Original Article

Soil Adsorption and Its Mechanism of the Fungicide Mepanipyrim

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Soil adsorption of mepanipyrim labeled with ^{14}C was investigated using a batch equilibrium method, and isotherms were calculated by the Freundlich equation for five different Japanese soils collected from the upland fields. The Freundlich equation described mepanipyrim adsorption adequately. Adsorption coefficients (K_f) ranged from 12.9 to 427, and normalized K_f based on the soil organic carbon content ($K_{f,oc}$) from 1090 to 5210. The values of $1/n$ were smaller than unity for all soils tested. Desorption of mepanipyrim was hysteretic. Soil adsorption of mepanipyrim was pH dependent, showing the maximum adsorption at a pH value in the vicinity of its pK_a 2.9. It is considered that the ionic bond between protonated mepanipyrim and the minus charge on soil colloid contributes to this pH effect. After decomposition of the soil organic matter with H_2O_2 , K_f values decreased for all soils tested. Adsorption of mepanipyrim on the H_2O_2 treated soils increased with the decreasing pH in the pH range above the pK_a value.

Key words: pesticide, mepanipyrim, adsorption, soil pH.

INTRODUCTION

Mepanipyrim, *N*-(4-methyl-6-prop-1-ynylpyrimidin-2-yl)aniline is a fungicide developed by Kumiai Chemical Industry Co., Ltd. and Ihara Chemical Industry Co., Ltd.¹⁾ Mepanipyrim has a good disease control activity for gray mould, scab, and brown rot and has been used on several horticultural crops and fruit trees.²⁾

Soil adsorption governs the environmental fate of agrochemicals by controlling directly the mobility, the leaching potential, and the availability for chemical and biological degradation in soils. Therefore the information on soil adsorption of mepanipyrim is essential for predicting its environmental fate and behavior. Soil adsorption of weak bases like atrazine is known to be pH dependent.^{3–5)} Mepanipyrim is also a weak base having the pK_a of 2.9 (private data determined by the spectrophotometric method in K-I Chemical Research Institute Co., Ltd.) and it was expected that its soil adsorption was influenced by pH. In this report we deal with the adsorption characteristics of mepanipyrim on five Japanese soils, the effect of pH on the soil adsorption, and the adsorption on soils treated with H_2O_2 to oxidize soil organic matters to clarify the role of soil organic matter and mineral constituents.

MATERIALS AND METHODS

1. ^{14}C -Labeled Compound and Authentic Compound

The structural formula of mepanipyrim is shown in Fig. 1. Mepanipyrim labeled with ^{14}C uniformly on its benzene ring was synthesized by Daiichi Pure Chemicals Co., Ltd. It had a specific activity of 808 MBq/mmol and a radiochemical purity of 96.2%. The authentic compound of non-labeled mepanipyrim was synthesized by K-I Chemical Research Institute Co., Ltd. The water solubility of mepanipyrim is $3.10\ \mu\text{g/ml}$ at 25°C . To prevent precipitation of mepanipyrim, the maximum concentration used was less than half of its water solubility.

2. Soils

Five Japanese soils collected from the plow layers of the upland fields in Nagano (Nagano-pref.), Kikugawa (Shizuoka-pref.), Ushiku (Ibaraki-pref.), Koriyama (Fukushima-pref.), and Kume (Okayama-pref.) were passed through a 2 mm screen prior to use. The physicochemical properties of the test soils are shown in Table 1.

3. Preparation of H_2O_2 Treated Soils

The five soils were heated at 80°C with 6% H_2O_2 solution being added with 6% H_2O_2 solution repeatedly until

Fig. 1 Structural formula of mepanipyrim.

drastic bubble generation ceased. The soils were rinsed with distilled water well and air-dried.

Organic carbon contents of the H_2O_2 treated soils are shown in Table 1. Though the H_2O_2 treatment reduced the carbon contents effectively for all soils used, Nagano and Ushiku H_2O_2 treated soils still had 0.82 and 0.58% of organic carbon, respectively.

