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Triazophos residues and dissipation rates in wheat crops and soil

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Abstract

The residual level and dissipation rate of triazophos in wheat crops and the soil in which they were grown were determined by gas chromatography (GC). Maximum final residues of triazophos in wheat grain, stems and leaves, and soil were 1.865, 44.506, and 0.973 mg/kg, respectively. The mean half-life of triazophos in wheat plants (grain, stems, and leaves) was 5.22 days with a dissipation rate of 90% over 14 days. The half-life in soil was 7.93 days with a dissipation rate of 90% over 21 days. Dissipation rates in two geographically separated experimental fields differed, suggesting that this was affected by local soil characteristics and climate. Although residual levels of triazophos in wheat plants may pose risks to the health of humans and other animals, comparatively low residues in soil suggest that this pesticide may be otherwise environmentally safe.

Keywords: Pesticide residues; Dissipation; Gas chromatography; Triazophos; China

1. Introduction

Triazophos [3-(*o*,*o*-diethyl)-1-phenyl thiophosphoryl-1,2,4-triazol] is a broad-spectrum organophosphate insecticide and acaricide with nematicidal properties (Coats, 1994; Rani et al., 2001). It is used to control aphids, bollworms, red spiders, fruit borers, leaf hoppers and cutworms on a variety of crops, such as fruits, cotton, maize, wheat, cereals, and vegetables, and is particularly effective in the control of plant nematodes (Hamey and Harris, 1999; Yen et al., 1999; Kranthi et al., 2001; Martin et al., 2003a, b; Nath et al., 2005). Wheat is an important crop in China that is cultivated throughout the country (Rozelle and Huang, 2000). Although triazophos residues have been reported in some vegetables and environmental materials (Hamey and Harris, 1999; Harris, 2000; Carter et al., 2000; Liao et al., 2002), we were unable to find any published information on triazophos residues in wheat. In this study, we investigated the persistence, dissipation, and kinetics of triazophos residues in wheat crops and the soil in which they were grown. Our objective was to determine the maximum safe application rate of triazophos for wheat crops.

2. Materials and methods

2.1. Materials

Pesticide: Triazophos (EC, 40%) was the pesticide used.

Crop: Winter wheat was the crop used.

Chemicals: Petroleum ether (60–90 °C), acetone, dichloromethane, sodium chloride, and anhydrous sodium sulfate were all AR grade. Florisil (60–80 mesh) was baked for 4 h at 650 °C. Before use, activated carbon and florisil were baked for 4 h at 135 °C to ensure that they were dry; 3% distilled water was added to the florisil to reduce its activity before use.

2.2. Experimental design

Experiments were conducted in 2003 and 2004 at two sites: one in Beijing and one in Shandong Province, China. Treatments were applied to 18, 30-m^2 plots at each site with each treatment replicated three times. A buffer area separated plots used for different treatments in the same field.

2.3. Triazophos dissipation

To investigate the dissipation of triazophos in wheat crops, wheat plants were simultaneously sprayed with triazophos and then sampled and

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tested for triazophos residues at different times post spraying. During the first 10 days of May in 2003 and 2004, triazophos (EC, 40%) was dissolved in water and sprayed onto the surface of wheat plants at a dosage of 900 g a.i. ha^{-1}. At 2 h after spraying, 2 kg of wheat plants was collected from 12 randomly selected 0.1-m^2 sampling points within each plot. Plants were severed about 10 cm from the base of each plant; the plant parts collected included the immature grain, leaves, and stems. This sampling regime was repeated 1, 3, 5, 7, 14, 21, and 30 days after spraying. Plants were sprayed on 6 May 2003 in Shandong and on 9 May 2003 in Beijing. Sampling took place on 6, 7, 9, 11, 13, 20, and 27 May and 6 June 2003 in Shandong and on 9, 10, 12, 14, 16, 23, and 30 May and 9 June 2003 in Beijing. The soil in which the plants were grown was sampled on days 0, 1, 3, 5, 7, 14, 21, and 30 after spraying; sampling dates were the same as those for the plant material. Soil was sampled to a depth of 0–15 cm at 18 randomly selected sampling points in each plot using soil-sampling apparatus. Both plant and soil samples were stored at −20 °C until analyzed.

