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Dissipation and environmental fate of herbicide H-9201 in carrot plantings under field conditions

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ABSTRACT

The dissipation of herbicide *O*-methyl-*O*-(2,4-dimethyl-6-nitrophenoxy)-*N*-isopropyl phosphoramidothioate (H-9201) in soil, water and its harvest residue in carrot was studied. The most likely pathway of hydrolysis was outlined and the initial hydrolysed metabolite was identified by GC/MS. Several simulation models were used to evaluate the experimental data, and the best-fit model for H-9201 was found to be the first-order Biphasic Model. It is postulated that rainy weather conditions following spraying favoured initial rapid residue removal; that is, the compound was washed into or bound with the soil and, with less surface loss, dissipation was slower. The hydrolysis study indicated that the herbicide hydrolysed faster in alkaline and acidic aqueous solutions where the hydrolysis process followed first-order kinetics, but followed pseudo first-order kinetics at pH 7. Degradation occurred as a first-order kinetic in natural pond water. The persistence of the herbicide residue in post-harvest carrot was lower than 0.02 mg/kg.

1. Introduction

Agrochemicals play important roles in modern agriculture. However, concerns about food safety and the environmental impact of agrochemical residues have increased. Due to agricultural and non-agricultural applications, and the subsequent surface runoff and leaching to groundwater, the environment is widely contaminated by agrochemicals (Rozemeijer & Broers, 2007), such as atrazine, which can be found in groundwater and surface water (Pereira, Rostad, & Leiker, 1990). Currently, most national governments pay considerable attention to the data requirements on environmental fate and animal toxicology in the process of agrochemical registration. In addition, even registered pesticides often require to pass through a re-registration process to ensure that they meet current guidelines, regulatory triggers and safety profiles. More recently, global conservation programmes have been developed to protect all countries from environmental contaminants. Thus, environmentally friendly herbicide application systems and farm system efficacy are ways of addressing environment impact issues and of helping to maintain food safety.

O-Methyl-*O*-(2,4-dimethyl-6-nitrophenoxy)-*N*-isopropyl phosphoramidothioate (H-9201) is an experimental compound with low toxicity and high herbicidal activity, which will be registered in China for agricultural applications. This chemical was designed by QSAR established by Corwin and Toshio (1964) and the quantitative correlation of structure–activity was first reported by Chen et al. (1981). Follow up studies have been reported by Yang, Wu, Ren, and Zhang (1995); Yang, Wu, Zhang, Wang, and Cheng (1991); Yang et al. (1986). Excellent broad-spectrum weed control against barnyard-grass and broadleaf weeds was documented with little or no side effect on the crops (Yang, Zou, Wang, & Cheng, 2006) in field studies. H-9201 could potentially reduce or replace some herbicides which are the cause of environmental concern, such as the sulfonylurea derivatives (residual carryover injury to the following crops). However, questions remain as to the kind of environmental concerns which H-9201 might raise. Is it safe to wild animals and other organisms? What is its environmental fate after application? Our work, therefore, seeks to provide baseline information on the environmental profile of H-9201 to contribute to the scientific assessment of the impact of this compound on public health, agriculture and the environment and to improve the efficacy of farming practices while helping to determine a maximum residue limit (MRL) value. We report here, for the first time, the results of a two-year field study of H-9201 from 2003 to 2004 in Nanjing, China.

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2. Material and methods

2.1. The analytical standard

The analytical standard was obtained from NanTongJiangShan Agrochemical and Chemical Co., Ltd and its purity was certified by the supplier to be greater than 98.5%. Solvents used in all analyses were analytical reagent or HPLC grade.

2.2. Climate information

Nanjing is located in the Yangtse delta (Jiangsu province, eastern China, 31°14′N, 118°22′E), in the lower reaches of the Yangtse River (Lu, Gong, Zhang, & Burghardt, 2003). The climate is characterised by a typical transition from tropical–subtropical to temperate and has profuse rainfall. The annual mean temperature is 15.5 °C, the maximum temperature is 42.6 °C, and the annual mean number of rainy days is 115, with a mean annual precipitation of 39.37 in. There is an intense period of rainfall from late June to mid-July (Niu, Dong, & Du, 2005; Yin, Ni, & Shi, 2001). During the trial period, the average daily minimum temperature was 8.7 °C, and the average daily maximum temperature was 16.2 °C.

