

# Metamitron and Chloridazon Dissipation in a Silty Clay Loam Soil†

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The dissipation of chloridazon in a silty clay loam soil under laboratory and field conditions was similar to that of metamitron, and they were both affected by temperature and soil moisture. The  $t_{1/2}$  of chloridazon, at 22% soil moisture, decreased from 76 to 14 days with temperature increase from 10 to 30 °C; the  $t_{1/2}$  of metamitron, in the same conditions, decreased from 40 to 7.5 days. At 10 °C the effects of an increase in soil moisture from 15 to 29% were larger on chloridazon degradation, with  $t_{1/2}$  decreasing from 134 to 41 days; the  $t_{1/2}$  of metamitron decreased from 46 to 21 days. DT<sub>50</sub> values measured in the topsoil (0–5 cm) were slightly different, 68 and 51 days, for chloridazon and metamitron, respectively, and no residues were detected in soil/water solutions at 20 cm depth 3 months after application. These results show that in Italian conditions during the first 80 days after herbicide application and in the absence of rainfall the soil persistence of the herbicides is high and the mobility in soil is low.

**Keywords:** Herbicide dissipation; soil mobility; chloridazon; metamitron

## INTRODUCTION

In the past 8 years there has been an increase in studies on pesticide fate in the environment as a response to large-scale pollution occurrence in many wells used for drinking water in Italy. Almost all identified and widely used herbicides in Italy are not of recent introduction; consequently, extensive literature on their environmental fate is available, but information for Italian or similar field conditions is missing. This represents a large gap because Italy is one of the main herbicide consumers in Europe (and in the world) and, given its pedoclimatic characteristics and the agronomic techniques adopted, is representative of the whole Mediterranean area.

Discussion of how herbicides might behave in Mediterranean areas compared with some other geographical locations is under way by several scientists. In fact, some recently published data (Capri et al., 1993) seem to confirm that herbicide soil dissipation may be much faster in the Mediterranean region than in the cooler and wetter areas of northern Europe (Walker, 1994), while the risk of leaching may be higher due to the deep cracks of the clay soil.

In 1987 our research group, in cooperation with governmental research agencies, began research on the soil dissipation (mainly persistence and mobility) of the most widely used herbicide mixtures applied on the main cultivated crops (sugarbeet, maize, soya). Field and laboratory measurements were integrated with simulations obtained from a mathematical model forecasting pesticide fate in soil as requested by the decision-making scheme for the environmental risk assessment of pesticides (EPP0, 1993) and EC Directive 91/414/EEC concerning the placing of pesticides on the market (EC, 1991).

As part of the wider program this paper reports results obtained with the herbicides metamitron and

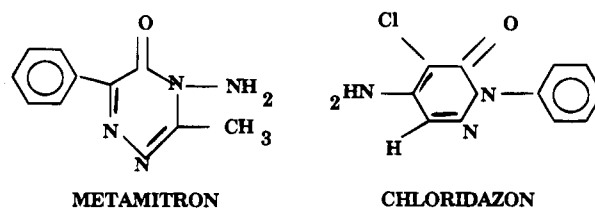


Figure 1. Chemical structures of the herbicides used.

chloridazon. Common objectives are as follows: to characterize the field dissipation; to evaluate the mobility in soil; to characterize the persistence under laboratory conditions and better define dependence on soil moisture and temperature; and to extrapolate the best parameters suitable as input for mathematical models.

## MATERIALS AND METHODS

**Chemicals.** Metamitron [3-methyl-4-amino-6-phenyl-1,2,4-triazin-5(4H)-one; trademark Goltix] and chloridazon [5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone; trademark Pyramin] are selective pre- and post-emergence herbicides, widely used in Italy for weed control in sugarbeet crops (*Beta vulgaris* L.) (Figure 1). They are often used together in mixtures for better weed control of graminaceous and dicotyledonous species.

Metamitron and chloridazon standards were from Pestanal (Riedel-de Haen Aktiengesellschaft, Germany). Goltix (70% metamitron) and Pyramin (65% chloridazon) were from Bayer and BASF/Solplant, respectively.

The other chemicals used for the chemical analysis were HPLC grade solvents (Merck, Germany); acetone, ammonium acetate, sodium sulfate, and dichloromethane were of RPE ACS grade (Carlo Erba, Italy).

