

Cross-enhancement of accelerated biodegradation of organophosphorus compounds in soils: Dependence on structural similarity of compounds

Brajesh K. Singh^{a,b,*}, Allan Walker^a, Denis J. Wright^b

^aHorticulture Research International, Wellesbourne, Warwick CV35 9EF, UK

^bDepartment of Biological Sciences, Imperial College London, Silwood Park Campus, Ascot, Berks SL57PY, UK

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Abstract

Rates of degradation of seven organophosphate nematicides and insecticides were examined in two soils known to show accelerated biodegradation of fenamiphos and one soil known to show accelerated biodegradation of chlorpyrifos. The results indicated that several organophosphate insecticides and one nematicide were susceptible to cross-enhanced degradation in the soil showing accelerated biodegradation of chlorpyrifos. No cross-enhancement was observed in the two soils showing accelerated degradation of fenamiphos. Fumigation resulted in the complete inhibition of pesticide degradation in all soils. The data suggested that the cross-enhancement of selected pesticides in chlorpyrifos-degrading soil was dependent on the structural similarity of the compounds. Mechanisms of degradation of pesticide in soil support this hypothesis, where structurally similar compounds (diazinon, parathion, coumaphos and isazofos) were hydrolysed by microbial activity in chlorpyrifos-degrading soil but the degradation products were accumulated. Enhanced degradation of chlorpyrifos and fenamiphos was found to be stable in the laboratory condition for a period of one year.

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1. Introduction

Extensive and repeated use of the same pesticides for a number of years without any crop or pesticide rotation has occasionally resulted in unexpected failures to control the target organisms. It has been demonstrated that a fraction of the soil biota can develop the ability to rapidly degrade certain soil-applied pesticides. This microorganism-mediated phenomenon has been described as enhanced or accelerated biodegradation. Enhanced degradation of pesticides can be a problem for farmers if the applied pesticides are degraded so quickly that they are unable to control the target pests. Induction of enhanced degradation typically requires several applications of the pesticide with a relatively short time interval between applications

(Walker et al., 1986), although there have been reports of induction of this phenomenon after a single treatment (Felsot and Shelton, 1993; Singh et al., 2003b). The role of abiotic factors such as soil pH in the induction and stability of enhanced degradation has been shown for several pesticides (Bending et al., 2003; Singh et al., 2003a, b). The problem of enhanced degradation becomes more significant if related pesticides can also be degraded rapidly in soil due to cross-enhancement (cross-adaptation) of degradation (Racke and Coats, 1990). Cross-adaptation of enhanced biodegradation has been reported within many groups of pesticide, such as the thiocarbamates (Wilson, 1984), carbamates (Horng and Kaufman, 1987; Morel-Chevillet et al., 1996), dicarboximides (Mitchell and Cain, 1996) and isothiocyanates (Warton et al., 2003).

Most organophosphorus pesticides have similar general structure. Fig. 1 contains structural formula of all organophosphorus compounds used in this study. The major pathway for their degradation involves hydrolysis of the phosphotriester bond (Munneck, 1976). These characteristics of similar chemical structures and similar degradation routes should make organophosphorus compounds susceptible to cross-enhancement. However, Racke and Coats

* Corresponding author. Present address: Environmental Science, Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK. Tel.: +44 1224 498200; fax: +44 1224 498207.

E-mail address: b.singh@macaulay.ac.uk (B.K. Singh).

