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Sorption and degradation of tebutam in soil under controlled laboratory conditions

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Abstract – This study investigates tebutam (N-benzyl-N-isopropylpivalamide) sorption and degradation in the surface level (0–20 cm) of a brown silty clay soil. All the experiments were conducted under controlled laboratory conditions using ^{14}C uniformly ring labelled tebutam. The sorption process was evaluated by adsorption kinetics, adsorption and desorption isotherms using a batch equilibration method. In our conditions, equilibration time for 95% of herbicide adsorbed was 0.21 h. This initial rapid sorption pattern, was followed by slower sorption continuing over 48 h. The adsorption isotherm was well described by the Freundlich equation with $K_f = 1.48$ and $n_f = 0.95$. This corresponds to a K_d of $1.48 \text{ l}\cdot\text{kg}^{-1}$ and a K_{oc} of $148 \text{ l}\cdot\text{kg}^{-1}$, comparable to the coefficients measured for atrazine. Desorption of tebutam was easy and weakly hysteretic, particularly for large adsorbed amounts. For degradation, data showed that 50% of tebutam was degraded in 14 days (as a percentage of extractable residues), and nearly 41% was mineralized in the same interval. Non-extractable residues reached 46% of initial applied amounts in 12 days. Their slow and gradual release determined after 12 days, appears to supply the mineralization process. Degradation products were formed from the fourth incubation day and three of them appeared to persist in soil media. They reached nearly 80% of extractable residual radioactivity at the end of incubation.

tebutam / adsorption / desorption / degradation / mineralization

Résumé – Rétention et dégradation du tébutame dans un sol en conditions contrôlées. La rétention et la dégradation du tébutame (N-benzyl-N-isopropylpivalamide) dans le sol, ont été évaluées en conditions de laboratoire à l'aide de la molécule uniformément marquée au ^{14}C sur le noyau aromatique. Le phénomène de rétention a été apprécié par une cinétique d'adsorption, une isotherme d'adsorption et une isotherme de désorption. Dans les conditions d'étude adoptées, le temps d'équilibre pour observer 95% de produit adsorbé est de 0,21 h. A cette adsorption rapide fait suite une adsorption lente qui se poursuit au delà de 48 h. L'isotherme d'adsorption est décrite par l'équation de Freundlich avec un coefficient K_f de 1,48 et une constante n_f de 0,95, ce qui conduit à un coefficient K_{oc} de $148 \text{ l}\cdot\text{kg}^{-1}$ comparable à celui de l'atrazine. Enfin, la désorption de l'herbicide est assez facile et le phénomène d'hystérésis est peu marqué, en particulier pour des quantités adsorbées importantes. Concernant la dégradation, les données obtenues ont montré que

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50 % du produit appliqué étaient dégradés en 14 jours et que près de 41 % étaient minéralisés dans le même temps. Les résidus non extractibles atteignent 46 % de la dose initialement apportée en 12 jours. Leur teneur diminue à partir de 14 jours. Ces résidus semblent alimenter le processus de minéralisation. Les produits de dégradation sont formés dès le 4^e jour et 3 d'entre-eux persistent dans le milieu. Ils atteignent près de 80 % de la radioactivité résiduelle extractible en fin d'incubation.

tébutame / adsorption / désorption / dégradation / minéralisation

1. Introduction

Tebutam is a nonionizable acetamide herbicide applied to the soil surface for weed control, mainly in rape farming and ranked third among the main cultivation crops in France in 1996 [5, 9, 15]. The widespread use of this chemical is reportedly held largely accountable for groundwater and surface water contamination [1, 2, 11]. However, dissipation in natural medium depends on many processes and factors, such as soil properties and climate just after treatment [12]. Among the overall parameters governing interaction between soil and pesticide, sorption properties, which limit dispersion, and degradation specifications, which contribute to conversion processes, are indispensable for appreciating the fate and behaviour of pesticides in the environment [18]. Thus, the sorption distribution coefficient (soil-water), normalized for soil organic carbon content (K_{oc}), and the half-life (DT_{50}) are used for chemical mobility classification [7], and for ecotoxicological risk assessment [8], and also in numerical models aimed to predict the transfer [3]. Although tebutam has been used since 1981, no study on it has been reported so far.