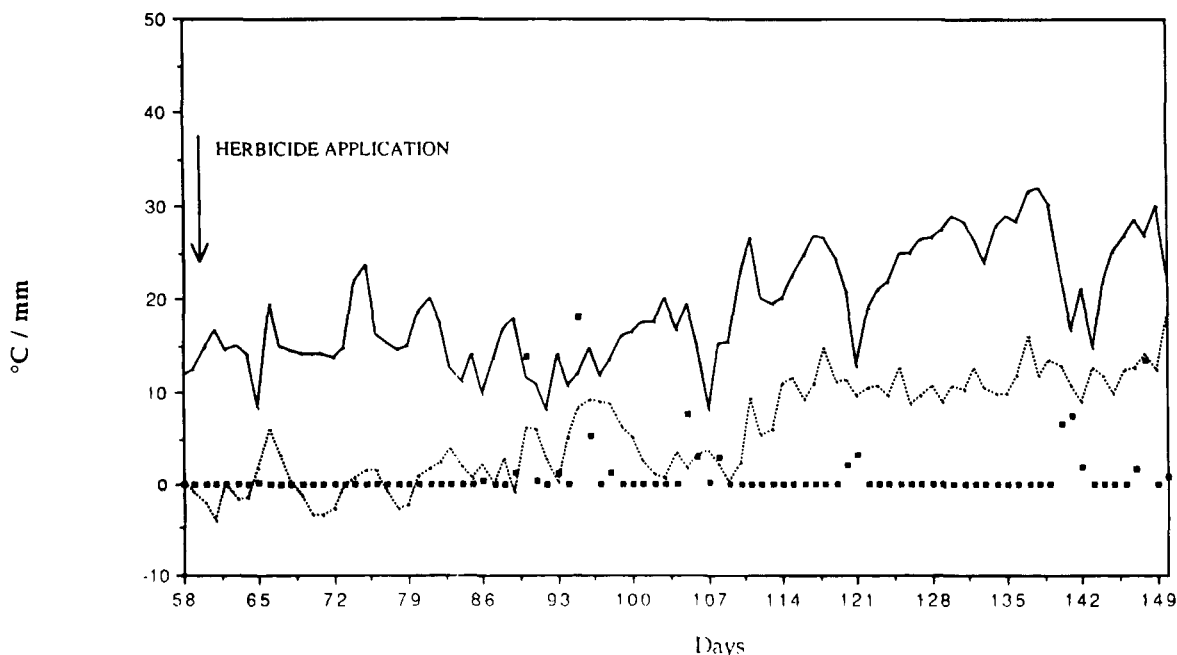
**Soil.** A silty clay loam, vertisolic xeric, was used for both field and laboratory experiments (Table 1).

Soil for chemical characterizations was sampled to a depth of 0–30 cm, air-dried to about 10% water content, and sieved through a 2 mm mesh sieve. Soil for physical characterizations and for the degradation experiment was sampled at the same depth and used fresh at 14% (w/w) moisture.

**Field Studies.** At a farm site representative of conditions typical of the Po Valley (northern Italy) three 250 m<sup>2</sup> sampling plots were separated within a large experimental field (3500 m<sup>2</sup>). All sampling plots were delineated along both the field length and tillage direction. Sugarbeet was cultivated following the standard agronomic practices used on the farm. The

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**Figure 2.** Climatic data for March–May 1992: (boxes) rainfall; (dotted line) minimum temperature; (solid line) maximum temperature.

**Table 1. Soil Chemico-physical Characteristics**

| characteristic                             | depth   |          |
|--|---------|----------|
|  | 0–10 cm | 10–30 cm |
| pH (in H <sub>2</sub> O)                   | 7.8     | 7.8      |
| organic matter, %                          | 2.21    | 2.14     |
| CEC, <sup>a</sup> mequiv/100 g             | 28.58   | 28.42    |
| clay, %                                    | 35.75   | 33.80    |
| silt, %                                    | 47.25   | 49.50    |
| sand, %                                    | 17.00   | 16.70    |
| bulk density, kg/L                         | 1.6     | 1.4      |
| field capacity (–0.05 bar), <sup>b</sup> % | 26.0    | 26.7     |
| wilting point (–15 bar), <sup>b</sup> %    | 18.7    | 19.2     |

<sup>a</sup> Cation exchange capacity. <sup>b</sup> Dry weight.

herbicide mixture was applied pre-emergence on March 3, 1992, using a tractor-mounted sprayer calibrated to distribute 600 L/ha. Application rates were 2.2 L/ha Goltix and 2.2 L/ha Pyramin. Sugarbeet (Break variety) was seeded at 25 plants/m<sup>2</sup>. To measure the amounts of herbicide mixtures applied and to test if the distribution was homogeneous, beckers installed on the soil surface were used to sample the mixture distributed. Weather data throughout the cropping season are shown in Figure 2. The crop was harvested on October 10, 1992.

**Soil Sampling.** Six soil cores (length 30 cm, diameter 3 cm), randomly distributed in each sampling plot, were taken using a continuous sampling tube (JMC Baksaver Handle). Sampling times were at 1 h and 1, 3, 6, 13, 38, 63, and 80 days after treatment. Soil cores, after determination of bulk density, were cut into three sections corresponding to 0–5, 5–10, and 10–20 cm depths. Collected samples were mixed and immediately frozen at –20 °C until analysis was carried out at the end of the experiment.

