



Influence of soil copper content on the kinetics of thiram adsorption and on thiram leachability from soils

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HIGHLIGHTS

- ▶ Soil copper content has a marked effect on the sorption process of thiram onto soil.
- ▶ Reactions of thiram with copper ions in soil occur.
- ▶ Reaction extension during adsorption may be strongly dependent on the Cu:Thi ratio.
- ▶ The persistence of thiram residues increases with soil copper content.
- ▶ Thiram is not easily leached and copper may contribute to its soil immobilization.

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ABSTRACT

This work aimed to assess the influence of soil copper content on the sorption processes of thiram, a fungicide widely used in agriculture, most of the times together with copper. Two different types of studies were performed: (1) desorption studies of thiram with acetonitrile after batch adsorption equilibration, and ageing of the wet soil for a variable period of time; (2) kinetic studies of thiram adsorption performed using the soil in its original form and after fortification with copper ions. In the desorption studies, with the increase of the ageing time, a decrease of the thiram peak and a simultaneous increase of a new peak, assigned to a copper complex, were observed in the chromatograms. This new peak increases sharply until an ageing period of about 4 d and then this area is maintained approximately constant until 18 d, the maximum ageing period studied. These results indicate that thiram reacts with copper ions along time giving rise to the formation of relatively persistent copper complexes in soil. Desorption studies with CaCl_2 0.01 M solution showed that this complex is not extracted. Thus, it is not easily leached to ground and surface waters and copper may contribute to thiram immobilization in soil. The kinetic studies of thiram adsorption were performed in both soils and for two initial thiram concentrations (~ 7 and 20 mg L^{-1}). For the soil fortified with copper the percentage of adsorbed thiram is higher than observed for the original soil at the same initial concentrations and equilibration times and 100% of adsorption is attained in 15 h or 48 h, depending on the thiram initial concentration. Four kinetic equations, the pseudo first- and second-order equations, the Elovich and the intraparticle diffusion equations were selected to fit the kinetic data of the adsorption process of thiram onto both original and fortified soil. The best model to describe the kinetics of thiram adsorption onto the original soil is the intraparticle diffusion model. For the soil fortified with copper ions we verified that for the highest initial thiram concentration, the best model is also the intraparticle diffusion model, however, for the lower initial thiram concentration the best model is the pseudo second-order kinetic equation, suggesting that, for a high Cu:Thi ratio, a chemical reaction of thiram with copper ions on the soil surface can occur, and it may be the rate controlling step. Since the kinetics of adsorption depends on both soil copper content and the initial thiram concentration in solution, i.e. depends on Cu:Thi ratio, it is difficult to choose a fixed batch equilibration time for adsorption studies of thiram.

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1. Introduction

In Portugal, according to 2002–2010 available reports, fungicides represent about 75–80% of pesticides market sales. Among the different chemical groups of fungicides, the inorganic fungicides are the largest contributors to fungicides sales corresponding to ~86% of the sales volume (~80% sulphur-based fungicides and ~6% copper-based fungicides) and the dithiocarbamate group contribute with ~10%. Among the various dithiocarbamates, thiram is the second most popular contact fungicide. During the 2002–2010 period, thiram selling rate registered a significant increase between 2002 and 2007 and a slight decrease after 2008, which reflects a decrease observed in the sells volume of all pesticides due to climatic and agronomic conditions, but thiram continues occupying a relevant position in the Portuguese market of fungicides, since in 2010 the sales increased again significantly (information available at <http://www.dgadr.pt/default.aspx>; last access 23 June, 2012). However, in comparison to other pesticides, there is a lack of information on thiram behaviour in soils. The literature reports adsorption studies of thiram onto lignins (Rupp and Zuman, 1992), specific adsorbents (e.g., waste resulting from a coal mine, SiO₂ particles, activated carbon or sepiolite) (González-Pradas et al., 1987; Misirli et al., 2004; Stathi et al., 2006) and different soil types (Valverde-García et al., 1988). In a previous work, (Filipe et al., 2009) we have reported a strong interaction between thiram and commercial humic acids, suggesting the relevance of the organic matter content on thiram sorption onto soils. That effect of soil organic matter on thiram sorption and desorption has been confirmed on a later study about the effect of organic amendments on thiram sorption onto a luvisol soil (Filipe et al., 2010), but the results obtained in this second study suggested that metals ions, namely copper ions, could have also a relevant effect on thiram desorption.

