



HAL
open science

Dissipation of pretilachlor in paddy water and sediment

Francesco Vidotto, Aldo Ferrero, Oriana Bertoia, Mara Gennari, Alessandro Cignetti

► **To cite this version:**

Francesco Vidotto, Aldo Ferrero, Oriana Bertoia, Mara Gennari, Alessandro Cignetti. Dissipation of pretilachlor in paddy water and sediment. *Agronomie*, 2004, 24 (8), pp.473-479. 10.1051/agro:2004043 . hal-00886233

HAL Id: hal-00886233

<https://hal.science/hal-00886233>

Submitted on 11 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Dissipation of pretilachlor in paddy water and sediment

Francesco VIDOTTO^{a*}, Aldo FERRERO^a, Oriana BERTOIA^a, Mara GENNARI^b, Alessandro CIGNETTI^c

^a Dipartimento di Agronomia, Selvicoltura e Gestione del Territorio, Università di Torino, Via Leonardo da Vinci, 44–10095 Grugliasco (TO), Italy

^b Dipartimento di Scienze agronomiche, Agrochimiche e delle Produzioni animali, Sezione di Scienze agrochimiche, Università di Catania, Via S. Sofia, 98–95123 Catania (CT), Italy

^c Dipartimento di Valorizzazione e Protezione delle Risorse Agroforestali, Settore di Chimica agraria, Università di Torino, Via Leonardo da Vinci, 44–10095 Grugliasco (TO), Italy

(Received 3 March 2004; accepted 28 May 2004)

Abstract – A two-year field study (2001–2002) was carried out in N-W Italy to study the behaviour of pretilachlor [2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide] in water and sediment of a rice field. Pretilachlor is a selective pre-emergence herbicide which is effective against annual grasses, sedges and broad-leaved weeds. The herbicide was applied in pre-seeding on a flooded rice field where water circulation was stopped for about 3 weeks after treatment. Pretilachlor concentration in the paddy water decreased by more than 90% during the first three weeks after the treatment. The amount of the herbicide in the paddy water gradually fell to levels below the sensitivity of the analytical method when water circulation was re-established. The pretilachlor concentration in the sediment gradually increased after the treatment, reaching the highest value 5 to 6 days later. The average DT_{50} in water and sediment were 6.77 and 28.76 days in 2001, 4.68 and 15.01 days in 2002, respectively. The low percolation rate (0.95 and 0.79 mm day⁻¹ in 2001 and 2002, respectively) and the high ratio of the herbicide adsorption on the sediment suggest that pretilachlor disappearance from the water was mainly the result of degradation.

rice / environmental fate

1. INTRODUCTION

Rice is cultivated in Europe in a total area of about 410 000 ha, most of which is in Italy (221 000 ha) and Spain (111 000) [5]. In all European countries rice is cultivated in permanent flooded conditions, with short periods during which soil is dried to favour rice rooting (in the early stages) or weed control treatments. The conventional irrigation system is also known as a “flow-through” system, because water is usually supplied in a series from the topmost to the bottommost basin and is regulated by floodgates by means of removable boards. Water circulation implies that effects of the herbicide application can also be observed in areas different from that of direct application. Moreover, paddy flooding favours the flow of solutes from the surface to the subsoil waters and may result in significant exchanges between these two aqueous bodies.

The extent to which water may contain residues of pesticide has become a public concern. Groundwater contamination has received increasing attention over the last few years as most of the drinking water is drawn from wells. Great activity in regulating the level of pesticide in water has been carried out in the European Union, in the last few years. The maximum allowable concentrations in ground waters (drinking and any other use) are set to 0.1 µg/L for any individual substance and 0.5 µg/L for total pesticide load. Following these regulations, the water authorities in Italy and all European Union countries are assess-

ing the extent to which pesticides are present in ground water. Under this investigation process, residues of several herbicides exceeding the allowed threshold have recently been found in Italy in ground water taken from wells, mainly located in the rice cultivation area. This has led to local restriction in the use of these pesticides [11].

Pretilachlor [2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide] is a chloroacetanilide herbicide which is widely used in transplanted and direct seeded rice (*Oryza sativa* L.) for the control of several grasses, broad-leaved weeds and sedges. Pretilachlor is used either as a pre-planting or post-emergence application. To improve its selectivity in post-emergence application, this herbicide is often mixed with the safener fenclorim. In Italy pre-seeding application has been authorised since 1998, primarily to control weedy rice (*Oryza sativa* L.) one of the most troublesome weeds of rice crops. Application of the product is currently performed when the paddy field is flooded. Afterwards the spraying water circulation is stopped for about 30 days, and a few days later rice is planted.