Hence, the aim of the work reported here was to assess sorption and degradation processes under controlled conditions, in an agricultural soil representative of those used for rape cultivation.

2. Materials and methods

2.1. Soil properties

The soil stems from a brown silty clay loam soil. Its main properties are: pH (in water), 7; % clay,

43.8; % silt, 43.5; % sand, 9 and % organic carbon, 1.0. The sampling was performed in May 1998 at the ploughing layer (0–20 cm) from the experimental site “La Bouzule”, 54-Champenoux in eastern France, only once previously cultivated with rape in 1996.

2.2. Chemicals

All the experiments were carried out with aqueous- CaCl_2 0.01 mol·l⁻¹ solutions, using uniformly ¹⁴C ring labelled tebutam (N-benzyl-N-isopropyl pivalamide; MW: 233.40; solubility in water: 0.79 g·l⁻¹ at pH 7 and 20 °C; specific radioactivity: 4.55 GBq·mmol⁻¹; 98.6% purity; Amersham). Isotopic dilutions were made in some cases with technical certified product (99.5 ± 0.5% purity; CIL Cluzeau).

2.3. Laboratory sorption studies

2.3.1. Soil preparation

After air-drying at room temperature, a whole soil sample was crushed and sieved to obtain a homogeneous sample of particles smaller than 50 µm in order to reduce diffusion phenomenon into aggregates.

2.3.2. Adsorption kinetics

The batch equilibration method (2:10, soil:tebutam aqueous- CaCl_2 0.01 mol·l⁻¹ solution) was used in the sorption studies. The initial radioactive level of the solution was close to 167 Bq·ml⁻¹. Because of the specific radioactivity of ¹⁴C-tebutam, the corresponding concentration of tebutam was 7.35 µg·l⁻¹. 10 ml of the initial solution was added to 2 g air dried soil in a 25 ml glass Corex centrifuge tube and sealed with an aluminium-lined

cap. After sample preparation the centrifuge tubes were shaken in a revolving agitator for 0, 2, 5, 10, 20, 30, 45 min and 1, 2, 4, 8, 12, 24, 48 h at 20 ± 1 °C. The suspensions were then centrifuged for 30 min at 3500 g, 20 °C (Beckman Avanti J-25). Three samples (1 ml) of each supernatant solution were collected and added to 10 ml of liquid scintillation cocktail (Ultima Gold, Packard). The amount of herbicide in solution was determined by radioactivity measurement by a liquid scintillation counter (Packard Tricarb 2100 TR). Blank samples were prepared similarly but without soil, and showed no adsorption on a glass Corex tube. Amounts of tebutam adsorbed on soil were calculated as the difference between the initial herbicide in solution and the supernatant content after centrifugation.

2.3.3. Adsorption isotherm

The procedure was identical to the one followed for kinetics. The aqueous solutions used for this study were prepared by isotopic dilution in order to provide a radioactivity close to $167 \text{ Bq}\cdot\text{ml}^{-1}$ for each solution and the following concentrations: 0.01, 0.1, 0.25, 0.5, 1, 2, 4, 10 and $20 \text{ mg}\cdot\text{l}^{-1}$. All adsorption studies were run in triplicate for each initial herbicide solution. Equilibration time for each modality was 4 h (95% of tebutam adsorbed).