4. Equilibration Time and ^{14}C -Material Balance

A preliminary study showed that the soil adsorption of mepanipyrim reached the equilibrium within 72 hr for all soils tested (data are not shown here).

The 72 hr sample of each soil in the preliminary study mentioned above and the 72 hr sample of each H_2O_2

treated soil from adsorption studies, which were centrifuged, were used for the determination of ^{14}C -material balance in the test systems. The supernatant and acetone extract from the precipitate were extracted with dichloromethane, respectively, and each dichloromethane extract was analyzed by co-chromatography using a silica gel TLC plate. The non-extractable ^{14}C remaining after the acetone extraction of each precipitate was oxidized using a Packard Sample Oxidizer and radioassayed.

The distribution of ^{14}C and ^{14}C -mepanipyrim were shown in Table 2. Since the recoveries of ^{14}C -mepanipyrim from the 72 hr samples were greater than 87%, it was considered that the degradation of mepanipyrim in the soil and water systems was slight after 72 hr shaking. Accordingly, 72 hr shaking time was employed for all studies reported in this report.

5. Adsorption

The adsorption studies were conducted using a batch equilibrium method. All treatments were duplicated.

Table 1 Physicochemical properties of the test soils.

Soil (Prefecture of sampling)	Particle size distribution(%)			Soil ^{a)} texture	Organic carbon content ^{b)} (%)	pH		CEC (me/100 g dry soil)	Main clay mineral ^{c)}		
	Sand	Silt	Clay			H_2O	KCl				
Nagano (Nagano)	54.5	35.6	9.9	L	12.5 (0.82)	4.7	4.2	47.5	V	K	A
Kikugawa (Shizuoka)	49.5	29.2	21.4	CL	0.43 (0.11)	5.1	3.9	9.6	K	I	
Ushiku (Ibaraki)	42.9	31.4	25.8	LiC	3.26 (0.58)	7.2	6.2	25.1	A		
Koriyama (Fukushima)	53.4	22.8	23.8	CL	1.08 (0.18)	7.6	6.7	13.5	K	V	
Kume (Okayama)	60.5	17.5	22.0	SCL	0.79 (0.09)	5.2	3.7	6.3	H		

^{a)} L :loam; CL: clay loam; LiC: light clay; SCL: sandy clay loam. ^{b)} Numbers in parenthesis are the organic carbon content after H_2O_2 treatment. ^{c)} A: allophane; H: halloysite; I: illite; K: kaolinite; V: vermiculite. Particle size distribution and soil texture were determined by the method of International Society of Soil Science.

Table 2 Distributions of ^{14}C and ^{14}C -mepanipyrim in the soil and H_2O_2 treated samples shaken for 72 hr.

Fraction and compound	Percentage to applied									
	Soil ^{a)}									
	Nagano		Kikugawa		Ushiku		Koriyama		Kume	
	Original	H_2O_2	Original	H_2O_2	Original	H_2O_2	Original	H_2O_2	Original	H_2O_2
Supernatant										
Mepanipyrim	0.5	9.6	8.6	27.6	8.3	42.0	15.3	36.5	17.1	79.5
Others ^{b)}	0.2	0.4	0.7	0.2	0.6	0.6	2.2	0.4	2.0	0.7
Precipitate										
Mepanipyrim	86.5	84.5	89.7	69.8	80.3	58.1	74.3	58.2	72.0	19.4
Others ^{b)}	3.0	0.9	2.5	4.2	1.8	0.6	2.7	0.7	2.8	0.4
Non-extractable ^{14}C	10.4	4.7	4.0	1.0	7.4	1.5	14.9	2.5	5.5	0.9
Recovery of mepanipyrim	87.0	94.1	98.3	97.4	88.6	100.1	89.6	94.7	89.1	98.9
Recovery of ^{14}C	100.6	100.1	105.5	102.8	98.4	102.8	109.4	98.3	99.4	100.9

^{a)} The left column of each soil shows the values for the original soil and the right column the values for the H_2O_2 treated soil.

