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Analysis of lindane, α- and β-endosulfan and endosulfan sulfate in greenhouse air by gas chromatography

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Abstract

A method to sample and analyse lindane and three endosulfan isomers in greenhouse air has been studied. The behaviour of Chromosorb 102, Porapak R, Supelpak-2, Amberlite XAD-2, Amberlite XAD-4 and polyurethane foam (PUF) as sorbents has been studied. Atmospheres containing known concentrations of these pesticides were generated. The desorption process of the analytes and the behaviour of sorbents in atmospheres with different relative humidities have been tested. No breakthrough was observed in the range of concentration studied. Personal samplers have been used with the selected sorbent (PUF), in order to sample lindane, α- and β-endosulfan and endosulfan sulfate in an experimental greenhouse. GC–electron-capture detection analysis and MS confirmation of the pesticides have been carried out. The dissipation process of the analytes in the 24 h period after application has been studied.

Keywords: Air analysis; Adsorbents; Sample preparation; Lindane; Endosulfan; Pesticides; Organochlorine compounds

1. Introduction

In the last few years considerable information has been acquired relating to human exposure to pesticide residues. Research is focusing on developing new technology to collect and quantify these levels, so that assessment can be made to determine possible short- or long-term effects on those living or working where pesticides are used.

Different sampling methods have been reported involving the use of liquids or solid adsorbents. Examples of these reports include liquids [1], chromatographic packings such as C_{18} hydrocarbons (e.g., Porapaks N and R) and Tenax GC [2,3], Chromosorb 102 [4] and resins such as XE-340 to trap organochlorine pesticides [5]. Both commercial sorbents and commercially available adsorbent tubes have been evaluated to determine the trapping efficiency of Chromosorb 102, polyurethane foam (PUF) and Tenax GC for chlorinated hydrocarbons, organophosphates and pyrethroids [6,7]. XAD-2 was evaluated for collecting pesticide aerosols and vapours simultaneously. Trapping efficiency was studied for dichlorvos, methomyl and chlorothalonil [8].

The use of PUF as trapping medium was developed by US Environmental Protection Agency (EPA) scientists [9–11] for both low and high volume samplers and has been accepted by the American Society for Testing and Materials (ASTM) as a standard method for collecting chlordane and heptachlor residues in air.

In the same way, Tenax GC, PUF, Amberlite XAD-2 and Amberlite XAD-4 have been evaluated

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in order to establish the optimum procedure for sampling organochlorine compounds such as hexachlorocyclohexanes and chlorobenzenes in the atmosphere using GC–electron-capture detection (ECD) analysis [12] and the trapping efficiency of PUF and Amberlite XAD-2 has been established for 15 organochlorine pesticides [13].

Greenhouse operations involve heavy use of pesticides to control pests, and the potential for worker exposure is high. However, few studies have been published on pesticide deposition and airborne residue in greenhouses. Waldron [14] summarised the results of a study performed with permethrin and dichlorvos and showed significant concentrations of airborne and surface residues during the initial hours after application until the greenhouse was effectively vented. Lindquist et al. [15] sampled airborne and surface residues of permethrin up to 12 h post-treatment after high and low volume applications. Jongen et al. [16] describe the procedure for sampling the respirable fraction of chlorthalonil containing aerosols in greenhouses while Olori et al. [17] report a procedure for greenhouse reentry time determination after fentin hydroxyde and cyhexatin treatment.

The results of these studies suggest that reentry may involve a potential hazard to workers, but few efforts have been devoted so far to solving the problem of greenhouse reentry time determination after pesticide treatment.

Samples of endosulfan in vapor phase and suspended particulates have been taken using PUF and quartz fiber filters [18,19] in order to study the air concentration of pesticides in area where agriculture is a primary source of semivolatile pollutants. However influence on sampling efficiency of factors such as ambient humidity, temperature, amount of solid sorbents, sampling flow-rate and breakthrough have not been fully established.