2.3.4. Desorption isotherm

Desorption from adsorbed herbicides was studied for concentrations of 0.01, 1, and $20 \text{ mg}\cdot\text{l}^{-1}$. After herbicide adsorption as previously described, 8 ml of equilibrated solution was replaced by the same volume of an aqueous CaCl_2 $0.01 \text{ mol}\cdot\text{l}^{-1}$ herbicide free solution, the volume of suspension (10 ml) being constant. Centrifuge tubes were hand shaken to disperse the soil pellets and the suspensions were rotary shaken for one hour at 20 ± 1 °C before centrifugation. The procedure was repeated five times to obtain the desorption isotherm. The herbicide concentration in the solution after each desorption was determined. The amount of herbicide remaining adsorbed on the soil was calculated as the difference between initial and desorbed amounts taking account of the aliquot removed from the previous sorption cycle.

2.4. Laboratory degradation studies

Incubation was carried out in a hermetically sealed enclosure in which the following elements were placed: a 60 mm diameter glass pot containing treated soil, a 10 ml NaOH $0.5 \text{ mol}\cdot\text{l}^{-1}$ solution ($^{14}\text{CO}_2$ trapping) and a 10 ml distilled water flask used to maintain constant humidity in the hermetic enclosure. The system was placed in a temperature controlled room at 20 ± 1 °C in darkness for 31 days with periodically change of CO_2 traps. Samples were analyzed in triplicate for tebutam residues, 13 times during the 31 day incubation period.

2.4.1. Soil preparation and treatment

After sampling the soil was air dried and sieved between 1 and 3.5 mm. This sample preparation procedure was chosen in order to standardize the particle size distribution and to prevent formation of an anaerobic compact layer in the bottom of the glass pot due to the accumulation of small particles. Samples of 40 g of soil were transferred to a glass pot. Each sample was treated with tebutam aqueous solution prepared by isotopic dilution in order to provide concentrations of $5 \text{ KBq}\cdot\text{ml}^{-1}$ and $125 \text{ mg}\cdot\text{l}^{-1}$. The volume of solution (8 ml) placed on each sample was calculated to make a treatment equivalent in surface area to $3600 \text{ g}\cdot\text{ha}^{-1}$ (1 mg) and to obtain a soil sample at 80% of its field capacity.

2.4.2. Residues mineralization

The mineralization of ^{14}C ring-labelled tebutam over the 31-days incubation period was monitored 14 times at each NaOH sampling date, between 2 to 31 days after treatment. Triplicate samples of NaOH solutions were analyzed for radioactivity. A 1 ml aliquot was removed from each sample and added to 10 ml Ultima Gold Scintillator (Packard), for liquid scintillation counting (Packard Tricarb 2100 TR). At each sampling date, the replacement of the CO_2 trapping solution by fresh solution allowed air renewal in the enclosures.

2.4.3. Residues in soil

2.4.3.1. Determination of extractable residues

^{14}C herbicide residues in soil were determined by exhaustive extraction with methanol. Triplicate samples were removed from incubation every other day up to 16 days and then 19, 22, and 31 days after treatment. The soil in each sample was transferred to a 250 ml PPCO (polypropylene copolymer) centrifuge flask. Tebutam and its metabolites were extracted from the soil by rotary shaking with 100 ml methanol at 20 °C for 16 h. After centrifugation at 5000 g for 20 min, supernatants were transferred to a volumetric flask and adjusted to 100 ml. The amount of extractable ^{14}C herbicide residue was determined for each sample by liquid scintillation counting using the Packard liquid scintillation analyzer. The extractions were repeated until the radioactivity in the supernatants was lower than two times the scintillation counter background (50 cpm). The combined extracts from the methanol extractions were concentrated by the following procedure. After filtration (Sartorius Minisart SRP15), they were evaporated just to dryness with a rotovapor (Heidolph 94200), and redissolved with 1 ml methanol before chromatographic analysis.

