fact that terbuthylazine was applied in the experiment at a concentration higher than its solubility; therefore the terbuthylazine LT value may be underestimated owing to the transport of herbicide in an insoluble mode (i.e. through colloidal particle transport).

In the second part of the experiment, a second curve (Figure 7) was elaborated with an exponential tendency curve that allowed the calculation of the herbicide half time under field conditions (50 days for linuron and 54 days for monolinuron). The values obtained are indicative, because of the limited number of values considered (three data), but they are in agreement with the half-time values reported in literature for laboratory studies (38–75 days for linuron; 45–60 days for monolinuron) [10, 11, 17]and confirm the similar biodegradability of linuron and monolinuron in soil matrix.

In conclusion, the worst weather condition simulated in the experiment promoted the rapid downward transport and the leaching of the tested herbicides.

The spatial heterogeneity of the soil horizons was revealed by the difference in the time taken by herbicides to reach a depth of 1 m (20 – 50 hours). The possible presence of preferential flow transport was underlined by the fact that the start of leaching of herbicides in the lysimeter samples corresponded to the leaching of chloride, without reflecting any chromatographic time delay.

As expected from the herbicide's environmental properties, monolinuron behaved as a more strongly leaching herbicide than linuron. The Leaching Time calculated for linuron was higher than for terbuthylazine, alachlor, metolachlor and monolinuron, indicating that linuron takes much longer to reach the groundwater table.

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