Supporting Information

Volatilization of parathion and chlorothalonil from a potato crop simulated by the PEARL model

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Introduction

Detailed reports of field studies are needed for testing a plant-volatilization model for pesticides. The volatilization of parathion and chlorothalonil from a potato crop was studied in a well-defined field experiment (8). Both pesticides are relevant in investigations of the emission to the air, as can be illustrated with some studies. The concentration of parathion measured in rainwater in Baden-Würtemberg, Germany, ranged from nil to 0.21 μ g L⁻¹ (34), while those measured in rainwater in Niedersachsen, Germany, ranged from nil to 0.32 μ g L⁻¹ (35). The concentration of chlorothalonil measured in rainwater in Niedersachsen, Germany (36), was on average 0.16 μ g L⁻¹ (range nil to 1.1 μ g L⁻¹). In an agricultural watershed in Maryland, USA, chlorothalonil was detected in 89% of the rainwater samples taken in the growing season (37), at an average concentration of 0.16 μ g L⁻¹ (range 0.01 to 2.01 μ g L⁻¹).

Procedures

Samples of the pesticides in air were taken (8) at 0.8 m, 1.0 m, 1.3 m and 1.5 m above the soil surface (top of the ridges). The pesticide vapors were trapped on XAD-4 adsorbent in glass cartridges, at an airflow rate of 50 mL min⁻¹. Total air volume sampled was measured using a gas meter. Four series of air samples (1 h of sampling each) were taken on the day of application and again on the first day after the day of application. Two series of samples were taken on the 2nd (1 h), 3rd (1 h) and 7th (2 h) days after the day of application. The XAD adsorbent was extracted using a mixture of ethyl acetate and hexane (1:1). Regular checks revealed that no breakthrough of pesticide vapor from the adsorbent had occurred. Upwind air samples did not contain measurable concentrations of the pesticides.

The rate of decline of the pesticides on/in the plant leaves was measured by taking samples of fully exposed leaves at seven time intervals, up to 7 days after application (8). The leaf samples were stored overnight in a mixture of ethyl acetate and hexane (1:1), the flask content was then shaken mechanically for 10 min. Parathion and chlorothalonil in the extracts of XAD adsorbent and leaves were analyzed using gasliquid chromatography.

The volatilization fluxes obtained with the AD and BR methods (8) in the measuring periods were averaged. These fluxes were multiplied by representative time periods to obtain the cumulative amount of pesticide volatilized after each day. The average of the fluxes in the two measuring periods in the first 4 hours after application were multiplied by this 4 hour period. The same was done for the second 4-hour period after application. Pesticide volatilization during the night (from 21 h to 6h30) was assumed to be negligible. The fluxes obtained on each of the days 1, 2, 3 and 7 after the day of application were averaged and multiplied by the 14.5 hour daylight period, to obtain the daily areic masses volatilized. The volatilization fluxes on days 4, 5 and 6 were obtained by interpolating linearly between the values for days 3 and 7. The latter values were also multiplied by the 14.5-h daylight period. The areic masses volatilized in each period were summed to obtain the cumulative volatilization at the

end of each day, as shown in Figures 1 and 2 for parathion and in Figure 3 for chlorothalonil.

The value of the vapor pressure of parathion at 25 °C was later confirmed (38), also by using the gas saturation method. The rate of volatilization of parathion from a glass surface was about half that of parathion-methyl (16, 39). In view of the vapor pressure of 1.2 mPa at 20 °C for parathion-methyl (16), the ratio of the volatilization rates was closely related to the ratio of the vapor pressures of parathion and parathion-methyl.

No direct measurements were found on the rate of phototransformation of chlorothalonil at plant surfaces. Chlorothalonil dissolved in water absorbs sunlight in the wavelength range of 300 to 340 nm (31), so it can be subjected to direct phototransformation. The rate of photolysis of chlorothalonil in water, obtained in laboratory and outdoor experiments, shows a wide range of values (Table S1).

Type of water	Light source	Details	Half-life	Reference
			(d)	No
Distilled	Simulated sunlight,	Calculated for 50 °N from	22	(40)
	translated to sunlight	experimental results		
De-ionised	Sunlight	Spain, August	4.2	(41)
Distilled	Sunlight	Greece, May	2.0	(42)
River	Sunlight	Greece, May	0.4	(42)
Lake	Sunlight	Greece, May	0.3	(42)
Distilled and	Simulated sunlight		1.2	(31
de-ionised				
Creek	Simulated sunlight		< 0.4	(31)
Pond	Simulated sunlight		< 0.4	(31)

Table S1. Half-lives of photolysis by (simulated) sunlight measured or calculated for chlorothalonil in water.

