



## Effect of long term organic amendments on adsorption–desorption of thiram onto a luvisol soil derived from loess

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### ARTICLE INFO

#### Article history:

Received 8 October 2009

Received in revised form 31 March 2010

Accepted 4 April 2010

#### Keywords:

Thiram

Adsorption–desorption

Soil

Organic amendments

### ABSTRACT

The objective of this work was to assess the influence of soil organic amendments on the sorption properties of the fungicide thiram. The organic amendments studied were organic household compost (COM), sewage sludge from municipal water treatment facilities (SLU) and farmyard manure (FYM), which were compared to mineral fertilizer application (MIN). Sorption–desorption experiments were performed using the batch method and the results indicated that the adsorption isotherms were non-linear and were found to conform to the Brunauer–Emmett–Teller (BET) model, suggesting multilayer adsorption and adsorbate–adsorbate interactions after the saturation of the surface layer. In general, distribution coefficient values,  $K_D$ , are dependent on, but not proportional to, the initial concentration of thiram. For a fixed thiram initial concentration, a significant correlation ( $r^2 > 0.851$ ;  $p < 0.001$ ) between  $K_D$  values and the soil organic carbon content (OC) was observed. The highest value of  $K_D$  was observed for the soil amended with compost, which is the one with the highest organic carbon content.  $K_D$  values were divided by the soil organic carbon contents in order to obtain organic carbon partition coefficients  $K_{OC}$ . Comparing  $K_{OC}$  means from 3 (initial concentrations)  $\times$  4 (soil organic matter compositions)  $\times$  3 (replicates) factorial ANOVA allow us to conclude that there is a significant but not proportional influence of the initial concentration of thiram on those values, but changes in the soil organic matter composition, associated to different soil amendments, have no significant influence on adsorption of thiram. To evaluate the reversibility of thiram adsorption, two consecutive desorption cycles were performed with  $\text{CaCl}_2$   $0.01 \text{ mol L}^{-1}$ . The desorption  $K_D$  values were consistently higher (approximately twice) than those for adsorption at the same equilibrium concentrations for all soil samples supporting the existence of hysteresis in the adsorption–desorption behavior of thiram. Despite the fact that the adsorption  $K_D$  values were proportionally increased with increasing total organic carbon content, this was not the case for the desorption  $K_D$  values.

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### 1. Introduction

In the latest years, our research group has given special attention to thiram (Filipe et al., 2009), since it is one of the most used contact fungicides all over the world (Sharma et al., 2003). Thiram, a dithiocarbamate compound, has been used to prevent crop damages, either in the field or during its transport and storage, protecting seeds, fruits, vegetables and ornamental plants from a variety of fungi (*Botrytis* spp., *Anthracois*, *Fusarium* and *Manil-ia*). It is also used as a repellent for fruit and ornamental trees protection from damages caused by rabbits and rodents (Sharma et al., 2003). In Portugal, according to 2003–2008 available reports

(<http://www.dgadr.pt/default.aspx>; last access March 30, 2010), thiram is the second most popular contact fungicide, after traditionally used copper derivatives. For this 5 years period, thiram selling rate showed a significant increase. In spite of the reported burst on thiram application, and in comparison to other pesticides, there is a lack of information on thiram behavior in soils. As any other pesticide, thiram fate in the environment can be ruled by *transformation* processes, which can include pesticide molecule breakdown by chemical, photochemical or biological degradation, or by *transfer processes*, such as adsorption/desorption, runoff, volatilisation and leaching. Among transfer processes, sorption is a key process that extensively controls the behavior of pesticides in soil, determining its distribution between soil and water systems (Senesi, 1992; Aboul-Kassim and Simoneit, 2001). In a previous work, we have reported a strong interaction

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between thiram and humic acids, suggesting the relevance of the soil organic matter on thiram sorption onto soils (Filipe et al., 2009). Other published works have reported adsorption studies of thiram onto lignins, specific adsorbents (e.g., waste resulting from a coal mine, SiO<sub>2</sub> particles, active carbon or sepiolite) (Gonzalez-Pradas et al., 1987; Rupp and Zuman, 1992; Misirli et al., 2004; Stathi et al., 2006) and soils (Valverde-Garcia et al., 1988). However, so far, and to the best of our knowledge, there are no studies reported in the literature about the effects of organic amendments on thiram sorption onto soil. The application of organic wastes, such as municipal solid waste compost, sewage sludge, and farmyard manure, to agricultural soils is a common practice nowadays, being an economically attractive solution to waste disposal, with benefits in terms of improvement of soil properties and fertility (Tejada and Gonzalez, 2007). However, if it is true that organic amendments improve soil fertility by enhancing organic matter levels, maintaining soil health, nutrition, fertility and crop productivity, it is also true that some of the amendments, such as sewage sludge, are prone to introduce several potentially toxic metals and organic contaminants in soils. Recently, an increasing interest has been focused on the effects of these organic amendments on pesticides behavior in soils (Briceno et al., 2007) and it has been demonstrated that organic amendments can significantly change pesticide sorption behavior onto the soil (Dolaptsoglou et al., 2007; El-Aswad, 2007; Majumdar and Singh, 2007; Ghosh and Singh, 2009).

In the present work, we investigate the influence of different organic amendments on the adsorption of thiram onto a luvisol soil derived from loess when compared to mineral fertilizer. The studied organic amendments were municipal solid waste compost, sewage sludge from municipal water treatment facilities and farmyard manure.