2.3. Soil properties

The dominant soils in and around Nanjing are Eutric and Mollic Gleysol and Gleyic Luvisol with inclusions of Plansol and Eutric Fluvisol, The dominant natural vegetation is deciduous broadleaf forest (Zhao, Zhang, Harald, & Yang, 2007). The study area was located southeast of Nanjing, where vegetable production is the main business in a gently undulating landscape comprised mainly of yellow brown soil (clay loamy typic-fe-accu argosols in Chinese Soil Taxonomy) (Zhang, Chen, Tan, & Sun, 2007), with 2.45% total C, 0.21% total N, pH(H_2O) 7.85. It has never been treated with H-9201.

2.4. Field trial

2.4.1. Experimental design

Two separate fields had been planted with carrot in previous years and had no history of H-9201 use. A formulation of H-9201 was sprayed at the recommended application rate (1050 g ai/hm^2) and at double the rate to the soil surface before seedling emergence by hand once with an air-powered sprayer on these separate lands, respectively; the double rate was to imitate overlap application of the herbicide. In addition, in each experiment, a control (water) experiment was carried out in the absence of H-9201. These single and double application rates were employed and tested in the harvest residue study; the double rate was also sprayed on the soil surface once for the study of residue degradation with time.

2.4.2. Harvest residue test process

2.4.2.1. Sample collection. Carrot samples were collected with the tops discarded at 143, 141, 139, 137, 135 and 130 days pre harvest and at the usual carrot harvest day. Two kilograms of carrot samples were collected for each replicate using the method of five plots sampling. After the leaves were discarded, the carrot samples were chopped and homogenised in a blender. The sub-samples were immediately subjected to analysis or stored at −20 °C for a short time.

Soil samples were collected at the same time as the carrot samples, by obtaining a 2 kg soil sample for each replicate using the method of five plots sampling from the earth surface to 15 cm deep. The samples were air-dried at 20 °C, sieved through nylon sieves with 40, 60 and 100 mesh to obtain sub-samples. All samples were placed in polyethylene bags and taken to the laboratory, where they were analysed.

2.4.2.2. Sample extraction. For carrots: a 10 g mincing sample was homogenised with 10 ml acetonitrile in a centrifuge tube, followed by liquid–liquid partitioning formed by the addition of 4 g anhydrous MgSO4 plus 1 g NaCl. After centrifugation, the 5 ml acetonitrile layer was removed and evaporated to dryness under a nitrogen stream. The obtained residue was re-dissolved in 2.0 ml acetone, and then cleaned by passing through an amino disposable cartridge (500 mg, 6 ml, SPE Supelclean, Supelco Inc., Bellefonte, PA, USA). Ten millilitres acetone was used as the elution solvent. The resulting extract was dried under a stream of nitrogen and dissolved in 2 ml of acetone ready for chromatograph injection. For soil: a 10 g soil sample was extracted with 20 ml acetone and processed using the same extraction steps as described above except that the elution solvent, a 10 ml mixture of acetone/*n*-hexane (1:1 V/V), was used to elute the same column. The residue was dissolved in 2 ml of acetone, and then analysed by gas chromatography.

2.4.2.3. Dynamic residue test process. Topsoil samples (0–15 cm) were collected using stainless-steel tools at 2 h, 1, 3, 7, 14, 21, 30, 45, 60, 75 and 144 days after treatment and processed using the same sample preparation steps as described in Section 2.4.2. Samples were extracted as described in Section 2.4.2.

2.5. Hydrolysis study

2.5.1. Experimental design

Distilled water at different pH values was added to 0.1 mol/l NaOH, 0.1 mol/l $KHC_8H_4O_4$, 0.1 mol/l KH_2PO_4, 0.1 mol/l H_3BO_3 and 0.1 mol/l KCL and disinfected at high temperature and pressure for 20 min, pH was measured by a pH metre and adjusted with 1 M H_2SO_4 or 1 M NaOH to provide pHs of 5, 7 and 9. Natural pond water was incubated at 35 °C for one week then stored in darkness to recover all the contents. The hydrolysis study was determined according to EPA guideline 161-1(Hitch, 1982).