The application of pretilachlor at 1.5 kg a.i. ha⁻¹ is reported to have an average efficacy of 80–90% against weedy rice [5]. Few studies are available on pretilachlor's behaviour in the soil and water of the paddy fields.

According to Fajardo et al. [4], in the 0–1 cm soil layer of the paddy field, dissipation of pretilachlor was quite rapid during the first 3 weeks but slowed down thereafter, with a DT_{50}

* Corresponding author: francesco.vidotto@unito.it

Table I. Soil granulometry, pH and organic carbon content in the paddy.

Layer (cm)	Clay (%)	Fine silt (%)	Coarse silt (%)	Fine sand (%)	Coarse sand (%)	Gravel (%)	pH (1:10 H ₂ O)	Organic carbon (%) K ₂ Cr ₂ O ₇ oxidation
0–20	8.4	24.4	11.8	31.1	24.4	5.58	5.5	1.3
20–40	7.5	23.3	11.5	31.5	26.1	11.70	6.1	1.0
40–60	6.0	19.0	7.0	31.1	37.0	43.32	6.4	1.1

ranging from 7 to 10 days. The herbicide was shown to leach to deeper layers (5–10 cm) within the first two weeks after the treatment and to quickly disappear afterwards. In the same study, the DT₅₀ of pretilachlor in paddy water was about 3.5 days. Kotula-Syka et al. [9] demonstrated that pretilachlor degradation is promoted by microorganism activity, as they observed a lower ¹⁴CO₂ evolution in sterilised compared with non-sterilised soils.

Balasubramanian et al. [3] found pretilachlor residues in rice plants when the herbicide was applied as a pre-planting treatment for two years in the same soil. Pretilachlor residues ranged between 36.2 and 29.6 µg kg⁻¹ in rice straw and 2.7 and 2.4 µg kg⁻¹ in rice grain. In soil samples, taken after harvest in the 0–15 cm deep layer, pretilachlor residues ranged between 292.0 and 220.0 µg kg⁻¹.

In a laboratory microcosm, Flori et al. [7] found that, 10 days after the treatment, 57.0% of the initially applied pretilachlor was still present in the surface water and 20.5% in the soil surface (0–2 cm). These amounts remained almost constant until 30 days after the treatment, showing that no degradation occurred in that time. Small amounts of pretilachlor (1.9–7.2%) were detected in deeper soil layers (2–25 cm).

Braschi et al. [3] reported a strong adsorption of pretilachlor both on sediment and dissolved organic matter (DOM). They also observed that the desorption from the sediment was highly hysteretic, suggesting a strong interaction between the herbicide and the sediment organic matter. An FT-IR analysis of pretilachlor-sediment complex revealed that a hydrophobic binding mechanism was involved in pretilachlor adsorption.

The purpose of this study was to investigate the behaviour of pretilachlor in paddy water and sediment of a rice field in which pretilachlor was applied as a pre-seeding treatment to control weedy rice.

2. MATERIALS AND METHODS

2.1. Experimental site and sampling

The experiments were carried out in 2001 and 2002 on a 35-ha study area located in the northern part of the East Sesia irrigation zone (municipality of Barengo; 45°33'30"N, 8°31'15"E). This area is part of the Po Valley and surrounded by the Po, Ticino and Sesia rivers and the prealpine foothills.

The choice of this area was justified by the need to fulfil two main requirements. First, the area is highly representative of the agronomic practices usually applied in the Italian rice-growing system. In particular, in this area the crop is grown from seeding to about 30 days before harvest in continuous flooding condi-

tions with only a few short periods (about 2–3 days each) in which water is temporarily removed from the field to promote crop establishment or allow herbicide treatment. Most of the paddy fields are connected in a flow-through system, in which water is supplied from the topmost to the bottommost field. The second reason is that the study area is located in a peripheral strip of the North-Italian rice growing area in which it is reasonable to exclude the presence of rice herbicides in the water bodies, since no other rice paddies are present uphill of this area. The 20-yr mean annual rainfall and temperature for the study area are 850.9 mm and 9.9 °C, respectively. A more detailed description of the study area is reported in a previous study carried out in the same site to evaluate the environmental behaviour of the herbicide cinosulfuron [6–11].

The fate of pretilachlor was studied in a test paddy located in the central part of the study area. The surface of the test paddy was 2.16 ha (90 × 240 m) and extended from W to E. The field was the last of a series of four connected fields and received water from the uphill paddy fields. It was fitted with water inlet and outlet floodgates set in prefabricated concrete housing and placed opposite each other near the western end of the field. As reported in Table I the 0–20 cm soil layer of the test paddy was sandy loam, with pH of 5.5 and 1.3% organic carbon.

