

Water and sediment dynamics of penoxsulam and molinate in paddy fields: field and lysimeter studies

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Abstract

BACKGROUND: In Chile, rice is cultivated under water-seeded and continuously flooded conditions. Because herbicide dynamics in paddy fields and non-flooded fields is different, 3 year experiments were performed to study the dissipation of molinate and penoxsulam in water and sediment.

RESULTS: In field experiments, both herbicides dissipated by 45–55% from the initial applied amounts during the first 6 h after application in all crop seasons; in lysimeter experiments, dissipation amounts were approximately 10% for penoxsulam and 16% for molinate. Penoxsulam field water DT₅₀ values varied from 1.28 to 1.96 days during the three study seasons, and DT₉₀ values from 4.07 to 6.22 days. Molinate field water DT₅₀ values varied from 0.89 to 1.73 days, and DT₉₀ values from 2.82 to 5.48 days. Sediment residues were determined 2 days after herbicide application into the paddy water, and maximum concentrations were found 4–8 days after application. In sediment, DT₅₀ values varied from 20.20 to 27.66 days for penoxsulam and from 15.02 to 29.83 days for molinate.

CONCLUSIONS: Results showed that penoxsulam and molinate losses under paddy conditions are dissipated rapidly from the water and then dissipate slowly from the sediment. Penoxsulam and molinate field water dissipation was facilitated by paddy water motion created by the wind. Sediment adsorption and degradation are considered to have a secondary effect on the dissipation of both herbicides in paddy fields.

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Keywords: dissipation; adsorption; desorption; herbicides

1 INTRODUCTION

In Chile, rice is cultivated under water-seeded and continuously flooded conditions. Unfortunately, most of the rice fields are not levelled properly, and water management facilitates the establishment of weeds that develop rapidly during initial rice growth. Under these conditions, aquatic weeds find a favourable habitat to compete with rice plants. The most troublesome aquatic weeds are water plantain (*Alisma plantago-aquatica*), small flower umbrella dode (*Cyperus difformis*), rice field bulrush (*Schoenoplectus mucronatus*) and barnyard grass (*Echinochloa* spp.). Weed interference in water-seeded and continuously flooded rice fields occurs mostly during the first 30–45 days after seeding.¹ If weeds are not controlled during the critical period, yields of Chilean rice are normally reduced by 40–60%.² The development of weed resistance to ALS-inhibitor herbicides in Chile has increased the number of herbicide applications per crop season.² Thus, environmental chemical load and the potential risk of contamination have increased recently.

In Chile, water contamination from herbicide use has not been an important issue; in other countries, however, it is a matter of permanent discussion.^{3–6} Some pesticides can be harmful to aquatic organisms, and contamination of drainage channels and creeks by pesticides used in rice production remains a concern in countries such as Australia.⁷

Because paddy fields function differently to non-flooded crop fields, research into herbicide dynamics is necessary to preserve water resources. Herbicide persistence in paddy fields is a potential risk for aquatic pollution through surface water flow and soil herbicide leaching.⁸ This is an important issue in Chile because the rice production area is irrigated principally with water from only two river basins.

Molinate has been used in paddy fields as a grass control herbicide for the past 30 years. Early studies indicated that the level of molinate reaching underground water would be negligible and generally eliminated by microbiota and plant metabolism.⁹ However, recent studies have shown the presence of trace amounts of molinate in surface and groundwater in California, Australia, Japan, Greece, Spain and Portugal.^{10–13} Penoxsulam is a relatively new, commercially introduced ALS-inhibitor herbicide recommended for the control of a broad spectrum of weeds in flooded rice fields. Chemically, it belongs to the triazolopyrimidine-sulfonamide group, and no long-term field environmental dynamic studies have been performed. Because the functions of herbicide dynamics are different between paddy