Water samples were stored at 25 ± 1 °C in darkness in 1-l amber bottles and spiked with H-9201 using acetone (500 μl) as a carrier and continuously mixed for 30 min prior to initiation of the test. The resulting water concentrations were 10 mg/l, which approached the residue range found in the soil.

2.5.2. Sample collection

Sampling was carried out after 2 h, 8 h, 1, 4, 7, 15, 21 and 30 days after treatment, by taking 10 ml water from each replicate and analysing as triplicate samples. Natural pond water was spiked with H-9201 and sampled at the same time intervals. It was possible that the experimental period needed to be extended, to establish the degradation pathway.

2.5.3. Sample extraction

A 10 ml water sample was mixed with NaCl and was extracted sequentially three times with *n*-hexane; the combined extracts were evaporated to dryness, and then re-dissolved in 5 ml acetone. For the distilled water samples, the extracts were ready for analysis without further treatment. For the natural pond water samples, the extracts were cleaned up by passing through a SPE-C18 column (500 mg, 6 mL, SPE Supelclean, Supelco Inc., Bellefonte, PA, USA), and acetone/hexane (1:1,V/V) was used as the elution solvent.

2.6. Analysis

All the extracts were analysed by gas chromatographs equipped with both flame photometric (FPD) and mass (GC–MS) detectors. Two capillary columns and detectors were used to provide qualitative data. One column was a DB-17 (1 μm film thickness, 30 m length, 0.53 mm ID, J&W Scientific, USA) connected with a flame photometric detector (FPD), the other column was a HP-5MS

(0.25 μm film thickness, 30 m length, 0.32 mm ID, J&W Scientific, USA) connected with MS. The inlet temperature was 250 °C and the injection was carried out in splitless mode using a 1 μl injection volume. For FPD, the detector temperature was 200 °C, the initial oven temperature was 150 °C, and was maintained for 2 min, the temperature was then increased 8 °C/min to 250 °C and held for 12 min. For GC–MS, the gas chromatograph settings were the same as described above. The ionisation potential of the mass selective detector was 70 eV and the scan range was 20–450 *m*/*z*. Helium was used as the carrier gas. All gases were ultra-pure quality.

This analytical procedure gave recoveries of 90.8–98.4% in soil and 89.2–101.8% in carrot, 97.43–100.91% in tap water and from 96.37–115.39% in natural pond water for a range of spiked H-9201 concentrations from 0.05 to 1.0 mg/kg. The analytical detection limit in soil, carrot, tap water and natural pond water was 0.01, 0.02, 0.008 and 0.02 mg/kg, respectively.

2.7. Statistics

Normally a simple first-order kinetic model is used to describe the persistence of a pesticide in the field. Statistical analysis in this study was carried out according to the formal approach proposed by Timme, Frehse, and Walter (1980) to profile the dissipation of the pesticide. However, when the dissipation cannot be adequately described by the first-order kinetic, more complex models and indices are required to better describe the pesticide dissipation and persistence (Bernard & Schaalje, 1985; Carlos & Zimdahl, 1989; Grover, Wolt, Cessna, & Schiefer, 1997), and DT_{50} may depend on the initial concentration and soil characteristics. Degradation of H-9201 in soil was followed for 5 months, and the results obtained were modelled according to the new EU guideline (Boesten et al., 2006). The modeling was performed using GraphPad PRISM version 5.0 and Excel with Solver Package. Three different category models were compared for fitting H-9201: single first-order (SFO), first-order multi compartment (FOMC) and Double First-Order in Parallel (DFOP or Bi-Exponential model). As a general purpose spreadsheet, Excel with the additional Solver Package installed (add-in module of EXCEL) can be used for estimating the degradation parameters, for example, FOMC, HS and DFOP for the parent compound. Software of GraphPad PRISM is another package that can handle a single substance in a single compartment; kinetic models can be implemented or chosen from its built-in models. More generic parameter estimation packages can handle more substances and/or more compartments (Beulke & Brown, 2001; Boesten et al., 2006; Simonsen, Fomsgaard, Svensmark, & Spliid, 2008). In our case, both GraphPad PRISM version 5.0 and Excel with Solver Package were employed to compare results.