Lindane is an organochlorine pesticide of moderate toxicity which is slowly degraded in the environment and can accumulate in tissue. It is effective as contact and stomach poison against most insects and mites (it has been particularly effective against biting flies, lice, fleas, ticks and mites attacking livestock), it has also been used in public health programmes as a residual spray against mosquito vector of malaria and tratomid vectors of Chagas disease. Its use in soils requires long post-treatment intervals. It is used alone or in combination with fungicides, and is applied as an aerosol, as smoke or as vapour on vegetables and fruit crops in greenhouses. Endosulfan is another organochlorine pesticide of moderate toxicity which penetrates the intact skin and is also absorbed by inhalation and from the gastrointestinal tract. Technical endosulfan contains two stereoisomers: α- and β-endosulfan, while endosulfan sulfate is the main metabolite in vegetables. It is effective against a wide range of insects and aphids by contact and stomach action. This pesticide is widely used combined with insecticides such as methomyl, bifenthrin, pirimicarb, clorpyrifos and parathion methyl, and its application on fruits and vegetables grown in greenhouses can be as an emulsifiable concentrate, dispersible powder or dust to control pests such as *Frankliniella occidentalis*, *Myzus persicae* or *Aphis gossypii*.

This paper reports the results of studies carried out with solid sorbents in order to establish the optimum procedure for sampling and analysing lindane and α- and β-endosulfan and endosulfan sulfate in greenhouse air. In addition, the dissipation process of the analytes during 24 h after application in an experimental greenhouse has been studied.

2. Experimental

2.1. Chemicals

The solvents were *n*-hexane, light petroleum and acetone (residue analysis grade, Panreac, Barcelona, Spain). Pesticide standards (pestanal quality) were obtained from Riedel-de Haën, Seelze, Germany). Solid standards (>99% purity) were dissolved in *n*-hexane (100 μg ml^{-1}) to obtain primary calibration solutions. Other solutions of lower concentration (0.01–2 μg ml^{-1}) were prepared from these by dilution with *n*-hexane.

The sorbents used (supplier in parentheses) were: PUF plugs of 0.022 g ml^{-1} density (Pikolin, Zaragoza, Spain); Chromosorb 102, 60–80 mesh; Porapak R, 80–100 mesh; Supelpak-2; Amberlite XAD-2 and Amberlite XAD-4, (Supelco, Bellefonte, PA, USA).

PL 80 (lindane 80%, w/v, suspensible liquid,

Inagra, Valencia, Spain) and Cotolita Tio (endosulfan 35%, w/v, emulsifiable concentrate, KenoGard, Nobel Industries, Sweden) were used as commercial formulations.

2.2. Equipment

A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 gas chromatograph equipped with an ^{63}Ni electronic capture detector, a fused-silica capillary HP-1 (Hewlett-Packard) column containing 100% methylpolisiloxane as stationary phase (60 m×0.25 mm I.D. and 0.25 mm film thickness) and an autosampler HP 7673, was used for quantification. HP 3365 Chemstation software was used for instrument control and data treatment.

A Hewlett-Packard Model 5890 Series II gas chromatograph coupled with an HP 5971 A mass spectrometer detector, on column injector and an autosampler HP 7673 with an HP-UX Chemsystem software was used for GC–MS analysis with a Chrompak (Middelburg, Netherlands) CP-Sil 5 capillary column (25 m×0.25 mm I.D. and 0.25 mm film thickness) connected to a deactivated fused-silica uncoated precolumn (1 m×0.53 mm I.D.).

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

2.3. Analytical procedures

2.3.1. GC–ECD operating conditions

These were: injector temperature 250°C; detector temperature 300°C; splitless time 2 min; initial temperature 105°C for 2 min, 20°C min^{-1} up to 150°C, 10°C min^{-1} up to 250°C and then held at 250°C for 25 min. The carrier gas was nitrogen at 0.85 ml min^{-1} and the same gas at a flow-rate of 60 ml min^{-1} was used as make-up.

2.3.2. GC–MS conditions

The initial oven temperature was 60°C for 1 min, then raised at 10°C min^{-1} up to 270°C (5 min hold); on column injection was used, the initial injector temperature being 63°C and then programmed at the same rate as the oven; helium was used as carrier gas with 55 MPa column head pressure. The mass spectrometer settings were: electron impact ionization mode with 70 eV electron energy, scan mass range 40–440.