2.4. Determination of final triazophos residues

The growth period of the winter wheat used in this experiment, which is typically sown in late autumn and harvested in early summer, is about 8 or 9 months. To investigate the effects of triazophos dosage and spray frequency, a two-by-two experimental design was used. High (900 g a.i. ha^{-1}) and low (600 g a.i. ha^{-1}) dosage treatment groups were each composed of two separate plots, one of which was sprayed three and the other four times, with an interval of 7 days between sprays. In addition to stem and leaf material and soil, matured or nearly matured wheat seed, excluding that with a milky color, was sampled to determine final triazophos residues in harvested grain. Wheat seed, stem and leaf material, and the soil in which these had grown were sampled on days 3, 7, and 14 postspraying, respectively.

2.5. Analytical methods

2.5.1. Sample preparation

Samples (20 g) of wheat grain, stem and leaf material, and soil were tested for triazophos residues using gas chromatography (GC). The 20-g samples of grain meal were obtained by threshing 1–2 kg of wheat grain and concentrating this using the quartation method. Then 200 g of this threshed, concentrated grain was dried, ground into a coarse meal with a vegetation disintegrator, and divided into 20-g samples. Stem and leaf material was cut into small pieces before GC analysis. The 20-g soil samples were measured on a dry matter basis after the soil had been dried in the shade and sifted through a 40-mesh sieve.

2.5.2. Extraction

The extraction process followed the method described by Gong et al. (2004) with slight modifications. Samples (20 g) of the prepared grain meal, stem and leaf material, and soil were placed in three separate beakers to which 40, 80, and 40 ml of acetone was added, respectively. Samples were then left overnight after which extraction was conducted, with surging, for 1 h. The samples were filtered using an 80-mm glass filter and air pump. Grain and plant residues were filtered with 100 ml acetone and soil samples with 80 ml acetone. Filtrates for each type of sample were combined and transferred to a funnel with a little acetone after which 200 ml of 5% sodium chloride and 50 ml dichloromethane were added and surged for 2 min. The dichloromethane phase was collected after partitioning and transferred to a funnel with anhydrous sodium sulfate. The resultant solution was then filtered with 10 ml dichloromethane. The water phase was extracted by surging twice with dichloromethane (30, 30 ml). All extracts were combined and concentrated to near dryness on a rotary vacuum flash evaporator (Eyela Model NE-IS). Soil samples were filtered with an acetone–petroleum ether mixture (35:65, v/v) (APEM), put into a flask, and made up to a final volume of 5 ml for GC analysis.

2.5.3. Clean-up

A little absorbent cotton was put in the bottom of the glass cleanup column (1 cm i.d.) and then a 4-cm-thick layer of anhydrous sodium sulfate, 5 g florisil, a 1-g mixture of florisil and activated carbon (4:0.2), and another 4-cm-thick layer of anhydrous sodium sulfate were successively added. The ratio of the adsorbent to sample weight was 30:100. The column was prewashed in 30 ml of APEM and the first 15 ml elution discarded. The concentrated samples of wheat meal and stem and leaf material were dissolved in a little APEM, placed in the cleanup column, and filtered with 100 ml APEM. The resultant eluate was evaporated on a rotary evaporator at 30 °C until just 1–2 ml remained. The concentrated samples were transferred to a flask and made up to a volume of 5 ml with APEM for GC analysis.

2.5.4. GC estimation

GC analysis used a combination of published methods (Rani et al., 2001; Kumari et al., 2003; Nath et al., 2005). Estimation of triazophos residues was performed using a GC machine (Model HP-5890 II) equipped with a SGE BPX50 column (50% phenyl equivalent polysilphenylene–siloxane; 30 m × 0.53 mm i.d. × 0.5-μm film thickness). Other GC parameters were as follows: temperature (°C), oven 280, injection port 300, detector (NPD) 300; gas flow (ml/min), nitrogen 30, hydrogen 3, air 79. The relative retention time (Rt) for triazophos was observed to be 3.6 min.

