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Monitoring Movement of Fenamiphos through Soil Water in Peach Orchards Using Quantitation by Gas Chromatography/Mass Spectrometry

James B. Kotcon[1] and Mary Wimmer[2]

[1]Division of Plant and Soil Sciences, West Virginia University, P.O. Box 6057, Morgantown, West Virginia 26506-6057, USA and [2]Department of Biochemistry, Health Sciences Center, West Virginia University, Morgantown, West Virginia 26506, USA

Ground water contamination by pesticides has become an increasingly important issue. Nematicides have received added attention in this regard because they are highly toxic to mammmalian systems, are relatively water soluble, and are applied directly to soil at high rates. The organophosphate nematicide, fenamiphos, is the only material still registered for nematode control in bearing peach and apple orchards in West Virginia and surrounding fruit producing areas. In spite of their potential environmental hazards and their economic cost, nematicides are currently the only effective means of reducing population densities of plant-parasitic nematodes in established orchards (Kotcon 1990). Pesticide applications through drip irrigation systems greatly reduce the quantity of pesticide applied because only a portion of the root zone is treated compared to broadcast applications; however, irrigation water may accelerate leaching of pesticides through the soil to ground water. Because much of the fruit production in this area occurs on highly vulnerable karst topography (Hogmire et al. 1990), this study was undertaken to assess the rate of movement of fenamiphos in soil water through the tree root zone, and to evaluate the potential for ground water contamination among three application methods. In the course of this study, a gas chromatography/mass spectrometric method for quantifying fenamiphos was developed.

MATERIALS AND METHODS

This study was conducted in a newly planted peach orchard in Jefferson County, WV on Hagerstown cherty silt loam soils (pH 5.2, 38% rock fragments with the remaining soil composed of 26% sand, 58% silt, 16% clay, CEC 9.36 cmol/kg) with clay subsoils (25% rock fragments, 19% sand, 28% silt, 53% clay,) and outcrops of limestone bedrock. Soil suction lysimeters were installed at depths of 15, 30, and 90 cm within the tree row. One lysimeter was placed at each depth in each of two replicate plots per treatment at locations both inside and outside of the anticipated wetted zone from drip irrigation emitters. Pretreatment water samples were collected from lysimeters on May 28, 1987. Fenamiphos was applied to five replicate, eight-tree plots on June 5 in the following treatments: 1) as a broadcast spray at 20 kg active ingredient (ai)/treated ha, 2) via drip irrigation at 20 kg ai/treated ha, or 3) via drip irrigation at 10 kg ai/treated ha. Two untreated plots served as controls and were monitored with one lysimeter each at the 30-cm

Send reprint requests to J. B. Kotcon at the above address.

depth. Water samples were collected 1 day after treatment, 25 days later, and approximately monthly thereafter. Plots treated with 10 kg/ha received a second application Sept. 25 to evaluate the effects of split applications. Lysimeters were left in place over winter. Only minimal maintenance was required to obtain water samples in the spring of 1988; thus, the soil profile was not disturbed. Fenamiphos treatments were repeated with applications on May 5, 1988 and Sept. 22, 1988 (split treatment). Water samples were collected May 4 (pretreatment) and at 9, 20, 41, 63, 92, 128 and 146 days after application.

Soil water samples collected from lysimeters were analyzed for concentrations of fenamiphos and its primary degradation products, fenamiphos sulfoxide and fenamiphos sulfone via gas chromatography/mass spectrometry. Prior to extraction of fenamiphos from water samples, 200 ul of 500 ppm fenthion (technical grade) in methanol was added as an internal standard. All solvents used in the pesticide extraction and analysis were of pesticide grade or better. Water samples were extracted according to U. S. Environmental Protection Agency methods (US-EPA 1978) with 60 ml hexane:methylene chloride (85:15) per liter of sample. The extraction was repeated two more times and the pooled organic layers were dried over anhydrous sodium sulphate and evaporated to 5-10 ml on a rotary evaporator equipped with a dual aspirator pump, holding the sample temperature at approximately 15 C to prevent evaporative losses. After addition of one small drop of mineral oil as a keeper, the extract was further concentrated to 0.2-1.0 ml using a Kuderna-Danish aparatus at 110 C.