2.4. Clean-up procedure of sorbents

PUF plugs of 100 mm length and 20 mm diameter were cleaned using 100 ml of *n*-hexane–light petroleum (85:15, v/v) mixture for 12 h in a Soxhlet extractor siphoning at 20 min $cycle^{-1}$; this step was repeated using acetone as solvent. After this treatment, the plugs 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 as described above. After clean-up, the sorbents were packed with a nitrogen current in cartridges containing 500 mg of each sorbent, put into a precleaned vessel and stored at room temperature in the dark.

2.5. Desorption procedure

The sorbents were spiked with 0.4 μg of pesticides by using a micropipette and dried with a slight nitrogen current for 10 min. A Soxhlet extractor was used siphoning at 20 min $cycle^{-1}$ for 8 h using 100 ml of *n*-hexane–light petroleum (85:15, v/v) or 100 ml of acetone as extractants. Another method, by sonication, was employed treating the sorbents with three sequential portions of 20 ml each of *n*-hexane–light petroleum (85:15, v/v) or acetone, for 20 min each. The extracts were poured through a filter tube packed with 15 g of anhydrous sodium sulfate into a 200 ml Kuderna–Danish, 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. 0.4 μg of dieldrin were added as internal standard for quantification and the solution was diluted to 4 ml with *n*-hexane.

2.6. Sampling method

SKC personal samplers Model PCEX3KB provided with a 10 cm length PUF cartridge and calibrated to sample air at a flow-rate of 2 l min^{-1} were used. Three samplers were placed at random in

the greenhouse at 160 cm from the ground and another one was carried by the operator.

Air samples were taken at intervals during and after application varying sampling time if high or low concentration of pesticides in the air was suspected. The sorbents were transferred into glass tubes, capped and stored out of light at 4°C until extraction and analysis.

Greenhouse air temperature and relative humidity were monitored and registered during the experiment by using a Jules Richard Model 16352.47 thermohygrographer (Argenteuil, France).

2.7. Validation of sampling and analysis

2.7.1. Generation of a standard atmosphere

In order to generate a standard atmosphere of a known analyte concentration, 200 μl of a *n*-hexane solution containing 2 μg ml^{-1} of the mentioned compounds were injected in a device as described by Nerin et al. [12] under the following conditions: injector temperature: 100°C; oven temperature: 100°C; detector temperature: 200°C; carrier gas: dry air at a flow-rate of 2 l min^{-1} for 15 min. Breakthrough during sampling was determined by connecting two glass cartridges in series containing the solid sorbents and drawing different volumes of air through them.

2.8. Dissipation study

The dissipation experiment was conducted in a flat roof experimental greenhouse of polyethylene (200 mm of thickness) (15×40×2.50) m^3 volume which was in use for the growth of peppers. Lateral windows remained closed during the experiment. Application rate was 1250 l ha^{-1}. Lindane was applied at a dose rate of 0.4 kg ha^{-1} of active ingredient (a.i.) and endosulfan was applied at a dose rate of 0.6 kg ha^{-1} of a.i. A semi-stationary high volume 2-stroke sprayer operating at a nominal flow-rate of 3 l min^{-1} was used for application spraying from ground level upwards to a height of approximately 2 m for 25 min. Air samples were taken during application and just after the end of the application (45 min sampling time), 5 h later (60 min), 12 h later (60 min) and 24 h later (120 min).

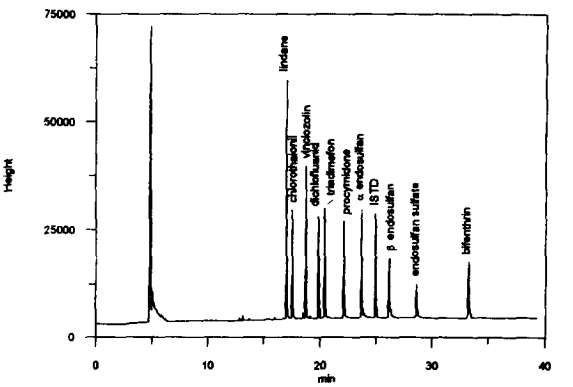

Fig. 1. Chromatogram of a standard mixture of pesticides frequently used in the area.