2.4.3.2. Determination of non-extractable residues

After the extraction sequence, the soil samples were air dried and pulverized. The non-extractable ^{14}C residues were determined by combustion of three soil aliquots (1 g) under O_2 flow, at 900 °C, for 10 min, in order to produce $^{14}\text{CO}_2$. The $^{14}\text{CO}_2$ was trapped in 15 ml of ethyleneglycol-monomethylether/ethanolamine mixture (80/20, v/v). Radioactivity of the trapping solution was determined by liquid scintillation counting on 10 ml of the mixture in 10 ml Scintillator Plus cocktail (Packard).

2.4.4. Analysis of residues

Soil extracts were analyzed by HPLC in a Varian chromatograph equipped with a diode array detector and a β radioactivity detector (Flo-one β , Packard), with the following operating conditions: C18 Lichrospher column, 4.6 \times 250 mm (Merck), wavelength 190 nm, injection volume 94 μl , analy-

sis time 20 min, flow rate 0.8 ml·min⁻¹, gradient elution acetonitrile/water buffered at 3% H_3PO_4 0 min (40/60, v/v), 6 min (55/45, v/v), 9 min (60/40, v/v). Qualitative peak identification was performed by β radioactivity detector in the following conditions: Scintillator Ultima-Flo, flow 1.2 ml·min⁻¹, counting cell 500 μl . The extracts in triplicate were combined to provide enough radioactivity for the qualitative analysis.

3. Results and discussion

3.1. Sorption under controlled conditions

3.1.1. Adsorption kinetics

Data from the kinetic adsorption experiment (Fig. 1) revealed a two-step reaction:

- the first is nearly instantaneous. The speed of this step can be attributed mainly to the particle size (50 μm), which offers large sorption surface area and readily available sites. 29.17% of the chemical was adsorbed after shaking the suspension for 2 min, although this value may be overes-

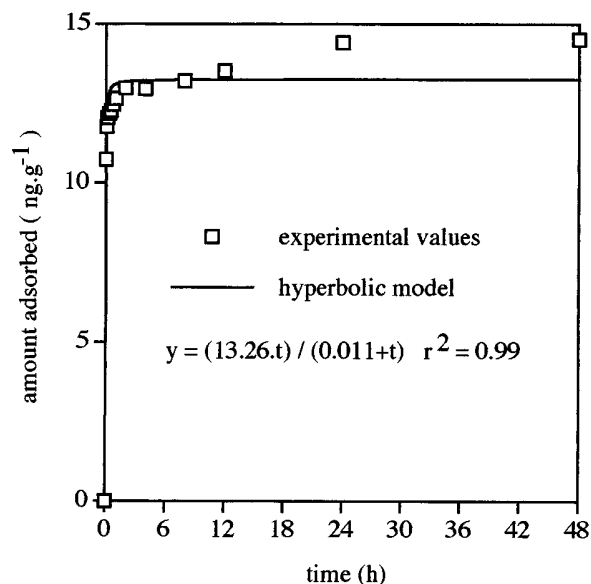


Figure 1. Tebutam sorption kinetics on brown silty clay soil at $C_0 = 7.35 \mu\text{g}\cdot\text{l}^{-1}$. (Standard deviation of experimental values are not noticeable.)

timated by the amount which can be adsorbed during centrifugation (30 min);

– the second is slower, with equilibrium still not reached after 48 h. The slow adsorption suggests the involvement of less accessible sites, implying a diffusion mechanism within the particles [4, 10].

The amount adsorbed and the time required to reach equilibrium are estimated by the hyperbolic model.

$$Q_{\text{ads}} = (Q_{\text{max}} \cdot t) / (K + t) \quad (1)$$

K: empirical constant of adsorption

Q_{max} : maximum amount of adsorbed tebutam ($\text{ng} \cdot \text{g}^{-1}$)

Q_{ads} : amount of adsorbed tebutam per mass unit ($\text{ng} \cdot \text{g}^{-1}$)

t: time required to reach equilibrium (h).