**Water Sampling.** In each plot eight soil water suction samplers were installed prior to herbicide treatment, at 20 cm depth. These samplers collect available soil water under a negative pressure between 35 and 80 cbar (Capri et al., 1992). Collected samples were mixed to obtain a sample sufficient for chemical analysis.

**Herbicide Extraction and HPLC Analysis.** Metamitron and chloridazon in soil were extracted (Ghebbioni and Trevisan, 1992) with acetone and water and analyzed by a Hewlett-Packard (Waldbronn, Germany) 1090 L liquid chromatograph with autoinjector and diode array detector set at 288 nm. Recoveries were 93% (±5.2) for metamitron and 82% (±5.2)

for chloridazon. Detection limits in soil samples were 0.034 and 0.025 mg/kg for metamitron and chloridazon, respectively.

Herbicide residues in water samples were extracted by solid-phase extraction on an SPE C<sub>18</sub> column (Trevisan et al., 1993), eluted by methanol. Recoveries were 95% (±3.2) for metamitron and 92% (±1.9) for chloridazon. The detection limits in water samples were 1.3 and 1.2 µg/L for metamitron and chloridazon, respectively.

**Laboratory Studies. Incubation Conditions.** Fresh soil samples (450 g each) were incubated in loosely capped glass containers (600 mL capacity) containing the soil as described in Capri et al. (1993). For each treatment, a water suspension of the herbicides was added to 1 kg of fresh soil sample and then divided into two replicated containers to obtain a final concentration of 2 mg/kg of dry soil. Trials with 22% soil moisture were incubated at temperatures of 10, 20, and 30 °C; trials with 15, 22, and 29% soil moisture were also incubated at temperatures of 10 and 30 °C. At 1, 3, 7, 14, 28, 45, and 60 days after herbicide treatment, 40 g of soil was sampled from each container for herbicide determination.

In these trials the effects of temperature and soil moisture on the degradation rate in conditions similar to field conditions were evaluated. The temperature and moisture values used during these trials were representative of northern Italian weather conditions for the crop (sugarbeet) in the winter to spring period (Figure 2). A moisture level below wilting point (<15% soil moisture) and levels close to and above the field capacity (22 and 29% soil moisture) were used. Trials lasted 60 days to avoid a depression of the microbial activity, as reported by other authors (Anderson, 1987).

While the trials at 10 and 30 °C were carried out by maintaining the two herbicides combined in the same incubators as in field applications, in the second trial at 20 °C herbicides were kept separate to measure metabolites; results of these trials will be published separately. It seems that rates are the same whether the herbicides are used alone or combined with one another, as shown previously by Fan de Fang et al. (1983) and Pestemer and Malkomes (1983).

**Herbicide Extraction and HPLC Analysis.** Samples were extracted and analyzed as described above for field soil samples.

**Statistical Analysis.** Half-lives ( $t_{1/2}$ ) and dissipation times ( $DT_{50}$ ) were calculated by assuming that degradations of both herbicides follow first-order kinetics. In the paper we use the terms linear and nonlinear kinetics because the first-order constants were derived using two methods: from the slopes

**Table 2. Herbicide Half-Lives in Laboratory Conditions**

| trial | temp, °C | soil moisture, % | metamitron        |                 | chloridazon      |       |
|-------|----------|------------------|-------------------|-----------------|------------------|-------|
|       |          |                  | $t_{1/2}$ , days  | $R^2$           | $t_{1/2}$ , days | $R^2$ |
| 1     | 10       | 15               | 46.4              | 0.95            | 133.7            | 0.77  |
| 2     |          | 22               | 39.8              | 0.96            | 75.6             | 0.85  |
| 3     |          | 29               | 20.7              | 0.97            | 41.0             | 0.65  |
| 4     | 20       | 22               | 15.5              | 0.99            | 21.3             | 0.82  |
| 5     | 30       | 15               | 10.6 <sup>a</sup> | (9.533; 0.0071) | 12.2             | 0.83  |
| 6     |          | 22               | 7.5 <sup>a</sup>  | (4.706; 0.0211) | 13.6             | 0.94  |
| 7     |          | 29               | 8.0 <sup>a</sup>  | (8.973; 0.0100) | 7.9              | 0.98  |

<sup>a</sup> Nonlinear model was used to estimate  $t_{1/2}$ ; in parentheses are  $\alpha$  and  $\beta$  values.  $t_{1/2}$  values by linear model were 12.1 (0.99), 10.5 (0.98), and 9.7 (0.99). The  $F$  values were 574.3, 107.3, and 161.2, respectively, for 15, 22, and 29% soil moisture.