3. Results and discussion

The GC–ECD analysis yielded a satisfactory separation of the analytes of other pesticides currently used in the area as can be seen in Fig. 1.

The efficiency of the clean-up of sorbents can be observed in Fig. 2, where a chromatogram corresponding to an extract from a cleaned PUF is shown. The other sorbents yielded cleaner chromatograms.

3.1. Calibration

Table 1 summarises the retention time window (RTW) obtained for each pesticide in the two columns by injecting 1 μl of a solution containing 0.100 μg ml^{-1} of lindane, α- and β-endosulfan and endosulfan sulfate in the GC–ECD system and 4.0

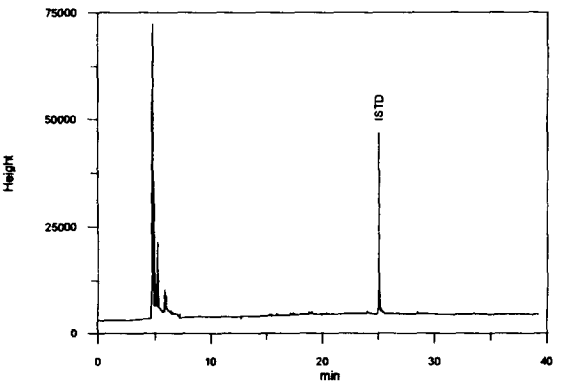

Fig. 2. Chromatogram of an extract from PUF after cleanup.

Table 1
Retention time window (RTW) for each pesticide in the two columns and calibration data ($n=8$)

Analyte	Column		Equation	Detection limit (ng ml^{-1})	Quantitation limit (ng ml^{-1})
	HP-1	CP-Sil5			
Lindane	16.79–16.81	14.16–14.20	$L=1.59$(amt ratio)-0.082	1.9	6.3
α-Endosulfan	23.47–23.49	18.03–18.07	$E_a=1.14$(amt ratio)-0.001	2.5	8.3
β-Endosulfan	25.88–25.91	18.92–18.96	$E_b=0.79$(amt ratio)$+0.006$	3.1	10.2
Endosulfan sulfate	28.27–28.30	19.68–19.72	$E_s=0.66$(amt ratio)-0.010	3.6	12.0
Dieldrin (ISTD)	25.01–25.04	19.21–9.25			

μg ml^{-1} of each pesticide in the GC–MS. The RTW is defined as the average of the retention times (8 measures) plus or minus three times the standard deviation (S.D.) of retention times (t_R).

The GC–ECD analysis has been used for quantification. Calibration data (Table 1), obtained from 8 experimental points by plotting height ratio vs. amount ratio show linear regression coefficients >0.9993. Internal standard calibration was used by adding to each calibration point, 0.100 μg ml^{-1} of dieldrin. 1 μl of each calibration solution has been injected in the GC–ECD system in order to determine quantification and detection limits [20] (Table 1). Dynamic ranges were also studied [21] obtaining relative standard deviation (R.S.D.) of the response factors measured between 5 and 100 times the quantification limit of each pesticide lower than 11%.

According to previous studies one of the major sources of error in the analysis of volatile compounds is attributed to the loss of compounds during the concentration step when evaporation is carried out. In order to evaluate this loss, 0.4 μg of each pesticide was added to a 100 ml of extractant solvents (acetone or *n*-hexane–light petroleum, 85:15, v/v). The solution was concentrated as described above. Results obtained showed that the analytes were not lost in the process, obtaining recoveries in both cases between 99 and 103% and R.S.D. <5%.

3.2. Desorption procedure

Sorbents were spiked, as is described above, in order to study the reliability of the desorption procedure using both Soxhlet extractor or ultrasonic bath (Tables 2 and 3).

