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Residual effect of tembotrione in soil with distinct textures and humidity

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ABSTRACT: The use of herbicides with extended residual periods enables a longer time of weed control, although it may cause toxicity in more sensitive crops after application. The aim of our study was to evaluate the residual effect of tembotrione in soil with distinct textures and humidity. In the first experiment, two bioassays were carried out in one clay-textured Oxisol, with different relative humidities - irrigated and with water deficit. In the second experiment, two bioassays were carried out in a medium-textured and in a clay-textured Oxisol, in different relative humidities. The residual tembotrione effect in soils with water deficit was up to 300 days after application, independently from soil texture. In humid soils, however, the period of this effect is reduced to 200 days long.

Key words: bioassays; crop rotation; phytotoxicity; soil persistence

Efeito residual do tembotrione em solo de textura e umidade contrastantes

RESUMO: O uso de herbicidas com longo efeito residual possibilita o controle das plantas daninhas por um período de tempo maior, mas podem proporcionar toxicidade em culturas sensíveis plantadas após sua utilização. O objetivo desta pesquisa foi avaliar o efeito residual do tembotrione no solo de textura e umidade contrastantes. No primeiro experimento, foram conduzidos dois bioensaios em Latossolo Vermelho-Amarelo de textura argilosa, com umidade contrastantes - irrigado e com déficit hídrico; no segundo experimento, dois bioensaios em Latossolo Vermelho-Amarelo de textura média e argilosa, ambos com umidades contrastantes. O efeito residual do tembotrione em solos com déficit hídrico é de até 300 dias da aplicação, independente da textura do solo. Entretanto, esse efeito é reduzido para 200 dias em solos úmidos.

Palavras-chave: bioensaios; fitointoxicação; persistência no solo; rotação de cultura

Introduction

Tembotrione (2-[2-chloro-4-mesyl-3-((2,2,2-trifluoroethoxy) methyl)benzoyl]cyclohexane-1,3-dione) is an herbicide registered in Brazil for maize crop, used in post-emergence weed control, with solubility of 71,000 mg L^{-1} and pKa of 3.2 (Tarara et al., 2009; Agriculture & Environment Research Unit, 2017), being a triketone, classified as a weak acid, showing molecular neutrality in low pH values and the anionic form in neutral or alkaline pH ranges (Barchanska et al., 2016). This molecule inhibits the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD), affecting the carotenoid synthesis resulting leaves whitening in sensitive plants, evolving to necrosis and death (Karam et al., 2009).

According to studies of tembotrione degradation in soil at field conditions, the 90% dissipation period exceeds 105 days (Austria, 2011). On the other hand, this property in laboratory conditions is longer than 342 days (Health Canada Pest Management Regulatory Agency, 2014), being dependent on humidity and soil physical-chemical characteristics. Tembotrione is not persistent in field conditions, except when loamy sands are present (US EPA, 2007), and may be toxic to sensitive crops, as beet (França et al., 2016), and carrot (Bontempo et al., 2016).

The toxicity of an herbicide is a property that varies according to many field conditions, including crop species, type of soil and humidity. In crop rotation, beet crop (*Beta vulgaris* L.) is usually followed by corn plantation. However, beet is very sensitive to herbicide residuals in the soil, being a good bioindicator to various compounds as atrazine and tembotrione (Bontempo et al., 2016), sulfentrazone (Blanco & Velini, 2005), 2,4-D and picloram (Santos et al., 2013) at bioassays. Nevertheless, there is a lack of scientific information about tembotrione behavior in Brazilian soils, especially related to a sensitive plantation, as beet. Thus, this work aims to evaluate the effect of tembotrione residuals onto a sensitive crop at two Oxisols Red-Yellow with different textures and humidities.

Materials and Methods

Oxisols were characterized by X-ray diffraction (XRD) in a XRD-6000, Shimadzu X-ray diffractometer (Cu-Kα1 radiation, 30 kV, 30 mA, 0.02º step) and by Fourier transform infrared spectroscopy (FT-IR) in a FT-IR 4100, JASCO spectrometer, 400 to 4,000 cm^{-1} (resolution of 4 cm^{-1} and accumulation of 256 scannings).