Pretilachlor was applied over the total surface of the study area, including the test paddy and the uphill fields, at 1125 g a.i. ha⁻¹, as the commercial herbicide Rifit (pretilachlor at 500 g L⁻¹; Syngenta) with a rear-mounted boom sprayer equipped with flat-fan nozzles. The treatment was carried out with forward speed of 1.8 m/s, a pressure of 250 Kpa and application volume of 200 L ha⁻¹. The test paddy was flooded 6 days before treatment. During the treatment the water level in the test paddy was 12 and 9 cm in 2001 and 2002, respectively. The treatment was done on 5 April, in both 2001 and 2002. After the treatment, the inlet and outlet floodgates were kept closed for a period of time (CAT, closure after treatment), in order to prevent water circulation. The CAT had a duration of 23 days in 2001 and 18 days in 2002.

Cinosulfuron (60 g a.i. ha⁻¹), propanil (4000 g a.i. ha⁻¹), quinclorac (500 g a.i. ha⁻¹), and triclopyr (500 g a.i. ha⁻¹) were sprayed in the entire study area in both years in order to control weeds different from weedy rice such as sedges (Cyperaceae family), barnyard grass [*Echinochloa crus-galli* (L) P. Beauv] and mudplantain (*Heteranthera reniformis* Ruiz et Pavon). A standard Class A pan evaporimeter was used to determine the amount of water evaporated daily from the field during the CAT period. For this period, it is reasonable to approximate that the actual evapotranspiration of the field was equal to the pan evaporation, as the field surface was actually made up of free water and the crop stand was absent. In order to improve adherence between the pan evaporation data and actual field evaporation,

the evaporimeter was placed on a slatted wooden frame within the test paddy. Records of the water level in the evaporimeter and test paddy, as well as rainfall data, were collected daily during this period. These data were used to calculate the average daily water percolation during the CAT period, by averaging the results of the following equation:

$$Perc_{n \rightarrow n+1} = (PW_n - PW_{n+1} - R_{n \rightarrow n+1}) - (PE_n - PE_{n+1} - R_{n \rightarrow n+1}) \quad (1)$$

where $Perc_{n \rightarrow n+1}$ is the percolation (in mm) occurring from day n to day $n+1$, PW and PE are the water level (mm) in the paddy field and in the pan evaporimeter, respectively. $R_{n \rightarrow n+1}$ is the rain (mm) occurring in the same period and affecting in the same way both PW and PE .

In the test paddy two 1-L subsamples of water were taken in the eastern, central and western parts of the paddy before and immediately after the treatment and 2, 8, 15, 21, 29, 36, 44, 57 and 74 days after treatment (DAT) in 2001 and 1, 5, 7, 14, 21, 31, 45, 56, 73 and 84 DAT in 2002. On each sampling date, paddy water was taken from the top 5-cm layer by directly filling 1-L flasks. Two subsamples of the sediment of approximately 1.8 kg were taken in the eastern, central and western parts of the test paddy before and immediately after the treatment, and at 2, 6, 29, 36, 44, 57, 85 and 110 DAT in 2001 and at 1, 5, 14, 31, 45, 56, 73 and 84 DAT in 2002. The sediments were manually collected by using a stainless steel shovel shaped to take the top 1 cm of soil. Both water and sediment samples were collected in LD_PE flasks and immediately stored at -20°C until they were analysed. Previous tests showed that pretilachlor adsorption on the used flasks is negligible and that storage at -20°C is appropriate (data not reported).

2.2. Sample analysis

The extraction of pretilachlor residues from each water sample was performed by liquid/liquid partition with dichloromethane starting from 100 mL of water. This was done three times with 50 mL of dichloromethane. The organic phase was collected in a vacuum flask and dried with a rotary evaporator at 30°C . The residue was taken up with 2 mL of hexane and analysed by gas-chromatography.

Extraction of pretilachlor from the sediment was carried out on water-saturated samples. The excess water was drawn off with a pipette and then with blotting paper. The samples then had an average of 50% (v/v) water. Extraction was done on 20 g of sediment by adding 20 g of Extrelut[®] (Merck) and 100 ml of extraction mixture (5% v/v methanol in dichloromethane). The suspension was transferred to 250-mL screw-top Sovirel bottles and shaken mechanically for 30 min. Following decantation of the suspended material phase, the liquid phase was transferred to a vacuum flask. The solid phase underwent two other extraction operations, each with 75 mL of the extraction mixture and 15 min of shaking. The combined liquid extracts were dried with a rotary evaporator. The residue was taken up with 2 mL of hexane then purified on a silica column (LC-18) and eluted with 2 ml of methanol.

