THE EFFECT OF ORGANIC MATTER AND COPPER IONS ON THE BEHAVIOUR AND FATE OF THIRAM IN ENVIRONMENT

FILIPE O.M.S.[1,2], **VIDAL M.M.**[1,2] **and SANTOS E.B.H.**[3]

[1]Instituto Politécnico de Coimbra, ESAC, DCE, Rua Pedro Nunes, 3030-199 Coimbra, Portugal
[2]CERNAS, Campus da ESAC, Bencanta, 3040-316 Coimbra, Portugal
[3]CESAM, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
E-mail: olga@esac.pt

ABSTRACT

The effect of organic matter and copper ions on the behaviour and fate of thiram in the environment was studied. Adsorption-desorption and kinetic studies in soils with different organic amendments and with different copper contents were performed to assess the behaviour of thiram in soils, and we concluded that copper ions can contribute to the thiram immobilization onto soil. In addition, copper ions can affect degradation of thiram in natural waters and several copper complexes, more persistent than thiram, were identified as result from the degradation of thiram in the presence of copper ions in aqueous solutions.

Keywords: thiram, copper ions, soils, natural water, adsorption-desorption, persistence, dimethyildiothiocarbamates, HPLC-UV-MS/MS^n

1. Introduction

Thiram, tetramethylthiuramdisulfide, is a dithiocarbamate compound that has been used as a contact fungicide with preventive action, worldwide applied not only in agriculture, but also in rubber industry as an accelerator and vulcanization agent. In Portugal thiram is one of the most used fungicides, whose sales have increased significantly along the years and it is also one of the most used fungicides all over the world. However, comparing to other pesticides, there is a lack of information in the literature about the behaviour of thiram in environmental systems, namely, in what concerns its degradation in soil or in water systems and products formed. Furthermore, the effect of Cu(II) on the behavior of thiram in the environment is scarce, despite the fact that Cu(II) based fungicides are frequently applied in the same season and/or in the same crops as thiram, increasing the effectiveness of thiram fungicidal action. Although many studies have been published on the behaviour of pesticides and heavy metals independently, little attention has been given to the phenomena which take place when both are present together.

In this context, the aim of this work was to assess the influence of humic substances and copper ions on the behaviour and fate of thiram in the environment. Different studies were performed to assess the behaviour of thiram in soils and in natural water, studding how humic substances and copper ions can affect its degradation.

2. Experimental

Adsorption-desorption and kinetic studies of thiram onto soil with different organic amendments and with different copper contents were performed as described elsewhere [1,2,3].

River water samples were collected in River Vouga (Carvoeiro station), Aveiro, Portugal and were filtered through a 0.45 mm filter, stored at 4 ºC, spiked with thiram, and analysed by C18-SPE-HPLC-UV as described by Filipe *et al*. [4], after different incubation times

The effect of Cu(II) on the degradation of thiram in aqueous solutions containing different molar ratios thiram:Cu(II) was followed by both UV-Vis and HPLC-MS^n as described by Filipe *et al*. [5]

3. Results

3.1. Behaviour of thiram in soil

Adsorption-desorption studies of thiram onto soil revealed that organic matter [1,2] and soil copper contents [3] affect thiram adsorption-desorption processes, influencing its leachability and persistence in soil. In fact, soil copper content has a marked effect on the sorption process of thiram onto soil. Thiram reacts with soil copper ions and the rate of those reactions depends on the ratio thiram:Cu. Thus, the rate and extent of those reactionsduring adsorption studies can be strongly dependent on the soil copper content and on the initial thiram concentration in solution, making the choice of the equilibration time for batch sorption studies and adsorption isotherms determination a difficult task. The complexes formed with copper in soil are persistent, and they are not easily leached from soil to groundwater. Thus, we can conclude that copper may contribute to the immobilization of thiram in soil.

3.2. Behaviour of thiram in natural waters

Data about thiram recovery from natural waters [4] showed fast thiram degradation in environmental matrices. Thiram was completely recovered (>80%) from river water samples when analyzed immediately after spiking but scarcely recovered when analyzed after one or two days (Table 1). However, several thiram recovery experiences in the presence of EDTA, as chelating agent, suggested that metal ions, namely copper ions, were involved in thiram degradation. This mechanism may be environmentally relevant since copper based fungicides are often applied either in the same season or in the same crops as thiram.

Table 1: Thiram recoveries (R) from 1 L of river water sample spiked with thiram (SD=standard deviation, n=number of experiments performed in each case).

Sampling Date	Equilibration time (h)	[Thi] (μg L^{-1})	R ± SD (%)
Jun 2006	0	2.82	77.6 ± 1.4 (n=3)
		11.3	79.6 ± 1.1 (n=2)
	24	2.82	< LOD (n=2)
		11.3	40.9 ± 2.4 (n=2)
Oct 2006	0	11.1	98.0 ± 1.3 (n=2)
	24	11.1	41.8 ± 0.8 (n=2)
Mar 2007	0	11.2	98.8
	24	11.2	61.3 ± 6.3 (n=6)
	48	11.2	25.0
Apr 2007	0	11.2	83.1
	24	11.2	20.1 ± 2.7 (n=3)
	48	11.2	< LOD (n=3)

Thus, a deeper study [5] about the effect of copper ions on the degradation of thiram in aqueous solutions by UV-Vis and HPLC-MS/MS^n, allowed us to conclude that the presence of an excess of Cu(II) accelerates the degradation of thiram in aqueous solutions. The evolution of the UV–Vis spectra overtime for 2 mg L^{-1} thiram solution in the presence of Cu(II) is shown in Fig. 1. In the presence of Cu(II), the spectrum of thiram gives rise to spectra dominated by two absorption maxima at 260 and 420 n. Over time, the maximum at 420 nm decreases and gives rise to a new maximum at 385 nm. The formation of the species responsible for the absorption at 420 nm and the conversion to those responsible for the absorption at 385 nm occur faster when the excess of copper is higher. Besides, the results allowed us to identified a $[CuThi]^{2+}$ complex which degrades into $[(DMDTC)Cu]^{+}$. This complex readily decomposes to other copper complexes which are quite persistent, and that were identified for the first time.