The experiment was carried out in two bioassays, placed in a greenhouse from the experimental area at Rio Paranaíba, Minas Gerais state, Brazil (Latitude: 19º12'29" S and Longitude: 46º07'57" W). In the first bioassay, the influence of humidity on the tembotrione residual was evaluated for two years, in which a dystrophic Red-Yellow Oxisol was used as the substrate. This soil was clay-textured, containing 42% of clay, 51% of silt and 7% of sand, cation exchange capacity (CEC) of 8.77 $cmol_c dm^{-3}$, 2.9% of organic matter and pH 5.5.

In the second bio-essay, the same objectives of the first experiment were sought, although using two different Oxisols as substrates: the dystrophic Red-Yellow Oxisol from the first experiment and a Red-Yellow Oxisol from a plantation areas of Serra do Salitre, Minas Gerais state (Latitude: 19º05'50" S and Longitude: 46º40'25" W). This soil was medium-textured, containing 19.4% of clay, 2.7% of silt and 77.9% of sand, CEC of 5.79 $cmol_c$ dm^{-3}, 2.25% of organic matter and pH 6.2.

In both essays, soil and tembotrione (75.6 g ha^{-1}) were added to vases (5.0 dm^3 of capacity) perforated in the bottom in order to allow water flow. Six seeds of beet (*Beta vulgaris*) were sowed in each vase. After five days of emergence, thinning was carried out, keeping four remaining plants in each vase - the experimental unit.

Treatments were represented for an evaluation period (30, 90, 150, 200 and 300 days after tembotrione application) and for presence or absence of daily irrigation. The absence of irrigation was maintained until the end of the corresponding evaluation period. In the first year, treatments were called clay-Oxisol irrigated and dried. At the 28th day after emergence (DAE), the aerial sections of plants were collected and stored in paper bags for oven drying under forced ventilation under 72 ºC, until constant weight, for dry matter (DM) determination. Data were converted to a percentage of DM reduction compared to the reference.

The experimental treatment was completely randomized with four replicates. The database was statistically described and graphics were plotted by SigmaPlot 11.0 software.

Results and Discussion

Characterization of Oxisols samples

Vibrational spectroscopy in the infrared region with Fourier transform (FTIR) may describe the main functional groups presented in soil minerals. Figure 1 presents the FTIR spectra of Oxisols applied in the experiments. The two types of Oxisol show characteristic bands assigned to axial

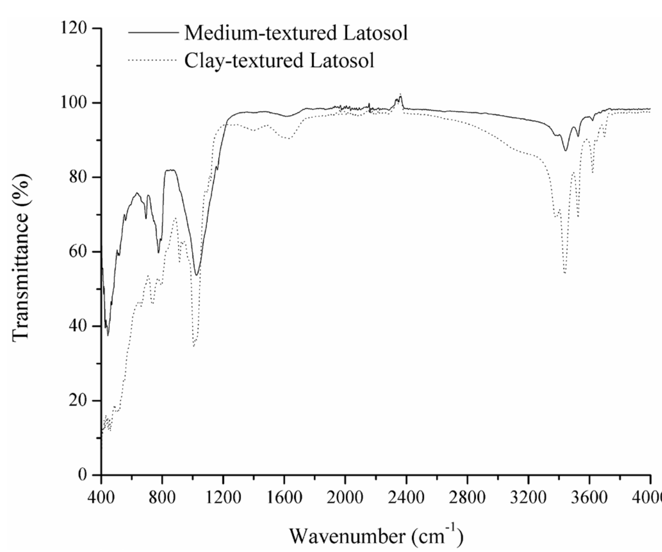

Figure 1. FTIR spectra of Oxisols.

