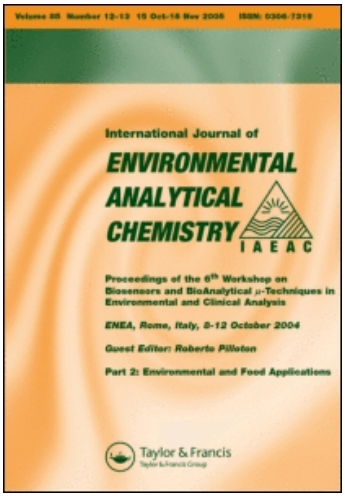

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ANALYSES OF PROCYMIDONE AND VINCLOZOLIN IN GREENHOUSE AIR

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A method for sampling and analysis of procymidone and vinclozolin in greenhouse air was investigated. The behaviour of Chromosorb 102, Porapak R, Supelpak–2, Amberlite XAD–2, Amberlite XAD–4 and polyurethane foam (PUF) as sorbents was studied. Atmospheres containing known concentrations of these pesticides were generated. The desorption process of the analytes, concentration step and behaviour of sorbents in air with different relative humidities were tested. No breakthrough was observed in the range of concentrations studied.

Personal samplers were used with the selected sorbent (PUF), for sampling procymidone and vinclozolin in an experimental greenhouse. GC-ECD analysis and MS confirmation were performed. The dissipation process of the analytes in the 24 h period after application was studied.

Keywords: Sampling; greenhouse-air; procymidone; vinclozolin; solid-sorbent; standard atmosphere

INTRODUCTION

Occupational exposure to pesticides during application and re-entry is a health hazard that is being evaluated in many countries. Greenhouse operations involve heavy use of pesticides and the potential for worker exposure is high. However, not much is known about because little has been published on the analysis of pesticides in air. To this end, four steps must be considered: air sampling, sample storage, recovery of the sorbed analytes and determination.

Adsorption on solids at room temperature as a sampling method, is a substitute for absorption in suitable solvents[1–4] or cold trapping methods[5,6]. Nerín et al[7,8] and Yeary et al[9] have evaluated the trapping efficiencies of Tenax GC, Polyurethane foam (PUF), Amberlite XAD–2 and Amberlite XAD–4 to establish

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optimum conditions for sampling chlorobenzenes and hexachlorocyclohexanes in air. Other porous polymers such as Porapak and Chromosorb or graphitized carbon as Carbopack are used almost as widely as charcoal. Martinez-Vidal et al [10] have evaluated the desorption process of five organochlorine pesticides from Chromosorb, Porapak, PUF, Amberlite XAD–2 and Amberlite XAD–4. Some factors must be considered in choosing the sorbent: (1) breakthrough and concentration of saturation; (2) background signal; (3) influence of air humidity and temperature on trapping efficiency.

The degree of decomposition of the analytes during sampling and storage must also be studied for the possibility of chemical reaction with the sorbent [11]. Desorption of compounds trapped on solid sorbents may be performed using either liquid solvents with different polarities [12] or thermal desorption [13,14]. For liquid desorption, the unavoidable dilution of an enriched sample could lead to a decrease in sensitivity. Thermal desorption efficiency depends on the volatility of the analyte and the adsorption capacity of the sorbent. Desorption temperature should be as low as possible in order to avoid thermal decomposition of the more labile compounds present in the sample.

The pesticides studied in this paper have been selected from among the most widely used in an area with a great concentration of greenhouses located in Almeria (Spain). These pesticides are procymidone and vinclozolin. Some physicochemical properties of interest are given in Table I. Procymidone is a fungicide with moderate systemic activity and vinclozolin is another fungicide which acts by contact. Both pesticides are used on field crops and on fruits and vegetables, particularly those grown in greenhouses. GLC and HPLC are techniques used to analyze procymidone and vinclozolin in different environmental media. Different multiresidue methods employing acetone extraction followed by partitioning into different solvents and GLC determination [15–17] are efficient in extracting and determining by GLC [18] and HPLC in groundwater after SPE.