For the hydrolysis study, the presence of herbicides in water is also indicated by DT_{50}. Normally, degradation in water can be adequately described by first-order kinetics, DT_{50} is equal to the first-order dissipation half-life. However, when the dissipation cannot be adequately described by first-order kinetics or if it has different rates at different times, the persistence of the herbicide may not be sufficiently represented by a single half-life and more complex models may need to be used. In our case, pseudo first-order equation was also fitted to the data.

3. Results and discussion

3.1. Degradation study

Degradation curves obtained for H-9201 residue data by fitting different kinetics models and the experimental data from the trial are shown in Fig. 1. The results indicated that a first-order discontinuous biphasic model matched the data well, and from around 30 days after application the degradation of H-9201 slowed down. From this we assumed that the fast dissipation phase occurred between 0 to 30 days which meant that the t_1 domain was (0–30 days), and that the slow dissipation phase occurred thereafter. A single DT_{50} value was not good enough to describe the total herbicide dissipation in soil with time, thus both DT_{50} and DT_{90} were used to indicate dissipation of the herbicide. Model parameters were obtained from the best-fit models using Microsoft Excel Solver, and the add-in analysis of Toolpak, as reported by Ma, Rahman, Holland, James, and McNaughton (2004). The Solver uses the Generalized Reduced Gradient (GRG2) nonlinear optimisation algorithm and returns the best-fit parameters by minimising the sum of squares of the residuals between the measured and fitted values. Visual graphical comparison, r^2 and root mean squares error (RMSE) (Loaguea & Green, 1991) were used to evaluate the goodness of fit. For the first-order biphasic model, which describes log-nonlinear, fast and slow dissipation of the herbicide with time, the errors and bias caused at the phase boundary identification induced an initial concern, in our case the correlation coefficient was $r^2 = 0.9944$ and the RMSE = 0.1398, which showed a higher correlation than the simple first-order model.

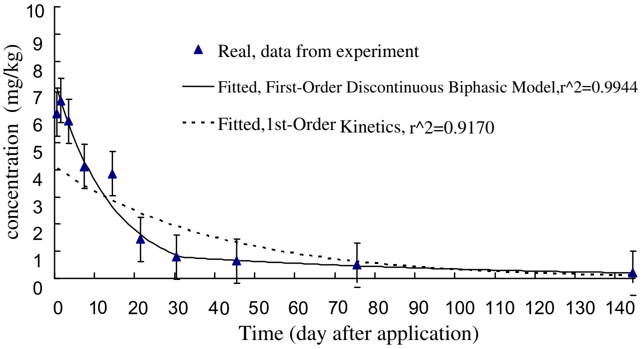

Fig. 1. Dissipation of H-9201 residue in soil.

Dynamic equations for the description of H-9201 dissipation in soil are given in Table 1. Dissipation models derived from Excel have been used to describe the herbicide degradation dynamics: the simple first-order kinetics equation with $DT_{50} = 27.8$ days and $DT_{90} = 92.4$ days; the first-order discontinuous biphasic model had a $DT_{50} = 9.9$ days and $DT_{90} = 70.2$ days, which meant that rapid and slow dissipation occur at different rates (k_1 and k_2) within the two time domains (t_1 and t_2), each following the first-order kinetics. The results showed that the representation of herbicide persistence by the first-order discontinuous biphasic model was better than that by the simple first-order model.

The outputs of kinetic models derived by fitting both the data to one phase exponential decay and to two phase exponential decay equations are also shown in Table 1. The one phase exponential decay model was preferred by the software of GraphPad Prism 5.0. Based on visual agreement between observed and simulated data, r^2 value and RMSE value, the best-fit model for H-9201 was finally found to be the first-order biphasic model, and the endpoints derived from this model were accepted for assessment the fate of H-9201.

An adequate description of pesticide degradation in soil is important for the risk assessments within the pesticide registration process. Normally, the first-order equation is considered and used to describe the degradation of pesticides (Simonsen et al., 2008). Often, kinetics other than first-order may be more suitable for describing the decline of measured concentrations. In addition, the use of different simulation models or of different options within one program and the initial concentration may impact on the

Table 1
Dynamic equation for H-9201 dissipation in soil.