deformation of SiO-H groups (3445 cm^{-1}), which are related with strong bands of Si-O found in the fingerprint region (1020 cm^{-1}) (Silverstein & Webster, 2000). Si-H bending is presented with presented in a band and on a shoulder in clay and medium-textured spectra, respectively. Sharp bands found I the region of 3700-3600 cm^{-1} may be caused by vibrational modes of Al-OH groups (Oliveira et al. 1998; Dick et al. 2003). In the fingerprint region, some differences are observed between the two Oxisols studied. Clay-textured Oxisol present exclusive bands of silicon groups as follows: angular deformation of Si-H (914 cm^{-1}) and stretching of Si-O-Si (975 cm^{-1}).

In general, the transmittance percentage in clay textured Oxisol is lower than that observed in medium-textured soil. Functional groups described above do not provide precise identification of mineral composition of soil samples not even give an overall explanation of adsorption/desorption phenomena. The mineral composition or its variety may offer a better understanding of how tembotrione interacts with the system soil particles surface/water/beetroot seeds.

X-ray diffraction was applied to show the variation in mineral phase composition between medium-textured Oxisol and clay-textured Oxisol. Diffractograms presented in Figures 2A and 2B indicate the presence of mineral phases

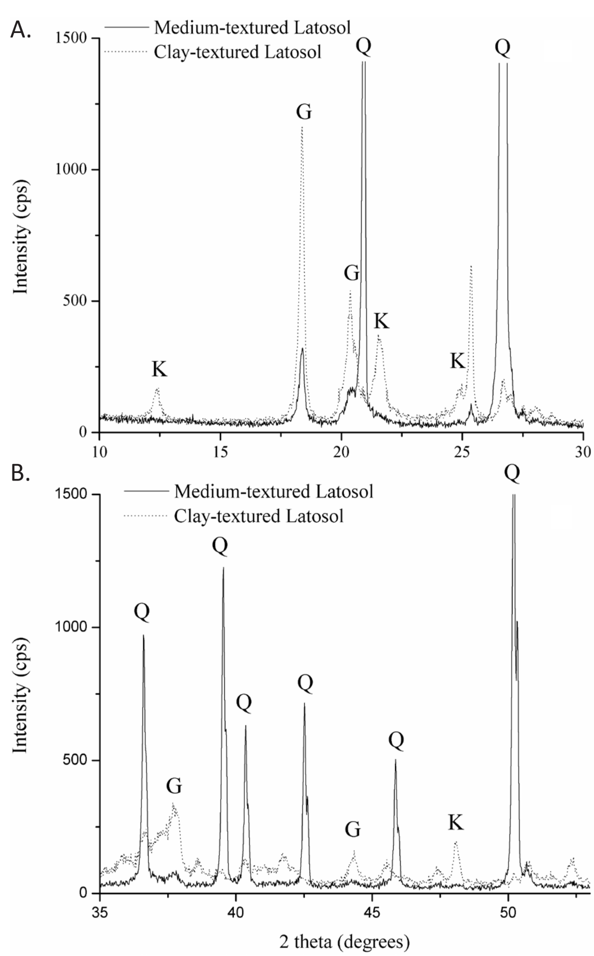

Figure 2. X-ray diffraction patterns of Medium-textured Oxisol and Clay-textured Oxisol in the 2-theta range of 10-30° (A) and 35-55° (B).

commonly associated with clay composition in the clay-textured Oxisol, featuring kaolinite (K) and gibbsite peaks (G). On the other hand, almost all peaks of medium-textured Oxisol are assigned to quartz (Q).

Another difference observed between the soils analyzed is that Medium-textured Oxisol is more ordered than clay-textured Oxisol. This crystal-like behavior of medium-texture Oxisol in X-ray diffraction suggests that this Oxisol may present a lower specific surface area (SSA) when compared to the other soil sample. Generally, the higher the SSA, the higher the adsorption capacity, due to an increase of the number adsorption sites available to immobilize tembotrione. According to The Pesticides Properties Database, when pH decreases, tembotrione presents a higher immobilization in the same type of adsorbent (Agriculture & Environment Research Unit, 2017). In our study, clay-textured Oxisol may be able to reduce pH of the suspension owing to aluminum hydroxyl groups presented in the chemical structure of kaolinite and gibbsite, and consequently, immobilize a higher amount of tembotrione than medium-textured Oxisol.

