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Transformation of metamitron in a sandy clay loam soil

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Abstract – The degradation of metamitron, a sugar beet herbicide, in soil was studied in laboratory conditions and in field lysimeters under different irrigation water volumes. An identification of degradation compounds was also attempted. Laboratory degradation followed a first-order kinetics with a half-life of 18.2 days while lysimeter dissipation was consistently rapid with a half-life ranging from 4.4 to 8.0 days under the different irrigation conditions. A degradation compound appeared as early as the first few days in both laboratory and lysimeter samples and was identified as 4-(dimethylimino)-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one by GC/MS and NMR spectra. (© Inra/Elsevier, Paris.)

metamitron / pesticide degradation / field lysimeters / degradation compounds

Résumé – Filière de transformation du métamitron dans un sol argilo-sableux. La dégradation dans le sol du métamitron, un herbicide de la betterave à sucre, a été étudiée en conditions de laboratoire et, sur le terrain, au moyen de lysimètres, sous différents volumes d'eau d'irrigation. On a également tenté d'identifier les composés de dégradation. La dégradation en laboratoire a suivi une cinétique de tout premier ordre, avec une demi-vie 18,2 j, tandis que la dissipation observée avec les lysimètres a été constamment rapide, la durée de demi-vie s'échelonnant entre 4.4 et 8 j suivant les différentes conditions d'irrigation. Un composant de dégradation est apparu dès les premiers jours tant dans les échantillons de laboratoire que dans ceux des lysimètres, et a, par le biais des analyses spectrales GC/MS et NMR, été identifié comme étant du 4-(diméthylimino)-3-méthyl-6-phényl-1,2,4-triazine-5(4H)-one. (© Inra/Elsevier, Paris.)

métamitron / dégradation du pesticide / lysimètres de terrain / composés de dégradation

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1. Introduction

The environmental fate of pesticides depends on a number of processes including leaching, sorption and degradation in soil, crop growth, meteorological conditions and soil hydrology [10]. Pesticide degradation in soil is a process which has a high impact on groundwater contamination.

Metamitron, 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4*H*)-one, has been used in Italy for 30 years as a herbicide in sugar beet crops for the post-emergence control of annual broad-leaved weeds and grasses.

Numerous studies have been carried out on the soil degradation of metamitron [1, 2, 8] and have indicated that laboratory half-lives range from 7 to 50 days, depending on soil and incubation conditions. Some studies performed on the fate of metamitron in field conditions in the Mediterranean area [2, 7] have suggested a low hazard of groundwater pollution. Again, this may have been because the herbicide remained in the top soil layer owing to the lack of rainfall during the experiments.

None of the above experiments give information as to the degradation pathway of metamitron and the possible identification of degradation products.

In this paper the degradation of metamitron in a sandy clay loam soil was studied in the laboratory at 20 °C and 20 % soil moisture with the aim of

singling out and identifying possible transformation products and hypothesizing the mechanism through which they had been formed. Samples from a field lysimeter study [9] carried out with the same soil from the laboratory experiment where the lysimeters were subjected to different water regimes were used to investigate the presence of these compounds in field conditions.

2. Materials and methods

2.1. Soil and chemical standards

A sandy clay loam soil was used for degradation studies in laboratory conditions and for the lysimeter trial. *Table 1* reports the main physico-chemical characteristics of the experimental soil collected from lysimeters in the 0–30-cm layer. Analyses were carried out according to Cavazza [3] for hydrologic properties and Page [6] and Klute [5] for physico-chemical properties.

Analytical-grade metamitron (99.0 % purity) produced by the Institute of Organic Industrial Chemistry (Warsaw, Poland) was used as the analytical standard.

The analytical standard of the transformation product of metamitron was obtained by *in vitro* hydrolysis conducted in the dark: metamitron was added to a 0.2-M carbonate buffer solution at pH = 10.8 and continuously shaken at room temperature for 4 days, the solution was then extracted three times with CH₂Cl₂ and the collected extracts were concentrated at reduced pressure. The residue was rinsed with EtOAc and purified by silica-gel chromatography using a ratio of *n*-hexane:EtOAc (9:1) as eluent.

2.2. Degradation studies

A 50-g portion of finely powdered soil sample was placed in a 250-mL flask and 100 mL methanol solution containing 3 mg of metamitron were added. After the complete evaporation of methanol, the powdered soil was used to fortify a 1-kg sample of 2-mm-sieved air-dried soil in order to obtain a final concentration in the three soil samples of 3.0 mg kg⁻¹. The container was covered with perforated tin-foil and incubated in the dark at 20 °C and 20 % soil moisture. Soil moisture content was maintained by daily additions of water. At different times after the treatment, duplicate 50-g samples were extracted and analysed.

Table 1. Main properties of the experimental soil collected from lysimeters in the 0–30-cm layer.

Sand (%)	49
Silt (%)	23
Clay (%)	28
Field capacity (% w/w, 0.033 MPa)	24.5
Wilting point (% w/w, 0.15 MPa)	10.5
pH (H ₂ O)	7.5
Organic matter (%)	2.8
CEC (meq 100 g ⁻¹)	16.5
Bulk density (g cm ⁻³)	1.10

2.3. Field lysimeter experiment

The trial is reported in detail by Vischetti et al. [9]. The study consisted of a 200-m² plot cultivated with a sugar beet crop including six buried drainage lysimeters. Pre-emergence herbicide treatment was applied using a commercially formulated product (Goltix, 70 % a.i.) distributing 3.5 kg ha⁻¹ a.i. Soil cores were taken at various increments to a depth of 120 cm at different times after treatment and duplicate 50-g samples for each increment were extracted and analysed.