Gas chromatography was done on a 30-m SE30 capillary column (0.25 mm I.D., J&W Scientific, Inc., Folsom, CA 95630) with isothermal elution at 235 C. Although not necessary due to the distinctive monitoring method, complete separation of fenthion (5.5 min. elution) and fenamiphos (7.1 min. elution) was observed. Detection and quantitation of pesticides was by mass spectrometry using selective ion monitoring for m/e 154 and 303 (unoxidized fenamiphos major ions); 186 (major ion of fenamiphos sulfone); and 278 (major ion of fenthion). A standard of fenamiphos was run prior to and after every approximately six samples to determine the ratio of m/e 278 to m/e 303 for equal amounts of the two pesticides. This factor (which averaged 0.69) was used to calculate the amount of fenamiphos in unknown samples, each of which contained a known amount of the fenthion standard. No interference from other compounds in the sample was seen when monitoring these two ions. By concentrating the extract of a 1-liter water sample to 0.2 ml, a detection limit of less than 2.5 ppb is attainable with this method.

RESULTS AND DISCUSSION

The major molecular ions in the mass spectra of fenamiphos, its sulfoxide, and its sulfone are m/e 303 (the molecular weight of fenamiphos), 319, and 335, respectively, due to the addition of one and two atoms of oxygen to the parent compound as it becomes oxidized. The major fragments resulting from the molecular ions are at m/e 154, 170, and 186. These ions are observed in Figure 1 which shows the major ions in a gas chromatographic peak of a mixture of oxidized and non-oxidized forms under conditions in which the forms elute unresolved.

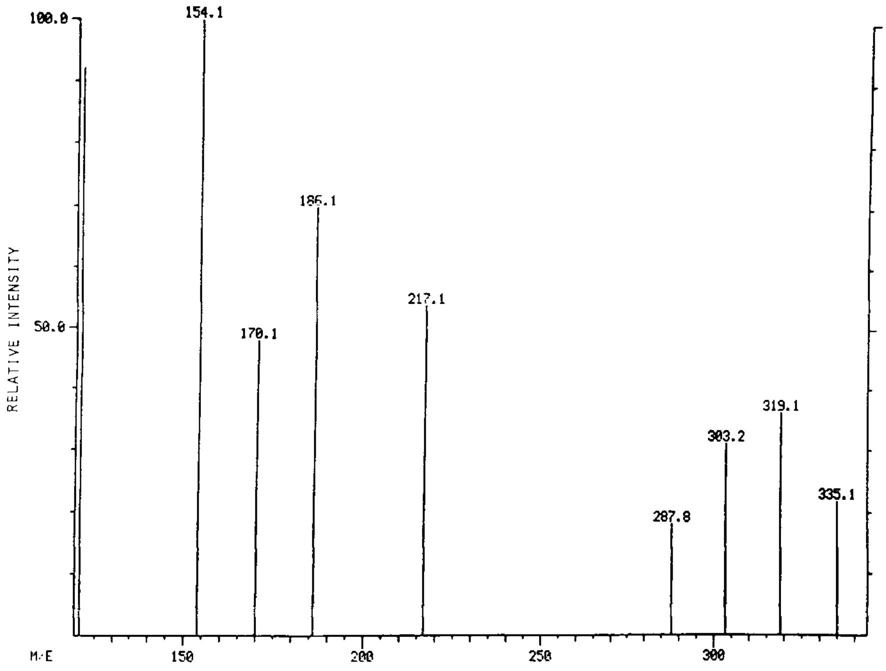

Figure 1. Major ions in a mixture of oxidized and non-oxidized Fenamiphos. The Fenamiphos sample originated from a twelve-day-old 60 ppm solution in HPLC-grade water. Ionizing voltage was 70 ev.

The oxidized forms of fenamiphos, the sulfoxide and sulfone, have been reported to be the major metabolites of the pesticide found in soils and plants (Waggoner 1972). Therefore, the initial gas chromatographic runs of lysimeter field sample extracts were monitored using the major ions for the oxidized forms, m/e 170, 186, and 335. An example of one field sample analysis shows a small peak eluting with the correct retention time for fenamiphos forms following the peak for internal standard fenthion (Figure 2A). The ion profile of the minor peak (Figure 2B) is consistent with the presence of small amounts of the oxidized forms (m/e 170 and 186, with m/e 335 too low to detect).