The best recoveries of α- and β-endosulfan and

Table 2
Recovery percentages and relative standard deviations (R.S.D.%) in the extraction procedure by Soxhlet with *n*-hexane–light petroleum (85:15, v/v) ($n=4$)

Analyte	Chromosorb	Porapak	Supelpak	XAD-2	XAD-4	PUF
Lindane	72.4 (2.4)	78.1 (6.8)	80.1 (3.9)	54.8 (3.2)	50.9 (8.6)	70.6 (0.4)
α-Endosulfan	103.9 (4.6)	96.4 (1.7)	67.3 (4.5)	87.0 (5.3)	68.7 (10.8)	76.9 (1.1)
β-Endosulfan	105.1 (1.9)	92.3 (6.6)	49.2 (6.1)	50.6 (7.7)	45.3 (7.7)	67.3 (0.7)
Endosulfan sulfate	114.9 (0.3)	88.5 (8.5)	65.3 (3.6)	71.7 (4.0)	42.3 (8.9)	60.4 (3.3)

Table 3
Recovery percentages (R.S.D.%) in the extraction procedure by sonication with *n*-hexane–light petroleum (85:15, v/v) ($n=4$)

Analyte	Chromosorb	Porapak	Supelpak	XAD-2	XAD-4	PUF
Lindane	70.4 (1.9)	68.6 (2.1)	41.0 (7.9)	33.9 (2.6)	64.6 (2.2)	82.2 (0.5)
α-Endosulfan	84.5 (2.9)	78.2 (1.3)	73.5 (11.4)	77.3 (1.5)	76.7 (0.5)	85.4 (1.8)
β-Endosulfan	87.3 (3.9)	85.9 (0.6)	72.8 (5.2)	62.4 (4.3)	60.3 (0.4)	81.4 (1.4)
Endosulfan sulfate	89.7 (4.5)	71.3 (0.7)	63.8 (1.7)	56.8 (5.2)	51.1 (2.5)	70.3 (4.5)

Table 4
Recovery percentages (R.S.D.%) in the extraction procedure by sonication with acetone (n=4)

Analyte	Chromosorb	Porapak	Supelpak	XAD-2	XAD-4	PUF
Lindane	93.4 (3.7)	95.1 (1.7)	65.6 (1.6)	78.3 (5.2)	80.3 (1.5)	98.6 (4.2)
α-Endosulfan	93.2 (2.2)	92.3 (2.2)	84.0 (1.1)	94.3 (4.3)	90.2 (2.4)	98.5 (3.1)
β-Endosulfan	95.9 (2.5)	101.1 (4.1)	84.7 (1.0)	95.5 (3.3)	95.0 (2.9)	97.7 (1.0)
Endosulfan sulfate	107.5 (2.7)	94.8 (5.1)	93.4 (1.2)	100.4 (3.0)	106.0 (4.4)	110.6 (4.3)

endosulfan sulfate using Soxhlet were between 88–115% (R.S.D. ranging 0.3–8.5%) from Chromosorb and Porapak. Lindane shows the best recovery from Supelpak, 80%. Recovery of the four analytes from PUF and Amberlite XAD-4, improves using sonication (recovery of α- and β-endosulfan and endosulfan sulfate also improves from Supelpak) but, in general, it decreases in Chromosorb, Porapak and Amberlite XAD-2. Finally, when acetone is used as solvent with sonication, noticeably better results were obtained, with recoveries >90% for endosulfan from PUF, Chromosorb, Porapak Amberlite XAD-2 and Amberlite XAD-4. Lindane shows good recoveries (also >90%) from Chromosorb, Porapak and PUF, as can be seen in Table 4.

3.3. Generation of standard atmosphere

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

Experiments were carried out by injecting 0.4 μg of the analytes in the chromatographic oven used to generate standard atmospheres. Pesticides were trapped in the first cartridge. After each experiment, 0.5 ml of hexane were injected into the system and a current of air was passed through the column, the exhaust being trapped in another cartridge.

The injection port and detector temperature between 80–200°C were optimized setting the oven temperature at 100°C. The best recoveries were obtained with injector at 100°C and detector at 200°C. In these conditions the oven temperature was tested. It can be seen in Table 5 that the best recoveries were obtained at 100°C oven temperature, ranging between 89 and 102% with R.S.D.s lower than 5%.