**Table 3. Constant for Temperature and Soil Moisture Effects Derived from Laboratory Data**

|             | temp effects at 22%  |       | soil moisture effects at |       |       |       |     |       |
|-------------|----------------------|-------|--------------------------|-------|-------|-------|-----|-------|
|             | soil moisture        |       | 10 °C                    |       |       | 30 °C |     |       |
|             | $\Delta H$ , cal/mol | $r^2$ | $b^a$                    | $A$   | $r^2$ | $b$   | $A$ | $r^2$ |
| chloridazon | 14177                | 0.996 | 1.775                    | 16900 | 0.987 | 0.478 | 35  | 0.600 |
| metamitron  | 14616                | 0.937 | 1.230                    | 1463  | 0.847 | 0.458 | 69  | 0.674 |

<sup>a</sup>  $b$  = slope.

of the linear regression of the logarithms of the concentration of all replicates against time, assuming the linear relationship

$$\ln C = \ln C_0 - kt \quad (1)$$

where  $C_0$  is the initial concentration and  $k$  is the rate constant; and from a first-order nonlinear kinetic model, developed by Gustafson and Holden (1990), based on the assumption of a spatially variable first-order rate constant

$$\ln C = \ln C_0 - \alpha \ln(1 + \beta t) \quad (2)$$

where the parameter  $\alpha$  is dimensionless and  $\beta$  has units of the rate constant.

If the nonlinear model met the convergent criterion, the hypothesis of a linear first order (eq 1) was tested with an  $F$  test for parameter  $\beta$  (eq 2), equal to zero (Gustafson and Holden, 1990).

Dissipation time and half-life were calculated from the relation  $\ln 2/k$  for eq 1 and  $[0.5^{-(1/\alpha)} - 1]/\beta$  for eq 2.

The effect of temperature on degradation was expressed using the Arrhenius equation:

$$\log(H_1/H_2) = (dE/2.303)R(1/T_1 - 1/T_2) \quad (3)$$

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 effects of moisture were analyzed by means of the empirical equation developed by Walker (1978):

$$H = AM^{-b} \quad (4)$$

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.

All of the statistical tests were performed using SAS software (SAS, 1989).

## RESULTS AND DISCUSSION

**Laboratory Studies.** Results of the laboratory trials are shown in Tables 2 and 3. All replicates have a standard deviation lower than 10% for both herbicides.

**Chloridazon and Metamitron Degradation.** For chloridazon soil moisture had a different effect on degrada-

tion. When the soil moisture was made to vary from 15 to 22 to 29% at 10 °C, degradation rates increased with a constant factor 1.8. At 30 °C, the highest used here, there was a meager soil moisture effect and the half-life decreased from 12.2 to 7.9 days as the soil moisture increased from 15 to 29%. Increasing the temperature to 30 °C strongly increases degradation, but the main increase occurs with a temperature variation from 10 to 20 °C (by a factor of 3.5) (Table 2). The half-life measured at 20 °C and 22% soil moisture (21.3 days), probably due to the different soil characteristics, was slightly longer than that measured by Fan de Fang et al. (1983), who, at 20 °C and 70% soil water saturation, measured a  $t_{1/2}$  of 15 days.

For metamitron temperature seems to influence the degradation more than soil moisture. At 10 °C, increasing soil moisture increases the degradation rate as for chloridazon; increasing soil moisture from 22 to 29% increases degradation by a factor of 1.9. Increasing soil temperature at constant soil moisture (22%) enhances degradation, with a marked effect from 10 to 20 °C (increase rate factor 2.6) and a lesser one from 20 to 30 °C (Table 2). Walker (1978), under laboratory conditions and with a lower soil moisture (9.9%, i.e. 15.8% of field capacity), measured a reduction in  $t_{1/2}$  by a factor of 3.7 (52.5 ÷ 14.1 days) with a temperature increasing from 10 to 30 °C. This factor is lower than our factor 5.3, perhaps because of the difference in moisture content, which strongly influences degradation. Our degradation rate for metamitron (0.0149 ÷ 0.0924) is in agreement with those reported in the literature by Allen and Walker (1987), who report a range in  $K_{deg}$  (days<sup>-1</sup>) of 0.014–0.065 in a large number of English soils, and by Walker (1978), who at different temperatures and soil moistures reports a  $K_{deg}$  of 0.0132 ÷ 0.0491.