Describing model	Kinetic equation	Parameters			
		DT_{50}	DT_{90}	R^2	RMSE
A: derived by Excel (Solver Package)					
First-order kinetic model	$C = 4.0655e^{-0.0249t}$	27.8	92.4	0.9170	0.5180
First-order discontinuous biphasic model	$C = 7.0264e^{-0.0700t_1} + 1.1396e^{-0.0120t_2}$	9.9	70.2	0.9944	0.1398

Describing model	Kinetic equation	Goodness of Fit				
		DT_{50}	DT_{90}	R^2	A.S.S.[b]	Sy.x
B: derived by GraphPad Prism 5.0						
[a]One phase exponential decay	$C = 6.4040e^{-0.06002t} + 0.1797$	11.6	38.4	0.9667	5.875	0.4365
Two phase exponential decay	$C = 5.7030e^{-0.06003t} + 0.700e^{-0.0600t} + 0.1798$	23.1	73.3	0.9667	5.875	0.4848

[a] Preferred by the software.

[b] A.S.S., absolute sum of squares.

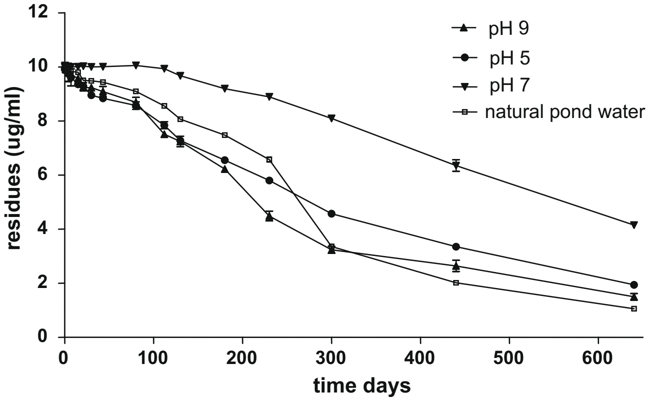

Fig. 2. Hydrolysis dynamics of H-9201 in water.

estimated DT_{50} values. In our study, different simulation models (biphasic model and first-order model) were employed to determine the best probable model to outline the environmental fate of H-9201.

The result of the biphasic model gave a good fit to the data and confirmed that during the period 0–30 days after application dissipation was faster and surface loss was occurring. It is postulated that with the assistance of organic carbon content in the soil, more herbicide was absorbed and remained near the soil surface (Yolcubal & Akyol, 2008), which offered more opportunity for the herbicide to be degraded by photochemical reactions, solar radiation, volatilisation, temperature or other dissipation processes. This led to more chemical and biological degradation (Fabbri, Bianco, Zelano, Ginepro, & Pramauro, 2008; Phanikrishna Sharmaa, Durga, & Subrahmanyam, 2008) with increasing soil moisture (irrigation, rainfall, etc.), and with H-9201 being soluble in water, the herbicide moved relatively deep into the soil or persisted in the aqueous layer, thus causing a noticeable reduction in the dissipation rate within the second phase domain. The hydrolysis study data also supported this assumption, showing that the dissipation rate of H-9201 was very slow in the dark, aqueous layer which indicated that photo-degradation, chemical and biological degradation processes may be involved in the herbicide's initial fast loss in the topsoil layer. The dissipation rate may be different under different field conditions, especially in the aqueous layer.

3.2. Hydrolysis

The results of the hydrolysis experiments are shown in Fig. 2 and indicate that hydrolysis of H-9201 started during the 112 days of incubation at pH 7. After this period hydrolysis of H-9201 slowed down. Characteristic of the behaviour of herbicides in water can be described by means of a modified first-order equation also known as pseudo first-order equation (Farran & Ruiz, 2004; Ma et al., 2004): $\text{Ln}C - \text{Ln}C_0 = k(t - t_0)$, where t_0 is the time of the initial phase (between the initial time and the time when degradation begins). Table 2 shows the kinetic equations of H-9201 hydrolysed in water at different pH values. Dissipation followed the first-order kinetic equation except at pH 7. Hydrolysis accelerated in the eleventh week, and then the hydrolysis rate at pH 9 was faster than at pH 5. The inorganic contents of the natural pond water or biological effects may accelerate the degradation and shorten the half-life, which was 197.2 days. The final pH value of sterile water changed from 5 to 4.24–4.38, from 7 to 5.87–5.88 and from 9 to 7.07–7.15, and the pH value of natural pond water changed from 7.12 to 7.75. It should be pointed out that the DT_{90} for H-9201 hydrolysis in all pH solutions was determined by extrapolation beyond the time period of the experiment. A metabolite was found in the extraction of sterile water. The mass-spectrum data and molecular structure are shown in Fig. 3. When an understanding of the molecular structure and mass-spectrum of H-9201 is obtained (profiled in Fig. 4), the most likely pathway of H-9201 hydrolysis can be proposed (see below).

