Journal of Environmental Sciences Vol. 7, No. 2, pp. 157—162, 1995 ISSN 1001-0742

Chemical behavior and risk assessment of four pesticides in soil and water

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Abstract—The degradation of pesticides in the environment is a very important index in evaluation the ecological risk of pesticides, the degradation of pesticides varies with their physico - chemical properties. In this paper, four pesticides including methyl - ISP [(N - isopropyl - o - methyl - o -(2- isopropyl oxo - carbonyl) phenyl phosphorthia midoate]; monocarboxoldehyde [N -(2,4-dimethylbenzyl - N - methyl amidine) hydrochloride]; pyrimyxthion [o,o diethenyl - o -(2- methoxy -4- methyl pyrimidine -6-)phosphorothioate] which are three effective insecticides used to control many pests of paddy field and cotton field and propachlor [2- ethenyl - N - (ethongmethyl)-2- monochloroacetamide] which is an effective herbicide used to control annual weeds, were selected and their degradation dynamics in soil and water under different conditions were studied.

Keywords: pesticide; chemical behavior; soil and water; risk assessment.

1 Introduction

The pesticides studied in a laboratory modelling system were Methyl - ISP, monocarboxoldehyde, propachlor and pyrimyxthion in this paper. The degradation dynamics and hydrolysis of these compounds in soil and water were determined under different conditions. The results showed that the degradation of the four pesticides in dryland soil and paddy soil was very rapidly and the half - lives of methyl - ISP, monocarboxoldehyde, propachlor and pyrimyxthion were 32, 3.3, 5.2 and 5.0 days, respectively. The degradation rates of these pesticides were varies with water content in soils.

The hydrolysis rates of the four pesticides accelerated with increase of temperature. Methyl —ISP and monocarboxoldehyde hydrolyzed rapidly as pH increased. Propachlor was very stable in neutral and basic aqueous mediums, but became less stable in acidic condition. Pyrimyxthion was more easily hydrolyzed in acidic or basic conditions than in neutral condition.

According to "The guideline of environment risk assessment of pesticides", the four pesticides could be classified as easily degradable ones.

2 Materials and methods

2.1 Materials

2.1.1 Chemicals

Methyl - ISP (99.5% purity); monocarboxodehyde (98% purity); pyrimyxthion (96%

purity); propachlor (98% purity).

Soil samples Taihu alluvial rice soil was collected from Jiangsu Province and Northeastern black soil was collected from Heilongjiang Province. Their physico - chemical properties are presented in Table 1.

Table 1 Characteristics of two soil used for the studies

Soil type	pH	Organic matter, %	Cation exchange capacity, meq/100g soil	Soil texture(<0.01 mm clay content), %
Northeastern black soil	8.40	3.34	24.03	48.0
Taihu rice soil	6.50	3.34	19.82	34.2

2.1.2 Buffer solution

pH 5: 500 ml 0.1 mol/L potassium K_2HPO_4 hydrogen phosphate + 226 ml 0.1 mol/L NaOH + distilled water to 1000 ml. pH 7: 500 ml 0.1 mol/L potassium dihydrogen phosphate + 291 ml 0.1 mol/L NaOH + distilled water to 1000 ml. pH 9: 500 ml 0.1 mol/L boric acid in 0.1 mol/L KCl (1:1) + 208 ml NaOH + distilled water to 1000 ml.

The buffer solution and all glassware should be sterilized for 1 h at high temperature and high pressure to avoid the biodegradation effects on the hydrolysis experiment. The pH of each sterilized buffer solution should be readjusted.

2.3 Degradation of the pesticides in soils

Degradation in dryland field: soil samples were air - dried and passed through a 20 mesh sieve. Each type of the soil samples was weighed 50 g into culture dishes, treated with the four pesticides at a concentration of 10 ppm, respectively, and then mixed thoroughly, transferred to 100 ml Erlenmeyer flask. Soil moisture content was adjusted to 60% of saturated water retaining capacity. The Erlenmeyer flask were then sealed with cotton plugs and cultured in incubator at a temperature of 25℃±1℃. The samples were taken periodically for further extraction and clean up and determined by GC.