Analytical determination was carried out with a Perkin Elmer 8500 gas chromatograph equipped with a medium polar capillary

column, J and W Scientific (30 m length, 0.33 mm int.dia. with 0.25 μm fused silica film), and an ECD detector on a dual channel (310°C) with nitrogen as a make-up gas. Helium was used as the carrier gas at a flow rate of about $1\text{--}2\text{ mL min}^{-1}$. The oven temperature was programmed to stay for 10 min at 200°C and then increased from 200 to 245°C (at a rate of $30^\circ\text{C min}^{-1}$) during the course of each injection analysis. The injector temperature (PTV) was set to 280°C ; the detector to 310°C . Recovery of pretilachlor was $95\% \pm 3$ from water and $81\% \pm 5$ from sediments. The limits of detection (LOD) were $0.1\text{ }\mu\text{g L}^{-1}$ for water and $0.2\text{ }\mu\text{g kg}^{-1}$ for sediment.

2.3. Data analysis

The data of pretilachlor concentration in paddy water were fitted to the following exponential decay model:

$$y = ae^{(-b\text{DAT})} \quad (2)$$

where y is the pretilachlor concentration and DAT represents the number of days after the treatment. The parameter a was correspondent to the highest concentration, recorded immediately after the treatment (DAT = 0). In the sediment, an increase in pretilachlor concentration was observed in the first 6 (2001) and 5 (2002) DAT. Afterwards, the concentration fell progressively, showing a behaviour similar to that observed in paddy water. For this reason, the data of pretilachlor concentration in the sediment were fitted to two distinct exponential models. The following exponential growth model was used to describe the pretilachlor concentration dynamics in the sediment during the first 6 (2001) or 5 (2002) DAT:

$$y = ae^{(b\text{DAT})} \quad (3)$$

where a was correspondent to the concentration recorded immediately after the treatment (DAT = 0).

For the subsequent values, the following exponential decay model was adopted:

$$y = ae^{(-b\text{DAP})} \quad (4)$$

where DAP (days after peak) is the number of days after the reaching of the maximum concentration in the sediment (occurred at 6 and 5 DAT, in 2001 and 2002, respectively). Regression analysis was conducted using the Sigma Plot analysis version 6.00 (2000) statistical software. The estimated time required for 50% and 90% of pretilachlor disappearance (DT_{50} and DT_{90} , respectively) was calculated from the regression equations.

3. RESULTS AND DISCUSSION

3.1. Pretilachlor in paddy water

No pretilachlor was present in the paddy water before treatment, in 2001 or 2002. Samples taken immediately after the treatment gave a mean content of $936\text{ }\mu\text{g L}^{-1}$ in 2001 and $1233\text{ }\mu\text{g L}^{-1}$ in 2002. In 2001 the maximum concentration of the herbicide in the water was recorded the same day as the treatment in the western and central part (984 and $1063\text{ }\mu\text{g L}^{-1}$, respectively) of the test paddy, while, in the eastern part, the

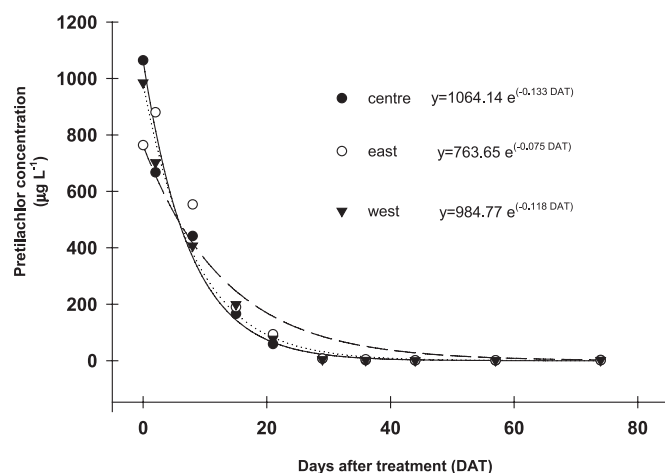


Figure 1. Pretilachlor concentration ($\mu\text{g L}^{-1}$) in paddy water in 2001. Solid, dashed and dotted lines refer to fitted regressions of central, eastern and western data, respectively.

