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Hydrolysis of Methyl Parathion in a Flooded Soil

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Methyl parathion (O,O-dimethyl O-p-nitrophenyl phosphorothioate) (MP) is used widely for controlling insect pests and vectors of diseases in agriculture and public health. MP, like ethyl parathion (Sethunathan et al. 1977), may undergo degradation in soil and water environments by hydrolysis, nitro group reduction or both. Hydrolysis is the major pathway in nonflooded soil while MP is degraded essentially by nitro group reduction in predominantly anaerobic ecosystems such as flooded soil. In a few instances, hydrolysis is the major or only pathway of MP degradation in soils even under flooded conditions (Ou 1985). Adhya et al. (1987) found that nitro group reduction was the major pathway of MP degradation in 4 out of 5 selected soils under flooded conditions while in one soil viz. Sukinda, degradation of MP proceeded exclusively by hydrolysis even under flooded condtions. The reason for rapid hydrolysis of MP in Sukinda soil even under flooded conditions is not clear. The present study is aimed at exploring the reason for the hydrolytic pathway of MP in flooded Sukinda soil. Also, the effect of temperature on the persistence and degradation pathway of MP in flooded Sukinda soil was studied.

MATERIALS AND METHODS

Three soils, a laterite (Sukinda) soil (pH 6.9, organic matter 0.62%, total nitrogen 0.04%), an acid sulfate (Pokkali) soil (pH 5.4, organic matter 5.51%, total nitrogen 0.21%) and a laterite (Pattambi) soil (pH 6.0, organic matter 1.04%, total nitrogen 0.063%) were air-dried and sieved (< 2 mm). Twenty-gram portions of the soil were flooded with 25 ml of sterile distilled water in pre-sterilized test tubes (200- x 25-mm) and incubated at 25 ± 1°C and 35 ± 1°C. After 10 days, an aqueous solution (1 ml) of a commercial formulation of MP (Metacid EC 50% obtained from Bayer, India) was added to flooded soil samples to provide a final concentration of 50 µg active ingredient (a.i.)/g soil. At periodic intervals after incubation at 25 and 35°C, residues of MP in duplicate soil samples were separated by thin-layer chromatography and analyzed colorimetrically after alkaline hydrolysis of MP as described earlier (Sharmila et al. 1988).

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Experiments were conducted to determine whether more reduced conditions generated through prolonged flooding or organic matter addition, would trigger nitro group reduction in Sukinda soil. In one approach, Sukinda soil was flooded and incubated at 25 and 35°C as in the previous experiment, but for 30 days instead of 10 days to allow more reduction of the soil prior to the addition of MP. The persistence and degradation pathways of MP added to a 30-day flooded soil were determined as in the earlier experiment. In another approach, rice straw was added to the flooded soil to accelerate its reduction. Soil samples (20 g) were amended with 100 mg of rice straw powder (0.5% w/w) and incubated under flooded conditions at 25 and 35°C as in the earlier experiments. After 10 days, an aqueous solution of MP (50 µg a.i/g soil) was added to the flooded soil samples and MP residues were extracted and analyzed at periodic intervals as in the first experiment.

The redox potentials of flooded soil were measured with a compound platinum-calomel electrode as described earlier (Pal et al. 1979). The pH of these soil samples (1:1:25 soil-water ratio) was also measured.

RESULTS AND DISCUSSION

MP disappeared more rapidly at 35°C than at 25°C in all the three soils under flooded conditions (Table 1).The insecticide was degraded more rapidly in Pokkali and Pattambi soils than in Sukinda soil. In Pokkali and Pattambi soils held at 35°C, the insecticide reached undetectable levels in 12 days. In Sukinda soil, hydrolysis was the only pathway of MP degradation at both temperatures. In Pokkali and Pattambi soils, degradation proceeded by both nitro group reduction and hydrolysis at both temperatures; but nitro group reduction was more pronounced than hydrolysis. According to an earlier study (Sharmila et al. 1988), degradation of MP in a flooded alluvial soil proceeded essentially by hydrolysis and to a less extent by nitro group reduction at 35°C and solely by nitro group reduction at 25°C. Such a temperature-dependent shift in the pathway of MP degradation was not noticed in the three soils used in this study. Evidently, the rate and route of degradation of MP in soil are governed by soil type and temperature.

The onset of reducing conditions in a soil following incubation under flooded conditions (Ponnamperuma 1972) should generally favor reduction reactions such as nitro group reduction as noticed in two of the three soils used in this study. Interestingly, however, nitro group reduction of MP, when added to 10-day preflooded Sukinda soil, was totally inhibited. In a follow-up experiment, Sukinda soil was flooded for 30 days prior to the addition of MP to generate more reduced conditions. The redox potential of the soil was -100 mV after 10 days of flooding and -145 mV after 30 days of flooding.

Table 1. Persistence of methyl parathion[a] in 10-day preflooded Sukinda, Pokkali and Pattambi soils held at 25 and 35°C

Incubation (days after MP addition)	Soil type	μg compound recovered/20 g soil					
		25°C			35°C		
		MP[b]	PNP[c]	MAP[d]	MP[b]	PNP[c]	MAP[d]
0	Sukinda (laterite)	710±5[e]	nd	nd	724±10	nd	nd
	Pokkali (acid sulfate)	720±10	nd	nd	717±7	nd	nd
	Pattambi (laterite)	790±5	nd	nd	795±7	nd	nd
4	Sukinda (laterite)	622±7	45±5	nd	585±14	102±8	nd
	Pokkali (acid sulfate)	557±20	57±5	98±7	340±8	59±10	257±5
	Pattambi (laterite)	332±3	85±5	275±12	240±5	123±4	260±5
12	Sukinda (laterite)	590±10	55±10	nd	185±8	75±10	nd
	Pokkali (acid sulfate)	217±12	50±15	277±4	tr	48±5	245±10
	Pattambi (laterite)	150±7	50±10	200±12	nd	40±10	170±8

[a]1000 μg/ml MP was added to 20 g soil.
[b]Methyl parathion, [c]*p*-nitrophenol, [d]methyl aminoparathion.
[e]Mean of duplicate estimations, ± deviation.
nd not detected.
tr trace.