General discussion

Most of the measurements on the rate of phototransformation of pesticides by sunlight have been done for solutions in water. The rate of photolysis of parathion-methyl dissolved in four types of fresh water (distilled, aquifer, river, lake) under natural sunlight conditions (Greece, summer) corresponded to half-lives in the range of 25 to 35 d (43). These half-lives are much longer than those of around 0.5 d for reference sunlight intensity (sunny day) derived for parathion–methyl on plant surfaces in three wind tunnel studies (14). In most cases, rather short half-lives were measured for the photolysis of chlorothalonil in water (Table S1). Experimental results in combination with the present computations indicate that the half-lives due to phototransformation of chlorothalonil on leaf surfaces are longer than those for photolysis in water. These differences in half-lives indicate that the rate of pesticide phototransformation is highly dependent on the medium.

The half-life of the phototransformation of parathion at the plant surface (0.69 d at reference sunlight radiation of 500 W m⁻²) introduced into the Run 2 simulation can be compared with the half-lives measured previously (44). These researchers applied ¹⁴C-labeled parathion to surfaces of glass, tomato leaf wax and tomato fruit wax. The surfaces were radiated in a photo-reactor with a xenon arc lamp emitting light with a light spectrum similar to that of sunlight. The decrease of parathion in a period of 8 hours corresponded to half-lives of 0.7 d (glass), 1.3 d (leaf wax) and 1.0 d (fruit wax). Unfortunately, the intensity of the light on the surfaces (in W m⁻²) was not given.

The average half-life of the residue of parathion measured on and in crop leaves in many reported studies (45) was 2.6 d (n = 43; SD = 1.5 d). In the computation of Run 2, the sum of the deposit left (8.4%) and of the penetrated residue (35.5%) was 43.9% of the dosage at 3.1 d (which is 2.6 d after application). So the simulated rate of decline of parathion on/in the leaves (corresponding half-life of 2.2 d) is slightly greater than the average rate in the reported measurements, but is well within the wide range of variation.

The computed decline of chlorothalonil on and in the potato plants can be compared with measurements (30) of the residue by soaking the potato leaves in acetone for 45 min. The half-life of the residue measured in this way was on average 4.4 days (n = 8; SD = 2.5 d). At 4.9 d (4.4 d after application) in the present study, the computed deposit left (18.5%) and the computed penetration into the plants (37.9%) give a total plant residue of 56.4% of the dosage. When chlorothalonil was measured on/in cranberry leaves by shaking them with methanol for 45 s (32), 56.1% of the dosage was found in the extract after 7 days. In the present computation for potato leaves, the sum of deposit left (9.9%) and of penetrated residue (42.9%) totalled 52.8% of the dosage at 7.5 d (7 d after application). The rather good simulation indicates that chlorothalonil penetrated only superficially into the plant leaves, which corresponds to the behaviour measured for the radio-labeled compound applied to plants (27).

In most studies on residues of pesticides on/in plants, an extraction method for the total residue was used. This makes it impossible to estimate the fraction of the residue available for volatilization at the plant surfaces. In other studies, the information on

extraction methods is inadequate to allow the fraction of the residue available for volatilization to be estimated. Even when the residue is obtained by rinsing the leaves for a short time, the use of an organic solvent can be expected to release part of the plant-penetrated residue. In order to make progress in studying the processes for pesticides at the plant surface, it is essential that the fractions of surface deposit and plant-penetrated residue as a function of time can be distinguished.

Measurements of parathion and chlorothalonil in the air above a field with cereal crops had already been carried out before (46), up to 1.4 days after spraying. These measurements do not allow volatilization fluxes to be calculated, so only a qualitative interpretation of the results is possible. Although the dosage of parathion was lower than that of chlorothalonil, its concentrations in air due to volatilization were initially higher than those for chlorothalonil. This confirms the fact that the vapor pressure of parathion is substantially higher than that of chlorothalonil. The concentration of parathion in the air above the crop decreased more rapidly than that of chlorothalonil. This corresponds to a comparatively fast dissipation of parathion residue at the plant surfaces. So the tendencies in that study correspond to those in our simulation results shown in Figure 2 for parathion and in Figure 3 for chlorothalonil.

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