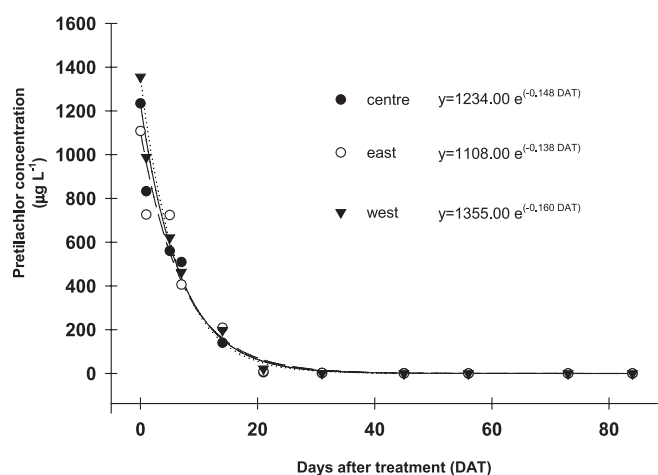


Figure 2. Pretilachlor concentration ($\mu\text{g L}^{-1}$) in paddy water in 2002. Solid, dashed and dotted lines refer to fitted regressions of central, eastern and western data, respectively.

maximum value was reached 2 DAT ($880 \mu\text{g L}^{-1}$). In 2002 the highest content of pretilachlor was detected just after the treatment in all parts of the paddy and ranged from $1108 \mu\text{g L}^{-1}$ at the eastern point, to $1234 \mu\text{g L}^{-1}$ in the centre and $1355 \mu\text{g L}^{-1}$ in the west. In both years the concentration fell by about 90% during the first 3 weeks, while the inlet and outlet floodgates were kept closed. When the water circulation was re-established, the pretilachlor content continued to decrease and was no longer detectable 44 DAT and 45 DAT in 2001 and 2002, respectively.

The dissipation of pretilachlor in the paddy water in 2001–02 was described by a first-order kinetic model (Figs. 1, 2). The regressions describing pretilachlor dissipation in the different positions of the test paddy (east, centre and west) were similar in both years. The calculated DT_{50} ranged from 9.22 days (centre, 2001) to 4.32 days (west, 2002) (Tab. II). With the exception of the eastern position in 2001, the DT_{50} were very similar between positions and years. These DT_{50} values are in agreement with the DT values reported by Fajardo et al. [4] in paddy water. The CAT periods (23 days in 2001 and 18 days in 2002) were roughly correspondent to the time required for a 90% disappearance of pretilachlor (DT_{90}). The calculated DT_{90} ranged from 17.32 (centre) to 30.59 (east) days in 2001 and from 14.36 (west) to 16.70 (east) days in 2002.

In an experiment carried out in laboratory conditions using a microcosm, Flori et al. [7] obtained different results, reporting a 43% dissipation of pretilachlor in water in the first 10 days after the application and no further dissipation during the following 20 days. They observed that 20.5% of the herbicide that was not recovered in water was found in the sediment.

3.2. Pretilachlor in paddy sediment

No pretilachlor residues were found in the paddy sediment before treatment, in 2001 or 2002. In opposition to the results obtained for the paddy water, an increase in herbicide concentration was observed during the first few days after the treatment. This increase was significantly different between the two

years. With respect to the values recorded immediately after the treatment, the pretilachlor concentration increased, on average, 1.5 times in two days in 2001 and 4.4 times in only one day in 2002. The increase in concentration in the sediment during the first few days after the treatment suggests that an adsorption process occurs, which is in agreement with the observations reported by Braschi et al. [3]. This behaviour was observed in both years and it is in agreement with the results of a previous study carried out in the same site with the herbicide cinosulfuron [6].

The highest mean concentrations were recorded at 6 DAT ($171 \mu\text{g kg}^{-1}$) and 5 DAT ($556 \mu\text{g kg}^{-1}$) in 2001 and 2002, respectively. As the $1/n$ value of the Freundlich equation obtained by Braschi et al. [3] for pretilachlor adsorption on the same sediment is close to 1, it is possible to use the K_f value (15.66) of the same equation to calculate the amount of the herbicide that was adsorbed on the sediment and that was present in the sediment water solution. On the basis of this computation, only 6.25% of the herbicide remained in the sediment water solution and could be prone to leaching.

After reaching a peak, concentration of the herbicide fell progressively to $1\text{--}3 \mu\text{g kg}^{-1}$ at 110 DAT in 2001 and below the limit of detection at 84 DAT in 2002. For the sediment data also, in both years, the regression models adopted gave a good fit with the pattern of pretilachlor dissipation (Figs. 3, 4).

Table II. Calculated mean time required for 50% and 90% pretilachlor disappearance (DT_{50} and DT_{90} , respectively) in paddy water (days after the treatment).