The general mechanism for the hydrolysis of thiophosphoric acid esters is that the esters react with a nucleophile by nucleophilic displacement (S_N2) at either the phosphorus or the carbon atom bound to the sulphur of the thiol moiety (Schwarzenbach, Gschwend, & Imboden, 1993). For nucleophilic displacement, OH^- is a better nucleophile than H_2O, and cleavage of the –P–N– bond could be the main mechanism of alkaline hydrolysis of H-9201. In addition, the –P–O– bond may also be easily cleaved, especially in acidic conditions, so a different cleavage order and activity of these two bonds would allow different dissipation rates at different pH values. Based on the mechanism of bond cleavage behaviour at different pH values described above, and the almost matched molecular structure of the metabolite, the most likely pathway of H-9201 hydrolysis is outlined in Fig. 5. It is also shown that the hydrolysis of H-9201 is pH dependent and light dependent; cleavage of the phosphoramide bond ($-NH-PO_2-$) would play an important role in the process activity. Further studies need to be carried out to identify metabolites of hydrolysis to achieve a better understanding of the degradation pathways.

3.3. H-9201 residue in post-harvest carrot and in soil

The residues of H-9201 present in carrot and soil sampled from 130 days to 143 days after application (harvest at 144 days) were less than 0.02 mg/kg in carrot, and less than 0.4 mg/kg in soil.

The residue of H-9201 in harvested carrots only came from the environment where the herbicide had been applied before seedling

Table 2
Hydrolysis dynamic equation of H-9201 in water.

pH	Parameter					
	Kinetic equation	*n*	*K*	DT_{50} (d)	DT_{90} (d)	*r*
Natural pond water (pH 7.12–7.75)	$C = 10.9240e^{-0.0035t}$	17	3.51×10^{-3}	197.16	654.95	−0.9773
5	$C = 9.9684e^{-0.0025t}$	17	2.51×10^{-3}	276.27	917.74	−0.9983
7	$C = 9.6837e^{-0.0016(t112)}$	17	1.63×10^{-3}	538.29	1528.09	−0.9880
9	$C = 10.0921e^{-0.0031t}$	17	3.09×10^{-3}	224.67	746.34	−0.9917

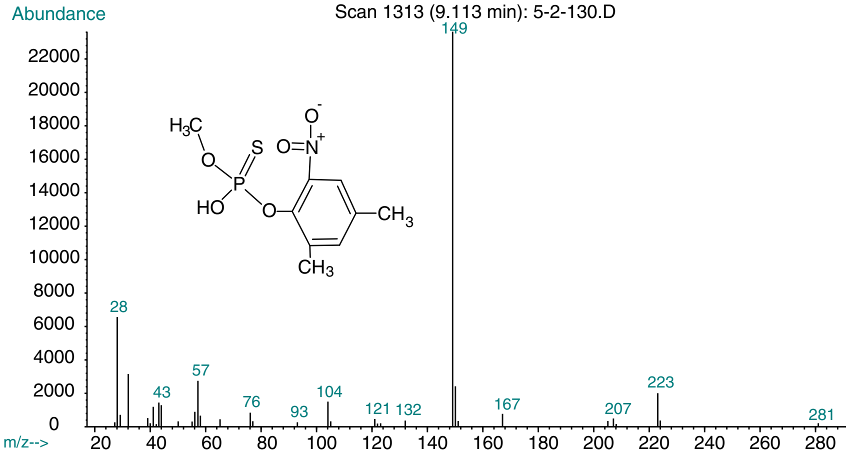

Fig. 3. Mass-spectrum graph of hydrolytic metabolite of H-9201 by EI-MASS.