The equilibrium time was calculated from the following approximation:

$$Q_{\text{ads}} = 0.95 Q_{\text{max}} \quad (2)$$

The correlation coefficient (r^2) was used to estimate the goodness-of-fit of the model to the data. The results showed that experimental data were accurately described by the hyperbolic model with an r^2 of 0.99. However, the model offered a poor representation of the final adsorption phase. In fact, it accounts for most of the values obtained between 0 and 4 hours (Fig. 1).

Model predictions indicated that the time required to reach 95% adsorption was 0.21 h. This short time traduces that the model badly takes into account the longer adsorption phase. However, the value was comparable to that of trifluralin (value obtained in the same conditions), another herbicide used on rape and tested on the same soil material. As opposed to trifluralin, however, the scale of adsorption was limited. After shaking for 48 h, only 39.5% of the tebutam was adsorbed against 97% for trifluraline [10].

3.1.2. Adsorption isotherm

Experimental adsorption data were correctly described by the Freundlich model of equation (3) according to an r^2 of 0.99 (Fig. 2).

$$Q_{\text{ads}} = K_f \cdot C_e^{n_f} \quad (3)$$

Q_{ads} : amount of adsorbed tebutam ($\mu\text{g} \cdot \text{g}^{-1}$)

K_f : Freundlich coefficient

C_e : equilibrium herbicide concentration ($\mu\text{g} \cdot \text{ml}^{-1}$)

n_f : empirical sorption coefficient.

The sorption coefficient ($n_f = 0.95$) reflects a low isotherm curvature and a ratio close to proportionality between the amount adsorbed ($\mu\text{g} \cdot \text{g}^{-1}$) and the equilibrium concentration which can be represented by K_d (K_d = amount adsorbed ($\mu\text{g} \cdot \text{g}^{-1}$) per equilibrium concentration ($\mu\text{g} \cdot \text{ml}^{-1}$)). This value revealed weak chemical affinity for the soil samples used. To normalize K_f variability, Rao and Davidson [16] suggested to refer to soil organic carbon (OC) and to use $K_{\text{oc}} = (K_d / \% \text{OC}) \cdot 100$. This variable is often used to compare the adsorption of substances on varied substrates. The lower the K_{oc} is, the weaker the adsorption occurs. The value obtained (148), is comparable to the one for atrazine [6], while the figure was 19500 for trifluraline in the same conditions and for the same soil material [10]. At last, percentages of adsorbed tebutam slowly decreased when herbicide concentration of the aqueous solution increased (26% of tebutam in solution is adsorbed for the concentration $0.008 \text{ mg} \cdot \text{l}^{-1}$, against 21% for the concentration $20 \text{ mg} \cdot \text{l}^{-1}$). This may suppose, on one hand the influence of soil-water partition because of tebutam's high affinity for water (solubility in water at 20°C , pH 7: $790 \text{ mg} \cdot \text{l}^{-1}$; [14]), and on the other hand the involvement of non-limited binding sites because of an empirical n_f coefficient near to 1.

3.1.3. Desorption isotherm

The desorption isotherm is described by the Freundlich modified equation (5), [17]:

$$Q_{\text{ads}} = Q_{\text{ads0}} - K_{\text{fd}} \cdot (C_{\text{e0}} - C_e)^{n_{\text{fd}}} \quad (5)$$

Q_{ads0} : initial amount of adsorbed herbicide ($\mu\text{g} \cdot \text{g}^{-1}$)

Q_{ads} : amount of adsorbed herbicide ($\mu\text{g} \cdot \text{g}^{-1}$)

C_{e0} : initial equilibrium herbicide concentration ($\mu\text{g} \cdot \text{ml}^{-1}$)

C_e : equilibrium herbicide concentration ($\mu\text{g} \cdot \text{ml}^{-1}$)

K_{fd} : empirical constant of desorption

n_{fd} : empirical desorption coefficient

$Q_{\text{ads}0}$ and $C_{\text{e}0}$ correspond to the values measured after the adsorption experiment.