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Table 1. Physicochemical properties of soil

| Soil (cm) | pH | CEC (meq 100 g ⁻¹) | Inorganic soil phase | | | Organic soil phase | |
|-----------|------|--------------------------------|----------------------|-------|-------|--------------------|----------------|
| | | | Sand | Clay | Loam | Organic matter | Organic carbon |
| | | | % | | | | |
| 0–15 | 5.81 | 21.16 | 34.20 | 34.40 | 31.40 | 2.09 | 1.14 |
| 15–30 | 6.22 | 19.1 | 29.2 | 36.20 | 34.6 | 1.28 | 0.86 |
| 30–45 | 7.52 | 43.1 | 13.9 | 66.20 | 19.9 | 0.95 | 0.55 |
| 45–60 | 8.12 | 41.7 | 21.9 | 60.20 | 17.9 | 0.80 | 0.46 |

Table 2. Physicochemical properties of herbicides (adapted from IUPAC Agrochemicals Database)²⁹

| Herbicide | Water solubility (mg L ⁻¹) | Vapour pressure (mPa) | Henry constant (Pa m ³ mol ⁻¹) | logK _{ow} | pK _a | Aqueous photolysis (days) | Aqueous hydrolysis (days) |
|------------|--|--------------------------|---|--------------------|-----------------|---------------------------|---------------------------|
| Penoxsulam | 408 | 2.49 × 10 ⁻¹¹ | 2.94 × 10 ⁻¹⁴ | -0.602 | 5.1 | 2 | Stable |
| Molinate | 1100 | 500 | 3.5 × 10 ⁻⁵ | 2.86 | N/A | Stable | 365 |

N/A: not applicable.

fields and non-flooded crop fields, 3 year field and lysimeter experiments were performed to study the dynamics and principal dissipation mechanisms of molinate and penoxsulam in water and sediments.

2 MATERIALS AND METHODS

2.1 Field study conditions and herbicide treatments

During the rice-growing seasons of 2007, 2008 and 2009, field studies were performed at the main paddy fields in the VI region of Chile (36° 08' S, 71° 52' W). After spring tillage, the experimental plots were built and flooded to a depth of approximately 12 cm. Individual plots were surrounded by 45 cm high, 40 cm wide levees. Rice seed (cv. Diamante) was presoaked for 48 h, allowed to dry for 24 h and then broadcast into the water over the plots (140 kg ha⁻¹). Soil physicochemical characteristics are presented in Table 1.

Penoxsulam (Ricer[®]) and molinate (Molirox[®]) herbicides were applied at their commercial rates, equivalent to 50.4 and 4890 g AI ha⁻¹ respectively. Herbicides were applied with a manual backpack sprayer (15 L) equipped with four antidrift nozzles (Albuz-Ari 11 001), covering a 2.5 m swath and spraying at 300 kPa to deliver 140 L ha⁻¹. The main characteristics of the herbicides are presented in Table 2.

After herbicide applications (12 days after seeding), water on the plots was maintained without flow, and water was added to compensate for losses from evaporation to retain the initial 12 cm water layer. Water that entered the experimental area was permanently monitored using an automatic water sampler (ISCO Model 6712) to detect any possible herbicide contamination from other sources.

2.2 Lysimeter studies

After spring tillage and before the experimental plots were built, six soil cores (0.6 m height, 0.22 m diameter) were removed intact from the experimental area. Soil core lysimeters were collected using a PVC cylinder with a 0.22 m internal diameter, 1.0 m height and 4 mm wall thickness. The PVC cylinders were inserted into steel

tubes with a cutting edge, and the tubes were driven vertically into the ground. The PVC lysimeters were removed, and a steel base cap with glass wool was secured to the base of each PVC soil core. The middle of the steel base cap was threaded and sealed to a 1 m PVC pipe (20 mm diameter) filled with glass wool, forming a continuum with the glass wool base cap. Leachates were collected in a plastic flask screwed to the bottom of each PVC pipe. Microinfiltrometers with non-reactive ceramic caps were installed in the lysimeters at the 30 cm soil depth to collect soil water samples to detect any herbicide lixiviation.