Position	2001		2002	
	DT_{50}	DT_{90}	DT_{50}	DT_{90}
Centre	5.22	17.32	4.68	15.56
East	9.22	30.59	5.03	16.70
West	5.86	19.45	4.32	14.36
Mean	6.77	22.45	4.68	15.54

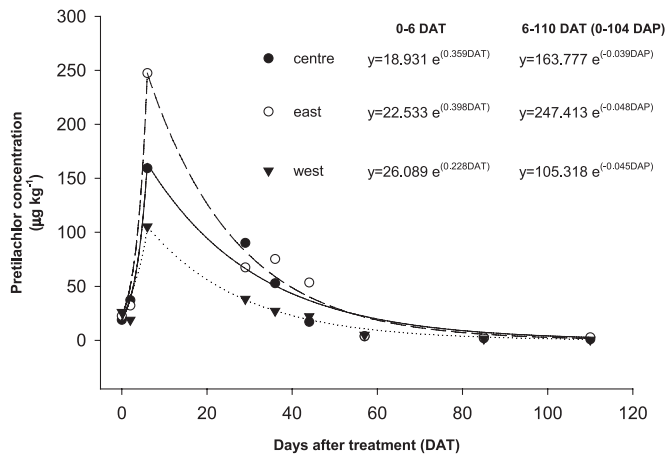


Figure 3. Pretilachlor concentration ($\mu\text{g kg}^{-1}$) in soil sediment in 2001. Solid, dashed and dotted lines refer to fitted regressions of central, eastern and western data, respectively. DAP (days after peak) is the number of days after the sampling in which the highest concentration was found.

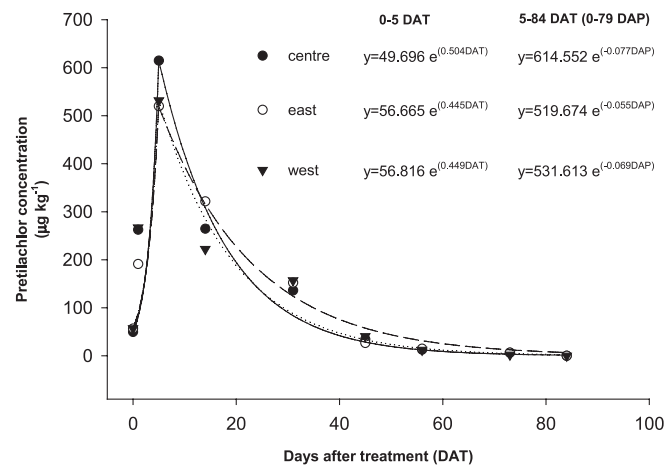


Figure 4. Pretilachlor concentration ($\mu\text{g kg}^{-1}$) in soil sediment in 2002. Solid, dashed and dotted lines refer to fitted regressions of central, eastern and western data, respectively. DAP (days after peak) is the number of days after the sampling in which the highest concentration was found.

The higher rate of increase of pretilachlor concentration recorded immediately after the treatment in 2002 also resulted in a faster disappearance of the herbicide after the peak. The DT_{50} values calculated from the day of pretilachlor application ranged from 25.32 to 30.76 days in 2001 (correspondent to 19.32 and 24.76 days after the sampling date in which the highest concentration was recorded), and from 14.64 to 15.24 days in 2002 (9.64 and 10.24 days after reaching the highest concentration). The calculated DT_{90} ranged from 37.42 to 51.57 days in 2001 (31.41 and 45.57 days after reaching the highest concentration) and from 25.18 to 26.24 days in 2002 (20.18 and 21.24 days after reaching the highest concentration; Tab. III).

Table III. Calculated mean time required for 50 and 90% pretilachlor disappearance (DT_{50} and DT_{90} , respectively) in paddy sediment (days after the treatment). The value correspondent to 100% is the highest concentration recorded in each position, which occurred at 6 and 5 DAT in 2001 and 2002, respectively.

Position	2001*		2002**	
	DT_{50}	DT_{90}	DT_{50}	DT_{90}
Centre	25.32	37.42	14.64	26.20
East	30.19	51.57	15.24	26.24
West	30.76	44.35	15.15	25.18
Mean	28.76	44.45	15.01	25.87

*, **: values are calculated starting from the equations $y = ae^{(-b \text{ DAP})}$ reported in Figures 3, 4, and adding 6 (2001) or 5 (2002) days.

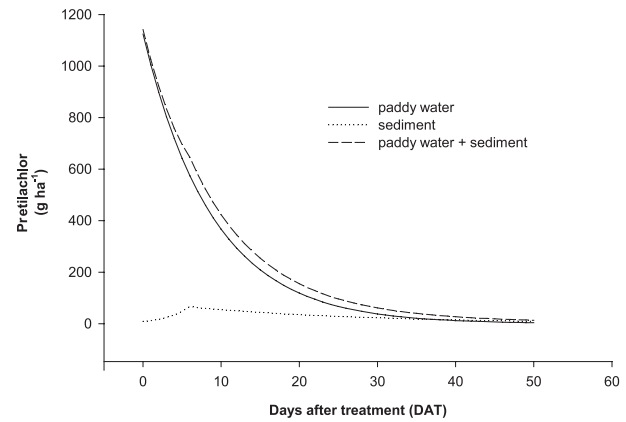


Figure 5. Estimated absolute pretilachlor amount in paddy water (solid line), sediment (top 22 mm, dotted line) and paddy water + sediment (dashed line) in 2001 experiment. Calculations are made on the basis of the estimated disappearance regressions in paddy water and sediment.