^{b)} Others contain ^{14}C in the water layers obtained from the dichloromethane partition.

Three mepanipyrin solutions were prepared at the concentrations of 0.0402 $\mu\text{g/ml}$; 146 Bq/ml, 0.20 $\mu\text{g/ml}$; 728 Bq/ml, and 1.02 $\mu\text{g/ml}$; 708 Bq/ml by dissolving non-labeled and ^{14}C -labeled mepanipyrin in 0.01 M CaCl_2 . A 20 ml aliquot of each mepanipyrin solution was added to 5 g of each soil (wet weight basis) in a 50-ml glass centrifuge tube. The tube was shaken gently on a reciprocal shaker at 25°C for 72 hr to achieve equilibrium. Following the equilibration the suspension was centrifuged at 3000 rpm ($1400 \times g$) for 15 min. An aliquot of the supernatant was taken from each tube to determine the radioactivity by a Packard Tri-Carb 2750TR/LL liquid scintillation counter. Hereafter the same manner of shaking, centrifugation, and radioassay was employed.

For the H_2O_2 treated soils three solutions of mepanipyrin were prepared at the concentrations of 0.0816 $\mu\text{g/ml}$; 296 Bq/ml, 0.408 $\mu\text{g/ml}$; 1478 Bq/ml, and 2.04 $\mu\text{g/ml}$; 1478 Bq/ml. A 2 ml aliquot of 0.01 M CaCl_2 was added to 500 mg of each H_2O_2 treated soil (air-dry weight basis) in a 10-ml glass test tube and the test tube was shaken gently for 24 hr to re-equilibrate the H_2O_2 treated soil with water. Then a 2 ml aliquot of each mepanipyrin solution was added to the test tube. The sample was shaken and centrifuged, and the supernatant was radioassayed in the same manner described above.

The pH of the supernatant was measured for the samples of each soil and its H_2O_2 treated soil with the highest initial concentration by a pH meter.

6. Desorption

The desorption studies were conducted using the samples with the highest initial concentration in the adsorption studies. The supernatant in each centrifuge tube was replaced with the equivalent volume of 0.01 M CaCl_2 . After the precipitate was dispersed by vibration, the sample was shaken and centrifuged, and the supernatant was radioassayed in the same manner described above.

7. Effect of pH on Mepanipyrin Adsorption

The effect of pH on mepanipyrin adsorption was examined using mepanipyrin solutions whose acidity was controlled with HCl or NaOH. All treatments were duplicated. Solutions of mepanipyrin at the concentration of 1.04 $\mu\text{g/ml}$ containing ^{14}C -mepanipyrin at 358 Bq/ml were prepared by dissolving non-labeled and ^{14}C -labeled mepanipyrin in 0.01 M CaCl_2 made in distilled water, 0.1, 0.075, 0.05, 0.025, 0.01, and 0.005 N HCl, and 0.01 N NaOH. Kikugawa and Koriyama soils were selected as one of the low pH and of high pH soils, respectively. Five grams of each soil (wet weight basis) and 20 ml of each mepanipyrin solution were shaken and centrifuged, and the supernatant was radioassayed in the same manner described above.