As in the field studies, the PVC lysimeters were maintained flooded with a water depth of 12 cm, and no flow was allowed. The herbicides were applied to the water at the same rate as that used in the field studies. A micropipette was used to deliver 1 mL of herbicide solution into each lysimeter (three for each herbicide). The applied solutions contained 0.19 mg mL⁻¹ of penoxsulam and 17.04 mg mL⁻¹ of molinate.

2.3 Herbicide dissipation in water and sediments

Water samples were obtained from each experimental plot and lysimeter 0, 1, 2, 4 and 6 h after herbicide applications. In addition, water and sediment samples were collected 2, 4, 8, 16, 32 and 72 days after applications. Sediment samples were collected at a depth of 10 cm using an 8 cm diameter PVC cylinder. Sediment samples were collected from the lysimeters using a 2 cm plastic cylinder. All samples were stored in the dark at 4 °C, frozen for 1 h and transferred to the laboratory, where they were maintained at -22 °C ± 2 °C until analysis.

2.4 Herbicide analysis

2.4.1 Sediment

Penoxsulam was extracted from 10 g of sediment with 10 mL of acetonitrile-HCl 1 N (90:10 v/v) (acetonitrile: LiChrosolv, Merck; HCl Pa analysis, Merck). The mixture was shaken for 1 h at 180 rpm, and the suspension was centrifuged at 3500 rpm. This procedure was repeated twice. The supernatants were combined, filtered and concentrated to dryness in a rotary evaporator, and then

resuspended with HCl 0.1 N, filtered through a Uniflo nylon filter (Whatman 13/02 nylon) and quantified by HPLC-UV.

Molinate was extracted from 10 g of sediment with 1 mL of water (LiChrosolv, Merck) and 10 mL of acetonitrile. The mixture was shaken for 30 min and centrifuged at 3500 rpm. This procedure was repeated 3 times. A 3 mL sample was removed from the combined extracts and added to 3 mL of *n*-hexane (LiChrosolv, Merck). This mixture was shaken for 30 min at 500 rpm, and the organic phase was separated and used for quantification by GC-MS.

2.4.2 Water

Penoxsulam was extracted from water samples using solid-phase extraction columns (Bakerbond SPE Octadecyl C-18, 5 mg/6 mL). The C-18 columns were conditioned with methanol (2 mL) and water (2 mL) (LiChrosolv, Merck). The water samples (500 mL) were passed through the SPE C-18 at a flow rate of 1 mL min⁻¹, and penoxsulam was eluted from the SPE column with two washes of 1 mL of acetonitrile to perform HPLC-UV analysis.

Molinate water samples were partitioned with dichloromethane (LiChrosolv, Merck). Water samples (250 mL) were transferred into 500 mL separation funnels with 10 mL of NaCl-saturated solution and 30 mL of dichloromethane. The mixtures were shaken for 20 s and placed in a support to separate the organic phase. The organic phase from each sample was collected and partitioned again with 30 mL of dichloromethane, and the general procedure was repeated again. The two organic phases were combined and concentrated at 1 µL in a rotary evaporator, resuspended in 1 mL of ethyl acetate (LiChrosolv, Merck) and quantified by GC-MS.

2.4.3 Chromatography conditions

The HPLC unit (Hitachi LaChrom Elite Model L-2300) was equipped with a LiChrospher 100 RP-18 (5 µm) column (125 mm length). The liquid phase used was ammonium acetate (80%)–acetonitrile (20%). The column temperature was 30 °C, and the flow rate was 1 mL min⁻¹. Injection volume was 20 µL, and the UV detector (Hitachi LaChrom Elite Model L-2450) was set at 230 nm.

The GC (Shimadzu Model GC-2010) was equipped with a 30 m capillary column RTX-5 MS (0.25 mm/0.25 µm). The oven conditions were 90 °C (1 min), 25 °C min⁻¹ – 160 °C – 25 °C min⁻¹ – 290 °C (1 min). The helium flow was 1 mL min⁻¹, and the injection volume was 1 µL. The MS (Shimadzu GCMS-QP2010 Plus) was set in the SIM mode with selected *m/z* of 126, 55 and 41.