K_{fd} and n_{fd} are calculated from non-linear regression using the statistical soft STATITCF.

The results showed that the experimental data were correctly described by the model according to an r^2 of 0.97 to 0.99 (Tab. I).

Desorption intensity (n_{fd}) was equivalent to adsorption intensity (n_{f}) for the lowest concentration, but greater than adsorption for 1 and 20 $\text{mg}\cdot\text{l}^{-1}$ initial concentrations. Figure 2 shows that tebutam is easily desorbed and weakly hysteretic.

Nevertheless, the total percentages of desorbed herbicide are clearly smaller when the initial amounts held by adsorbent are lower.

Percentages desorbed were 85.9, 86.6 and 93.0 respectively for initial tebutam concentrations of 0.008, 1 and 20 $\text{mg}\cdot\text{l}^{-1}$. This tends to show that weak reversible bonds, which accounted for most of the adsorption, become significant for small adsorbed amounts. These bonds slowed down and limited desorption in our conditions.

3.2. Degradation under controlled conditions

3.2.1. Degradation of tebutam

After a one-week latency period, measured extractable tebutam during incubation showed a first order kinetics for herbicide dissipation and a

herbicide half-life (DT_{50}) of 14 days (Fig. 3) approaching the figure for isoproturon in the same conditions [13]. Degradation products were observed early during incubation. Solvent extract analysis by HPLC equipped with a β radioactivity detector, allowed the separation of four unidentified metabolites (A to C) and tebutam. After 16 days of incubation, degradation compounds accounted for nearly 61% of extractable radioactivity. Metabolite A disappeared quickly, but compounds B and C tended to persist in soil medium. Metabolite D was observed 19 days after treatment, reaching 9% of extractable residues at the end of incubation.

3.2.2. Tebutam mineralization and non-extractable residues

The results given in Figure 4 show that after a very short latency period of 5 days, nearly 34% of ^{14}C tebutam was mineralized in 12 days. The intensity of this process then slowed down and gradually reached 58% of the initial applied amount in 31 days. The shortness of the latency phase and the speed of mineralization could result from the low resistance of tebutam to degradation. Possible microflora adaptation can be discounted since the soil was only treated once with tebutam 2 years earlier. The slower mineralization, from the 14th day after treatment, does not result from resistance to mineralization, but from a lack of bioavailable residues. The latter are part of the strongly adsorbed products, not accessible by

Table I. Parameters of the modified Freundlich equation describing the desorption isotherm of tebutam.

Concentration $\text{mg}\cdot\text{l}^{-1}$	$Q_{\text{ads}0}$	K_{fd}	$C_{\text{e}0}$	n_{fd}	r^2
0.008	0.011	1.190 ± 0.03	0.006	0.94 ± 0.07	0.98
1	1.145	1.367 ± 0.04	0.752	1.17 ± 0.11	0.97
20	19.830	0.268 ± 0.02	15.680	1.65 ± 0.05	0.99

$Q_{\text{ads}0}$: initial amount of adsorbed herbicide

K_{fd} : empirical constant of desorption

$C_{\text{e}0}$: initial equilibrium herbicide concentration ($\text{mg}\cdot\text{l}^{-1}$)

n_{fd} : empirical constant of intensity of desorption

r^2 : correlation coefficient of linearized Freundlich isotherms.