For the H_2O_2 treated soils solutions of mepanipyrin at 2.04 $\mu\text{g/ml}$ containing ^{14}C -mepanipyrin at 1478 Bq/ml were prepared by dissolving non-labeled and ^{14}C -labeled mepanipyrin in 0.01 M CaCl_2 made in distilled water, 0.04, 0.01, 0.008, 0.006, 0.004, and 0.002 N HCl and 0.004, and 0.008 N NaOH. The solution made in distilled water were used for all soils. The 0.01 N HCl and 0.008 N NaOH solutions were used for Nagano H_2O_2 treated soil, 0.004 and 0.002 N HCl and 0.004 N NaOH solutions for Kikugawa and Kume H_2O_2 treated soils, 0.004 and 0.002 N HCl and 0.004 N NaOH solutions for Koriyama H_2O_2 treated soil, and 0.04 and 0.008 N HCl and 0.004 N NaOH for Ushiku H_2O_2 treated soil. A 2 ml aliquot of 0.01 M CaCl_2 was added to 500 mg of each H_2O_2 treated soil (air-dry weight basis) in a 10-ml glass test tube and the test tube was shaken gently for 24 hr to re-equilibrate the soil with water. Then a 2 ml aliquot of each mepanipyrin solution was added to the test tube. The sample was shaken and centrifuged, and the supernatant was radioassayed in the same manner described above.

The pH of all supernatants was also measured.

8. Calculations

The concentration of mepanipyrin in the supernatant was calculated by assuming that all radioactivity in the supernatant was derived from mepanipyrin. The amount adsorbed was obtained as the difference between the amount in supernatant and the amount added to the centrifuge tube.

Adsorption isotherms were calculated using the logarithmic form of the Freundlich equation with the least square method:

$$\text{Log } (x/m) = \text{log}(K_f) + (1/n) \cdot \text{log}(C_e)$$

where x/m is the amount of mepanipyrin adsorbed on soil ($\mu\text{g/g}$), C_e is the concentration in the supernatant after the equilibration ($\mu\text{g/ml}$), K_f is the adsorption coefficient, and $1/n$ is the slope.

$K_{f,oc}$, which is the normalized K_f value based on the soil organic carbon content, was obtained by the following equation:

$$K_{f,oc} = (K_f / OC\%) \cdot 100$$

where $OC\%$ is the organic carbon content of soil.

Distribution coefficient was calculated to describe the desorption and pH effects on mepanipyrin adsorption by the following equation:

$$K_d = (x/m) / C_e$$

where K_d is the distribution coefficient. K_d values were also calculated with the equilibrium concentrations observed in desorption studies and the adsorption amounts obtained from the adsorption isotherms at the equilibrium concentrations.

RESULTS AND DISCUSSION

1. Adsorption Isotherms for the Soils

Adsorption isotherms are shown in Fig. 2. K_f , $1/n$, the coefficient of determination (r^2), $K_{f,oc}$, and pH of the supernatant are listed in Table 3.

The r^2 values, 1.000 for all soils tested, mean that the Freundlich equation well described the soil adsorption of mepanipyrim. The slopes ($1/n$) which were smaller than unity for all soils indicate that mepanipyrim adsorption was dependent on the initial mepanipyrim concentration in the solution and the proportion of molecules adsorbed decreased as the initial concentration increased. The K_f values for Nagano, Kikugawa, Ushiku, Koriyama, and Kume soils were 427, 22.4, 35.5, 14.5, and 12.9, respectively. And the $K_{f,oc}$ values were 3420, 5210, 1090, 1340, and 1630, respectively.

Though the soil adsorption of chemicals is generally governed by the soil organic matter, pH can be influential in the case of ionizable compounds. It was reported that the adsorption of a weak base atrazine on geologic materials was correlated with pH more highly than with

Fig. 2 Adsorption isotherms for the soils.

Error bars represent one standard deviation of the duplicate samples.

$OC\%$.⁶⁾ Also, it has been known that atrazine is adsorbed more at low pH than at high pH.³⁻⁵⁾ Mepanipyrim is also a weak base compound having the pK_a value of 2.9 and it was expected that its adsorption was influenced by pH as well as atrazine.

The pH values of equilibrium solutions were 6.4 for the Ushiku soil, 6.2 for Koriyama soil, and 5.0 for the other soils. The $K_{f,oc}$ values were greater for Kikugawa and Nagano soils having the lower pH value than those for Ushiku and Koriyama soils having the higher pH values. Especially Kikugawa soil having the lowest $OC\%$ gave the third greatest K_f value among the five soils. The $K_{f,oc}$ value for Kume soil, however, was relatively low in spite of its low pH.