Penoxsulam recoveries from sediment and water samples were 81 and 90% respectively, with a retention time of 2.03 min and quantification limits of 1.439 µg L⁻¹ for sediment and 0.227 µg L⁻¹ for water. Molinate recovery from sediment and water was 81%, with a retention time of 8.617 min and quantification limits of 4.977 µg L⁻¹ for sediment and 0.202 µg L⁻¹ for water. Sediment and water samples, laboratory blanks and spiked and no-herbicide soil samples were included.

2.5 Statistical analysis

Herbicide dissipation in water and sediment was fitted to an exponential model [equation (1)] using non-linear regression analysis PROC NLIN (SAS[®]) defined for the following equations:

$$C = C_0 \times \exp(-k_1 \times t) \quad (1)$$

$$DT_{50} = \frac{\ln(2)}{k_1} \quad (2)$$

where *C* (mg kg⁻¹) is the herbicide concentration at time *t* (days), *C*₀ (mg kg⁻¹) is the initial water or sediment herbicide concentration and *k*₁ (day⁻¹) determines the decline of the curve. The goodness of fit of the model was calculated according to Schabenberger.¹⁴ The DT₅₀ values were estimated using equation (2).

3 RESULTS AND DISCUSSION

Both herbicides dissipated quickly from paddy water. In the first 6 h after application, 45–55% of the initial applied amount was dissipated. This result was similar for all crop seasons, without significant differences between them (Table 3). Contrary to expectations, there was no effect of water and air temperature during the volatilisation process,⁹ because water and air temperatures during the crop-growing seasons of 2007 and 2009 were approximately 5 °C below that recorded during the 2008 crop-growing season, but herbicide losses from the water were almost the same (Table 3).

In contrast, lysimeter study results showed that no more than 19% of either herbicide was dissipated during the first 6 h after herbicide application (Table 4). Dissipation rates between herbicides and seasons in the lysimeter studies did not show significant differences and, similarly to the field studies, did not

Table 3. Water DT₅₀ and DT₉₀ for penoxsulam and molinate under field and lysimeter conditions

| Herbicide | Parameter | Season | | | | | |
|------------|--|--------------|---------------|--------------|---------------|--------------|---------------|
| | | 2007 | | 2008 | | 2009 | |
| | | Field | Lysimeter | Field | Lysimeter | Field | Lysimeter |
| Penoxsulam | <i>k</i> ₁ (1 day ⁻¹) | 0.41 (±0.03) | 0.04 (±0.002) | 0.35 (±0.02) | 0.09 (±0.01) | 0.54 (±0.04) | 0.06 (±0.004) |
| | DT ₅₀ ^a | 1.68 (±0.01) | 17.89 (±0.92) | 1.96 (±0.11) | 6.97 (±0.48) | 1.28 (±0.11) | 11.54 (±0.71) |
| | DT ₉₀ ^b | 5.32 (±0.04) | 56.73 (±2.93) | 6.22 (±0.33) | 22.08 (±1.51) | 4.07 (±0.32) | 36.59 (±2.22) |
| | <i>R</i> ² | 0.97 | 0.98 | 0.98 | 0.98 | 0.97 | 0.98 |
| Molinate | <i>k</i> ₁ (1 day ⁻¹) | 0.51 (±0.03) | 0.16 (±0.01) | 0.41 (±0.04) | 0.3 (±0.02) | 0.78 (±0.06) | 0.173 (±0.01) |
| | DT ₅₀ ^a | 1.36 (±0.08) | 4.46 (±0.32) | 1.73 (±0.16) | 2.31 (±0.16) | 0.89 (±0.06) | 4.02 (±0.24) |
| | DT ₉₀ ^b | 4.31 (±0.26) | 14.13 (±1.0) | 5.48 (±0.49) | 7.32 (±0.51) | 2.82 (±0.21) | 12.73 (±0.76) |
| | <i>R</i> ² | 0.98 | 0.98 | 0.95 | 0.98 | 0.98 | 0.98 |

^a Time (days) to 50% herbicide dissipation: DT₅₀ = ln(2)/*k*₁.