Soil was flooded for 30 days prior to the addition of MP to generate more reduced conditions. The redox potential of the soil was -100 mV after 10 days of flooding and -145 mV after 30 days of flooding. Even more reduced conditions of 30-day preflooded soil did not seem to trigger the nitro group reduction of MP in Sukinda soil (Table 2). As in 10-day preflooded soil, MP was degraded essentially by hydrolysis in 30-day preflooded soil. The pH of 10- or 30-day preflooded soil ranged between 6.9 and 7.04. Chemical hydrolysis of MP is expected to be not very rapid at this pH (Faust and Gomaa 1972). Hydrolysis of MP in 10-day preflooded soil is mediated essentially by microorganisms, because no hydrolysis occurred in soil preflooded for 10 days and then sterilized by autoclaving. In nonsterilized soil, the insecticide declined from the original level of 715 ± 12 μg/20 g soil to 137 ± 12 μg/20 g soil after 12 days with concomitant accumulation of p-nitrophenol in substantial amounts. During the same period, the amount of MP disappeared from sterilized soil was only 112 μg/20 g soil and p-nitrophenol was recovered only in traces.

Addition of organic sources such as rice straw would hasten the reduction of a flooded soil. The addition of rice straw distinctly increased the degradation rate of MP at both 25 and 35°C. As in the earlier experiments, in unamended soil hydrolysis was the sole pathway of MP metabolism (Table 3). In rice straw amended soil, the insecticide was degraded by both nitro group reduction and hydrolysis. In terms of the amounts of the metabolites accumulated in the soil, hydrolysis outstripped nitro group reduction. But, it is likely that some of the amino analog formed might have been immediately bound to the soil (Katan et al. 1976, Katan and Lichtenstein 1977). In fact, not all MP disappeared from rice straw amended soil was accounted for as p-nitrophenol + methyl aminoparathion.

According to an earlier report (Sethunathan 1973), addition of rice straw inhibited the hydrolysis of parathion in a flooded alluvial soil and accelerated nitro group reduction. In the present study, addition of rice straw to flooded Sukinda soil triggered nitro group reduction. Sukinda soil had very low organic matter content (0.62%) when compared to Pokkali (5.51%) and Pattambi (1.04%) soils. Soils poor in organic matter undergo slow reduction upon submergence (Ponnamperuma 1972) and, therefore, may not be congenial for nitro group reduction. Even 30-day preflooded Sukinda soil at 35° C (-145 mV) had higher redox potential than 10-day preflooded Pokkali (-200 mV) and Pattambi (-175 mV) soils. Addition of rice straw to flooded Sukinda soil accelerated its reduction. Thus, in 10 days after flooding, the redox potential of rice straw amended Sukinda soil dropped to -187 mV at 25°C and -205 mV at 35°C. Evidently, the inhibition of nitro group reduction of MP in flooded Sukinda soil is related to its low organic matter content and higher redox

Table 2. Persistence of methyl parathion[a] in 30-day preflooded Sukinda soil (30 days) and incubated at 25 and 35°C

Incubation (days)	μg compound recovered/20 g soil					
	25°C			35°C		
	MP[b]	PNP[c]	MAP[d]	MP[b]	PNP[c]	MAP[d]
0	750 ± 10[e]	nd	nd	754 ± 7	nd	nd
2	661 ± 9	nd	nd	501 ± 10	85 ± 5	nd
4	557 ± 11	80 ± 5	nd	350 ± 8	106 ± 4	nd
6	330 ± 7	65 ± 10	nd	104 ± 9	85 ± 5	nd
12	187 ± 11	nd	nd	nd	nd	nd

[a] 1000 μg/ml methyl parathion was added to 20 g soil.
[b] Methyl parathion, [c] p-nitrophenol, [d] methyl aminoparathion.
[e] Mean of duplicate estimation, ± deviation.
nd not detected.

Table 3 . Persistence of methyl parathion[a] in flooded Sukinda soil, unamended and amended with rice straw and incubated at 25 and 35°C

Incubation (days)	25°C						35°C					
	Unamended			Amended[b]			Unamended			Amended[b]		
	MP[c]	PNP[d]	MAP[c]	MP[c]	PNP[d]	MAP[e]	MP[c]	PNP[d]	MAP[e]	MP[c]	PNP[d]	MAP[e]
0	718±10[f]	nd	nd	708±8	nd	nd	715±10	nd	nd	720±12	nd	nd
2	670±12	nd	nd	364±14	60±7	45±5	619±20	68±5	nd	279±13	75±10	58±5
4	624±8	40±5	nd	255±10	90±3	43±3	540±7	102±7	nd	165±20	110±12	34±11
6	580±10	65±10	nd	189±10	48±5	nd	375±14	124±10	nd	nd	nd	nd
12	550±15	50±7	nd	nd	nd	nd	150±5	75±12	nd	nd	nd	nd

[a] 1000 μg/ml methyl parathion was added to 20 g soil.

[b] Soil was amended with 0.5% rice straw.

[c] Methyl parathion, [d] p-nitrophenol, [e] methyl aminoparathion,

[f] Mean, of duplicate estimations, ± deviation, μg compound recovered/20 g soil.

nd not detected.

potential Based on the data presented in this study, degradation of MP in this soil proceeded exclusively by hydrolysis under flooded conditions.

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