To check for the presence of non-oxidized fenamiphos in this peak, an identical run was made with ion monitoring at m/e 154 and 303 along with m/e 186. The gas chromatographic profile (Figure 3A) is markedly different from that of Figure 2. The ratio of areas of the fenamiphos and fenthion peaks is reversed, with the former now predominating. The profile of ions (Figure 3B) confirms that most of the fenamiphos in the sample is in the non-oxidized form. Therefore, in all subsequent analyses, gas chromatographic monitoring is done at m/e 154, 186, 278 and 303 to check for all forms. In no instance was more than a trace of oxidized fenamiphos observed.

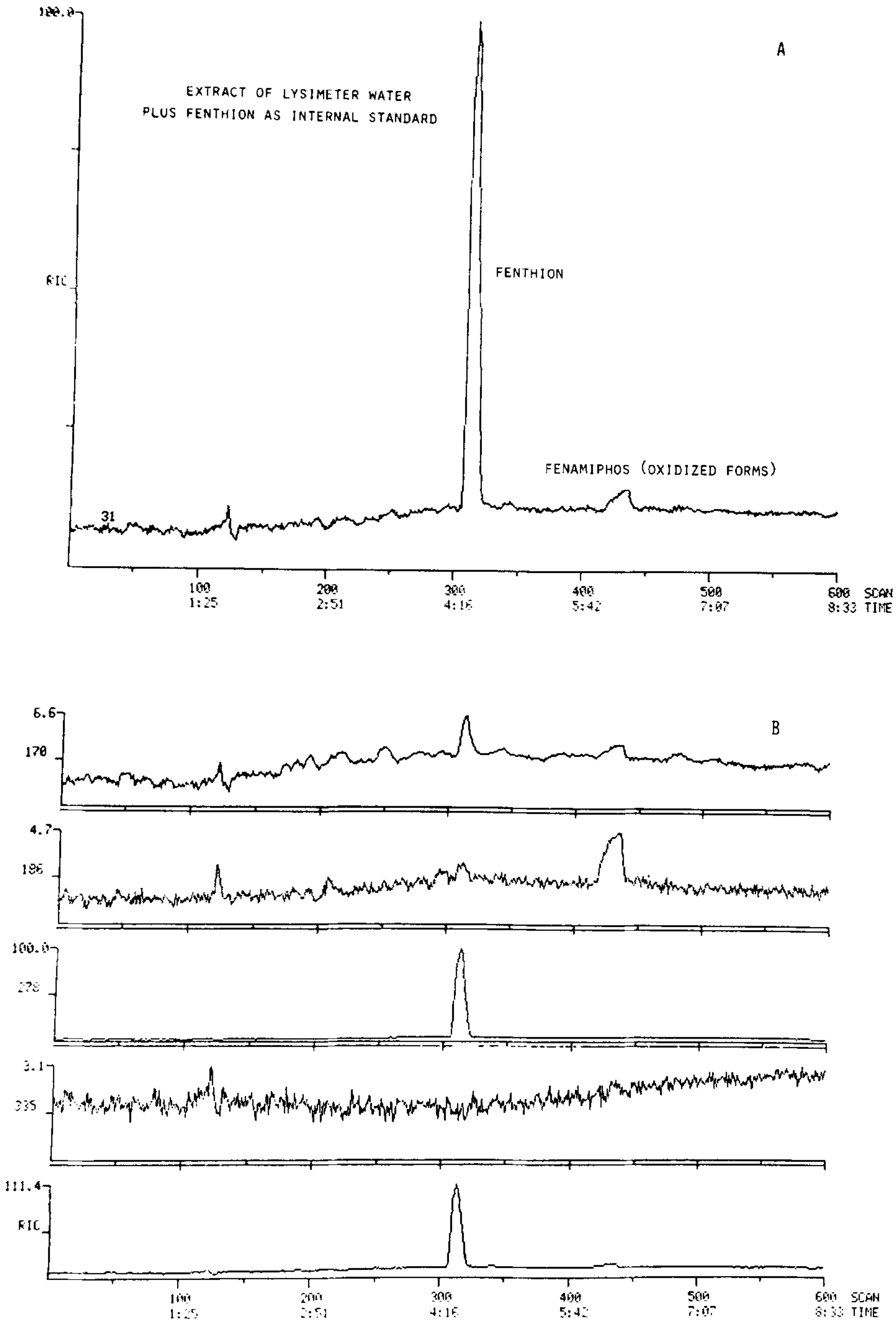

Figure 2. A) Gas chromatographic profile of an extract of lysimeter water after Fenamiphos field application. Ions monitored were those of oxidized Fenamiphos (m/e 170, 186, and 335) and Fenthion internal standard (m/e 278). RIC is the total ion current. Ionizing voltage was 35 ev. B) Profile of each selected ion.