Degradation in paddy field: This experiment was similar to the one described above, except that the water content of each soil sample in Erlenmeyer flask was adjusted to 2 cm higher than soil surface.

2.4 Hydrolysis

The hydrolysis of the four pesticides was performed at 25℃ and 50℃ in pH 5.7 and 9 in duplicate.

Buffers were added to 250 ml Erlenmeyer flask treated with the four pesticides respectively, so that the concentration of each pesticide in solution was 10 ppm. The Erlenmeyer flasks were sealed and shook thoroughly, then put into incubators at the temperature of 25℃±1℃ and 50℃ ±1℃. After incubation at proper intervals, the solutions were sampled for determination. The Erlenmeyer flask were put in dark and were keep air - tight in order to avoid the interference of photodegradation, volatilization and oxidation.

2.5 The condition of instrument analysis

The extracts of the four pesticides were dissolved in petroleum ether and determined by GC. Hewlett - Packard 5890 a gas chromatography, 10m×0. 53 mm i. d flexible capillary column with 2. 65μm film thickness of methyl silicone gum was used. The analytical condition and retention time of the pesticides are shown in Table 2.

Table 2 Analytical condition and retention time of the four pesticides

Pesticides	Detector[1]	Temperature of detection,			Carrier gas, ml/min	Retention time, min
		Column	Injector	Detector		
Methyl - ISP	NPD	180	270	300	20	3. 46
Monocarboxoldehyde	NPD	140	180	300	20	2. 02
Pyrimyxthion	ECD	170	220	200	25	1. 93
Propachlor	ECD	180	250	270	25	1. 26

1 NPD: nitrogen phosphorus detector; ECD: electron capture detector

3 Results and discussion

3.1 Degradation of the pesticides in dryland soil

The degradation of the pesticides in soil can be usually described as a pseudo - first order reaction. Therefore, the degradation constant (K) and half - life ($T_{1/2}$) can be obtained from the relationship:

$$K_t = 2.303 \log C_0/C_1, \tag{1}$$

$$T_{1/2} = \frac{\ln 2}{k}. \tag{2}$$

Where t is the time of pesticide degradation, d; C_0 is the initial concentration of pesticide in soil; C_1 is the concentration of pesticide in soil at time t.

Using the two formulas, the degradation constants K and half - lives $T_{1/2}$ of the four pesticides were determined (Table 3).

Table 3 Degradation constants and half - lives of the four pesticides in dryland soil

Pesticide	Soil type	K, d^{-1}	$T_{1/2}$, d	r
Methyl - ISP	Northeastern black soil	-3.11×10^{-2}	22. 29	−0. 9908
	Taihu rice soil	-2.91×10^{-2}	23. 82	−0. 9948
Monocarboxoldehyde	Northeastern black soil	-1.75×10^{-1}	3. 96	−0. 9737
	Taihu rice soil	-1.73×10^{-1}	4. 01	−0. 9819
Pyrimyxthion	Northeastern black soil	-1.61×10^{-1}	4. 31	−0. 9981
	Taihu rice soil	-1.45×10^{-1}	4. 78	−0. 9920
Propachlor	Northeastern black soil	-2.80×10^{-1}	2. 48	−0. 9668
	Taihu rice soil	-2.30×10^{-1}	3. 01	−0. 9229

The residue dynamics of the four pesticides in two different soils indicated that they were broken down quite rapidly in dryland. Their half - lives were within 5 days, except methyl - ISP, which had the longer half - live. The difference between degradation rates of the same kind of pesticide in different soils was very little. While the different pesticides differed much in their degradation rates in the same type of soil because of their own physico - chemical properties.

3.2 Degradation of pesticides in paddy soil

The data of this experiment are listed in Table 4.