Influence of humidity in tembotrione residual after two years period

Dry matter (DM) accumulation in aerial sections of beet was inhibited (without growth) for tembotrione until 150 days and was affected (< 40%) up to 300 days after herbicide dosage when treatments were irrigated in years I and II (Figure 3). Thus, daily irrigation may have favored desorption of tembotrione, shifting it from colloids sites to the soil. In soil, tembotrione would be available for dissipative processes, which probably occurred after 200 days, when residuals decreased. In this environment, it is known that tembotrione hydrolysis takes place, due mainly to biotic degradation and photolysis as a secondary cleavage process (Calvayrac et al., 2013).

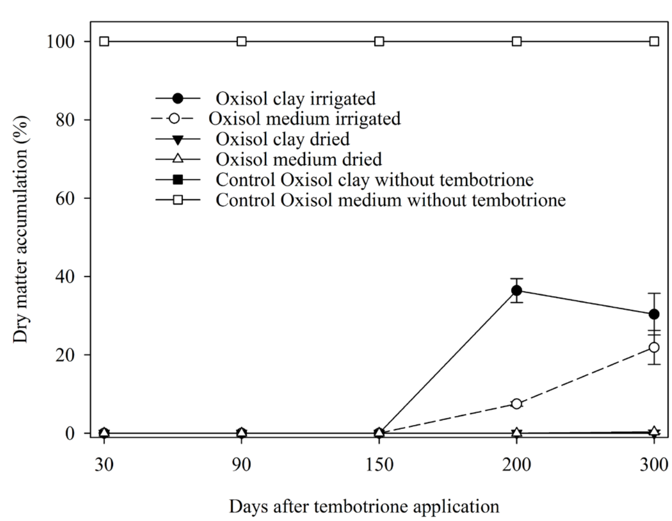

Figure 3. Dry matter accumulation percentage of beet sowed in clay-textured Oxisol, dried or irrigated in years I and II, contaminated with tembotrione (75.6 g ha^{-1}) up to 300 days. Vertical lines associated to each symbol represent the standard deviation (n = 5).

In the treatments with dried soil, however, there were no aerial sections to collect, due to germination of beet before 28 DAE and occurrence of whitening in leaves, necrosis and death, up to 300 days after tembotrione dosage (Figure 3). These results show that beet is very sensitive to tembotrione, which has a residual content in e soil during the evaluated period, as also reported for França et al. (2016).

The results from treatments with irrigated medium-textured Oxisol were similar to those presented for clay-textured Oxisol, on years I and II: the percentage of DM from aerial sections of beet were reduced by tembotrione up to 150 days after dosage. In the 300 day-period, the DM percentage maximum values ranged from 10 to 20%. In the dried soil, there was no beet seedling growth up to 300 days (Figure 4).

As can be seen, the adsorption of herbicide in organic matter may have occurred on both soil types, by the production of weakly bonded ligand residues. At this stage, tembotrione is available to return to soil suspension by desorption mechanisms. This may be explained by the low sorption coefficient (K_f = 1.59), giving mobility to tembotrione, and also by the herbicide sorption increase when pH reaches low levels (Agriculture & Environment Research Unit, 2017).