The six lysimeters were irrigated two by two with varying amounts of water. The leachates at the bottom of the lysimeters were collected whenever irrigation induced drainage of water along the soil profile.

2.4. Analyses

Soil residues of metamitron were extracted with methanol (2 × 100 mL × 2 h) and the extracts were diluted in water (150 mL), partitioned in chloroform (3 × 100 mL), evaporated to dryness and rinsed with methanol (1 mL). The samples were analysed by HPLC according to the procedure described by Ghebbioni and Trevisan [4].

Under these conditions retention time of the transformation compound was 16.5 min. Average recoveries were 98.7 (s.d. ± 0.4) and quantification limit was 9.8 µg kg⁻¹.

2.5. GC/MS and NMR analyses

GC/MS analyses were performed using a Varian Star model 3 400 chromatograph, equipped with a split-splitless injector and a DB5 column (0.25 mm i.d. × 30 m length), coupled with a Varian Saturn II mass-spectrometer operating in electron impact mode. Experimental conditions for GC/MS analyses were: initial temperature of 60 °C (1 min) ramped at 20 °C min⁻¹ to a final temperature of 250 °C (10 min); the injector temperature was 200 °C; the carrier gas was helium (1 mL min⁻¹); the ionization voltage was 70 eV and the emission current 10 µA. Methane was used as the ionizing agent. In these conditions the retention times were 22.5 and 23.0 min for transformation product and metamitron, respectively.

¹H-NMR and ¹³C-NMR were performed using a Varian NMR spectrometer 300 Mhz. NMR spectra were determined in deuterochloroform.

3. Results and discussion

Figure 1 reports the degradation of metamitron in laboratory conditions and the trend of formation and disappearance of the transformation compound which was found in all soil samples as early as the first few days after treatment. Degradation in laboratory conditions followed a first-order kinetics (R^2 significant at $P < 0.001$) and the corresponding half-life value was 18.2 days. The presence of the transformation product increased until day 3 after treatment, followed by a decrease until its complete disappearance at day 32 after treatment.

Dissipation in lysimeters was faster in the pair of most leached lysimeters. However, DT50 values, though different up to a two-fold increase (from 4.4 to 8.1 days), were similar from a practical point of view and indicate a fast dissipation in the conditions tested, independent of the amounts of water used [9].

Figure 1. Degradation of metamitron and formation and disappearance of the transformation compound in soil.

The transformation product found in laboratory samples was not the only unknown compound which appeared in the treated soil, but was the only product to appear in lysimeter soil samples, albeit in a very small amount. For this reason, the kinetics and identification of this single product was followed.

On the contrary, the transformation product was not found in the water leached by lysimeters at 4 and 56 days after treatment.

Figure 2 shows the mass spectra of metamitron (A) and of the transformation compound (B). In A the fragment at m/e 203 corresponds to the protonated molecular ion, m/e 186 derives from the loss of $-NH_2$ group, m/e 174 derives from the loss of $C=O$ group, while the signal at m/e 104 (parent ion) represents the benzonitril cation, at m/e 89 the benzylic fragment and at m/e 77 the benzene fragment. In B the most intense signals were at m/e 243 and m/e 227. The former is the protonated molecular ion, whilst the latter is consistent with the loss of the methyl group from this ion. The signal at m/e 214 is consistent with the loss of $C=O$ group from the molecular ion and the signal at m/e 199 could derive from 214 by loss of methylic group or from 227 by loss of $C=O$ group.

For a better understanding of the structure of the transformation compound, 1H -NMR and ^{13}C -NMR analyses were performed in deuterochloroform. Figure 3 shows the 1H -NMR spectra of metamitron (A) and transformation compound (B). 1H -NMR spectrum of metamitron shows the presence of a singlet at $\delta = 5.15$ ppm ascribable to the two aminic protons, which is absent in the 1H -NMR spectrum of the transformation compound. Metamitron has a singlet corresponding to three methylic protons at $\delta = 2.7$ ppm, while the transformation compound has three singlets at $\delta = 1.9$, 2.35 and 2.45 ppm, corresponding to three methylic protons (three isolated methyl groups). The aromatic protons show the same chemical shift for both metamitron and the transformation compound ($\delta = 7.5$ ppm, m, 3H; $\delta = 8.25$ ppm, m, 2H).

The ^{13}C -NMR spectrum of the transformation compound (not shown) confirms the presence of three methylic carbons at $\delta = 19.1$, 20.6 and 25.2

Figure 2. Mass spectra of metamitron (A) and of the transformation compound (B).

and the presence of the carbonylic carbon at $\delta = 181.1$.

Therefore, the structure of the transformation compound should be as follows:

This compound originates from metamitron by the addition of a $=C(CH_3)_2$ group, which may arise from other molecules of metamitron or from unstable metabolites. The formation of this compound

Figure 3. ^1H -NMR spectra of metamitron (A) and of the transformation compound (B).

could be independent of soil microbial activity since it was obtained also by *in vitro* hydrolysis.

4. Conclusion

Degradation of metamitron in a clay loam soil was faster in field lysimeters than in the laboratory experiment. The appearance of a transformation product, identified as 4-(dimethylimino)-3-methyl-6-phenyl-1,2,4-triazin-5(4H)-one, in the first few days after treatment in both laboratory and lysimeter trials, indicates the need to follow not only the pesticide but also its transformation products when assessing the environmental fate of xenobiotics.

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