Overall, chloridazon is more persistent than metamitron, mainly at low temperatures (Table 2). Both herbicides are affected by soil moisture and temperature, but different amounts of variation occur with increasing moisture and temperature. The degradation rate always increases with temperature, while it does not always rise with soil moisture increases, e.g. at 30 °C (Table 2). The similar behaviors of these herbicides would be supported by the analogy of some functional groups present in their molecules such as C=O, -NH<sub>2</sub>, and heterocyclic N (Figure 1). It has been demonstrated by several authors (Egvild and Jensen, 1969; Fuhr and Mittelstaedt, 1979) that degradation is the main process and it is mainly microbic. Some evidence indicates that this process evolves throughout a number of biotic and abiotic steps: Blecher et al. (1979) demonstrated that these compounds could be degraded by the same bacteria; furthermore, it is also possible that the disappearance of the aryl group occurs along the same pathways in the two cases. One or two metabolites are known for chloridazon (Muller and Lingens, 1983), and a larger number have been identified by Engelhardt et al. (1982) for metamitron. It appears that the heterocyclic ring of chloridazon is not broken, while it has been demonstrated that the triazin ring of metamitron may be broken down by different species of microorganisms (Engelhardt et al., 1982).

**Soil Moisture and Temperature Effects.** Arrhenius and Walker constants that summarize the effects of temperature and moisture on metamitron and chloridazon degradation in soil are reported in Table 3. All data

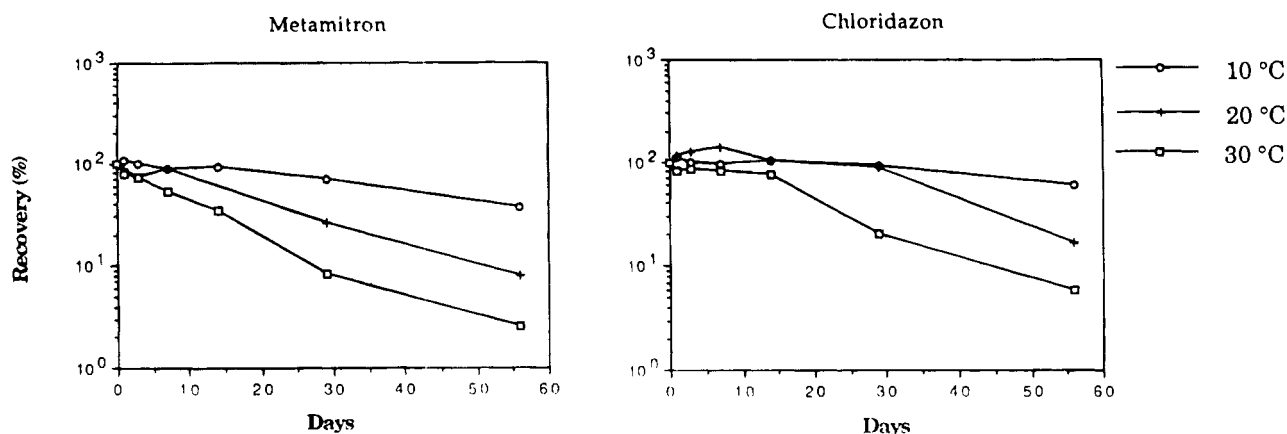


Figure 3. Degradation of metamitron and chloridazon at different temperatures.