3.3. Water percolation and pretilachlor degradation

The average evaporation recorded during the CAT period was 3.38 and 4.29 mm day^{-1} in 2001 and 2002, respectively. The correspondent water level reduction in the test paddy was 4.33 and 5.08 mm day^{-1} , respectively. These values lead to an estimated water percolation of about 0.95 and 0.79 mm day^{-1} for 2001 and 2002, respectively, which are within the range reported in literature (0.2–15.6 mm day^{-1}) for similar conditions [8, 10, 12, 13]. The thickness of the soil layer involved in vertical water movement during CAT was estimated for each year by multiplying the daily water percolation by the duration of CAT. According to this calculation, total vertical water movement during CAT was 22 mm and 14 mm in 2001 and 2002, respectively. The reduction of pretilachlor concentration in paddy water during the CAT period was the result of the combination of degradation and adsorption, as no dilution from flowing water could occur.

Pretilachlor degradation was determined by estimating the daily herbicide absolute amount present in the paddy water and in the topsoil layer of the paddy field (Figs. 5, 6). The absolute

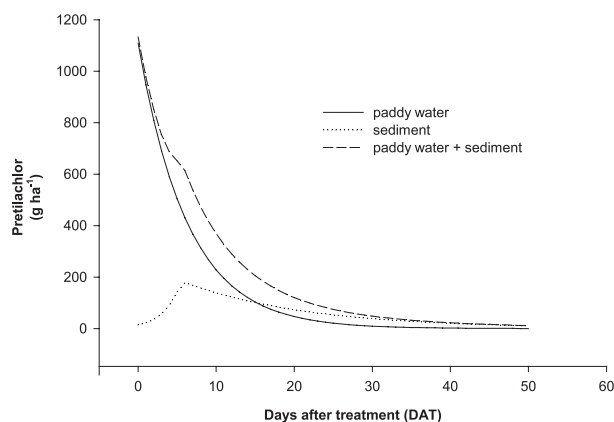


Figure 6. Estimated absolute pretilachlor amount in paddy water (solid line), sediment (top 14 mm, dotted line) and paddy water + sediment (dashed line) in 2002 experiment. Calculations are made on the basis of the estimated disappearance regressions in paddy water and sediment.

amount of pretilachlor present in the water was calculated by multiplying the herbicide concentration (in $\mu\text{g L}^{-1}$) estimated daily using the decay regression model [1] (averaging the concentration values recorded in central, eastern and western positions) by the flooding water volume per hectare, measured in the rice field. According to this calculation the amount of pretilachlor present in the water just before the floodgate opening was 95 and 75 g ha^{-1} in 2001 and 2002, respectively, which represents about 8.4 and 6.7% of the herbicide sprayed on the paddy field.

In the case of soil, it was assumed that in the CAT period pretilachlor could be found only in the soil layer involved in vertical water movement. The absolute amount of pretilachlor present in this layer was calculated by multiplying the herbicide concentration (in $\mu\text{g kg}^{-1}$) estimated daily using equations (3, 4) (averaging the concentration values recorded in central, eastern and western positions) by the weight per hectare of the soil layer. It was assumed that soil bulk density was 1800 kg m^{-3} and that herbicide concentration in the considered layer (22 mm and 14 mm in 2001 and 2002, respectively) was the same as that found in the 1-cm top layer, in which samplings and analyses were actually carried out. According to these assumptions, the actual content of pretilachlor in the soil was most likely overestimated for the CAT period.

The results of these calculations show that pretilachlor content estimated in the soil ranged from 67 and 143 g ha^{-1} at 6 and 5 DAT in 2001 and 2002, respectively, to 32 and 89 g ha^{-1} (in 2001 and 2002, respectively) before the floodgate opening. Before the opening of the floodgates the total absolute amount of pretilachlor per hectare (water and sediment) was 128 and 165 g ha^{-1} in 2001 and 2002, respectively, corresponding to about 11.4% and 14.7% of the herbicide sprayed in the paddy field, respectively. On the basis of these results, pretilachlor disappearance from paddy water is believed to be mainly the result of degradation.

