APPLIED SOIL ECOLOGY 40 (2008) 138–145

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Ecological detoxification of methamidophos by earthworms in phaiozem co-contaminated with acetochlor and copper

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ARTICLE INFO

Article history:
Received 6 March 2008
Accepted 27 March 2008

Keywords:
Ecological detoxification
Bioremediation
Earthworm
Methamidophos
Multiple pollution
Soil ecology

ABSTRACT

In view of the ubiquitous co-existence of methamidophos, acetochlor and copper (Cu) in agricultural soils, ecological detoxification of methamidophos in phaiozem by earthworms was examined using the detoxic incubation experiments with illumination. It was validated that the earthworm *Eisenia fetida* is a useful soil animal in the process of methamidophos detoxification as the assistance of soil microbes and enzymes. Due to the action of earthworms, the half life of methamidophos with concentration of 15 mg/kg in phaiozem could decrease from 5.61 days to 5.08 days. Dynamics of methamidophos detoxification by earthworms could conform to the logistic model. Under the condition of multiple pollution combined with acetochlor (20 mg/kg) and Cu (300 mg/kg), ecological detoxification of methamidophos by earthworms became complicated. Acetochlor played a promoting role in the biodegradation of methamidophos to some extent, while it was basically inhibited by Cu.

1. Introduction

As a typical organophosphorus insecticide, methamidophos has been widely applied to agricultural production in China, USA, the Netherlands and other countries in the world in view of its high effectiveness in killing various pests (Lin et al., 2000; Wu and Miyata, 2005; de Castro and Chiorato, 2007). Even in 1990, the amount of methamidophos applied to agricultural fields was up to 3.5×10^4 t (Lin et al., 2000), ranking the first in the application of insecticides in China. The normal dosage of methamidophos per hectare ranges from 187.5 to 900.0 g as the purified compound. Due to its effectiveness in killing various pests, it may be applied frequently according to the occurrence of pests in an agricultural field and other areas. And spraying is the normal method of application in fields. Because of its relatively short half-life, readily degradable property by chemical, biological, biochemical and ecological processes and high mobility in soils, methamidophos residues in soils have been seldom investigated (Hung et al., 2002; Athanasopoulos et al., 2005; Yen et al., 2000). However, with the increasing dosage of methamidophos applied and continual input to agricultural soils (Sun and Zhang, 2002), the amount of methamidophos residues in agricultural soils has even exceeded the self-purifying capacity of soil ecosystems (Liao et al., 2003; Zhou et al., 2004; García-de la Parra et al., 2006; Zhou and Wang, 2006). As a result, methamidophos has been detected in high concentrations in plants such as vegetables and crops, and thus leading to some direct and potential adverse effects on ecosystem health and environmental safety (de Castro et al., 2000; Spassova et al., 2000; Karlen et al., 2003;

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0929-1393/$ – see front matter
doi:10.1016/j.apsoil.2008.03.014

Battershill et al., 2004; Li et al., 2005). In other words, more and more attention has been paid to the ''pseudo-persistence'' of methamidophos in ecosystems in despite of its relatively short half-life.

According to our previous investigation, methamidophos is also one of the most frequently applied pesticides in Chinese coastal areas with a high economy-increasing rate, particularly in the phaiozem area of northeast China (Yu and Zhou, 2003; Zhou et al., 2004). With frequent application of the pesticide in agricultural production, there is a continual accumulation of methamidophos in soil environment (Yu and Zhou, 2005; Yu et al., 2005); although various environmental factors such as soil components, solution pH, and cationic exchange (CEC) had some influences on methamidophos sorption in soils, with the increase of mineral contents, organic matter, pH and CEC in soils the sorption of methamidophos increasing accordingly (Koleli et al., 2007). At the same time, some herbicides such as acethochlor and fungicides containing metals such as copper (Cu) are also applied widely in order to achieve high cropping rates (Yu and Zhou, 2003; Zhang et al., 2003). In addition, many large thermal power plants in the same area have been built in order to produce sufficient electric and heat energy for winter, and as a result, the fly ash containing Cu from coal combustion in the power plants becomes a point source of Cu pollution when waste material is finally deposited in the soil (Zhou et al., 2004; Klose and Makeschin, 2005; Wang and Zhou, 2005).