## 2. Materials and methods

### 2.1. Chemicals

All chemicals were of analytical grade. Thiram (pure substance, 97%) was purchased from Aldrich, methanol and acetonitrile (HPLC grade) were obtained from Riedel-de Haen and LabScan, respectively. An aqueous 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution was prepared from anhydrous CaCl<sub>2</sub> (Fluka, p.a.). Ultra pure water for aqueous solutions was obtained with a Milli-Q water purification system (Millipore).

Standard stock solutions of thiram (~35 mg L<sup>-1</sup>) were prepared by previous dissolution of the solid in acetonitrile, followed by dilution with 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> aqueous solution (percentage of acetonitrile in the final solution was always lower than 1%). Further dilutions were made in 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>. The stock solution and the diluted ones were prepared just before application to soil samples. A stock solution of 100 mg L<sup>-1</sup> thiram in acetonitrile was used to prepare more diluted standard aqueous solutions of thiram for the HPLC-UV method calibration.

### 2.2. Soils

Soils used in this study were collected on an agricultural field systematically submitted to controlled fertilization since 1962 (Scherer and Sharma, 2002). It is a luvisol soil derived from loess (17.8% clay, 76.3% silt, 5.9% sand) that has followed a cereal-root crop sequence. The field was divided into plots which were treated with different organic amendments and with a regular mineral fertilizer (MIN), this one acting as the control fertilization. The organic fertilizers were: organic household compost (COM, 58 t ha<sup>-1</sup>), sewage sludge from municipal water treatment facilities (SLU,

14.9 t ha<sup>-1</sup>) and farmyard manure (FYM, 9 t ha<sup>-1</sup>). These amounts, given on a dry weight basis, were applied every second year until 1997, then the amounts were changed to 90 t ha<sup>-1</sup> for COM and 10 t ha<sup>-1</sup> for SLU once in 3 years. The amendments were distributed in a completely randomized block design. A total of 12 samples were collected for the present work, corresponding to three replicates (three different plots) for each of the four soil amendment treatments. Soil samples were taken from the topsoil layer (0–30 cm) of each plot. They were air-dried, ground, passed through a 2 mm mesh size sieve, and stored in plastic containers until further use.

Some properties of the soils were determined by Lima et al. (2009). The total organic carbon contents (TOC) are 2.8%, 2.0%, 1.5% and 1.2% for COM, SLU, FYM and MIN soils, respectively.

### 2.3. Batch adsorption/desorption studies

Batch adsorption studies were performed using a soil:solution ratio of 1:5, according to OECD guideline (OECD, 2000). Portions of 1.2 g of soil were taken into 10 mL Pyrex centrifuge tubes and mixed with 6 mL of a thiram solution prepared in 0.01 M CaCl<sub>2</sub>. The concentration of thiram used was in the range 3–35 mg L<sup>-1</sup>. The centrifuge tubes were shaken on an end-over-end shaker (Heidolph Reax) at 100 rpm, during 15 h at 21 ± 1 °C to achieve equilibrium (Filipe et al., 2009). Next, the suspensions were centrifuged at 4000 rpm for 30 min and the supernatant was filtered by 0.22 µm filters (Millex-GV, PVDF membrane) and cleaned-up using a SPE procedure described by Filipe et al. (2007). The thiram concentration in the supernatant was then determined by HPLC-UV, with detection at 270 nm following a procedure described in section 2.5. For each batch experiment, a blank (without thiram) and a control sample (only thiram, without soil) have been performed.

For the soil samples equilibrated with the initial concentration of thiram of 22 mg L<sup>-1</sup>, desorption studies were performed. After the adsorption period and centrifugation of the aqueous suspensions, the supernatant was decanted; the residual supernatant that could not be removed was determined by gravimetry. Thiram concentration in this residual solution was considered to be the same as that measured in the bulk supernatant. A 6 mL portion of fresh 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> solution (without thiram) was added to the centrifuge tubes. The tubes were shaken for another 15 h, centrifuged at 4000 rpm for 30 min and the supernatants were collected and submitted to the same clean-up and analysis procedure as described in the adsorption experiment. The CaCl<sub>2</sub> desorption cycle was repeated once more. At last, two desorption cycles using 5 mL of methanol (4 h) and 5 mL of acetonitrile (48 h) were also performed. The organic extracts were analysed by HPLC-UV without any previous clean-up procedure. All experiments were done at 21 ± 1 °C.

Additionally, in another set of adsorption–desorption experiments, after 15 h of equilibration of soil with a thiram initial concentration of approximately 22 mg L<sup>-1</sup> the supernatant was removed by centrifugation and decantation, and thiram was immediately desorbed with 5 mL of acetonitrile. The acetonitrile desorption cycle was repeated once more. After the desorption period, the supernatant was immediately centrifuged, filtered and analysed by HPLC-UV.

### 2.4. SPE clean-up procedure

The SPE cartridges used in this work were purchased from Supelco (500 mg commercial supelclean envi-18 cartridges, 75 Å pore diameter and 56 µm particle size). The cartridges were set up in a 12-place manifold from Phenomenex and pre-conditioned with 6 mL of methanol, 6 mL of Milli-Q water and 6 mL of 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> aqueous solutions (the sample matrix). An

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