^b Time (days) to 90% herbicide dissipation: DT₉₀ = ln(9)/*k*₁.

Table 4. Sediment DT₅₀ and DT₉₀ for penoxsulam and molinate under field and lysimeter conditions

| Herbicide | Parameter | Season | | | | | |
|------------|-------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | | 2007 | | 2008 | | 2009 | |
| | | Field | Lysimeter | Field | Lysimeter | Field | Lysimeter |
| Penoxsulam | k_1 (1 day ⁻¹) | 0.04 (±0.01) | 0.03 (±0.01) | 0.03 (±0.01) | 0.03 (±0.01) | 0.03 (±0.01) | 0.04 (±0.02) |
| | DT ₅₀ ^a | 20.20 (±3.51) | 27.32 (±8.46) | 22.32 (±8.39) | 21.48 (±5.52) | 27.66 (±6.56) | 18.00 (±7.41) |
| | DT ₉₀ ^b | 64.05 (±11.14) | 86.60 (±26.82) | 70.75 (±26.59) | 68.08 (±17.51) | 87.68 (±20.78) | 57.06 (±23.48) |
| | R ² | 0.81 | 0.68 | 0.54 | 0.78 | 0.70 | 0.61 |
| Molinate | k_1 (1 day ⁻¹) | 0.06 (±0.03) | 0.03 (±0.01) | 0.04 (±0.02) | 0.04 (±0.01) | 0.03 (±0.01) | 0.05 (±0.02) |
| | DT ₅₀ ^a | 15.02 (±7.95) | 24.42 (±8.19) | 16.98 (±6.47) | 18.2 (±6.03) | 29.83 (±15.43) | 18.26 (±9.52) |
| | DT ₉₀ ^b | 47.61 (±25.21) | 77.41 (±25.96) | 53.83 (±20.5) | 57.68 (±19.13) | 94.57 (±49.08) | 57.89 (±30.17) |
| | R ² | 0.45 | 0.63 | 0.54 | 0.70 | 0.50 | 0.78 |

^a Time (days) to 50% herbicide dissipation: $DT_{50} = \ln(2)/k_1$.

^b Time (days) to 90% herbicide dissipation: $DT_{90} = \ln(9)/k_1$.

show any relation to air and/or water temperature during the first 6 h.

Penoxsulam is recognised as a non-volatile compound (Table 2); however, the present field results showed that penoxsulam losses from the paddy water were as large and as rapid as molinate losses during the first 6 h after application. Jabush and Tjeerdema¹⁵ did not find significant production of volatile degradation products from the total initial mass applied (less than 0.01%). However, values of field DT₅₀ and DT₉₀ in water were smaller than those reported previously.^{16,17} Other authors^{9,18,19} report that molinate volatilisation represented 75–85% of the total losses from water, and photolysis and adsorption represented less than 20%. Results from this study are in agreement with those in the literature, with molinate water dissipation values closer to the reported ones and DT₅₀ values between 1 and 10 days.^{20–24}

Both herbicides are highly stable in water (Table 2), and only penoxsulam can be degraded significantly by photolysis.¹⁵ However, these authors indicated that, in glass tube experiments, the principal metabolite of penoxsulam photolysis reached a maximum level after 28 h; the tubes were maintained in distilled water at 29 °C for 15 days and were continuously irradiated with simulated solar light (252 W m⁻²). In the present field and lysimeter studies, air and water temperature during the first 6 h after herbicide applications did not reach more than 26 °C, and solar irradiation was approximately 220 and 240 W m⁻² in the field and lysimeter studies, respectively, and lasted for only 6 h (between 12:00 and 6:00 p.m.) each year. Thus, photolysis degradation alone cannot explain the rapid loss of penoxsulam from the paddy fields.