This paper is a comparative study of sorbents for sampling procymidone and vinclozolin. The desorption process and their analyses using GLC and MS were also examined. The optimum conditions for obtaining a standard atmosphere with both pesticides were determined.

TABLE I Physicochemical properties of the compounds

Analyte	*Vapour pressure 20°C (mPa)*	*Kow*	*Solubility in water (mg/L)*
Procymidone	10.5	1380	4.5
Vinclozolin	0.016	1000	3.4

EXPERIMENTAL

Reagents

The solvents were n-hexane, acetone and petroleum ether (residue analysis grade, Panreac). Pesticide standards (pestanal quality) and internal standard (dieldrin) were obtained from Riedel-de Haën (Seelze, Germany). Solid standards (> 99% purity) were dissolved in n-hexane (0.1–1.0 mg/mL) to obtain primary calibration solutions. Other solutions of lower concentration (0.1 mg/mL) were prepared from these by dilution with n-hexane.

The sorbents used were: PUF plugs of 0.022 g/cm^3 density (Pikolin, Taragota, Spain); Chromosorb 102, 60/80 mesh; Porapak R, 80/100 mesh; Supelpak–2; Amberlite XAD–2 and Amberlite XAD–4 (Supelco, Bellefonte, PA).

Ronilan^{TM} (vinclozolin 50% w/v suspension concentrate, BASF Aktiengesellschaft, Germany) and Salithiex^{TM} (procymidone 50% w/w wettable powder, Sumitomo Chemical Co. Ltd., Japan) were the commercial preparations used.

Apparatus

A Hewlett-Packard (Palo Alto, CA) Model 5890 gas chromatograph equipped with an Electron Capture Detector (ECD-^{63}Ni) and an autosampler HP 7673 was used to analyse the samples. An HP 3365 Chemstation software was used for instrument control and data treatment.

A fused silica capillary (HP–1) column containing 100% methylpolysiloxane as stationary phase (60 m. length, 0.25 mm i.d. and 0.25 mm film thickness) was used for quantification.

A Hewlett Packard Model 5890 Series II gas chromatograph coupled with a HP5971 A mass spectrometer detector, on column injector and an autosampler HP7673 with a HP-UX Chemsystem software was used for GC-MS analysis using a Chrompak (Middelburg, The Netherlands) CP-Sil 5 capillary column (25 m length, 0.25 mm id and 0.25 mm film thickness) connected to a deactivated fused silica uncoated precolumn (1 m length, 0.53 mm id).

A Konik Model Cromatix KNK–2000 gas chromatograph and a silanized hollow glass column (2 m length and 5 mm id) were used to generate the standard atmosphere.

Chromatographic conditions

GC-ECD operating conditions: Injector temperature 250°C; detector temperature 300°C; Splitless time 2 min.; Initial temperature 105°C for 2 min, 20°C/min up

to 150°C, 10°C/min up to 250°C and then held at this temperature for 25 min. The carrier gas was nitrogen at 0.85 mL/min, and the same gas at a flow rate of 60 mL/min was used as make-up.

GC-MS operating conditions

On column injection, initial oven temperature 60°C for 1 min, 10°C/min up to 270°C (5 min hold); initial injector temperature 63°C and then heated at the same rate as the oven; helium carrier gas with column head pressure 8 psi. Mass spectrometer setting: electron impact ionization mode with 70 eV electron energy, scan mass range 40–400.

Clean-up procedure of sorbents

PUF plugs of 100 mm length and 20 mm diameter were cleaned using 100 mL of a n-hexane : petroleum ether (85:15 v/v) mixture for 12 h in a Soxhlet extractor operating at 20 min/cycle. This step was repeated using acetone as the solvent. The cartridges were dried under a nitrogen current and stored in a clean glass container in the dark. Chromosorb, Porapak, Supelpak and Amberlites XAD–2 and XAD–4 were also cleaned using the same procedure described above. After clean-up, the sorbents were packed under a N_2 current in cartridges containing 500 mg of each sorbent and kept in darkness in a precleaned, capped vessel at room temperature.

