Adsorption Experiments of Etridiazole and Oxamyl on Polyethylene Sheets and Poly(vinyl chloride) Tubing Used in Horticulture

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In laboratory experiments the adsorption and desorption of etridiazole and oxamyl on polyethylene (PE) and poly(vinyl chloride) (PVC) were studied. These fungicides and materials are commonly used in the culture of vegetables on artificial rooting medium. Capillary gas chromatography was used for quantitative analysis. Oxamyl was found not to adsorb on PE and PVC, and etridiazole, not on PVC. A substantial amount of etridiazole was adsorbed by PE. Equilibrium is reached after 4 h. Equilibrium concentrations after adsorption and desorption could be described quantitatively by Freundlich's adsorption isotherm. The results obtained can be used to adjust the effective dosage of the fungicide. They may also contribute to assessment of environmental risks when plastic materials containing residual amounts of fungicide are discarded.

A new and promising development in horticulture is growing cultures on artificial rooting medium. That technique implies that plants root in a rockwool slab fed with water containing all components essential to growth. The liquid rooting medium is transported by way of poly(vinyl chloride) (PVC) tubing and polyethylene (PE) sheets. Fungal diseases in plants may be suppressed by fungicides dissolved in the medium. To dose the fungicides effectively, it is important to know if and how much fungicide might adsorb to the PVC tubing and PE sheets. If a fungicide adsorbs, there are two reasons why it is important to know the rate of desorption after supplementation: First, undesirable residues of the fungicide must be avoided when crops are harvested. Second, discarded sheets should not cause environmental pollution.

Vonk (1985) describes the permeation of organic compounds through plastic tubing material. Bodyfelt et al. (1979) describe surface contamination of reuseable milk containers by several pesticides and herbicides. Steinwandter and Schlüter (1977) describe the adsorption of 11 chlorinated hydrocarbons on polyethylene from the gas phase. Finally Sharom and Solomon (1980) describe the adsorption of permethrin and other pesticides on glass and plastic materials used in bioassay procedures. However, to the best of our knowledge, adsorption and desorption of etridiazole and oxamyl on plastic materials have not been described to date.

The purpose of our investigation was to determine the adsorption and desorption behavior of etridiazole and oxamyl on PVC tubing and PE sheets. These fungicides were chosen because of their common use in horticulture.

To relate the amount of a substance adsorbed to the concentration of the substance in the surrounding phase at equilibrium, Freundlich's adsorption isotherm is often used (Mansfield, 1948; Blüh and Elder, 1955). This isotherm may be represented by

$$a/m = kc^{1/n} \quad (1)$$

where a is the mass of substance adsorbed (mg), m is the mass of the adsorbent (g), c is the concentration of the substance in the phase surrounding the adsorbent (mg/L), and k and n are constants depending on the temperature and the specific adsorption system. Equation 1 may be converted to

$$\log (a/m) = \log k + 1/n \log c \quad (2)$$

If the determined values of log (a/m) are plotted against the determined values of log c, the data should lie on a straight line having the slope $1/n$ and intersecting the ordinate at log (a/m) = log k where $c = 1$.

EXPERIMENTAL SECTION

The materials, fungicide concentrations, and conditions chosen largely corresponded with common practice.

Materials. Artificial rooting medium, polyethylene sheet, and poly(vinyl chloride) tubing (rigid) were obtained from the Glasshouse Crops Research Station (Naaldwijk, The Netherlands). Artificial rooting medium contained the following components: nitrate, 15–20 mmol/L; phosphate, 0.7–1.5 mmol/L; sulfate, 3–5 mmol/L; potassium, 5–10 mmol/L; calcium, 5–10 mmol/L; magnesium, 2–5 mmol/L; iron, 10–15 μmol/L; manganese, 5–10 μmol/L; zinc, 5–10 μmol/L; boron, 40–70 μmol/L; copper, 1 μmol/L; molybdenum, 1 μmol/L.

All reagents were of analytical quality. Ethyl acetate and sodium sulfate were obtained from Baker (Deventer, The Netherlands); hexane, pure etridiazole, pure oxamyl, and EPTC (*S*-ethyl dipropylthiocarbamate) were from Promochem (Wesel, FRG); and a commercial formulation of etridiazole was from AAqrunol (Groningen, The Netherlands).

Preliminary Experiments. Preliminary experiments were carried out to check whether any measurable adsorption of oxamyl and etridiazole on PE and PVC could be detected. These experiments were carried out in duplicate with contact liquid containing pure etridiazole and oxamyl. These liquids were prepared by diluting stock solutions of the fungicides in ethyl acetate, with artificial rooting medium. A piece of PE sheet of 10 cm × 7.5 cm × 0.008 cm (0.484 g) was put into a 500-mL conical flask containing 200 mL of contact liquid. The concentrations of etridiazole and oxamyl in this liquid were 15 mg/L. The same was done with a piece of PVC tubing (length 5 cm, diameter 5 cm, thickness 0.22 cm).