The influence of the time it takes for air to pass through the empty glass column as well as the

Table 5
Effect of "oven temperature" on trapping efficiency expressed as recovery percentages (R.S.D.%)

Analyte	Oven temp (°C)	Chromosorb	Porapak	PUF
Lindane	100	96.4 (4.8)	93.0 (4.6)	97.7 (1.2)
	80	84.5 (3.3)	81.9 (3.9)	84.9 (4.0)
	60	61.9 (5.0)	59.7 (4.8)	60.8 (4.6)
α-Endosulfan	100	92.2 (4.7)	91.5 (2.9)	102.1 (3.3)
	80	80.2 (6.1)	81.0 (6.8)	80.5 (4.2)
	60	45.7 (9.8)	60.6 (12.8)	63.5 (14.1)
β-Endosulfan	100	95.7 (4.8)	92.6 (3.9)	96.5 (3.8)
	80	75.7 (5.9)	78.2 (6.2)	71.2 (5.1)
	60	45.7 (9.8)	60.6 (12.8)	63.5 (14.1)
Endosulfan sulfate	100	90.0 (3.9)	89.9 (4.1)	94.1 (3.4)
	80	70.1 (6.7)	85.1 (7.1)	75.0 (6.9)
	60	55.0 (12.9)	43.5 (11.1)	45.8 (19.8)

Air flow-rate, 2 l min^{-1}; volume of dry air sampled, 30 l (n=4).

Table 6
Effects of sampling rate and sampling time on pesticide collection, expressed as recovery percentages (R.S.D.%)

Analyte	Sorbent	1 l min^{-1}			2 l min^{-1}		
		10 min	20 min	30 min	10 min	20 min	30 min
Lindane	Chromosorb	79.3 (4.1)	93.1 (5.0)	95.4 (3.6)	72.1 (3.3	88.6 (5.0)	95.8 (3.2)
	Porapak	76.1 (5.1)	90.3 (2.5)	92.8 (4.3)	70.6 (5.2)	89.9 (4.6)	93.5 (4.3)
	PUF	76.6 (5.2)	91.2 (3.8)	96.4 (2.9)	74.3 (4.1)	95.6 (5.0)	96.8 (2.2)
α-Endosulfan	Chromosorb	85.1 (4.9)	91.1 (3.3)	92.2 (4.7)	79.3 (7.7)	90.8 (4.8)	90.3 (5.2)
	Porapak	80.0 (5.9)	92.0 (5.1)	91.5 (2.9)	74.3 (8.1)	90.1 (6.0)	90.1 (4.4)
	PUF	86.7 (6.2)	98.7 (4.4)	102.1 (3.3)	80.0 (9.1)	92.0 (6.1)	99.7 (5.3)
β-Endosulfan	Chromosorb	75.9 (5.8)	90.2 (4.4)	95.7 (4.8)	66.4 (10.3)	88.3 (5.4)	94.3 (5.2)
	Porapak	77.3 (7.4)	89.7 (5.1)	92.6 (3.9)	70.9 (8.8)	86.2 (5.1)	93.7 (4.9)
	PUF	82.9 (6.9)	92.7 (3.3)	96.5 (3.8)	70.9 (9.2)	90.2 (5.0)	93.2 (5.1)
Endosulfan sulfate	Chromosorb	72.3 (6.8)	91.4 (4.0)	90.0 (3.9)	65.3 (8.7)	90.2 (5.1)	90.1 (5.6)
	Porapak	70.9 (7.4)	86.3 (5.4)	89.9 (4.1)	62.9 (9.1)	84.1 (4.9)	87.7 (4.8)
	PUF	71.9 (8.0)	90.9 (2.2)	94.1 (3.4)	66.5 (7.4)	90.1 (5.6)	92.7 (4.4)

flow-rate was also studied (Table 6). No significant differences were observed between 1 and 2 l min^{-1} air flow-rate with air volume sampled of 20 and 30 l in both cases.