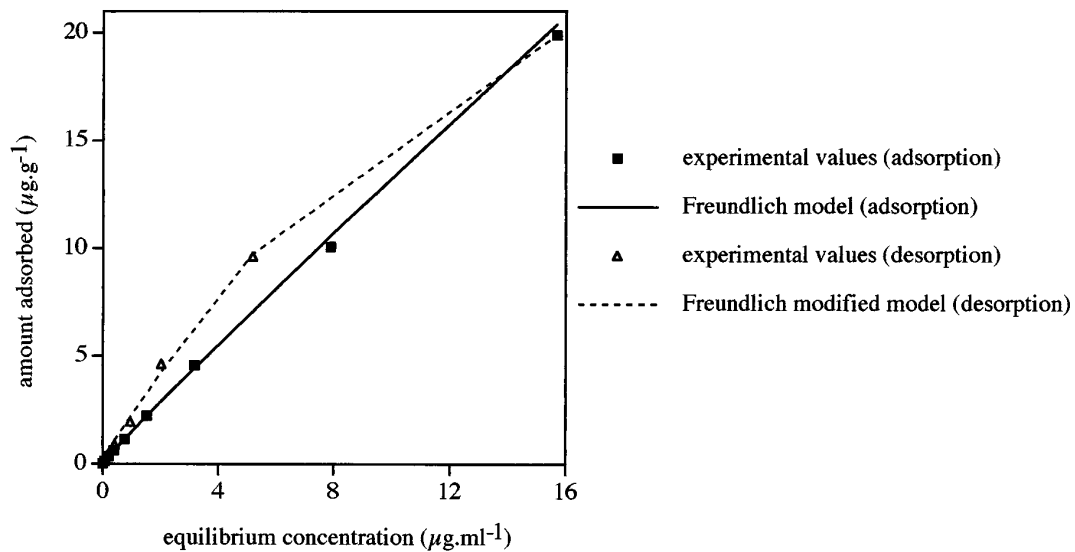


Figure 2. Example of experimental and predicted tebutam adsorption-desorption isotherm on brown silty clay soil. (Standard deviation of experimental values are not noticeable.)

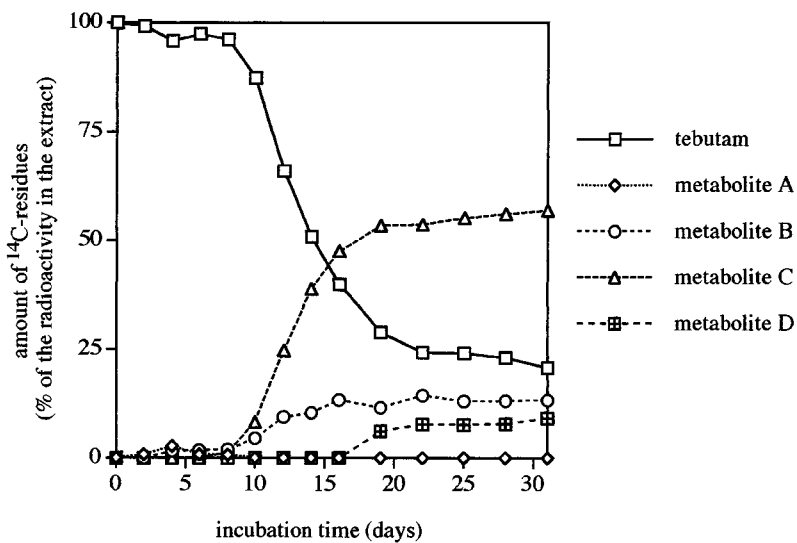


Figure 3. Evolution of ¹⁴C tebutam and ¹⁴C tebutam degradation products during incubation time. (Standard deviation of experimental values are not noticeable.)

microorganisms, and represent a share of non-extractable residues.

Like mineralization, non-extractable residue formation is rapid, reaching nearly 46% of the initial amount applied 12 days after treatment (Fig. 4).