2.5.5. Calculations

Different amounts of standard triazophos (99.0% purity) were added to samples of grain meal, stem and leaf material, and soil collected from unsprayed control plots and the triazophos residue in these control samples was determined by the external standard method. Recovery was determined with single-point calibration. There was a positive linear relationship ($y = 472.98 + 15{,}699x$, $R^2 = 0.9996$) between the peak area (y) for triazophos and its concentration (x) in the range 0.125–6.000 ng/μl. The limit of detection (LOD) for triazophos was 0.075 ng and the limit of quantification (LOQ) was 0.05 mg/kg.

The residual amount and half-life of triazophos were calculated by the equations, $C_T = C_0 e^{-KT}$ and $T_{1/2} = -1/K \ln 0.5$, respectively, where T is the time (days or hours) after application of the pesticide, C_T is the residue of the pesticide at time T, C_0 is an initial residue after application (at $T = 0$), K is a dissipation coefficient, and $T_{1/2}$ is the time required for the pesticide residue level to fall to half the initial postapplication level.

3. Results

3.1. Recovery

Recovery was determined as described above. Recovery from soil, leaf and stem, and grain samples was 91.54–101.24%, 86.29–97.99%, and 88.86–99.75%, respectively (Table 1). Recovery data and their coefficients of variance (CV) did not exceed the permissible range (Table 1).

3.2. Dissipation of triazophos in wheat plants and soil

The initial residue of triazophos in wheat plants grown in Shandong was 32.19 mg/kg with a half-life ($T_{1/2}$) of 4.86 days; 98.58% of this initial residue had dissipated after 30 days. However, initial residue of triazophos in the wheat plants grown in Beijing was only 13.38 mg/kg with a half-life of 5.59 days; 97.42% of this residue had dissipated after 30 days (Table 2).

The initial residue of triazophos in soil from the Shandong experimental field was 1.3052 mg/kg with a half-life of 9.51 days; 91.47% of this residue had dissipated

Table 1
Recovery (%) of triazophos from wheat grain, leaf and stem material, and soil from unsprayed control plots

Sample type	Amount added (mg/kg)	Recovery (%) 1	2	3	Average	CV[a] (%)
Soil	5.00	93.43	86.06	95.13	91.54±4.82	5.27
	0.50	94.82	105.56	103.33	101.24±5.67	5.60
	0.05	97.59	103.42	98.33	99.78±3.17	3.18
Leaf and stem	5.00	93.60	93.56	92.95	93.37±0.36	0.39
	0.50	80.96	89.05	88.88	86.30±4.62	5.36
	0.05	97.97	95.39	100.62	97.99±2.62	2.67
Grain	5.00	99.07	98.47	101.17	99.57±1.42	1.42
	0.50	96.45	97.11	104.41	99.33±4.42	4.45
	0.05	81.92	88.05	96.62	88.86±7.38	8.31

[a]CV, coefficient of variance.

Table 2
Dissipation of triazophos residues in wheat crops grown in Shandong and Beijing, China

Days after spraying	SD03 Residue (mg/kg)	SD03 Dissipation (%)	BJ03 Residue (mg/kg)	BJ03 Dissipation (%)
0.042	32.447±1.903	—	19.411±5.771	—
1	31.012±0.363	4.42	14.951±2.811	22.63
3	25.648±1.004	20.95	11.135±4.407	42.37
5	16.768±1.308	48.32	6.262±1.215	67.60
7	9.355±0.195	71.17	4.581±1.522	76.30
14	2.694±0.158	91.70	1.366±0.102	92.93
21	2.195±0.183	93.24	0.713±0.272	96.31
30	0.460±0.049	98.58	0.499±0.231	97.42

SD03, Shandong, 2003; BJ03, Beijing, 2003.