3.4. Influence of atmospheric humidity in the trapping efficiency

Carrier gas in the previous experiments was synthetic dry air. Relative humidity conditions were obtained with a similar system to that described by Anderson et al. [22] by humidifying air in gas dispersion bottles and diluting it with dry air in a mixing chamber. Different relative humidities 50, 75 and 99% have been obtained. No significant differences have been observed in the trapping efficiency for the relative humidities tested PUF showing, a slightly better recovery than the other sorbents as can be seen in Table 7.

3.5. Influence of variables affecting the breakthrough

The breakthrough occurred for lindane and β-endosulfan when using 75 mg of sorbent or 2.5 cm length of PUF, but when 500 mg of sorbent (Chro-

Table 7
Recovery percentages (R.S.D.%) in the study of influence of relative air humidity in the trapping efficiency

Sorbent	Relative humidity (%)	Lindane	α-Endosulfan	β-Endosulfan	Endosulfan sulfate
Chromosorb	50	93.4 (5.0)	89.6 (5.1)	90.9 (4.9)	88.4 (5.3)
	75	94.3 (4.7)	91.3 (3.6)	95.2 (3.1)	91.2 (5.4)
	99	94.6 (3.4)	90.1 (4.8)	93.8 (5.4)	89.9 (5.8)
Porapak	50	93.6 (5.2)	90.3 (2.6)	90.3 (5.4)	88.6 (5.2)
	75	90.7 (4.6)	93.1 (3.6)	89.6 (3.7)	90.1 (6.4)
	99	93.0 (4.1)	91.0 (2.9)	91.3 (4.7)	89.7 (5.1)
PUF	50	96.3 (3.3)	98.7 (4.2)	94.3 (5.4)	94.1 (4.6)
	75	97.1 (2.5)	97.6 (3.3)	96.3 (5.7)	93.7 (4.2)
	99	97.0 (2.2)	100.3 (4.5)	97.2 (5.5)	92.8 (5.0)

Air flow-rate 2 l min^{-1}; total volume of air 30 l (n=4).

Table 8
Stability test of pesticides trapped in the sorbents after storage in different conditions, expressed as percentage recovery at day 0 ($n=4$)

Day	Storage conditions	Lindane			α-Endosulfan			β-Endosulfan			Endosulfan sulfate		
		Chromosorb	Porapak	PUF	Chromosorb	Porapak	PUF	Chromosorb	Porapak	PUF	Chromosorb	Porapak	PUF
1	Room light[a]	98.1 (3.3)	97.2 (4.2)	99.3 (2.1)	99.9 (4.6)	98.1 (3.2)	98.6 (5.1)	104.7 (4.8)	99.0 (4.5)	97.7 (5.9)	99.7 (5.0)	97.4 (5.0)	94.1 (5.3)
	4°C[b]	98.1 (3.5)	98.4 (4.9)	98.6 (3.3)	100.7 (4.4)	99.1 (3.5)	99.1 (2.6)	99.4 (4.4)	98.6 (4.2)	97.2 (3.1)	99.0 (4.8)	96.4 (4.7)	97.2 (3.4)
	−25°C[b]	98.4 (3.8)	98.8 (4.5)	99.0 (2.1)	99.2 (4.4)	101.1 (3.7)	99.3 (2.2)	102.8 (4.7)	103.7 (3.9)	97.2 (3.4)	98.7 (4.9)	98.7 (5.7)	99.9 (4.1)
4	Room light[a]	98.7 (5.5)	97.6 (5.7)	97.3 (5.3)	92.7 (5.5)	92.6 (7.2)	89.3 (9.6)	96.7 (6.1)	94.7 (7.9)	90.1 (10.4)	92.1 (6.9)	91.9 (7.4)	88.6 (8.2)
	4°C[b]	98.3 (3.9)	98.1 (4.7)	99.1 (2.4)	95.7 (4.7)	96.4 (4.1)	95.1 (3.2)	97.9 (4.4)	97.5 (4.2)	96.6 (3.1)	98.4 (4.8)	98.7 (5.0)	97.0 (3.4)
	−25°C[b]	99.0 (3.7)	98.7 (4.7)	98.7 (2.6)	99.1 (4.3)	100.3 (3.1)	99.8 (1.6)	99.4 (4.8)	98.1 (5.3)	97.0 (4.1)	75.4 (8.9)	98.2 (4.6)	101.0 (2.1)
21	Room light[a]	90.2 (8.9)	91.1 (9.7)	90.6 (15.2)	89.0 (10.3)	88.3 (9.7)	88.7 (14.7)	77.6 (14.3)	79.1 (12.7)	74.3 (17.2)	92.7 (5.3)	78.4 (15.6)	77.9 (18.3)
	4°C[b]	96.4 (4.1)	97.2 (5.0)	98.7 (3.4)	96.1 (4.9)	95.4 (3.9)	99.6 (2.6)	91.2 (5.2)	95.8 (4.8)	95.1 (1.2)	90.2 (5.0)	90.9 (5.7)	91.9 (3.1)
	−25°C[b]	96.7 (4.8)	97.9 (5.2)	99.1 (2.5)	95.8 (4.7)	96.4 (4.6)	98.8 (4.5)	93.1 (5.7)	95.6 (5.1)	96.1 (4.2)		91.8 (5.1)	93.9 (3.3)