The conical flask was shaken at low speed, to prevent dashing, for 4 h at 21 °C. After the piece of PE or PVC was removed with a pair of tweezers, the contact liquid was extracted with three portions of 50 mL of hexane. To determine the amount of adherent liquid, the PE or PVC was washed with water. Determination of the remaining etridiazole and oxamyl showed that the amount of adherent liquid was negligible. This step was hence omitted in further experiments.

The combined extracts were dried on anhydrous sodium sulfate and made to 200 mL with ethyl acetate containing the internal standard (EPTC). Of this solution 5 μL was injected into the gas chromatograph.

Main Experiments. From the preliminary experiments it appeared that etridiazole adsorbs to PE, but not to PVC, and that oxamyl adsorbs neither to PE nor to PVC. Further exper-

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iments were hence limited to the combination of etridiazole and PE.

The main adsorption/desorption experiments were carried out with contact liquid containing a commercial formulation of etridiazole. This liquid was prepared by diluting stock solutions of the formulation in ethyl acetate, with artificial rooting medium. The experiments were carried out in duplicate.

Adsorption/Desorption of Etridiazole on/from PE as a Function of Time. Eight aliquots of contact liquid containing 15 mg of etridiazole/L were shaken with PE sheet at 21 °C for various periods of time: 5, 10, 15, 30, 60, 240, 360, and 720 min. To measure desorption each piece of PE sheet containing adsorbed etridiazole was put into a conical flask containing artificial rooting medium without etridiazole. The flasks were shaken for the same periods of time and at the same temperature as was done for adsorption. Finally, all contact liquid was extracted as described for the preliminary experiments.

Adsorption/Desorption of Etridiazole on/from PE as a Function of Concentration. Three aliquots of contact liquid containing 7.5, 15, and 25 mg of etridiazole/L, respectively, were shaken with PE sheet for 240 min at 21 °C. Etridiazole was allowed to desorb from the three pieces of PE sheet for 240 min at 21 °C as described above. Finally, all contact liquid was extracted as described for the preliminary experiments.

Adsorption/Desorption of Etridiazole on/from PE as a Function of Temperature. Three aliquots of contact liquid containing 15 mg of etridiazole/L were shaken with PE sheet for 240 min at different temperatures. The conical flasks were shaken in conditioned rooms at 10, 21, and 30 °C, respectively. Etridiazole was allowed to desorb from the three pieces of PE sheet for 240 min at the temperatures mentioned above. Finally, all contact liquid was extracted as described for the preliminary experiments.

GC Analysis of Etridiazole. GC analyses were carried out on a Hewlett-Packard 5880 fitted with two alkali flame ionization (NIP) detectors. The instrument was equipped with an autosampler and two fused silica capillary columns: a CP-SIL5 CB (17 m × 0.32 mm (i.d.), film thickness 1.2 μm; Chrompak, Middelburg, The Netherlands) and a DB-1701 (30 m × 0.313 m (i.d.), film thickness 0.25 μm; J&W Scientific Inc., Rancho Cordova, CA). Helium was used as carrier gas (constant pressure 108 kPa) as well as makeup gas for the detectors (23 mL/min). The temperatures of the injection port and the detectors were 230 and 300 °C, respectively. The two columns were fitted into one inlet, and ca. 5 μL of the solution was injected splitless on the "cold" column at 60 °C. After 60 s the carrier gas splitting was restarted, and after another 60 s an oven temperature program was started as follows: 10 °C/min up to 100 °C, then 5 °C/min up to 140 °C, then 25 °C/min up to 270 °C, held for 2 min, then cooled to the initial temperature.

RESULTS AND DISCUSSION

Etridiazole adsorbs to PE, but not to PVC, and oxamyl adsorbs neither to PE nor to PVC. This finding was in agreement with permeation studies of Vonk (1985). Vonk (1985) states that permeation through PE is considerable for lipophilic organic compounds such as alkylated aromatics and chlorinated hydrocarbons and slight for polar organic compounds such as ketones and phenols. On the other hand, Vonk states that significant permeation through PVC does not take place with chlorinated hydrocarbons and ketones. Etridiazole is a lipophilic organic compound containing a chlorinated carbon atom. Oxamyl, however, is a more polar organic compound containing ketone groups.

The adsorption/desorption of etridiazole on/from PE as a function of time was studied to determine the length of time required to reach equilibrium. The results are presented in Figure 1. A substantial proportion of etridiazole (ca. 40%) adsorbed on PE. Equilibrium was reached after about 240 min. In subsequent experiments this period was taken as contact time.

For desorption, equilibrium was reached after 240 min. At the equilibrium stage, less than half of the adsorbed amount of etridiazole was released. The relative standard deviation of the results was 7.6%. The standard deviation was larger at the shorter contact times. This could be explained by the fact that the time of sampling is critical at short times.