Water may affect the tembotrione interaction with soil. In our study, low humidity in soil improved the sorption of tembotrione at organic colloids and minerals, partially resulting in herbicide unavailability for prior to weed control. This may be explained by the low amount of the herbicide ready to leaching, due to its limited solubility in dried soils. When water is available, tembotrione presents a low adsorption capacity at metal oxides, carbonates and clay surfaces of soil, due to its negatively charged structure at the ionic form (Zemelka, 2015). Thus, constant values of humidity may favor herbicide stability in soil suspension for a longer period, contributing to sorption at the root system of beet. Belo et al. (2007) described similar behavior, in which water interfered in the phytoremediation of tebuthiuron and trifloxysulfuron sodium for *Canavalia ensiformes* e *Stilozobium aterrimum*. The decrease in the tembotrione activity with the rise of water reposition in soil may be explained by microbial activity growth, followed by biodegradation.

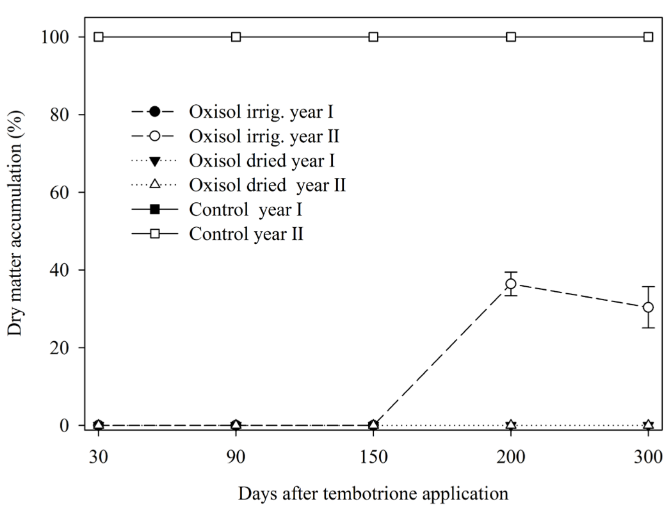

Figure 4. Dry matter accumulation percentage of beet sowed in clay-textured Oxisol, dried or irrigated, contamined with tembotrione (75.6 g ha^{-1}) up to 300 days. Vertical lines associated to each symbol represent the standard deviation (n = 5).

In dried soil, a slow dissipation of tembotrione is observed, independently of the texture of the soil, during the period of experiments. Blanco et al. (2010) reported the same behavior and explained that the dryness favored sorption of the herbicide onto soil colloids (clay and organic matter), not enabling dissipative processes, even chemical or biological.

Influence of humidity on the residual effect of tembotrione in two distinct soils

The lowest dry matter values from aerial sections of beet were observed in the medium-textured Oxisol (Figure 4). This fact indicates that sorption of tembotrione is higher in the clay-textured soil, prevailing its permanence in the soil. When constant values of humidity are observed, the release of the herbicide in soil occurs and absorption on roots by bioindicator species takes place.

In distinct textures of soil, the sorption of pesticides may be due to organic matter content. Firmino et al. (2008) described a low sorption of imazapyr in sandy soils (low organic matter content). In our study, the humidity on medium-textured soil, which presents lower contents of clay and organic matter when compared to clay textured soil, enabled availability of tembotrione in the soil solution, interfering with the growth of bioindicator species.

Taking into account that the sort of soil management may influence on content and characteristics of organic matter and humic substances, soils with different management may present a variation on herbicide sorption (Ferri et al., 2005). Thus, the interference on the carotenoid synthesis and its consequences to photosynthesis may affect productivity, probably make the beet plantation unfeasible in areas with tembotrione residues.

These results highlight the importance of the herbicide behavior in soil, as well as the sensitivity of the further species cultivated on areas with tembotrione residues. Thus, plantation problems in beet and other sensitive species due to tembotrione residues from earlier cultivation may be avoided if the behavior of the herbicide on soil is known.

Conclusions

Tembotrione residual show a possible synergistic inhibitory effect on the beet growth when medium-textured soil and no irrigation are applied.

In terms of soil texture, this effect is explained by the low adsorption capacity presented in medium textured soils, due to higher silicate content (from the sandy portion of soil) and low organic matter contents.

The lack of humidity in soil also contributes to the inhibition of beet growth due to the low dissipation or desorption of the tembotrione residual content, promoted usually by water.

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