Table 4 Degradation constants and half-lives of four pesticides in paddy soil

Pesticide	Soil type	K, d^{-1}	$T_{1/2}$, d	r
Methyl-ISP	Northeastern black soil	-1.73×10^{-2}	40	-0.9981
	Taihu rice soil	-2.17×10^{-2}	32	-0.9864
Monocarboxoldehyde	Northeastern black soil	-2.68×10^{-1}	3.00	-0.9750
	Taihu rice soil	-2.11×10^{-1}	3.30	-0.9829
Pyrimyxthion	Northeastern black soil	-1.80×10^{-1}	4.20	-0.9750
	Taihu rice soil	-1.46×10^{-1}	5.00	-0.9515
Propachlor	Northeastern black soil	-1.34×10^{-1}	5.00	-0.9644
	Taihu rice soil	1.32×10^{-1}	5.20	-0.9721

The results in Table 4 show that the degradation patterns of the pesticides in paddy soil and in dryland soil were similar. Compared with Table 3, the half-lives were changed little except a 10 days longer half-life of methyl-ISP in paddy soil than which in dryland soil.

It has been reported in many studies that the soil moisture was a factor responsible for causing the changes in the rates of the degradation of pesticides. Under temporary irrigation and anaerobic conditions, the degradation rates of some pesticides decreased and their persistence in soil changed obviously. On the contrary, some other pesticides were easier to be broken down in irrigated field than in aerobic field, and some pesticides were not affected by the soil moisture. The effects of soil moisture on the four pesticides were different. The half-lives of methyl-ISP and propachlor in paddy soil were 10 days and 2 days longer than which in dryland soil, respectively. While for monocarboxoldehyde and pyrimyxthion, the soil moisture had no significant effect on their degradation and their half-lives changed little.

3.3 Hydrolysis of the four pesticides

Table 5 presents the hydrolytic rates of the four pesticides at different temperatures and pH values.

Where E is the activation energy of hydrolysis reaction. According to the relationship between temperature and reaction rate, i.e. the formula of Arrhenius.

$$\ln K = -\frac{E}{RT} + \ln A, \tag{3}$$

$$\ln \frac{K_2}{K_1} = \frac{E}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right), \tag{4}$$

$$\text{i.e. } \log \frac{K_2}{K_1} = \frac{E}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right). \tag{5}$$

The activation energy of a pesticide at certain pH value can be obtained by substituting K_1, K_2 of the pesticide determined at different temperatures into Formula (5).

It is readily seen from Table 5 that the hydrolytic rates of pesticides were greatly influenced by the changes of temperature and pH values. Under neutral aqueous conditions, the degradation rates of the four pesticides at 25℃ were found to be in the order of monocarboxoldehyde > pyrimyxthion > methyl-ISP > propachlor, the half-lives were observed to be 6.5, 55.9, 270.8 and 602.7 days, respectively

Table 5 Hydrolysis of the four pesticides at different temperatures and pH values

Pesticides	pH	T, ℃	n	K, d^{-1}	r	E, J/mol
Methyl-ISP	5	25	6	1.85×10^{-3}	−0.9745	
		50	7	3.29×10^{-3}	−0.9913	18432.3
	7	25	6	2.56×10^{-3}	−0.9908	
		50	7	8.81×10^{-3}	−0.9975	39569.4
	9	25	6	3.78×10^{-2}	−0.9991	
		50	5	1.65×10^{-1}	−0.9992	47181.6
Monocarb-oxoldehyde	5	25	7	3.68×10^{-3}	−0.7431	
		50	7	5.04×10^{-2}	−0.9934	83791.4
	7	25	6	1.06×10^{-1}	−0.9847	
		50	5	1.16	−0.9880	76608.6
	9	25	5	15.76	−0.9819	
		50	5	24.65	−1.000	14321.3
Pyrimyx-thion	5	25	9	1.86×10^{-2}	−0.9967	
		50	5	1.05×10^{-1}	−0.9924	55415.2
	7	25	8	1.24×10^{-2}	−0.9949	
		50	6	9.62×10^{-2}	−0.9925	65594.6
	9	25	7	2.14×10^{-2}	−0.9932	
		50	6	4.28×10^{-1}	−0.9987	95914.8
Propachlor	5	25	8	2.16×10^{-3}	−0.9894	
		50	8	1.04×10^{-2}	−0.9858	50321.3
	7	25	8	1.15×10^{-3}	−0.9687	
		50	8	2.29×10^{-3}	−0.9843	22053.1
	9	25	8	7.82×10^{-4}	−0.8857	
		50	8	1.90×10^{-3}	−0.9804	29418.8

