



Influence of the isomerism on the sorption of imazamethabenz-methyl by soil

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HIGHLIGHTS

- ▶ Soil pH is the most important factor influencing the sorption of IMBM.
- ▶ Positional isomerism influence the sorption of *m*- and *p*-IMBM on clay-rich soil.
- ▶ The sorption on soil organic matter does not depend on positional isomerism.

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ABSTRACT

The sorption of meta and para isomers of the herbicide imazamethabenz-methyl, methyl 6-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*m*- or *p*-toluate, by three soils and soil organic matter, was studied. Sorption isotherms conformed to the Freundlich equation. It was found that pH was the main factor influencing the adsorption in all of the systems. The highest level of sorption was measured on soils with low pH and high organic carbon content. Moreover, at low pH value, the soil rich in smectite clays, favoured the sorption of *meta* rather than *para* isomer. The higher affinity of clay surfaces for the *meta* isomer of the herbicide is due to the stabilization of the *meta* protonated form by resonance. At all pH values, the sorption on soil organic matter did not differ between two isomers.

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1. Introduction

Imazamethabenz-methyl (IMBM) is an imidazolinone herbicide used for broadleaf weeds in corn and wheat (Hedlund and Andersson, 1987). As for other imidazolinone herbicides, its mode of action is related to the inhibition of acetohydroxyacid synthase (AHAS), a key enzyme involved in the biosynthesis of branched-chain amino acids in plants (Shaner et al., 1997). Although, according to Decision 2005/303/EC, EU does not permit the presence of IMBM in plant protection products, the IMBM herbicide is widely used to control wild oats and broadleaf weeds principally in Canada, US and China, under the trademark Assert.

Aerobic degradation accounts for most losses of IMBM herbicide from soil (Mangels, 1991). Moreover, photolytic degradation can also occur on soil surfaces (Curran et al., 1992).

Since IMBM undergoes protonation–deprotonation reactions in water (Pintado et al., 2009), the protonation state could be very important in both soil sorption and abiotic degradation (Pusino et al., 1995; Brigante et al., 2007).

The sorption of IMBM on soil conforms well to the Freundlich isotherm, with apparent increasing of adsorption with increasing of organic matter and clay content of the soils (Carton et al., 1997).

Commercial IMBM is composed of a mixture of two positional isomers: *meta* (methyl 6-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*m*-toluate, *m*-IMBM) and *para* (methyl 2-[(RS)-4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl]-*p*-toluate, *p*-IMBM), Fig. 1.

The effect of positional isomerism on the chemical and photochemical degradation of IMBM is known (Brigante et al., 2007). The degradation, either chemical or photochemical, is faster for the *meta* than for the *para* isomer. Analogously, *meta* IMBM is adsorbed on homoionic clays to a higher extent than *para* isomer if the positively charged protonated form of the herbicide is involved. On the other hand, if hydrogen-bonding is responsible for sorption, no difference is exhibited by the two isomers (Pusino et al., 1995).

To our knowledge, no analogous information is available concerning IMBM sorption on soil. Thus, this work was aimed at studying the influence of the isomerism on the sorption of IMBM isomers on soil in relation to possible environmental implications. For this purpose, the study was carried out on three soils with different physico-chemical properties. Further, the sorption of IMBM

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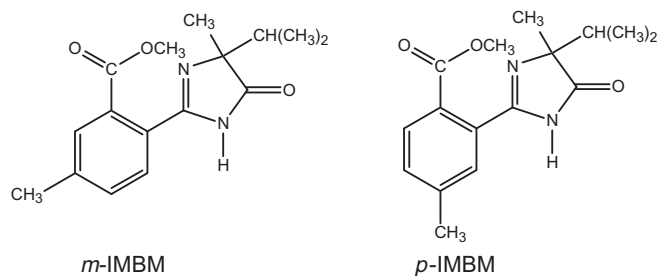


Fig. 1. Chemical structure of IMBM isomers.

isomers on humic acid was examined. The effect of pH on sorption was also analyzed.

2. Materials and methods

2.1. Materials

Imazamethabenz-methyl ($C_{16}H_{20}N_2O_3$), either as *para*-isomer (*p*-IMBM, 96.2% purity) or *meta*-isomer (*m*-IMBM, 96.8% purity), was supplied by American Cyanamid Co., Princeton, N. J. Both *p*-IMBM and *m*-IMBM are white solids with a solubility of 1370 and 857 mg L⁻¹ in water at 25 °C, respectively. The octanol/water partition coefficient (K_{ow}) of *p*-for *p*-IMBM and *m*-IMBM is 66 and 35, respectively (Tomlin, 1995).