Desorption procedure

Sonication was used by treating the sorbents with three sequential portions of 20 mL each of acetone for 20 min each. The extract was poured through a filter tube packed with 15 g of anhydrous sodium sulfate into a 200 mL Kuderna Danish. Then it was evaporated to approximately 4 mL at 40°C, and, subsequently, to approximately 0.4 mL with a nitrogen flow to avoid loss in the evaporation step. For quantification 0.1 μg/mL of dieldrin was added using internal standard calibration and the solution was diluted to 4 mL with n-hexane.

Generation of standard atmosphere

A device of the type depicted in Figure 1 was used under the following set of conditions: Injector temperature: 100°C; Oven temperature: 100°C; Detector temperature: 200°C; air volume: 30 L (1 L/min for 30 min). Two glass cartridges

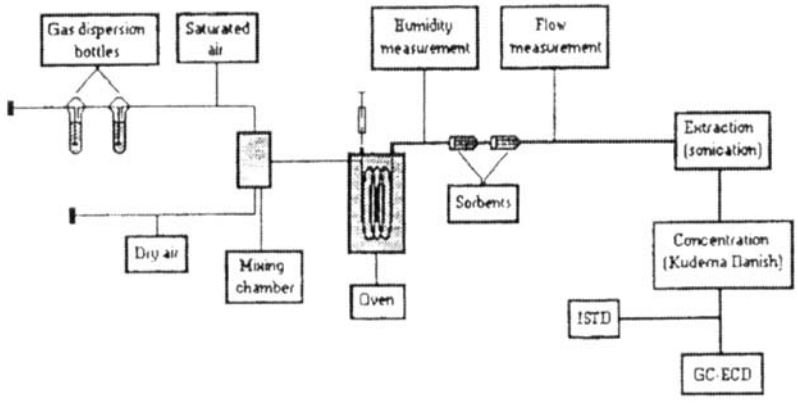

FIGURE 1 Process of standard atmosphere generation

containing the solid sorbents were placed in series at the detector outlet. Solutions of known concentration of both pesticides were injected into the injection port of the oven.

Sampling

SKC personal samplers (Model PCEX3KB) equipped with a 10 cm length PUF cartridge and calibrated to sample air at a flow rate of 2 L/min were used. They were placed randomly in the greenhouse at 160 cm from the ground. Another optional sampler was carried by the operator. Periodic air samples during and after application were taken. If a high or low concentration of pesticides in the air was suspected the sampling times were varied. Immediately following each sampling period, the sorbents were removed from the greenhouse and transfered to glass tubes. The tubes were capped and kept away from light. The PUF cartridges were stored in darkness at 4 °C until extraction and analysis was performed.

Greenhouse air temperature and relative humidity were monitored and registered during the experiment by using a Jules Richard Model 16352.47 Thermo-hygrographer.

Dissipation study

The dissipation experiment was conducted in February 1995 in a flat roof experimental greenhouse of 15 × 40 × 2.50 m and constructed of polyethylene

(200 mm of thickness). Lateral windows remained closed during the experiment. The doses applied were 0.6 Kg/ha of procymidone and vinclozolin active ingredient (a.i.). Formulations were dissolved in 100 L of water. A semi stationary high volume 2-stroke sprayer, operating at a flow rate of 3 L/min was used for application. This was carried out from ground level up to a height of approximately 2 m during a 25 min time period. Air samples were taken during application, immediately after application (45 min time sampling), 5 h after (60 min), 12 h after (60 min) and 24 h after (120 min).

RESULTS AND DISCUSSION

As can be seen in Figure 2 the GC-ECD analysis yielded a satisfactory separation of both analytes of other pesticides currently used in the area. This chromatogram corresponds to a standard solution containing 0.2 μg/mL of pesticides.