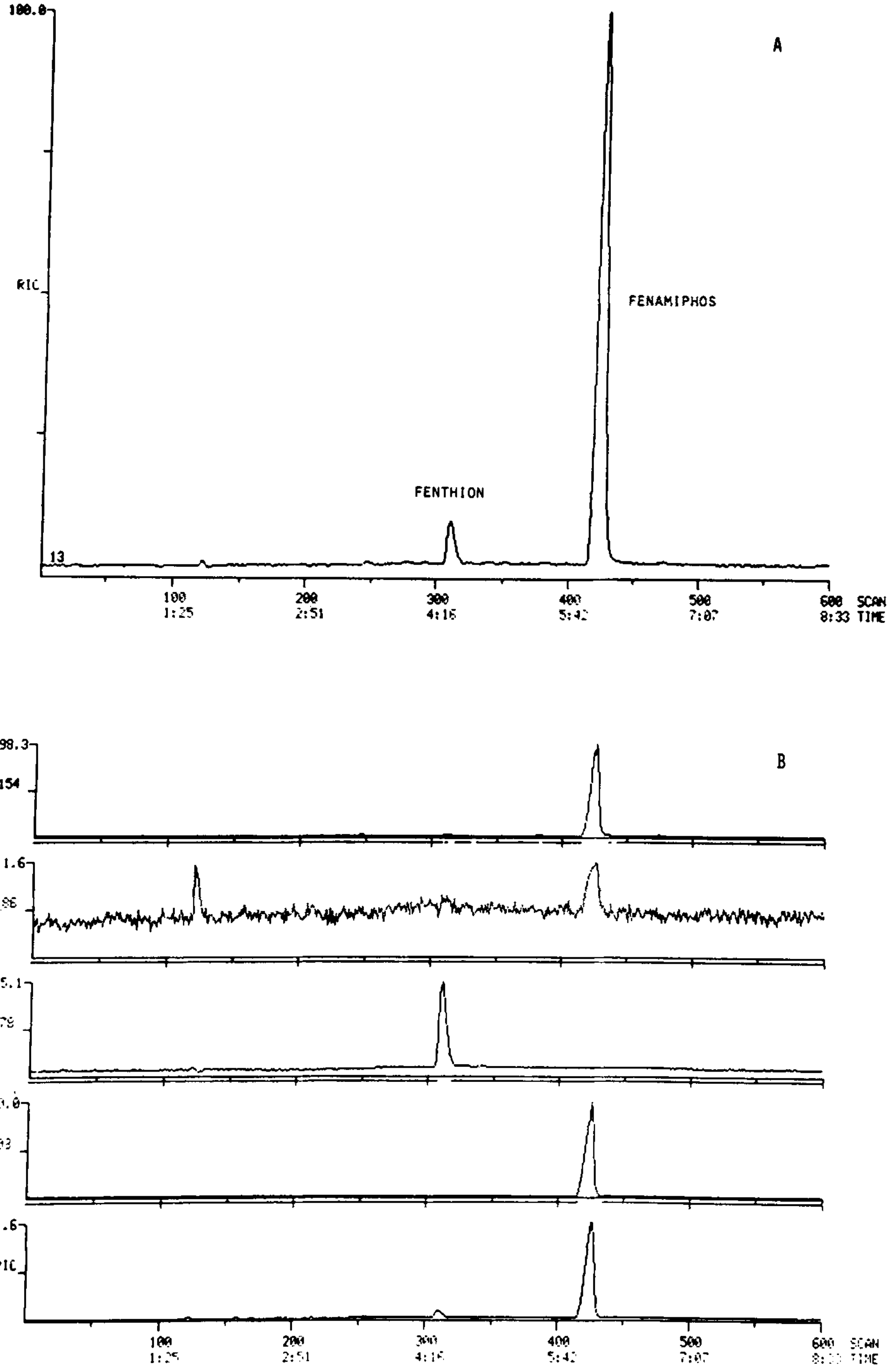

Figure 3. A) Gas chromatographic profile of the same extract as in Fig. 2, except ions monitored included those of non-oxidized Fenamiphos (m/e 154, 303). B) Profile of each selected ion.

Drip irrigation resulted in a 1.2-m diameter wetted zone; fenamiphos application rates were calculated accordingly. Much of the plot had slopes of 5 to 15 %, resulting in very irregular wetting patterns. Water samples from lysimeters varied in volume depending on the moisture content of soil. Dry soil resulted in no water being collected. Water samples ranging in volume from 2 to 980 ml were analyzed for fenamiphos. Detection limits were proportional to sample volume and ranged from 2 ppm to 2.5 ppb, respectively. Less than 1% of the fenamiphos observed in these samples was oxidized into fenamiphos sulfoxide or fenamiphos sulfone.

In 1987, fenamiphos was detected in one sample from an untreated plot and in one sample each at 15 cm and 30 cm depths in the 20 kg/ha drip treatment at the first sample date. No fenamiphos residues were detected in samples collected at later dates.

In 1988, fenamiphos was detected in samples collected 9 days after application from all treatments and at all depths. The fenamiphos concentrations found in the pre-treatment and first two post treatment replicate samples (5/4; 5/13; and 5/24 sample dates) are listed in Table I. The complete data set from days zero to 146 after fenamiphos application is illustrated in Figure 1. Fenamiphos was detected more consistently and in higher concentrations within the wetted zones beneath emitters than in nonwetted portions of the root zone. This was expected in the drip-applied treatments where fenamiphos was applied only to the wetted zone; however this was also observed in the broadcast application where fenamiphos was applied to both wetted and nonwetted soil zones. The high concentrations detected in May declined rapidly and no samples had detectable fenamiphos by 92 days after application (Figure 1). Fenamiphos was detected in water samples from all depths five days after the fall application to the 10kg/ha drip treated plots.