2. Desorption from the Soils

The K_d values obtained for desorption and those calculated from the adsorption isotherms at the equilibrium concentrations observed in the desorption studies are shown in Table 4.

The desorption K_d values were larger than those calculated. This suggests that mepanipyrim desorption from the soils is hysteretic and mepanipyrim once adsorbed on soils will be desorbed less than expected from the adsorption isotherm.

Table 4 Distribution coefficients (K_d) for the desorption of mepanipyrim from the soils and those calculated from the adsorption isotherms.

Soil	K_d obtained from desorption test	K_d calculated from the isotherm
Nagano	1260	803
Kikugawa	57.4	44.4
Ushiku	79.5	59.3
Koriyama	26.9	20.8
Kume	30.5	22.1

Table 3 Freundlich constants, coefficients of determination (r^2), and normalized K_f based on organic carbon content ($K_{f,oc}$) for the adsorption of mepanipyrim on five Japanese soils, and pH of supernatant.

Soil ^{a)}		$1/n^b)$	$K_f^c)$	r^2	$K_{f,oc}$	pH
Nagano	Original	0.887 (0.977-0.771)	427 (190-818)	1.000	3420	5.0
	H ₂ O ₂	0.852 (0.795-0.909)	48.7 (38.1-62.2)	0.998	5939	4.8
Kikugawa	Original	0.747 (0.723-0.774)	22.4 (20.0-25.5)	1.000	5210	5.0
	H ₂ O ₂	0.658 (0.574-0.740)	12.2 (8.87-16.8)	0.992	11100	5.7
Ushiku	Original	0.817 (0.790-0.846)	35.5 (31.6-40.9)	1.000	1090	6.4
	H ₂ O ₂	0.861 (0.845-0.875)	7.59 (7.25-7.89)	1.000	1310	6.0
Koriyama	Original	0.832 (0.821-0.845)	14.5 (13.7-15.1)	1.000	1340	6.2
	H ₂ O ₂	0.746 (0.678-0.814)	9.43 (7.57-11.8)	0.996	5240	5.9
Kume	Original	0.756 (0.734-0.779)	12.9 (11.9-14.2)	1.000	1630	5.0
	H ₂ O ₂	0.614 (0.287-0.703)	0.454 (0.411-0.821)	0.998	504	5.8

^{a)} The upper line for each soil shows the values for the original soil and the lower the values for the H₂O₂ treated soil. ^{b)} Numbers in parenthesis are the 95% confidential interval for $1/n$. ^{c)} Numbers in parenthesis are the 95% confidential interval for K_f .

3. Effect of pH on the Adsorption of Mepanipyrim

Fig. 3 shows the effect of pH of the equilibrium solution on the adsorption of mepanipyrim expressed in K_d value for Kikugawa and Koriyama soils. For both soils the K_d values increased as pH decreased, reaching the maximum at a pH value near the pK_a value of mepanipyrim. In the pH range below the pK_a value the K_d values decreased. This pH effect is analogous to that observed for the adsorption of s-triazine herbicides onto soil colloids,^{7),8)} and aniline and toluidines onto montmorillonite.⁹⁾ The increase in mepanipyrim adsorption with the decrease in pH would be attributed to the formation of the ionic bond between protonated mepanipyrim and the minus charge on the soil colloids in addition to other adsorption mechanisms. This increase in mepanipyrim adsorption got enhanced between pH 5 to 6 for both soils. The percentage protonated of a weak base in a solution is given by the following equation¹⁰⁾:

$$\% \text{ protonated} = 100 / (1 + 10^{(pH - pK_a)})$$

Calculated from the equation, more than 99% of mepanipyrim molecule exists as a neutral form in the pH range above 5 so that the ionic bond doesn't seem to be involved in the increase in adsorption within this pH range. But the acidity at the soil colloid surface can account for this. In the vicinity of the soil colloid surface, cations accumulate to neutralize the minus charge on the soil colloid surface and the pH may be lower than that of equilibrium solution by as much as 2 pH units.^{11),12)} On the basis of this pH difference mepanipyrim can be protonated and adsorbed through the ionic bond even when the pH of equilibrium solution is far above its pK_a value. Assuming the difference of 2 pH units, 44.3% of mepanipyrim molecule in the acidic layer at the soil colloid surface can be protonated in Nagano, Kikugawa, and Kume soils, whose equilibrium solutions gave the pH of 5.0. On the other hand in

Fig. 3 Effect of pH on the K_d values of mepanipyrim adsorption onto Kikugawa and Koriyama soils. Error bars represent one standard deviation of the duplicate samples.

Koriyama and Ushiku soils giving the pH of 6.2 and 6.4, respectively, the percentages protonated were 4.7 and 3.1. Accordingly, the ionic bond is considered to be available in Nagano, Kikugawa, and Kume soils, while it is negligible in Koriyama and Ushiku soils.

In the pH range below the pK_a value the competition with proton over the adsorption sites may decrease mepanipyrim adsorption as well as the case of the adsorption of s-triazines by clay minerals.⁸⁾

The mepanipyrim adsorption didn't change remarkably in the higher pH range above 5.2 for the Kikugawa soil and 5.9 for Koriyama soil. The reason is most likely that above a certain pH value all mepanipyrim molecules exist in a neutral form even in the vicinity of soil colloid surface and the adsorption of neutral molecule is little affected by pH.¹³⁾

Consequently, it is confirmed that the pH of equilibrium solution controls the affinity of the soils for mepanipyrim. The difference of the affinity between Kikugawa and Koriyama soils may be partly attributed to the pH difference between both soils.

4. Adsorption Isotherms and Effect of pH on the Adsorption for the H_2O_2 Treated Soils

K_f , $1/n$, r^2 , $K_{f,oc}$, and pH of supernatants for the H_2O_2 treated soils are shown in Table 3 and the effect of pH on the adsorption for the H_2O_2 treated soil expressed in K_d value is shown in Fig. 4.

The K_f values for Nagano, Kikugawa, Ushiku, Koriyama, and Kume H_2O_2 treated soils were 48.7, 12.2, 7.59, 9.43, and 0.454, respectively. After the H_2O_2 treatment K_f values for Nagano, Ushiku, and Kume soils decreased remarkably to 11.4, 21.4, and 3.5% of those for their respective original soils, while the decrease in K_f values for Kikugawa and Koriyama soils were less remarkable

Fig. 4 Effect of pH on the K_d values of mepanipyrim adsorption onto the H_2O_2 treated soils. Error bars represent one standard deviation of the duplicate samples.

giving the K_f values of 54.5 and 65.0% of those for their respective original soils.

Similar to the pH effect for Kikugawa and Koriyama original soils in the pH range above the pK_a value, the adsorption increased while the pH value decreased for all H_2O_2 treated soils. The pH effect was remarkable for Kikugawa, Koriyama, and Nagano soils, but not so for Ushiku and Kume soils.

5. Corrected K_f Values for the H_2O_2 Treated Soils and Discussion on the Adsorption Capacities

Since the H_2O_2 treatment induced some changes in the pH values of the supernatants as shown in Table 3, corrected K_f values for the H_2O_2 treated soils were calculated at the pH for their respective original soils to compare directly with the K_f values of the original soils. Using the K_d value at the pH of each original soil obtained from the Fig. 4 by interpolation or extrapolation, the amount adsorbed and the supernatant concentration were calculated with the initial concentration of 1.02 $\mu\text{g}/\text{ml}$ and then the corrected K_f value was obtained from the Freundlich equation:

$$x/m = K_f \cdot C_e^{1/n}$$

It was assumed that the $1/n$ value was equal to that of the isotherm for each H_2O_2 treated soil shown in Table 3.