The field study area is normally windy; therefore, wind conditions could have accounted for the enhanced volatilisation. According to Crosby,²⁵ temperature is not the only factor that can affect the rate of volatilisation. Wind speed and, consequently, water motion can also affect herbicide volatilisation in rice paddies. In the lysimeter experiments, with no water motion and no air circulation, the herbicide molecule concentration gradient between air and water diminished and resulted in a low rate of net mass transfer.²⁶ This result could explain why the losses of both herbicides from water in the lysimeter studies 6 h after application were only 29% of the losses from water in the field studies.

The field water dissipation rates for penoxsulam and molinate in 2009 were higher than those in 2007 and 2008, and water temperatures did not affect the dissipation process; paddy water temperature during 2007 was cooler than in 2008 and 2009, showing an average 18.3 ± 2.3 °C during the study time (October to March of each year). However, the differences in dissipation rates and DT₅₀ were not significant; the half-life variation between 2009 (major dissipation rate) and 2008 (smaller dissipation rate) was only 0.4 days (9.6 h) for penoxsulam and 1.25 days for molinate. Similarly, no differences in DT₅₀ and DT₉₀ in the sediment were observed between the two herbicides during any season (Table 4).

Conversely, in the lysimeter experiments, DT₅₀ and DT₉₀ values for penoxsulam in water were 3–10 times higher than the values determined in the field experiments. These differences were smaller, only 1.3–4-fold, for molinate (Table 4). As with the field experiments, the daily average water temperature in the lysimeter experiments did not significantly affect the dissipation process (average 18.5 ± 2.2 °C during October to March of each year).

No herbicide residues were determined in the sediment at the beginning of each study season. Sediment herbicide dynamics followed a similar pattern for penoxsulam and molinate; herbicides were determined in the sediment from the second day after application, reaching the maximum amount 4–8 days after application, and then decayed from the eighth day to the end of the study period. The maximum amount of herbicides found in the sediment, expressed as a percentage of the total herbicide mass applied, was lower in the field experiments (penoxsulam, $8.5 \pm 2.3\%$; molinate, $8.7 \pm 2.5\%$) than in the lysimeter experiments (penoxsulam, $16.2 \pm 2.4\%$; molinate, $27.9 \pm 6.1\%$). These results can be explained principally because of the rapid water dissipation produced in the field experiments.

In flooded fields, anaerobic degradation processes are expected to dominate the microbial transformation.²⁶ Jabusch and Tjeerdema²⁷ found DT₅₀ values for penoxsulam in freshly collected soils from 5.2 to 12.8 days; these values are lower than the values determined in the present study. However, sediment pH in this study was 5.81 (Table 1) and is probably one of the factors that can favour a low reductive potential in the sediment, resulting in a low microbiological degradation rate.²⁷

However, molinate sediment dissipation parameters (DT₅₀ and DT₉₀) in the present study were similar to previously reported

values,^{18,28} possibly because molinate sediment degradation is more closely related to macrobiotic and plant metabolism.²³

Contrary to other studies,^{12,13,18} no herbicide leaching was detected at a soil depth of 30 or 60 cm. Park *et al.*¹⁸ worked with ¹⁴C-molinate and found ¹⁴C residues at a soil depth of 60 cm; however, soil organic matter and clay contents are higher in Parral soils.

4 CONCLUSIONS

Results obtained during 3 years of field and lysimeter studies for penoxsulam and molinate applied to paddy fields showed that herbicides dissipated rapidly from the water and then slowly from the sediment. Dissipation of penoxsulam in water could be the result of photolysis and volatilisation and could be facilitated by paddy water motion caused by wind. However, in the field experiments, volatilisation was the principal phenomenon that explained molinate dissipation. Sediment adsorption and degradation would have a secondary effect on dissipation of both herbicides in paddy fields.

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