Significant concentrations of fenamiphos in Sept. 27 samples from the other treatments cannot be explained because no fenamiphos was applied to these plots in September. Conceivably, a 2-cm rain event just prior to the Sept. 27 sampling may have leached additional fenamiphos from the spring application; however, this had not been observed with similar rain events prior to the Aug. 4 and Sept. 9 sampling.

The rapid movement observed in 1988, compared to the very limited movement in 1987, was associated with rainfall and temperature differences. Average temperatures were 24 C or greater and rainfall was below normal following the June 1987 applications. In contrast, during the three weeks following the May 1988 application, soil temperatures were about five degrees C cooler than in June 1987 and the plots received almost eight inches of rain in addition to the irrigation.

The decline in fenamiphos concentrations over time may have been due to fenamiphos degradation, sorption to soil particles, or movement below the lysimeter. While degradation cannot be ruled out, it should be noted that very little of the residues detected were of the oxidized forms, fenamiphos sulfoxide or fenamiphos sulfone. Organophosphate pesticides such as fenamiphos are generally considered to have minimal leaching potential because of their moderate solubilities and soil partition coefficients (Ritter 1990). Schneider et al. (1988) found that fenamiphos was leached from the root zone more rapidly with weekly

Table I. Concentration of fenamiphos in water samples from lysimeters placed in wetted and nonwetted zones under peach trees irrigated as indicated. See Materials and Methods section for details.