Table 3
Dissipation of triazophos residues in the soil of experimental wheat fields in Shandong and Beijing, China

Days after spraying	SD03 Residue (mg/kg)	SD03 Dissipation (%)	BJ03 Residue (mg/kg)	BJ03 Dissipation (%)
0.042	2.533±0.079	—	1.169±0.020	—
1	1.140±0.333	54.99	0.189±0.010	—
3	0.592±0.025	—	0.895±0.019	23.44
5	0.822±0.134	67.55	0.409±0.007	65.01
7	0.517±0.040	79.59	0.206±0.004	82.38
14	0.362±0.040	85.71	0.158±0.002	86.48
21	0.227±0.012	91.04	0.067±0.001	94.27
30	0.216±0.012	91.47	0.043±0.002	96.32

SD03, Shandong, 2003; BJ03, Beijing, 2003.

after 30 days (Table 3). However, the initial residue in soil from the Beijing field was 0.8225 mg/kg with a half-life of 6.36 days; 96.32% of this residue had dissipated after 30 days (Table 3).

3.3. Final residues of triazophos in wheat grain, leaf and stem material, and soil

In 2003, residual triazophos levels in wheat grain, leaf and stem material, and soil were 0.187–1.865, 3.168–44.506, and 0.086–0.551 mg/kg, respectively (Tables 4–6). However, in 2004, the corresponding values were 0.023–1.396, 2.040–12.909, and 0.051–0.973 mg/kg, respectively. Although triazophos residues in soil did not vary as much between years, residues in grain and stem and leaf material were dramatically lower in 2004 than in 2003.

4. Discussion

Initial residues of triazophos in wheat plants and soil differed between the two experimental sites; plants grown in Shandong had twice the residual level of triazophos as those grown in Beijing. Dissipation of triazophos in stem and leaf material was faster in Beijing than in Shandong; 96.31% after 21 days compared to 93.24% over the same period of time. Similarly, dissipation in soil was faster in Beijing than in Shandong; the half-life of triazophos in soil was 6.36 days at Beijing compared to 9.51 days at Shandong. This difference probably reflects the lower initial residue in the soil at Beijing compared to that at Shandong (0.82 vs. 1.31 mg/kg). These between-site differences suggest that local soil characteristics and climate affect the dissipation of triazophos.

The amount of triazophos detected in wheat grain sampled on days 3, 7, and 14 postapplication did not exceed 1.865 mg/kg. However, the maximum residue recorded in stem and leaf material was 44.506 mg/kg. By comparison, triazophos residues in soil were less than 0.973 mg/kg. Therefore, despite the fact that triazophos dissipated more slowly in soil than in plant material, residues in soil were much lower than those detected in either wheat grain or stem and leaf material.

FAO/WHO has not established maximum residue limits (MRL) for triazophos. In some countries, such as Germany and South Africa, MRLs of triazophos in fruits, vegetables, and cereal are 0.05–2.00 mg/kg. The acceptable daily intake of triazophos is 0–0.001 mg/kg body weight. The application of triazophos has seldom followed the guidelines for pesticide residues in food specified by the FAO/WHO (FAO/WHO, 1983). Our results, particularly the high residues of triazophos we observed in wheat grain and stem and leaf material, provide a quantitative basis for revising the application of this pesticide to wheat crops. We recommend that wheat crops be sprayed with triazophos (EC, 40%) not more than 3 times at a dosage not exceeding 600 g a.i. ha^{-1} and with an interval of at least 7 days between each application. There should be a withholding period of at least 14 days between the last application and harvest. Repeated application of high dosages of triazophos to wheat crops is not advisable.