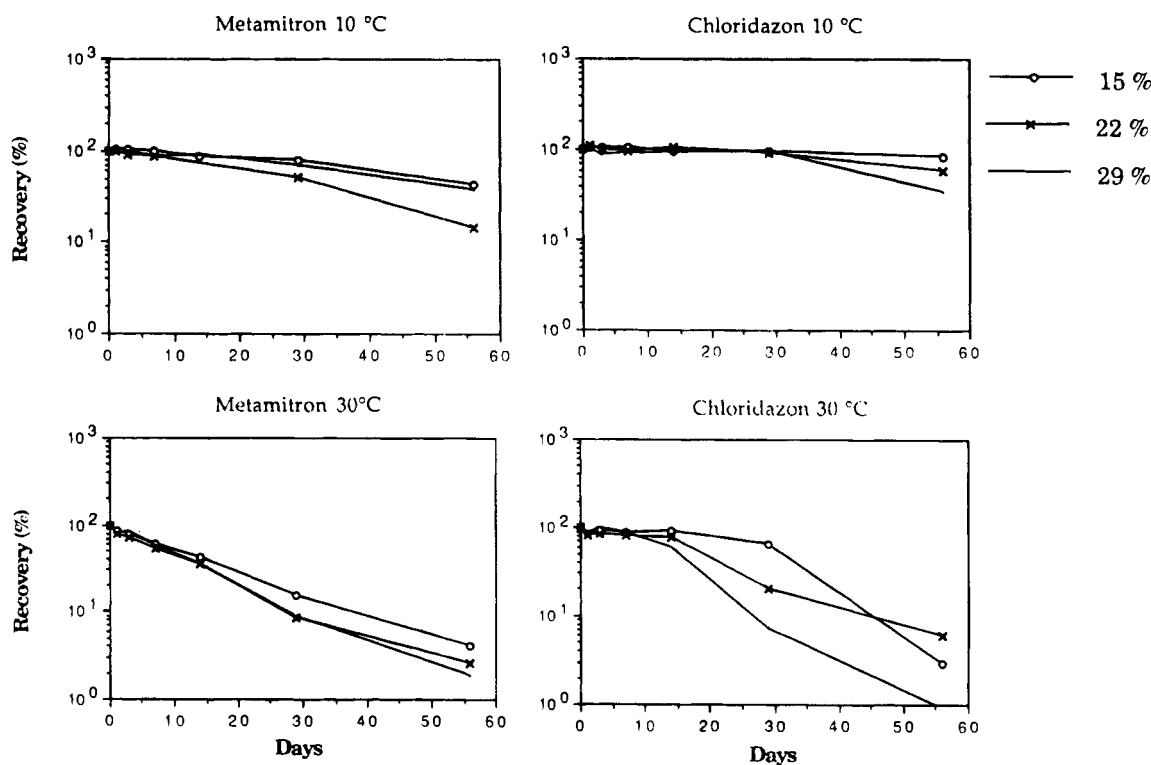


Figure 4. Degradation of metamitron and chloridazon at 10 and 30 °C and with different soil moisture contents (% dw).

for both herbicides gave regression coefficients statistically significant at  $P < 0.001$ . The activation energies were similar, 14 177 and 14 616 cal/mol for chloridazon and metamitron, respectively (Table 3). The value obtained for metamitron is not very dissimilar from the 11 140 cal/mol value obtained by Walker (1978) in a sandy loam soil (9–10% moisture content with 15.8% of field capacity and a temperature range from 15 to 25 °C). No  $A$  constant is reported in the literature for chloridazon. On the basis of the activation energies available for many herbicides, which range from 5460 to 24570 cal/mol (Boesten, 1986), it is possible to say that chloridazon and metamitron are moderately affected by temperature changes in comparison with other herbicides.

The empirical eq 4 gives a measure of degradation from moisture contents. In our soil type both herbicides were affected by soil moisture levels, more at 10 °C (slopes  $b$  of 1.775 and 1.230) than at 30 °C (slopes  $b$  of 0.478 and 0.458) for chloridazon and metamitron, respectively (Table 3). This effect at low temperature is strong one, given that for many herbi-

cides this value is in the range 0.1 ÷ 1.4 (Boesten, 1986). Walker (1978) reported  $b = 1.0$  and  $A = 255.3$ : these data fit well in the middle of the range of our experiment (Table 3).

**Measurements of the Degradation Fits.** The degradation of both herbicides follows a first-order kinetic, sometimes not very well (Table 2), but with regression coefficients that always are statistically significant ( $P < 0.005$ ). To assess the existence of a nonlinear trend in the degradation kinetic, all data were fitted both with the linear model (eq 1) and with a first-order nonlinear model (eq 2) based on the assumption of a spatially variable degradation rate. Very often the nonlinear model did not converge because of the data that fail to change in the initial 20-day step degradation; in that case the trend is better seen as a linear kinetic (metamitron) or as a semilinear or broken curve (chloridazon at 20 and 30 °C) (Figures 3 and 4). Only with the incubation of metamitron at 30 °C is the convergent reached and the test  $F$  significant ( $P < 0.001$ ).  $t_{1/2}$  values calculated in this way are slightly lower than those obtained with the linear model (Table 2).