The corrected K_f values for Nagano, Kikugawa, Ushiku, Koriyama, and Kume H_2O_2 treated soils were 33.7, 29.4, 4.89, 5.61, and 1.34, respectively. From the comparison between the corrected K_f values and K_f values for the original soils, in the Nagano, Ushiku, and Kume soils, whose K_f values decreased remarkably by the H_2O_2 treatment, the soil organic matter is considered to be the main adsorbent in mepanipyrim adsorption in their original soils. The K_f value for Koriyama soil also decreased but not remarkably. Therefore, both the organic matter and mineral constituents may play the major roles in the original soil. In the case of Kikugawa soil, the K_f value increased after the H_2O_2 treatment. This indicates the importance of soil mineral constituents in original Kikugawa soil on mepanipyrim adsorption.

Around pH 5 the adsorption capacities for Nagano, Kikugawa, and Koriyama H_2O_2 treated soils seemed almost the same. On the other hand Ushiku and Kume H_2O_2 treated soils showed relatively low adsorption capacities. Especially the adsorption capacity for the Kume H_2O_2 treated soil was the lowest over the pH range tested. It can be considered that the high affinity of the Kikugawa original soil in spite of its low OC% is due to the contribution of the high adsorption capacity of its mineral constituents besides its low pH, and the low affinity of the Kume soil having the lower pH value is attributed to the low adsorption capacity of mineral constituents in addition to its low OC%.

The difference in the adsorption capacities of the H_2O_2 treated soils may be due to the difference in the main clay minerals contained in the soils. Kikugawa, and Koriyama soils whose H_2O_2 treated soils had high adsorption capacities contained 2:1 type clay minerals, illite or vermiculite. On the other hand the main clay mineral in the Kume soil was halloysite which is a 1:1 type clay mineral. Because the 2:1 type clay minerals generally have a large surface area and a high layer charge independent of pH, compared to the 1:1 type clay minerals,¹⁴⁾ the 2:1 type clay minerals can adsorb protonated mepanipyrim more strongly than the 1:1 type clay minerals. Allophane, which was the main clay mineral in the Ushiku soil, has minus charge dependent on pH and its CEC decreases rapidly as pH decreases.¹⁵⁾ Therefore, it doesn't seem to work as an effective adsorbent for a weak base compound which becomes protonated as the pH decreases. This is because the pH change affected little on mepanipyrim adsorption on Ushiku H_2O_2 treated soil. Remaining organic carbon in Nagano H_2O_2 treated soil may contribute to its high adsorption capacity. However, the vermiculite contained in Nagano soil is also considered to be significant for its adsorption capacity.

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要 約

殺菌剤メパニピリムの土壌吸着とその機構

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^{14}C 標識メパニピリムを用い, その土壌吸着性および吸着特性を5種類の畑土壌について調べた。

3段階の濃度で実施した吸脱着試験の結果, メパニピリムの土壌吸着はフロイントリッヒの吸着等温式によく適合した。吸着係数 K_f は 12.9 から 427 であり, $1/n$ はすべての土壌で 1 より小さかった。また, K_f を有機炭素含量で割り

算出した $K_{f,oc}$ は, 1090 から 5210 であった。脱着においてヒステリシスが認められた。メパニピリムの吸着は pH 依存性であり, pH の低下に伴い増加し, pK_a (2.9) 付近で最大となった。この pH 依存性には, プロトネーションしたメパニピリムと土壌コロイドの負電荷との間のイオン結合が関与していると推察された。過酸化水素により土壌有機物を分解すると, 全ての土壌で K_f 値が減少した。 pK_a 以上の pH において, 過酸化水素処理した土壌への吸着も, pH の低下にともない増加した。