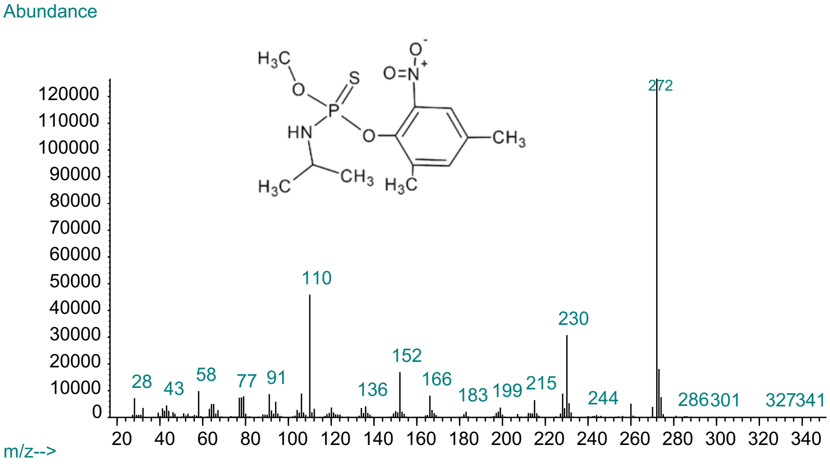

Fig. 4. Mass-spectrum graph and structure of H-9201.

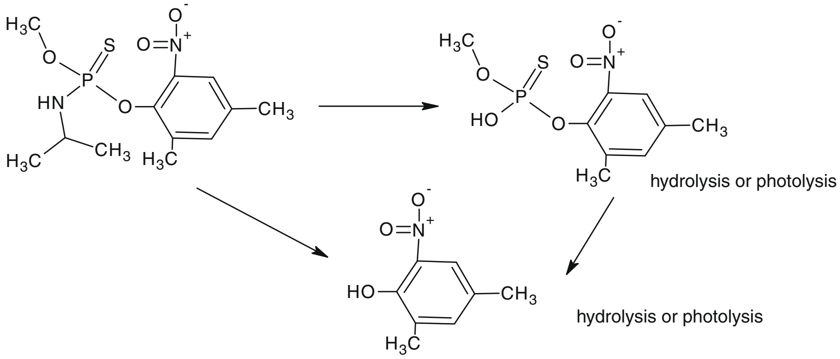

Fig. 5. Tentative degradation pathway of H-9201 in water.

emergence, implying that the residue probably accumulated in carrot via water delivery, since this chemical can persist in the aqueous layer as shown by our hydrolysis study. Other extended environmental exposure and toxicology experiments indicated that the toxicity of H-9201 to Silkworm larvae (*Bombyx mori*), honey bee (*Apis mellifera* L.) and quail (*Coturnix coturnix japonica*) is low, but medium toxicity to zebra fish was observed (*Brachydanio rerio*) (Yang et al., 2006). Our results indicated that this chemical could be accumulated in plants and is stable in the aqueous layer; therefore an environmental impact assessment is needed to determine the bioaccumulation of H-9201 residues in the aqueous environment. So far, no maximum residue limits (MRL) have been set in carrot and other agricultural products.

4. Conclusions

Overall, the degradation study showed that a first-order discontinuous biphasic model adequately described the dissipation of H-9201 in the soil. Both DT_{50} and DT_{90} were needed to describe the persistence of the herbicide under field conditions. H-9201 is 90% dissipated in the soil at carrot harvest time. The residue of H-9201 in harvested carrot was less than 0.02 mg/kg following application of double the recommended dose and was not detected following the recommended treatment dose at the same time intervals.

A decline in soil residues may be attributed primarily to growth dilution between application and sampling, as well as to volatilisation which occurs during the first few days following application, in addition to removal by weathering, heat decomposition, sunlight UV radiation or other complex conditions (Spynu, 1989). When considering the hydrolysis results (especially in natural pond water), non-aqueous factors may be more important in the herbicide's dissipation, and photochemical reactions may be involved in the degradation pathway. Since the herbicide was applied as a spray to the soil surface, its dissipation and degradation will vary depending on the soil type, pH, organic matter content and environmental conditions. On the soil surface, degradation may be due to the process of photolysis and soil binding, followed by slower biotic-mediated processes. Further laboratory studies need to be carried out to profile the degradation pathway below the soil surface to identify the effect of each factor on degradation.

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