Non-extractable amounts decreased progressively from 14 days after treatment and accounted for 35% of initial applied amounts at the end of incubation time. The results given in Figure 5 show that the released residues were not found in soil methanolic extracts. Hence it would appear that

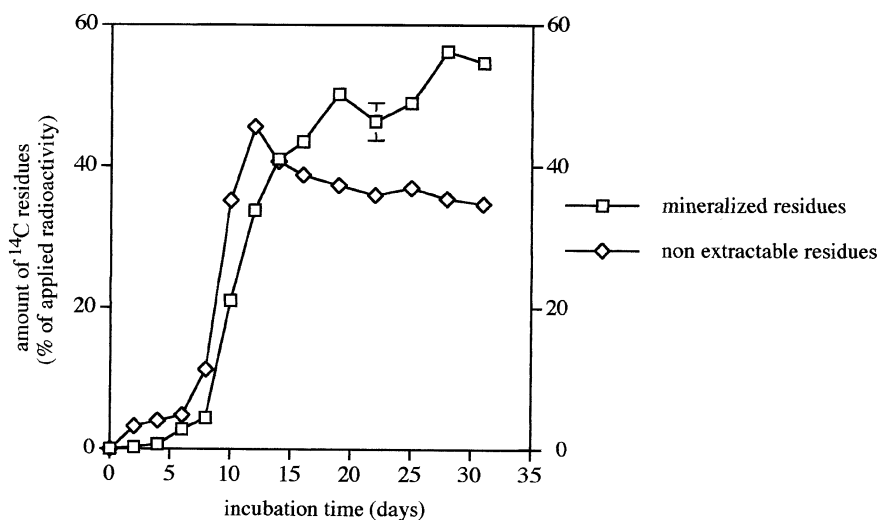


Figure 4. Evolution of tebutam mineralization and tebutam non-extractable residues during incubation time.

they supply the slow increase in mineralization observed from 14 days after treatment. Non-extractable residue releases appear to have stabilized 31 days after treatment, and this also applies to mineralization.

Alongside the rapid non-extractable residue formation and substantial mineralization, the methanol extractable residues become negligible (Fig. 5) and increasingly difficult to extract as incubation proceeds. Thus only 18% of the radioactivity present in the soil (^{14}C tebutam initially applied - mineralized ^{14}C residue), was still extractable at the time of the first extraction after 12 incubation days. These observations substantiate the hypothesis of slower mineralization due to the lack of bioavailable residues.

4. Conclusion

Our studies showed that tebutam is an herbicide that is adsorbed rapidly but in limited amounts (21 to 26% of initial applied amount). Sorption due to diffusion within the soil particles, only accounts for a small share of the immobilized chemical. Moreover, desorption is fairly easy and hysteresis is low, even though tebutam is more difficult to desorb with low adsorbed amounts. These observations tend to suggest that this herbicide may be

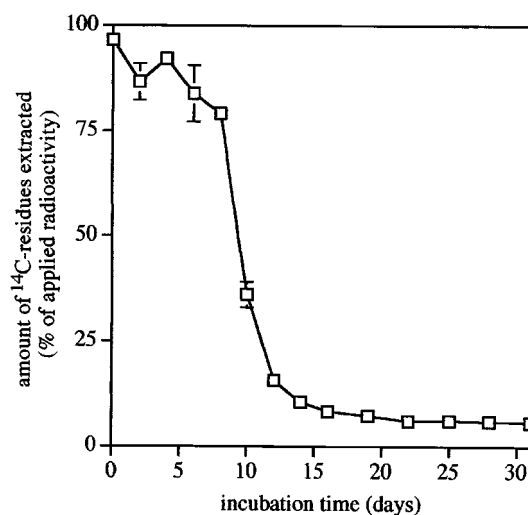


Figure 5. Quantitative evolution of soil methanolic extracts during incubation time.

easily entrained by water. However, environmental contamination may be limited by rapid transformation ($\text{DT}_{50} = 14$ days) to different metabolites (80% of extractable radioactivity at the end of incubation time). Mineralization is very fast (58% of initial amount applied is mineralized in 31 days) and appears to be hindered by the non-bioavailable and non-extractable residues present in the soil after 12 incubation days. Thus, non-extractable residues accounted for 46% of the initial applied

amount 12 days after treatment, but then decreased progressively. This could correspond to release of non extractable residues followed by mineralization.

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