Although many studies have been published on the adsorption of pesticides and heavy metals independently, little attention has been given to the phenomena which take place when both are present together. As far as we know, the first studies on the possible influence of copper ions on the adsorption and mobility of organic pesticides in soils were focused on glyphosate (Morillo et al., 1997, 2000, 2002). More recently, some studies about the effect of soil copper ions on other pesticides adsorption and degradation have emerged in the literature (Arias et al., 2006; Dousset et al., 2007; Liu et al., 2007; Pateiro-Moure et al., 2007). However, to our knowledge, no studies have been reported on the effects of heavy metals, namely copper ions, on thiram sorption and desorption onto/from soil. Copper ions are very important since several copper-based fungicides have been extensively used for more than 100 years and many thousands of tons are consumed annually all over the world to prevent plant diseases (Borkow and Gabbay, 2005). Besides, the supply of organic amendments, namely sewage sludge and municipal waste compost to agricultural land, which is an usual and economically attractive practice nowadays, can represent an important source of contamination with this metal (Santos et al., 2010). Thus, in the present work, a systematic study of the influence of copper ions on the adsorption and desorption of thiram from soil was performed in order to clarify the occurrence of reactions with copper ions which can affect the persistence and mobility of thiram.

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade. Thiram (pure substance, 97%) was purchased from Aldrich; HNO₃ (65%) was obtained from

Riedel-de Haen; methanol and acetonitrile (HPLC grade) were obtained from Riedel-de Haen and LabScan, respectively. An aqueous 0.01 M CaCl₂ solution was prepared from anhydrous CaCl₂ (Fluka, p.a.). Ultra pure water for aqueous solutions was obtained with a Milli-Q water purification system (Millipore). Standard solutions of thiram were prepared by previous dissolution of the solid in acetonitrile, followed by dilution with 0.01 M CaCl₂ aqueous solution (percentage of acetonitrile in the final solution was always lower than 1%). Thiram solutions were prepared just before application to soil samples. A stock solution of 100 mg L⁻¹ thiram in acetonitrile was used to prepare more diluted standard aqueous solutions of thiram for the HPLC–UV method calibration. Cu, Zn, Pb, Cd and Cr atomic spectroscopy standards 1000 mg L⁻¹ were from BDH Chemicals, Ltd.

2.2. Soil

Soil used in this study was kindly supplied by Professor Scherer of the Institute of Agricultural Chemistry, University of Bonn and was 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 follows a cereal-root crop sequence. The field was divided into plots which were treated with different organic amendments and with a regular mineral fertilizer. The fertilizer was distributed in a completely randomized block design. For this study we selected two different and aleatory soil plots that were treated with 58 t ha⁻¹ of compost from organic household waste (designated as COM soil). Soil samples (1000 g) were taken from the topsoil layer (0–30 cm) of each plot. They were air-dried, ground, sieved through a 2 mm mesh size, and stored in a plastic container until further use. Some characteristics of COM soil are pH = 7.1, TOC = 2.8%, OM = 5.4%, [Cu]_{total} = 39 mg kg⁻¹, [Pb]_{total} = 100 mg kg⁻¹; [Zn]_{total} = 177 mg kg⁻¹ (Santos et al., 2010), [Cr]_{total} = 35 mg kg⁻¹, [Ni]_{total} = 23 mg kg⁻¹ (Costa, 2008).

2.3. Batch adsorption–desorption studies of thiram

Although two different sets of adsorption–desorption experiments were performed (Experiment 1 and Experiment 2), the general conditions for all of them follow a procedure described previously (Filipe et al., 2010). Briefly, 1.2 g of soil was mixed with 6 mL of a 0.01 M CaCl₂ solution with a known initial thiram concentration in a Pyrex centrifuge tube. For each batch experiment, a blank (without thiram) and a control sample (only thiram, without soil) have been performed. The centrifuge tubes were shaken on an end-over-end shaker at 100 rpm. Next, suspensions were centrifuged at 4000 rpm for 30 min and the supernatant was filtered by a syringe filter unity (0.2 µm, Millex-GV) and cleaned-up using an SPE procedure described elsewhere (Filipe et al., 2010). The thiram concentration in the supernatant was determined by HPLC–UV with detection at 270 nm (Filipe et al., 2008). The residual supernatant that could not be removed was determined by gravimetry and thiram concentration in this residual solution was considered to be the same as that measured in the bulk supernatant. Thiram was desorbed from the residual wet soil with 5 mL of acetonitrile and shaking during 24 h. After the desorption cycle the extracts were centrifuged at 4000 rpm for 30 min, filtered by a syringe filter unit (0.2 µm, Millex-GV) and submitted to thiram analysis by HPLC–UV (Filipe et al., 2008). All experiments were done at 21 ± 1 °C. Experiments using 6 mL of CaCl₂ 0.01 M for desorption of thiram were also performed. The procedure was the same but the aqueous extract was previously cleaned-up as previously described (Filipe et al., 2010) before analysis by HPLC–UV. The specific conditions for the different sets of experiments are as follows. Experiment 1: batch adsorption equil-

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