Three Italian soils, a sandy loam Entisol from Fornace (Emilia-Romagna), a clay loam Vertisol from Bassona (Emilia-Romagna), a loamy sand Inceptisol from Monghidoro (Emilia-Romagna), were examined. The samples were air-dried and sieved to <2 mm. The particle size distribution was measured by the Purdue University Soil Testing Laboratory using the pipette method (Day, 1965). The organic carbon was determined according to the modified Walkley–Black method (Jackson, 1958). The cation exchange capacity (CEC) was determined by the BaCl₂ procedure (Hendershot and Duquette, 1986). Soil pH was determined on slurries with a soil/water ratio of 1:2.5 w/w. Selected physico-chemical properties of the soils are listed in Table 1. The clay mineralogy of all soils was determined by X-ray diffraction (XRD) analysis (see Table 1).

Humic acid (HA) was obtained from Monghidoro soil according to the procedure of Stevenson (Stevenson, 1972). After precipitation, it was centrifuged, redissolved, and precipitated three times, then dialyzed against distilled water until salt-free, and finally freeze-dried.

The solvents, of HPLC grade (Carlo Erba Reagenti, Milano, Italy), were used without further purification.

Table 1
Selected physical–chemical properties and mineralogical composition of investigated soils.

Property	Fornace	Bassona	Monghidoro
OM (%)	1.3	4.4	6.3
Clay (%)	18.0	61.0	20.0
Sand (%)	57.0	21.0	58.0
Silt (%)	25.0	18.0	22.0
pH	7.8	7.6	5.4
CEC ^a	17.5	51.2	23.5
Smectite (%)	12.0	46.0	3.0
Illite (%)	42.0	32.0	–
Chlorite (%)	–	9.0	34.0
Kaolinite (%)	24.0	7.0	3.0
Quartz (%)	–	6.0	53.0
Potash feldspar (%)	22.0	–	7.0

^a cmol kg⁻¹.

2.2. Sorption on soil

IMBM sorption isotherms were obtained using a batch equilibrium method. In general, triplicate samples of 5 g of air-dried soil, sieved through a 2-mm mesh screen, were equilibrated in polyallomer centrifuge tubes with 10 mL of aqueous herbicide solution. The initial concentrations of the herbicide ranged between 18.3 and 182.6 μM for *meta* isomer and 17.2 and 172.2 μM for *para* isomer. The tubes were shaken (end over end) for 24 h at 25 (±2 °C). Preliminary batch kinetic studies indicated that a pseudo-equilibrium was reached for both the isomers within 9 h and that no significant changes in concentration occurred after further shaking for 48 h. After equilibration, the suspension was centrifuged at 19000g for 15 min, and the supernatant was pipetted off and analyzed immediately. The amount adsorbed by soil was calculated from the difference between the initial and final concentrations of IMBM isomer in solution. The effect of pH of the soil solution on IMBM sorption was examined by using a batch equilibrium method after the addition of HCl.

2.3. Sorption on humic acid

Triplicate samples of HA (20 mg) were equilibrated at 25 ± 2 °C in polyallomer centrifuge tubes with 10 mL of herbicide aqueous solution (pH 3.5). IMBM concentrations before equilibration ranged between 18.3 and 182.6 μM for *meta* and 17.2 and 172.2 for *para* isomer. The tubes were shaken (end over end) for 20 h. After centrifugation, the supernatant solution was removed and analyzed. Sorption was also studied on humic acid brought to pH 4.6 (CaA) by the addition of Ca(OH)₂.

Preliminary kinetic studies indicated that equilibrium was reached and that no degradation took place within the aforementioned times.

2.4. HPLC analyses

The concentration of IMBM isomers was determined by HPLC. The system was assembled as follows: a Waters 1515 pump equipped with a Waters 2487 UV–Vis programmable detector operating at 238 nm; Breeze chromatography software; a μBondapak C₁₈ analytical column (10 μm, 300 × 3.9 mm i.d.) eluting with acetonitrile plus water (65 + 35 by volume) previously brought to pH 2.8 with phosphoric acid at a flow rate of 1 mL min⁻¹. The retention time of both IMBM isomers was 4.5 min.

The quantitative analysis of IMBM isomers was performed by using an external standard. Calculations were based on the average peak areas of the external standard. The detection limit for both

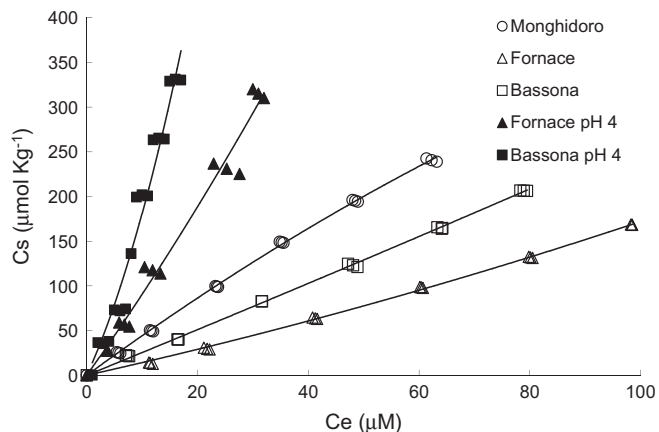


Fig. 2. Sorption isotherms of *m*-IMBM on soils.

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