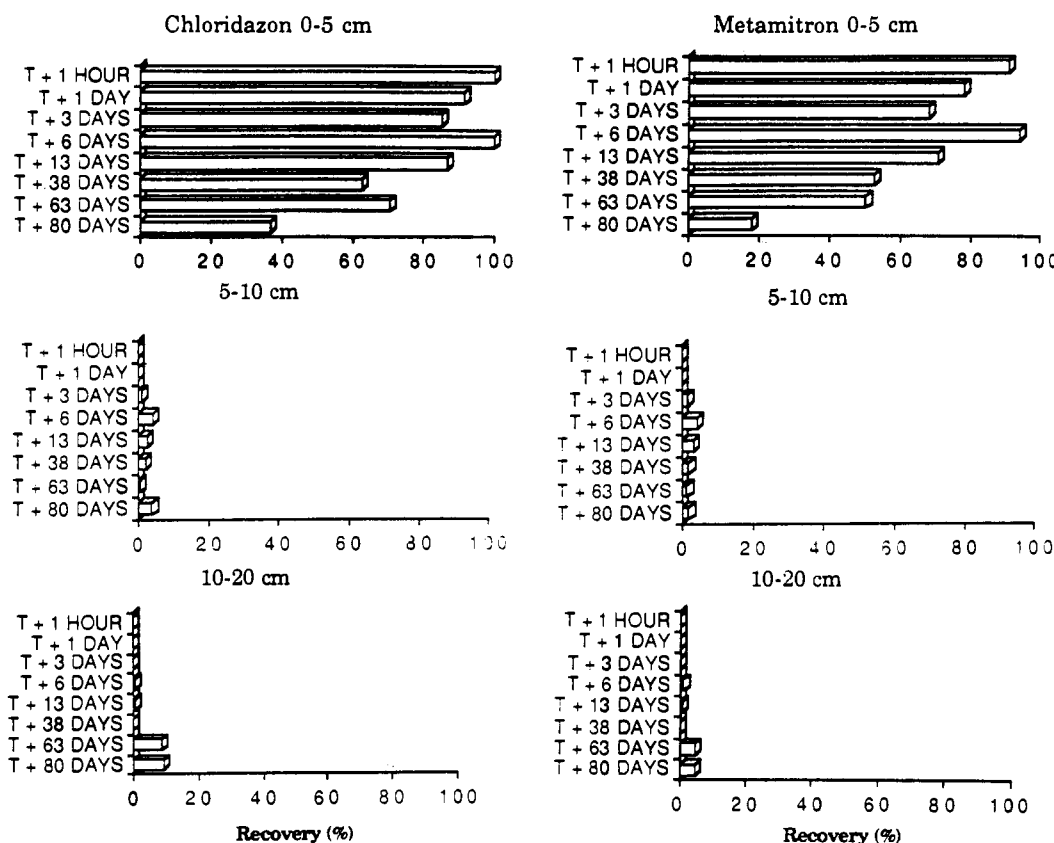


Figure 5. Herbicide dissipation at different sampling times (mean of three replicates).

The kinetic behaviors of chloridazon and metamitron appear to be different. Metamitron at different temperatures and soil moistures showed a first-order kinetic, confirming the results obtained by Allen and Walker (1987), who found  $1.44 \pm 0.224$  as the kinetic order for metamitron. Chloridazon showed, mainly at temperatures of 20 °C or less and at low soil moistures, kinetics different from a first order and not linear (Figures 3 and 4; Table 2). At 30 °C and at higher soil moisture, chloridazon shows a lag phase which persists for the first 15 days of incubation. This agrees with results obtained under laboratory conditions by Fan de Fang et al. (1983), who measured for chloridazon, both alone and combined with other herbicides, the kinetic order with an initial lag phase followed by a fast rate of degradation. It appears that microorganisms need an adaptative period as demonstrated in measurement of the rate of the  $^{14}\text{CO}_2$  evolved from the herbicide incubation (Führ and Mittelstaedt, 1979).

**Field Studies. Soil Residues.** Herbicide amounts applied to soil, calculated as the average of the sampling carried out during field application, were  $0.0995 \text{ g/m}^2$  of metamitron and  $0.097 \text{ g/m}^2$  of chloridazon. Herbicide distribution in the field was not spatially homogeneous, with a CV = 27% ( $n = 12$ ). This variability occurs when the herbicide is applied on soil using standard farming systems, and even in the presence of good agricultural practice (Walker and Brown, 1983; Smith and Parrish, 1993). That extrinsic variability, and the intrinsic soil spatial variability due to the large size of the field, are the main reasons for the variability between replicates, which for all the sampling ranges from 12 to 70% in CV.

Chloridazon is more persistent than metamitron with a  $\text{DT}_{50}$ , calculated by considering a first-order kinetic, of 68.3 days against 51.3 days for metamitron. Both

Table 4. Means of Climatic Conditions between Sampling Times

|                               | days after treatment |      |      |      |      |      |      |
|-------------------------------|----------------------|------|------|------|------|------|------|
|                               | 1                    | 3    | 6    | 13   | 38   | 63   | 80   |
| $T_{\min}^a$ , °C             | -2                   | 2.0  | 0.7  | -4   | 3.1  | 7.2  | 11.2 |
| $T_{\max}^b$ , °C             | 15                   | 13.9 | 14.4 | 16.8 | 14.1 | 20.2 | 25.7 |
| rainfall, <sup>c</sup> mm     | 0                    | 0.2  | 0    | 0    | 41.7 | 19.2 | 16.0 |
| soil moisture at 10 cm, % w/w | 14.2                 | 14.0 | 13.9 | 14.0 | 15.0 | 15.5 | 15.0 |
| soil temp 10 cm, °C           | 7.0                  | 7.2  | 7.5  | 7.8  | 10.9 | 16.3 | 23.0 |

<sup>a</sup> Minimum temperature. <sup>b</sup> Maximum temperature. <sup>c</sup> Cumulative value.