Besides the non-point pollution damage caused by the increasing use of methamidophos due to its mobile characteristics in soil environment, methamidophos also may affect the soil microbe directly. Su et al. (2007) examined toxic effects of methamidophos in agricultural phaiozem on *nifH* gene, namely the nitrogenase iron protein gene, which is one of the oldest functional genes in the history of gene evolution served in nitrogen fixation of bacteria using the denaturing gradient gel electrophoresis (DGGE) and the sequencing approaches in a microcosm experiment. It was showed that the medium tested concentration (150 mg/kg) of methamidophos caused the most apparent changes in *nifH* gene diversity at the first week, while the high concentration (250 mg/kg) of methamidophos produced prominent effects on *nifH* gene diversity in the following weeks, and joint toxic effects of methamidophos and acetochlor on *nifH* gene were also apparent.

On the other hand, the self-purification and detoxification function of soil ecosystems is increasingly degraded with unceasing application of chemical pesticides and the multiple pollution by more than one pollutant (Simonich and Hites, 1995; Zhou, 1995; Zhou, 2003; Wang and Zhou, 2005; Zhou, 2006), especially with the application of methamidophos, because the biological toxicity of the pesticide is very strong (Zhou et al., 2004) and the desorption of the pesticide from soils is very rapid and its bioavailability is also high (Yu, 2004; Worek et al., 2007). Although people know in theory that the self-purification ability of soil ecosystems are mainly related to the activity of microorganisms as the main force decomposing organic pollutants (Awasthi et al., 2000; Zhang et al., 2003; Zhou et al., 2004), whether earthworms themselves and enzymes from the activity of earthworms in soils can degrade methamidophos, contribute to the degradation of methamidophos and promote the decomposing function of microorganisms or not is still vague, especially under the condition of multiple pollution combined with other chemicals (Zhou, 1995; Zhou and Wang, 2006). Thus, the research on earthworm detoxification of methamidophos in phaiozem co-contaminated with other chemicals including acetochlor and Cu is of practical and scientific significance, and will provide a useful basis for strengthening methamidophos detoxification in complicated environments where the multiple pollution takes place (Zhou, 1995; Zhou and Wang, 2005).

2. Materials and methods

2.1. Soil sampling

Samples of the tested soil, phaiozem (black soil), as a typical zonal soil in northeast China, were collected from a fallow field (47°26′N, 126°38′E) in the Hailun Station of Agro-ecological Experimentation, Chinese Academy of Sciences, which is situated at Hailun County, Heilongjiang Province, China. No agricultural chemicals have been used in the past decades at the sampling site, which is located in the continental temperate monsoon zone, with a dry and cold winter and a warm and wet summer. Annual mean temperature is about 1.5 °C. Annual precipitation averages range between 500 and 600 mm, of which 70% occurs between May and September. The length of the annual frostless period is only around 30 days (Yu and Zhou, 2003; Zhang et al., 2003). Basic physical and chemical properties of the tested soil are listed in Table 1.

2.2. Chemicals and reagents used

Commercial formulations of methamidophos (O, S-dimethyl phosphoroamido thiolate, $CH_3SCH_3OPONH_2$), 40% of miscible oil reagent (pH 6.37), and acetochlor ($C_{14}H_{20}ClNO_2$), 50% of miscible oil reagent, were used as the tested agrochemicals. And $CuSO_4 \cdot 5H_2O$ of analytic grade was used as the added heavy metal. Besides, all other reagents used in this work were at analytic grade.

2.3. Detoxic experiments

The tested concentrations (Table 2) of methamidophos, acetochlor and Cu in phaiozem were set according to our

Table 1 – Basic physical and chemical properties of the tested soil

Sampling depth (cm)	0–20
Soil pH[a]	6.58
OM ($g\,kg^{-1}$)	37.83
Total N ($g\,kg^{-1}$)	2.56
Total P ($g\,kg^{-1}$)	0.61
Total K ($g\,kg^{-1}$)	26.00
Particle size (%)	
Sand	33.8
Silt	39.6
Clay	26.6

[a] Soil pH was determined on the basis of pH-H_2O.