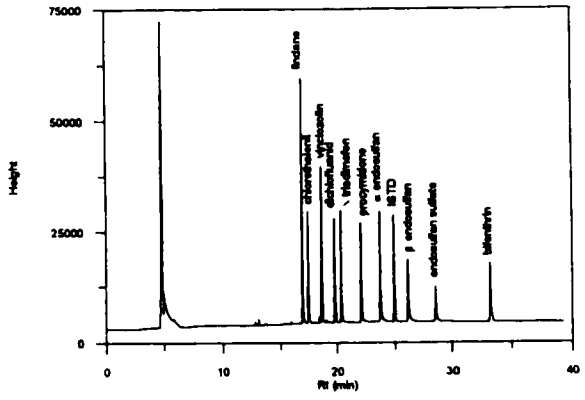

FIGURE 2 Chromatogram of a standard 0.2 μg/mL standard mixture of pesticides frequently used in the area of Almería, Spain.

Calibration

Table II summarizes the retention time window (RTW) determined for each pesticide in the two columns. 1 μL of solutions containing vinclozolin and procymidone were injected in the GC-ECD (0.1–1.0 mg/mL) and in the GC-MS (4.0 mg/mL), respectively. The RTW is defined as the average of the retention times (8 measurements) plus or minus three times the standard deviation (SD) of the retention times (RT).

TABLE II Retention time window (RTW) for each pesticide in the two columns, and calibration data (n = 8)

Analyte	*Column HP–1*			*Column CP-Sil5*		
	RT	*SD (10^3)*	*RTW*	*RT*	*SD (10^3)*	*RTW*
procymidone	21.89	5.3	16.79–16.81	17.40	4.2	14.16–14.20
vinclozolin	18.49	3.5	23.47–23.49	15.72	5.1	18.03–18.07
dieldrin (ISTD)	25.02	6.0	25.00–25.04	19.23	5.9	19.21–19.25

One microlitre of each calibration solution was injected in GC-ECD in order to determine dynamic ranges and quantification and detection limits[19,20] (Table III). The relative standard deviation (RSD) of the response factors (RF) measured between 5 and 100 times the quantification limit (QL) of each pesticide are lower than 7%. The values of detection and quantification limits[20] are given in Table IV.

TABLE III Dynamic range of GC-ECD for HP–1 capillary column

Analyte	*RF 100XQL*	*RF 80XQL*	*RF 40XQL*	*RF 20XQL*	*RF 10XQL*	*RF 5XQL*	*RSD (%)*
procymidone	89	92	97	98	108	107	6.8
vinclozolin	316	344	352	380	369	330	6.9

$$RF = \frac{Peak\ height\ of\ compound}{amount\ of\ compound\ injected}$$

$$RSD\% = \frac{Standard\ deviation}{average\ of\ RFs}$$

QL = Quantification Limit

TABLE IV Statistical parameters of the determination of the pesticides. n = 8

Analyte	*RSD %*	*Detection Limit ng/mL*	*Quantification Limit ng/mL*
Procymidone	4.8	13.2	44.0
Vinclozolin	4.6	1.8	6.0

Internal standard calibration was used by adding 0.100 µg/mL of dieldrin to each calibration point.

The reliability of the evaporation step with the Kuderna Danish was tested for both, acetone and n-hexane:petroleum ether (85:15 v/v) solutions of procymidone and vinclozolin. The analytes were not lost in the process, and recoveries in both cases between 103 and 107% and RSD lower than 5% were obtained in both cases.

Desorption procedure

Sorbents were spiked with both pesticides and dried with a slight nitrogen current for 10 minutes in order to study the reliability of the desorption procedure using both Soxhlet extractor or ultrasonic bath. The results are summarized in Table V and VI.

TABLE V Recovery percentages (RSD %) of the re-extraction procedure by Soxhlet. Solvent n-hexane-petroleum ether (85–15 v/v). n = 4

Analyte	*Chromosorb*	*Porapak*	*Supelpak*	*XAD–2*	*XAD–4*	*PUF*
Procymidone	97.0 (2.5)	98.1 (5.7)	42.3 (4.8)	87.0 (12.1)	63.2 (16.8)	83.1 (2.6)
Vinclozolin	99.0 (1.6)	103.6 (4.8)	98.0 (3.4)	59.6 (12.2)	16.1 (20.6)	85.1 (1.0)