It was demonstrated that the hydrolytic rates of different pesticides varied greatly under the same conditions. According to the hydrolysis behavior of the four pesticides, propachlor was easy to be broken down in acidic medium, while methyl-ISP hydrolyzed rapidly in basic medium. Monocarboxoldehyde was unstable under neutral and basic aqueous solutions. Pyrimyxthion was more easily to hydrolyze in both acidic and basic conditions.

It was observed that the hydrolysis rates of the four pesticides all increased with elevated temperature to different degree depending upon the variety of pesticide and the pH conditions. Propachlor hydrolyzed readily as temperature raising under acidic conditions but less affected by temperature at basic conditions. The effects of temperature on methyl-ISP was greater in basic conditions than in acidic conditions. Pyrimyxthion, which was similar to methyl-ISP, was affected by temperature at pH 9. The effects of temperment on monocarboxoldehyde was the greatest among four pesticides.

The hydrolysis rate of the four pesticides all increased as temperature raised under the three pH conditions. The effects of temperature on hydrolysis of pesticides can be explained by the concept of activation energy. In fact, the magnitude of activation energy E reflects the effects of temperature on the reaction rate constant K. When E is higher, the effects will be greater and K

values will increased obviously as the temperature raised. The adversed result can be seen when E is lower.

3.4 Environmental risk assessment of the chemical behavior of the four pesticides

The chemical behavior of pesticides in ecological environment plays an important role in evaluating their effects on the environment. The more rapidly the pesticide degrades the less pollution to environment the pesticides will cause. Thus in developing new pesticides their high effectiveness and low residue should be considered. How to evaluate the safety of pesticides in environment is the problem what people concern about. At present, the half-life of pesticide is usually considered to be the basis of evaluation. In the Metcalf study, the half-lives of pesticides in soil were divided into five grades. The first grade of which is <1 month, the second is within 1-4 months, the third: 4-12 months, the fourth: 1-3 years and the fifth: 3-10 years. No further details about the basis of grading were given in his report. According to "the Guideline for testing of safety evaluation of the pesticides in environment" formulated by Nanjing Institute of Environmental Sciences (NEPA, China) for the simplicity and practicability, the residue periods of pesticides were divided into three grades: the low residue pesticides of which the half-lives were <3 months, the medium residue pesticides (half-lives 3-12 months), and the long residue period pesticides (half-lives >1 year). Based on this criterion, the half-lives of four pesticides studied are within 3 months, they belong to low residue pesticides.

There has been no definite criterion for evaluating the hydrolysis behavior of pesticides in aqueous medium by now. In this study, the hydrolysis half-lives for propachlor, methyl-ISP, pyriyxthion and monocarboxoldehyde were observed to be 602, 270, 56 and 6.5 days, respectively. As a result, pyrimyxthion and monocarboxoldehyde can be classified as the readily hydrolyzing pesticides and propachlor and methyl-ISP as the difficulty hydrolyzing ones. In fact, the degradation of pesticides under natural conditions was comprehensive of various degradation procedures. Therefore, the half-lives were generally much shorter than which determined from laboratory hydrolysis test. It should be concerned that once the pesticides go into groundwater that has lower temperature and higher acidity, the hydrolysis and biodegradation will be much less than which in surface water, and the photolysis will not occur. Therefore, it is very important to prevent the pesticides from polluting groundwater.

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(Received July 19, 1993)