4. CONCLUSIONS

In the present study the behaviour of the herbicide pretilachlor in paddy water and sediment was investigated in field conditions. The concentration of pretilachlor in the paddy water decreased by more than 90% in the first 22.45 (2001) and 15.54 (2002) days after the treatment, during which the inlet and outlet floodgates were kept closed. The reduction of pretilachlor concentration was satisfactorily described by an exponential decay model. According to the literature, pretilachlor disappearance in field conditions is most likely attributable to degradation due to microbial activity [9]. Hydrolysis could play only a negligible role in degradation, as the molecule is relatively stable, the calculated DT_{50} in laboratory conditions being higher than 200 days in the range of pH from 1 to 9 [2]. A vapour pressure of 0.133 mPa and Henry's constant of $8.1 \times 10^{-4} \text{ Pa m}^3 \text{ mol}^{-1}$ indicate that volatilisation cannot be considered a main process in field dissipation of pretilachlor. No information is available from the literature about the effect of light on degradation of this herbicide.

In the specific experimental conditions, leaching of pretilachlor can be considered of limited importance, mainly because of the marked tendency of this herbicide to be adsorbed by the soil, and the low water percolation rate. It is anyway likely that similar results could be obtained even in conditions of higher percolation. Considering the highest values of water percolation reported in the literature (15.6 mm day^{-1}), in the first 20 days after the treatment, during which about 90% of degradation occurs, pretilachlor could reach the maximum depth of 31.2 cm.

Acknowledgements: This study was carried out within the framework of the Italian national project MIUR 2001–2002 “Herbicide Fate in Paddy Rice”. The authors are grateful to the Cerri brothers for allowing them to conduct the field study in their farm, Dr. Luca Barbero, Dr. Roberto Busi and Dr. Franco Tesio for their technical assistance and two anonymous referees for useful comments on the manuscript. The paper is attributable in equal parts to the authors.

REFERENCES

- [1] Balasubramanian R., Veerabadrán V., Kannathasan M., Influence of continuous use of herbicides in rice based system on residue accumulation and on performance of succeeding pulse crop, *Pest. Res. J.* 11 (1999) 200–203.
- [2] BCPC, The pesticide manual, XIth ed., C.D.S. Tomlin (Ed.), The British Crop Protection Council, Farnham, Surrey GU9 7PH, UK, 1997.
- [3] Braschi I., Pusino A., Gessa C., Adsorption-desorption of pretilachlor and cinosulfuron on paddy field sediment, in: *Proceedings of the XII Symposium Pesticide Chemistry*, Piacenza, Italy, 2003, pp. 161–167.
- [4] Fajardo F.F., Takagi K., Ishizaka M., Usui K., Pattern and rate of dissipation of pretilachlor and mefenacet in plow layer and paddy water under lowland field conditions: a three-year study, *J. Pestic. Sci.* 25 (2000) 94–100.
- [5] Ferrero A., Vidotto F., Biology and control of red rice (*Oryza sativa* L. var. *sylvatica*) infesting Italian rice fields, in: Hill J.E., Hardy B. (Eds.), 2002. *Proceedings 2nd Temperate Rice Conference*, International Rice Research Institute, Los Baños, Philippines, 2002, pp. 523–533.

- [6] Ferrero A., Vidotto F., Gennari M., Nègre M., Behavior of cinosulfuron in paddy surface waters, sediments, and groundwater, *J. Environ. Qual.* 30 (2001) 131–140.
- [7] Flori P., Pancaldi D., Braschi I., Gessa C., Behavior of four herbicides in a paddy field: simulation by a laboratory microcosm, in: *Proceedings of the XII Symposium Pesticide Chemistry*, Piacenza, 2003, pp. 223–232.
- [8] IRRI, *Soils & Rice*, IRRI, Los Baños, Philippines, 1978.
- [9] Kotoula-Syka E., Hatzios K.K., Berry D.F., Wilson H.P., Degradation of acetanilide herbicides in history and nonhistory soils from eastern Virginia, *Weed Technol.* 11 (1997) 403–409.
- [10] Luppi G., Finassi A., Riso (*Oryza* spp.), in: Pàtron (Ed.), *Coltivazioni erbacee*, Pàtron, 1981, pp. 219–268.
- [11] Miao Z., Cheplick M.J., Williams M.W., Trevisan M., Padovani L., Gennari M., Ferrero A., Vidotto F., Capri E., Simulating pesticide leaching and runoff in rice paddies with the RICEWQ-VAD-OFT model, *J. Environ. Qual.* 32 (2003) 2189–2199.
- [12] Mikkelsen, D.S., De Datta S.K., Rice culture, in: Bor S. Luh. (Ed.), *Rice. Vol. I – Production*, 2nd ed., Van Nostrand Reinhold, New York, 1981, pp. 103–186.
- [13] Yoshida S., *Fundamentals of rice crop science*, IRRI, Los Baños, Philippines, 1981.