TABLE VI Recovery percentages (RSD%) of the reextraction procedure by sonication. Solvent n-hexane-petroleum ether (85–15 v/v). n = 4

Analyte	*Chromosorb*	*Porapak*	*Supelpak*	*XAD–2*	*XAD–4*	*PUF*
Procymidone	83.1 (2.3)	69.2 (0.5)	75.2 (5.5)	71.9 (3.3)	80.5 (1.6)	95.8 (1.2)
Vinclozolin	82.8 (2.6)	59.3 (0.2)	88.9 (7.8)	62.2 (3.9)	74.7 (0.5)	97.2 (1.6)

The better recoveries of the analytes were obtained using Soxhlet extraction from Chromosorb and Porapak between 97–104% (RSD ranging 1.6–2.5%). Vinclozolin also showed a good recovery from Supelpak (98%). The recovery of procymidone from PUF, Supelpak and Amberlite XAD–4 improved when sonication was used but decreased from Chromosorb, Porapak and Amberlite XAD–2. The recovery of vinclozolin improved from PUF, XAD–2 and XAD–4, but decreased from the other sorbents. Finally, when acetone was used as the solvent with sonication, significantly better results were obtained with good recoveries of vinclozolin from all of the sorbents (between 96 and 118%). Also good recoveries of procymidone from Chromosorb, Porapak and PUF (between 90 and 93%) were achieved. Recoveries of procymidone from XAD–2, XAD–4 and Supelpak, ranged from 75 to 82%, as can be seen in Table VII.

TABLE VII Recovery percentages (RSD%) of the re-extraction procedure by sonication. Solvent acetone. n = 4

Analyte	*Chromosorb*	*Porapak*	*Supelpak*	*XAD–2*	*XAD–4*	*PUF*
Procymidone	92.6 (4.1)	90.1 (4.1)	80.1 (5.4)	75.6 (4.2)	82.3 (4.4)	92.7 (3.2)
Vinclozolin	117.6 (2.1)	101.1 (2.5)	96.5 (1.4)	99.5 (7.2)	111.1 (2.5)	114.8 (1.3)

Generation of standard atmosphere

In order to study the parameters affecting the efficiency of selected sorbents in trapping procymidone and vinclozolin in air, it is necessary to use standard atmospheres containing these pesticides.

Experiments were carried out by injecting 0.4 mg of vinclozolin and 0.8 mg of procymidone into the device shown in Figure 1. 0.5 mL of hexane were then injected into the system and the exhaust was trapped by another cartridge. No analytes were observed in this second cartridge.

The injection port and detector temperature, between 80 and 200°C, were optimized setting the oven temperature at 100°C. The best recoveries were obtained with injector and detector temperatures of 100 and 200°C, respectively. At these conditions the oven temperature was tested. As illustrated in Table VIII, the best recoveries were obtained at 100°C oven temperature, ranging between 89 and 92% with RSD lower than 5%.

TABLE VIII Recovery (RSD %) in the study of oven temperature effects on the trapping efficiency. Air flow rate 1 L/min; total volume of dry air passed 30 L. n = 4

Analyte	*Oven temp (°C)*	*Chromosorb*	*Porapak*	*PUF*
Procymidone	100	90.6 (3.6)	89.9 (4.4)	91.7 (3.9)
	80	76.3 (5.4)	86.0 (5.9)	80.6 (3.5)
	60	53.2 (10.6)	49.1 (6.9)	48.0 (12.4)
Vinclozolin	100	92.2 (3.4)	91.8 (3.4)	91.0 (3.5)
	80	81.5 (7.1)	83.4 (6.3)	88.0 (3.5)
	60	55.2 (9.9)	56.1 (10.1)	61.2 (11.2)

Furthermore, the effect of the air passage time through the empty glass column was also studied in addition to flow rate. Table IX summarizes the results. No significant differences were observed between air flow rates of 1 and 2 L/min with passage times of 20 and 30 min.