[a] Room temperature.
[b] Dark conditions.

mosorb and Porapak) or PUF cartridges of 10 cm length are used, no breakthrough was observed.

Also the influence on breakthrough of the amount of pesticides injected and the volume of air sampled has been studied by injecting different amounts (400, 200, 100, 50 and 25 μg) of pesticides and sampling at a constant flow-rate (1 l min^{-1}) during 30, 60, 120, 240 and 480 min, respectively.

No breakthrough was observed in the tested conditions, since the quantities found in the second cartridge were <1%.

No saturation was observed in sorbents in the concentration range of pesticides between 20 and 1250 μg m^{-3}.

3.6. Storage

Storage conditions of pesticides sampled with the sorbents have been established. Once the pesticides were trapped from the standard atmosphere, the cartridges were stored under different conditions of light, time and temperature in a capped glass vessel. The best storage conditions are in darkness at temperatures ranging between −25 to 4°C for all the sorbents, particularly PUF shows better results than the other sorbents after 21 days storage (Table 8). Light affects sorbents principally PUF, after four days of storage at room temperature, it yielded noisy baseline chromatograms and inaccurate quantification of pesticides.

3.7. Dissipation process of lindane, α- and β-endosulfan in greenhouse air

On the basis of the experiments carried out, we selected PUF for sampling lindane, α- and β-endosulfan and endosulfan sulfate in air because it is the most efficient in trapping these pesticides, its structure facilitates the handling of the cartridge, it is cheaper than the other sorbents and under real atmospheric conditions, humidity does not influence its trapping efficiency. Sampled air volume can range between 30 to 480 l. flow-rate can be between 1–2 l min^{-1}, consequently, a fast 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 all pesticides.

At three selected locations in the greenhouse, air samples have been collected, following the conditions described in Section 2.6. The relative humidity ranged between 39 and 98%, and the temperature ranged between 10 and 33°C. Peaks have been confirmed by GC–MS.

The decline of concentration, mean of all sampling stations, of α- and β-endosulfan and lindane during the period of time studied was established. The time averaged concentration during application of pesticides was 4.4 mg m^{-3} of α-endosulfan, 4.2 mg m^{-3} of β-endosulfan and 3.3 mg m^{-3} of lindane. No significant differences between sampling stations have been observed, whereas concentrations in the personal sampler carried by applicator were slightly less (4.0, 3.8 and 3.0 mg m^{-3}, respectively). In the samples taken just after the application the time averaged concentrations of α-endosulfan and lindane increase until 4.9 and 4.3 mg m^{-3}, respectively whereas β-endosulfan concentration (4.0 mg m^{-3}) is only slightly lower than that obtained during the application.

Results indicate that 24 h after application, at 7.5% of initial concentration of α- and β-endosulfan and at 8.7% of lindane 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 presence of volatile organic solvents in emulsifiable concentrates as in endosulfan formulation.

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