Table 4
Final residues of triazophos in wheat grain and stem and leaf material grown in Shandong, China

Days after spraying	Number of times sprayed	Dosage (g a.i. ha^{-1})	Residue (mg/kg)			
			2003		2004	
			Grain	Stem and leaf	Grain	Stem and leaf
3	3	600	0.829±0.016	17.513±1.761	0.905±0.064	4.650±0.470
		900	1.189±0.103	44.506±9.613	0.684±0.097	6.633±3.109
	4	600	1.481±0.046	24.618±2.130	0.573±0.084	2.594±0.465
		900	1.532±0.141	29.269±2.712	0.585±0.076	3.094±1.218
7	3	600	0.531±0.042	15.940±3.345	0.614±0.027	3.601±0.693
		900	1.176±0.160	21.980±2.504	0.534±0.082	5.719±0.747
	4	600	0.886±0.050	9.112±0.538	0.347±0.058	2.222±0.224
		900	1.624±0.133	10.812±0.788	0.448±0.079	4.138±1.001
14	3	600	0.187±0.014	9.179±1.998	0.280±0.027	2.221±0.310
		900	0.348±0.065	20.345±1.670	0.023±0.007	4.702±0.867
	4	600	0.438±0.118	7.845±0.609	0.121±0.039	2.040±0.162
		900	0.591±0.090	8.834±1.386	0.437±0.149	5.097±1.589

Table 5
Final residues of triazophos in wheat grain and stem and leaf material grown in Beijing, China

Days after spraying	Number of times sprayed	Dosage (g a.i. ha^{-1})	Residue (mg/kg)			
			2003		2004	
			Grain	Stem and leaf	Grain	Stem and leaf
3	3	600	1.101±0.189	12.232±3.076	0.750±0.094	5.442±0.155
		900	1.865±0.107	16.789±4.476	1.396±0.101	10.529±1.584
	4	600	1.345±0.281	11.162±2.555	0.524±0.015	7.745±0.762
		900	1.661±0.054	21.919±0.698	1.357±0.045	12.909±1.357
7	3	600	0.916±0.130	9.117±1.988	0.376±0.019	3.293±0.426
		900	1.262±0.268	16.034±2.469	0.582±0.053	4.432±0.268
	4	600	1.011±0.078	5.618±1.276	0.282±0.012	3.304±0.599
		900	1.409±0.195	20.126±2.966	0.551±0.013	4.933±0.946
14	3	600	0.442±0.037	4.367±1.892	0.329±0.078	2.294±0.081
		900	1.573±0.115	3.578±0.996	0.568±0.146	2.369±0.043
	4	600	0.729±0.096	3.168±0.869	0.241±0.053	2.244±0.061
		900	1.185±0.339	11.655±1.246	0.655±0.179	2.850±0.421

Table 6
Final residues of triazophos in the soil of experimental wheat fields in Shandong and Beijing, China

Days after spraying	Number of time sprayed	Dosage (g a.i. ha^{-1})	Residue (mg/kg)			
			SD03	SD04	BJ03	BJ04
3	3	600	0.238±0.006	0.284±0.046	0.298±0.062	0.329±0.088
		900	0.225±0.014	0.520±0.130	0.498±0.038	0.819±0.172
	4	600	0.459±0.010	0.268±0.048	0.354±0.038	0.467±0.019
		900	0.499±0.030	0.931±0.141	0.466±0.014	0.973±0.097
7	3	600	0.180±0.034	0.474±0.021	0.225±0.060	0.187±0.027
		900	0.285±0.007	0.473±0.012	0.437±0.160	0.424±0.044
	4	600	0.450±0.071	0.250±0.008	0.316±0.007	0.254±0.028
		900	0.680±0.188	0.241±0.011	0.374±0.062	0.553±0.057
14	3	600	0.105±0.039	0.391±0.007	0.169±0.013	0.064±0.015
		900	0.165±0.078	0.307±0.008	0.200±0.036	0.104±0.014
	4	600	0.130±0.080	0.256±0.004	0.196±0.018	0.051±0.005
		900	0.158±0.018	0.423±0.013	0.232±0.019	0.131±0.018

SD03, Shandong, 2003; SD04, Shandong, 2004; BJ03, Beijing, 2003; BJ04, Beijing, 2004.

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