TABLE IX Effect of dry air passage time through the cartridge at two differents flow rates. n = 4

Analyte	*Sorbent*	*1 L/min*			*2 L/min*		
		10 min	*20 min*	*30 min*	*10 min*	*20 min*	*30 min*
Procymidone	Chromosorb	77.6 (4.1)	88.2 (4.2)	90.6 (3.6)	74.3 (9.4)	86.3(4.3)	89.2 (5.1)
	Porapak	74.9 (4.2)	88.9 (4.1)	89.9 (4.4)	69.8 (8.7)	86.2 (4.1)	89.0 (5.0)
	PUF	78.2 (6.0)	90.3 (5.0)	91.7 (3.9)	70.3 (8.5)	88.8 (5.4)	90.2 (4.8)
Vinclozolin	Chromosorb	72.3 (5.5)	87.1 (3.0)	92.2 (3.4)	60.3 (4.3)	88.3 (5.0)	90.4 (6.1)
	Porapak	76.3 (3.3)	82.4 (7.6)	91.8 (3.4)	59.6 (6.4)	80.6 (5.3)	89.7 (3.6)
	PUF	81.2 (6.1)	88.3 (4.1)	91.0 (3.5)	63.4 (7.6)	87.1 (4.1)	92.4 (4.1)

Influence of atmospheric humidity in the trapping efficiency

The carrier gas in the previous experiments was synthetic dry air. Relative humidity conditions were obtained with a system similar to that described by Anderson et al.[21] Air was humidified in gas dispersion bottles and diluted with dry air in a mixing chamber. Different relative humidities of 50, 75 and 99% were obtained. No significant differences were observed in the trapping efficiencies for the relative humidities tested. However, as can be seen in Table X, PUF shows a slightly better recovery than the other sorbents.

TABLE X Recovery (RSD %) in the study of relative air humidity effects on the trapping efficiency. Air flow rate 1 L/min; total volume of air passed 30 L. n = 4

Sorbent	*Relative humidity (%)*	*Procymidone*	*Vinclozolin*
Chromosorb	50	87.3 (3.4)	88.7 (6.1)
	75	89.9 (5.2)	90.2 (4.1)
	99	91.3 (5.2)	90.6 (5.2)
Porapak	50	88.6 (5.2)	91.0 (4.4)
	75	89.3 (4.1)	89.3 (2.7)
	99	87.6 (5.0)	92.3 (4.3)
PUF	50	90.3 (5.4)	94.2 (5.0)
	75	92.1 (4.9)	93.6 (3.2)
	99	93.4 (5.4)	95.1 (2.3)

Effects of sorbent amounts in breakthrough and concentration of saturation

Breakthrough occurred when using 75 mg or 2.5 cm length of sorbent. However, when 500 mg of sorbent (Chromosorb and Porapak) or PUF cartridges of 10 cm length were used, no breakthrough was observed.

Also, the amount of pesticides injected and volume of air sampled has been studied for the effect on breakthrough by injecting amounts of 400, 200, 100, 50, and 25 mg of pesticides and sampling at a constant flow rate of 1 L/min during 30, 60, 120, 240 and 480 minutes, respectively. It can be assumed that no breakthrough occurred in the tested conditions, since the quantities found in the second cartridge were less than 1 %.

No saturation was observed in sorbents in the pesticide concentration range of 20 to 1250 $\mu g/m^3$.

Storage

Darkness and temperatures in the range of –25 to 4 °C provide the best storage conditions for all the sorbents. In particular, better results are found with PUF

than with the other sorbents after 21 days of storage. Light affects the sorbents, especially PUF. After four days of storage at room temperature, it yielded noisy baseline chromatograms and inaccurate quantification of pesticides (Table XI).