herbicides dissipate slowly in the first 80 days after field application (Figure 5). At the end of the field experiment metamitron residues in the topsoil (0–5 cm) were  $0.36 \pm 0.18 \text{ mg/kg}$  of dry soil ( $18.0 \pm 7.9\%$  in recovery), while chloridazon residues were  $0.74 \pm 0.38$  ( $36.9 \pm 17.1\%$ ) (Figure 5). The total recoveries for all soil layers were 47% and 25% for chloridazon and metamitron, respectively. These are comparable with recoveries obtained at the end of the laboratory trials (60 days), which range between 82.4 and 29.7% at 10 °C and between 3.1 and 0.9% at 30 °C for chloridazon and between 43.1 and 14.1% and between 4.0 and 1.9% for metamitron. Since herbicide field dissipation is influenced by different process such as leaching, volatilization, and phototransformation, these results may confirm that degradation in the absence of high rainfall is the principal process.

As already shown by the laboratory trials we can see that temperature and soil moisture influence the dissipation rate more than leaching. In fact, mean temperature and soil moisture in the field during sampling ranged from 6.5 to 18 °C and from 12 to 25% (Table 4), where  $\text{DT}_{50}$  values were similar to those obtained at 10

°C under laboratory conditions (68.3 against 75–134 for chloridazon and 51.3 against 40–46 for metamitron). We can assume that dissipation rate increases with time: this is confirmed by previous field trials carried out in a clay soil on sugarbeet crops, where the authors found a concentration of  $2.5 \div 10 \mu\text{g}/\text{kg}$  at 210 days after herbicide application, corresponding to a  $\text{DT}_{50}$  of 17–20 days (Flori et al., 1993; Del Re et al., 1993).

Both herbicides had similar leaching rates through the soil profile. Chloridazon reaches greater concentrations in the bottom soil because of its greater persistence (Figure 5). Both herbicides show residues in the 5–10 cm layer after 3 days from application (Figure 5), but only after 63 days do they reach significative concentrations at 10–20 cm. At the end of the experiment, 80 days after application, at 5–10 cm depth, there are recoveries of  $1.74 \pm 1.81$  and  $3.94 \pm 3.49\%$  of metamitron and chloridazon, respectively. At 10–20 cm depth, and at the same sampling time, metamitron and chloridazon recoveries were  $4.75 \pm 4.83$  and  $8.96 \pm 8.86\%$ , respectively.

Measurements of residues in soil water at 10–30 cm depth showed concentrations of  $95 \pm 118.6$  and  $88.1 \pm 110.4 \mu\text{g}/\text{L}$ , 6 days after treatment, and  $44.8 \pm 47.9$  and  $51.9 \pm 57.8 \mu\text{g}/\text{L}$  after 49 days for metamitron and chloridazon, respectively. In samples collected 3 months after herbicide application, chloridazon and metamitron were not detectable. This may be supported by ground-water monitoring carried out in recent years in our province, where chloridazon and metamitron were never detected (Russo et al., 1993).

**Conclusions.** Our results confirm that optimal conditions in temperature and soil moisture (or better water volumetric content) increase the degradation rates of metamitron and chloridazon. In northern Italian conditions both pre-emergence herbicides applied to sugarbeet should have a field dissipation characterized in two steps, one slower, in February–April, a second faster, between May and August, depending on rainfall and temperature patterns. This will influence the weed control ability and the environmental fate of both. In fact, since low temperatures with low moisture content retard degradation, chloridazon may become slightly to very persistent and metamitron slightly to moderately persistent, thereby increasing weed control efficacy as well as the risk of leaching and runoff in case of storms. Comparing  $t_{1/2}$  with  $\text{DT}_{50}$  and residue values in soil profile, it is possible to say that field dissipation is primarily due to degradation rather than leaching. In Italy the majority of soils cropped with sugarbeet are loamy and clay; the risk that chloridazon and metamitron reach the groundwater or the bottom layer of the soil is low, unless intensive rainfalls occur in the first step.

The use of the degradation constant measured in the experiment for input of the mathematical model must be checked carefully.  $t_{1/2}$  values must be chosen as close as possible to the temperature and soil moisture range of the field; otherwise, models may give unreliable results. Furthermore, the results indicate the clear not easily supported by the available model theories. In fact, these kinetics are not adopted by widely used models such as PRZM (Carsel et al., 1985) and LEACHMP (Hutson and Wagenet, 1992), and PELMO (Klein, 1993), which use kinetics with different orders, is not able to simulate trends with an initial lag phase, as shown in our data. To use mathematical models correctly, it is necessary to take into account these phenomena and

improvements are needed. Model evaluation has been in part already published (Trevisan et al., 1994).

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