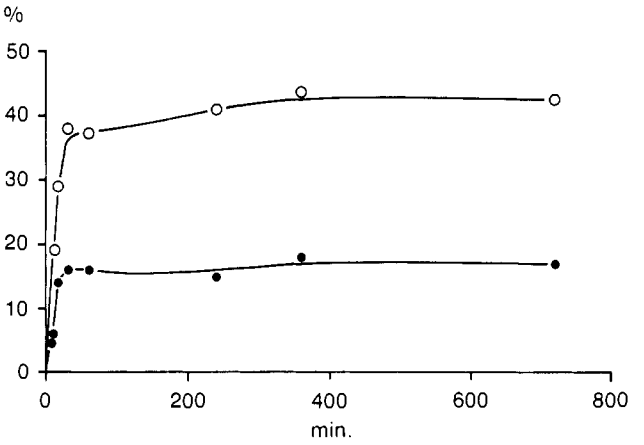

Figure 1. Adsorption (○) and desorption (●) of etridiazole on/from PE as a function of time at 21 °C. Results are expressed as a percentage of the etridiazole initially present in the contact liquid (15 mg/L).

Table I. Adsorption of Etridiazole on PE at Various Concentrations of the Compound in the Contacting Liquid Phase (t = 21 °C)

concn in contact liq at start, mg/L	concn in contact liq at equil, mg/L	etridiazole ads on PE at equil, mg/g
25.0	15.8	3.80
13.6	8.87	1.95
7.07	4.52	1.05

Table II. Desorption of Etridiazole from PE at Various Concentrations (t = 21 °C)

etridiazole abs on PE at start, mg/g	concn in contact liq at equil, mg/L	etridiazole ads on PE at equil, mg/g
3.80	6.06	1.28
1.95	3.12	0.68
1.05	1.63	0.38

The results of experiments to determine the adsorption of etridiazole on PE as a function of concentration are summarized in Table I. The results of the desorption experiments carried out with the samples referred to in Table I are presented in Table II.

A double-logarithmic plot of adsorbed amounts of etridiazole against concentrations in the liquid at equilibrium is shown in Figure 2. The data points refer to both the adsorption and desorption experiments. By linear regression, values of 0.22 and 0.99 were obtained for k and n, respectively (see eq 2). The correlation coefficient was 0.998. The results show that one and the same relationship, presented by eq 2, is valid for both adsorption and desorption.

The results of a single adsorption/desorption experiment conducted at 10 and 30 °C are included in Figure 2. The values obtained for 30 °C are close to the line for 21 °C, but those for 10 °C yield a line with a flatter slope.

More measurements should be performed to establish the isotherm at these (and other) temperatures.

CONCLUSION

The relationship between concentrations of etridiazole in artificial rooting medium and the amounts of fungicide adsorbed on polyethylene when equilibrium has been reached can be described by Freundlich's iso-

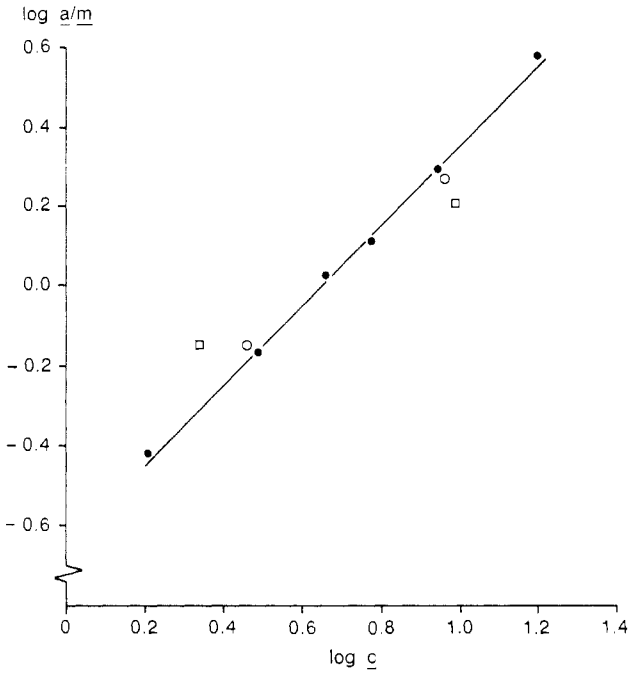

Figure 2. Relationship between the logarithm of concentrations (c, mg/L) of etridiazole in artificial rooting medium and the logarithm of amounts adsorbed on polyethylene (a/m, mg/g) at equilibrium. Key: ● = 21 °C, ○ = 30 °C, □ = 10 °C.

therm. This isotherm was determined at 21 °C. At other temperatures it can be established by means of relatively simple laboratory experiments. The adsorption is reversible; i.e., the same isotherm is valid for both adsorption and desorption. The results obtained in this study have to be taken into account when etridiazole is dosed in horticultural systems based on artificial rooting medium and polyethylene sheets. They may also contribute to assessment of environmental risks involved in the discard of used polyethylene sheets.

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