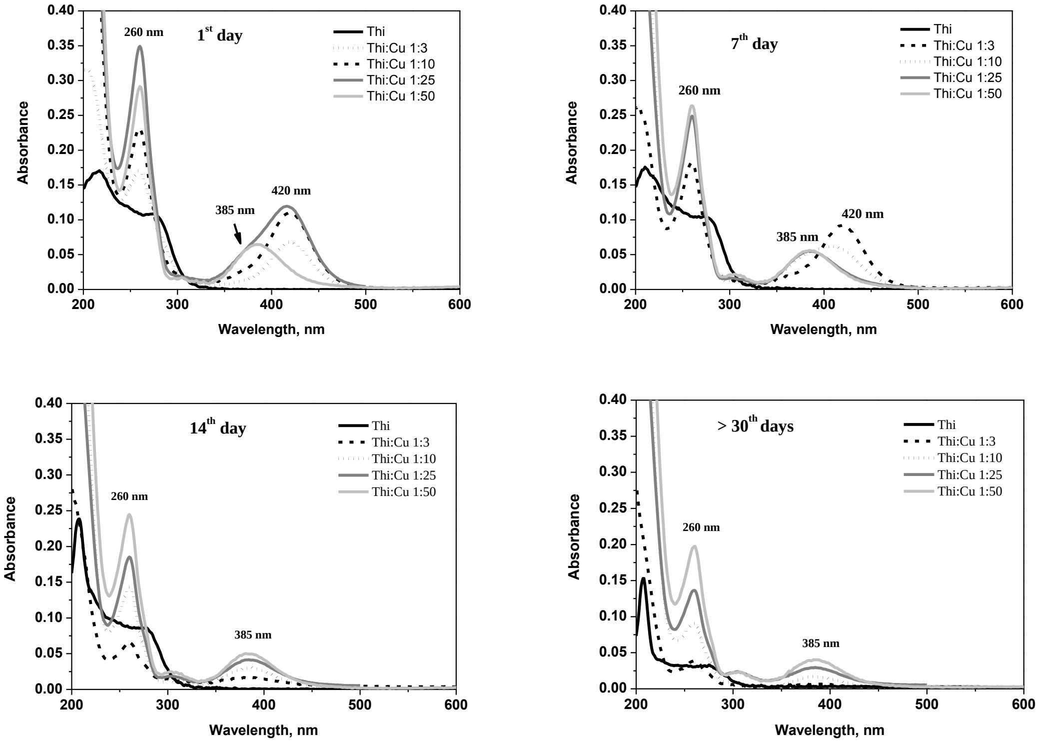

Figure 1: – UV-Vis spectra of a 2.0 mg L^{-1} thiram aqueous solution (─) containing molar ratios of Thi:Cu: (- - -) 1:3, (···)1:10, (─) 1:25 and (─) 1:50, and recorded 1, 7, 14 and 34 days after preparation.

4. Conclusions

Thus, we conclude that the organic matter and copper ions have important effects on the behaviour and fate of thiram in the environment. However it should be highlighted that copper ions have an extremely marked effect on the degradation of thiram giving rise to quite persistent degradation products. Some of those products have been identified for the first time by HPLC-MS/MS^n.

ACKNOWLEDGMENTS

O. Filipe wishes also to acknowledge a PhD grant from FCT (SFRH/BD/39551/2007). The authors also thank the financial support provided to CERNAS (PEst-OE/AGR/UI0681/2014) and CESAM (PEst-C/MAR/LA0017/2013) by the Portuguese Foundation for Science and Technology (FCT).

REFERENCES

1. Filipe O.M.S., Vidal M.M., Duarte A.C., Santos E.B.H. (2009) Adsorption-Desorption behavior of thiram onto humic acid, J. Agric. Food Chem., **57**, 4906-4912.
2. Filipe O.M.S., Vidal M.M., Duarte A.C., Scherer H.W., Schneider R.J., Santos E.B.H. (2010), Effect of long term organic amendments on adsorption–desorption of thiram onto a luvisol soil derived from loess,. Chemosphere, **80**, 293-300.
3. Filipe O.M.S., Costa C.A.E, Vidal M. M., Santos E.B.H. (2013), Influence of soil copper content on the kinetics of thiram adsorption and on thiram leachability from soils, Chemosphere **90**, 432-440.
4. Filipe O.M.S., Vidal M.M., Duarte A.C., Santos E.B.H. (2008), Influence of fulvic acids and copper ions on thiram determination in water, J. Agric. Food Chem., **56**, 7347–7354.
5. Filipe O.M.S., Santos S.A.O., Domingues M.R.M., Vidal M.M., Silvestre A.J.D., Neto C.P., Santos E.B.H. (2014), Effect of copper ions on the degradation of thiram in aqueous solution: identification of degradation products by HPLC-MS/MS, J Hazard Mater., 279, 125–132.