TABLE XI Stability test, after storage, of pesticides trapped in PUF, expressed as percentage of recovery at day 0. n = 4

Day	*Storage conditions*	*Recovery (RSD %)*	
		Procymidone	*Vinclozolin*
1	room light	98.3 (6.4)	97.2 (4.2)
	4°C	98.6 (3.3)	97.1 (3.4)
	–25°C	98.2 (3.7)	98.1 (5.0)
4	room light	90.6 (8.2)	90.0 (8.2)
	4°C	98.1 (4.0)	94.1 (4.9)
	–25°C	97.6 (4.1)	93.9 (8.1)
21	room light	86.3 (15.4)	88.4 (9.6)
	4°C	92.7 (4.0)	96.4 (3.4)
	–25°C	95.7 (3.9)	95.8 (4.1)

* room temperature **dark conditions

Based on the experimental data, PUF was selected for sampling procymidone and vinclozolin in air because it is the most efficient in trapping these pesticides, its structure facilitates handling of the cartridge, it is cheaper than the other sorbents and in real atmosphere, humidity does not influence its trapping efficiency. The volume of air samples can range between 30 and 480 L. The flow rate can range between 1 and 2 L/min. Consequently, a high flow rate could be used to reduce the sampling time as long as the total air volume is kept constant. The detection limit of the method is 10 ng for vinclozolin and 60 ng for procymidone.

Dissipation process of procymidone and vinclozolin in greenhouse air

Air samples were collected at three randomly selected locations in the greenhouse, following the conditions described in the experimental section. The relative humidity ranged between 39 and 98%, and the temperature ranged between 10 and 33°C. Peaks have been confirmed by GC-MS.

Figures 3 and 4 show the decline of concentration (as a mean of the values from all sampling locations) of procymidone and vinclozolin during the sampling time period. The time averaged concentration during the application of vinclozolin and procymidone were, respectively, of about 4.3 and 4 mg/m^3. No significant differences between sampling location were observed. However, concentrations in the personal sampler carried by the applicator was slightly lower

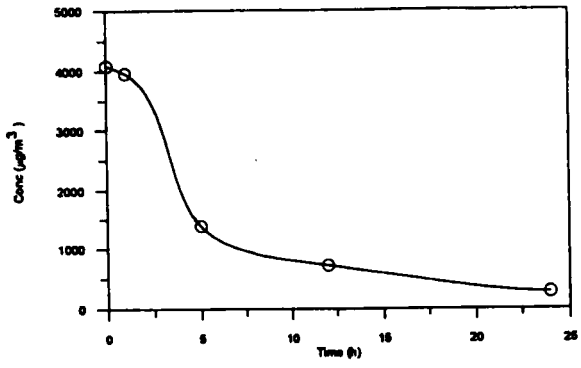

FIGURE 3 Dissipation process of procymidone in greenhouse air after application of 0.6 Kg a.i./ha. The application was carried out in February 1995, the ambient temperature into the greenhouse ranged between 10–33°C and the relative humidity between 39–98%

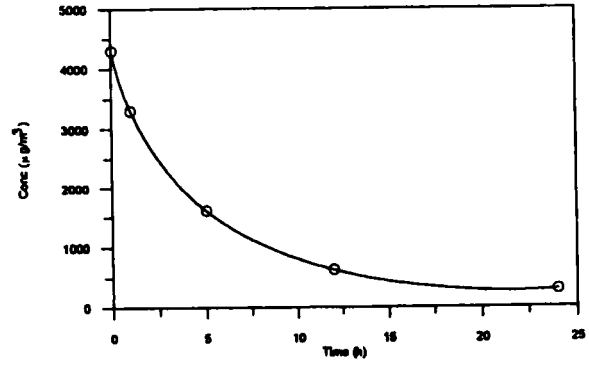

FIGURE 4 Dissipation process of vinclozolin in greenhouse air after application of 0.6 Kg a.i./ha. The application was carried out in February 1995, the ambient temperature into the greenhouse ranged between 10–33°C and the relative humidity between 39–98%

(about 3.9 and 3.3 mg/m^3 of vinclozolin and procymidone, respectively). In the samples taken just after the application, it can be observed that the time averaged concentrations are only slightly lower than those obtained during the application.

Results indicate that 24 hours after application, 6.9% and 6.8% of the initial concentrations of vinclozolin and procymidone (the latter having discrepancies between locations) remained in the greenhouse atmosphere. The dissipation and decline process may be influenced by parameters such as vapour pressure, temperature and relative humidity or the absence of volatile organic solvents in wettable powder as in procymidone formulation.

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