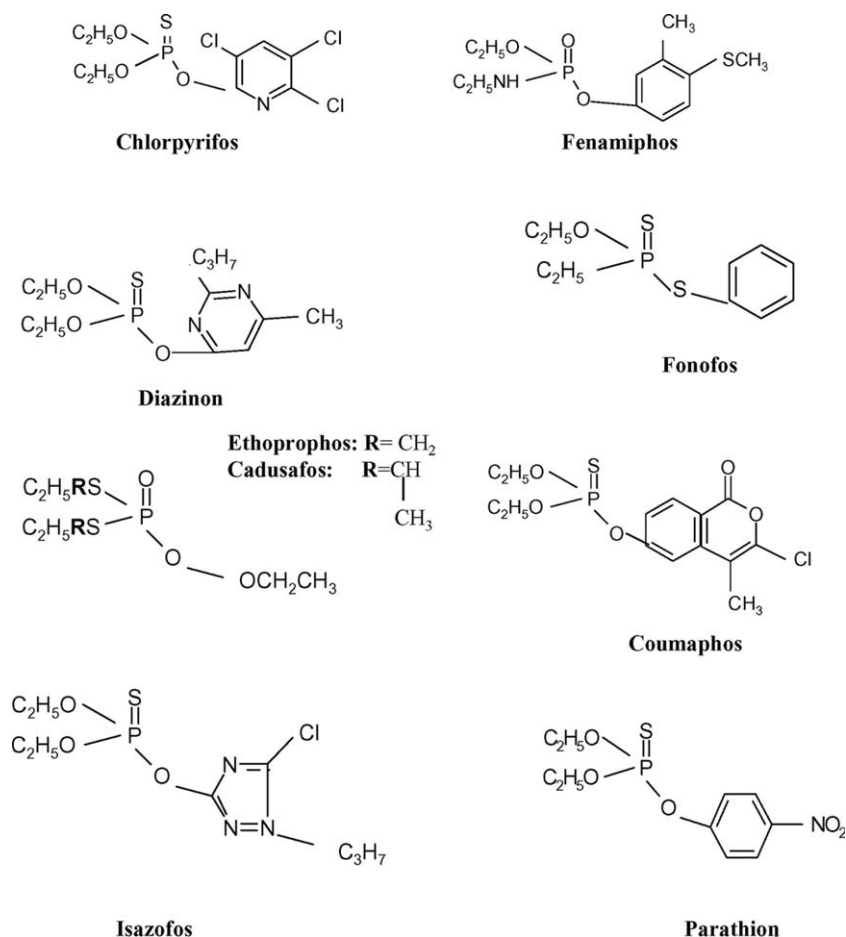


Fig. 1. Chemical structure of organophosphate pesticides used in experiments.

(1988) reported only limited cross-adaptation for enhanced biodegradation within this group.

Chlorpyrifos (O, O-diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) is used world-wide as an agricultural insecticide. Its environmental fate has been studied extensively and the reported half-life in soil varies from 10 to 120 days (Racke et al., 1988), with 3,5,6-trichloro-2-pyridinol (TCP) as the major degradation product. This large variation in half-life has been attributed to variation in factors such as soil pH, temperature, moisture content, organic carbon content and pesticide formulation (Getzin, 1981; Racke et al., 1988).

The biological efficacy of the plant nematicide fenamiphos (ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate) can be significantly reduced by enhanced biodegradation (Anderson and Lafuenza, 1992; Ou, 1991; Stirling et al., 1992; Singh et al., 2003b). It is oxidised rapidly in soil to fenamiphos sulfoxide (FSO) and fenamiphos sulfone (FSO₂), both of which have similar nematicidal activity to fenamiphos (Waggoner and Khasawinah, 1974) and degradation studies therefore usually include an estimation of their total toxic residues (TTR), a combination of the amounts of parent compound plus the two oxidation products. Chung and Ou (1996)

reported that in soils showing enhanced biodegradation of fenamiphos, the parent compound is oxidised to FSO, which is then rapidly hydrolysed to FSO-phenol (FSO-OH). FSO-OH is subsequently mineralised to CO₂. In this situation, the step involving transformation from FSO to FSO₂ is not important.

Previous studies have shown the lack of efficacy of chlorpyrifos and fenamiphos against target pests in Australian sugarcane and banana fields due to the development of enhanced biodegradation in the soil (Singh et al., 2003a, b). If there is cross-adaptation to related pesticides, this could cause major problems to farmers. Because enhanced degradation generally develops in response to extensive and repeated pesticide use, how long an enhanced degradation can persist in the absence of the pesticide, is an important aspect for pest management.

Smelt et al. (1996) reported that enhanced degradation of ethoprophos was stable for three years. The stability of enhanced degradation can be influenced by several abiotic factors and may vary from compound to compound and from field to field. Recent observations of pH effect on stability of enhanced degradation have signified the role of abiotic factors on stability of enhanced degradation (Bending et al., 2003; Singh et al., 2003b). In the present

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