Treatment	Depth	Fenamiphos Concentration (ppb) 5/4	5/13	5/24
Wetted Zone				
Broadcast	15 cm	0	1470	398
		*	*	*
Broadcast	30 cm	*	781	263
		--	*	*
Broadcast	90 cm	0	48	18
		0	90	6
18lb Drip	15 cm	0	1193	81
		0	248	24
18lb Drip	30 cm	0	1145	235
		0	0	19
18lb Drip	90 cm	0	18	599
		0	665	404
9lb Drip	15 cm	0	--	207
		0	103	22
9lb Drip	30 cm	0	34	7
		0	0	0
9lb Drip	90 cm	--	--	3
		0	3958	748
Untreated Control	30 cm	0	0	2
		--	7	*
Nonwetted Zone				
Broadcast	15 cm	0	*	*
		*	0	*
Broadcast	30 cm	0	--	20
		--	0	0
Broadcast	90 cm	0	*	15
		0	0	0
18lb Drip	15 cm	0	0	0
		--	0	*
18lb Drip	30 cm	0	102	2
		0	0	*
18lb Drip	90 cm	0	0	0
		0	0	4
9lb Drip	15 cm	--	0	*
		--	--	0
9lb Drip	30 cm	0	22	0
		0	0	7
9lb Drip	90 cm	0	0	0
		*	*	0

* Trace concentration detected

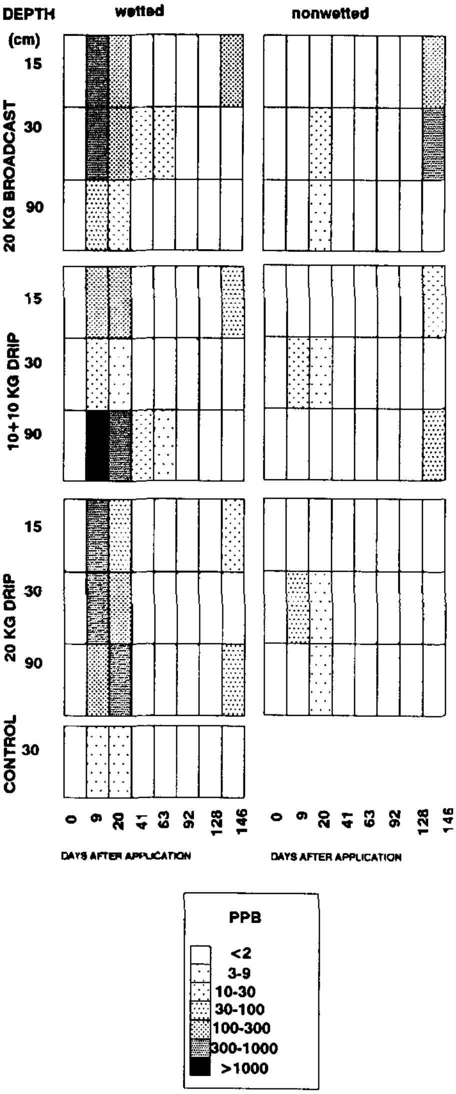

Figure 4. Mean concentration of fenamiphos in water samples from two replicate lysimeters placed at three depths in wetted and non-wetted soil under drip irrigated peach trees, 1988. Lysimeter samples were taken at 0, 9, 20, 41, 63, 92, 128, and 146(5) days after application on May 8, 1988 (Sept. 22 in the split treat-ment, 10+10 drip). Lysimeters were installed at one depth in control (untreated) plots.

irrigation than when irrigation was restricted after application.

The use of drip irrigation increased the leaching of fenamiphos in this study; however, this occurred only after high rainfall accumulation. Furthermore, fenamiphos concentrations were highly variable indicating substantial spatial variability (Table I). To minimize the potential for groundwater contamination, applications should be timed to avoid periods of excessive rainfall. Unfortunately, other restrictions on use and practical aspects of pest and crop biology often limit the window for nematicide applications. The use of drip irrigation applications has the added advantage of greatly reducing the total amount of pesticide applied because a smaller ground area is treated (74 % less than with broadcast applications in this trial). Because of the ease of application, drip applications also encourage the use of multiple, low-dose applications which would tend to reduce the concentration of nematicide leaching to groundwater during high rainfall events. Nematicide applications should also be timed to avoid seasonal ground water recharge periods (Boesten and van der Linden 1991) which occur during fall and winter in West Virginia. If further research shows that adequate pest control can be achieved (Kotcon 1988), properly timed drip applications may actually reduce the overall threat to groundwater, in spite of the increased leaching associated with unusually heavy rain events.

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