Sorption of Diazinon and Other Chemical Vapors by Mushrooms and Agricultural Substrates in Enclosed Systems

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Glass desiccators are used as a model for various enclosed systems and in which conditions of minimal ventilation are simulated. Agricultural substrates including mushrooms sorb various amounts of diazinon vapor when grown in or placed into atmospheres that maximize the concentration of diazinon in the vapor state. In only one test in several that simulated the worst possible case situation was the tolerance of 0.75 ppm (mg/kg) for diazinon residues on or in mushrooms exceeded. The walls of the desiccator act both as a sink and as a mobile reservoir for the chemical vapors introduced. The relative amounts of vapors that may become sorbed by a particular sorbent not only depend on the vapor pressure of the particular agrochemical sorbate, but more importantly on the degree of ventilation of the particular enclosed system. Environmental considerations are implied by the data.

INTRODUCTION

The established tolerance of 0.75 ppm for diazinon in mushrooms is consistent with tolerance levels established on a majority of raw agricultural crops and is based on data obtained in tests conducted at the United States Department of Agriculture in Beltsville, MD, and in tests in commercial mushroom houses (Cantelo et al., 1982). A review of the data shows that in several cases mushrooms grown in both treated and untreated mushroom beds contained 0.004 ppm diazinon. Diazinon had been used prior to the tests to treat the ceilings, walls, and frames of the mushroom house in order to control mushroom flies. In addition diazinon treated compost had been placed in treated beds placed beside the untreated control beds. In related work with an organophosphorus pesticide with a vapor pressure similar to diazinon (Argauer and Feldmesser, 1978) we had attributed trace amounts of residues found in several samples of cantaloupe to sorption of the chemical directly from the treated soil on which the fruit rested. We are reporting a study in which we attempted to exceed the established tolerance through transfer of diazinon vapors to the mushrooms in a simulated worst possible case situation. We grew mushrooms in glass desiccators in order to maximize the number of molecules of insecticide vapor in contact with the surface of the growing mushrooms. We extended the investigations to include other agriculturally related sorbents in order to predict the amounts of diazinon and of other chemicals with different vapor pressures that might be expected to be sorbed under conditions of minimum ventilation.

METHODS AND MATERIAL

Diazinon Sorption on Mushrooms Grown in Glass Desiccators. Figure 1 illustrates the system used for growing mushrooms in glass desiccators. Intact sections of mushroom growing media were removed from a production bed and placed in the desiccator. The media consisted of two layers, the upper called casing, and the lower compost. The compost was a mixture of straw-bedded horse manure, chicken manure, brewers grains, and gypsum. This material had been subjected to an outdoor composting process where caramelization of carbohydrates occurred and then to indoor composting to kill undesirable organisms and to remove the ammonia and produce carbohydrate forms readily available to the mushrooms. Mushroom spawn, which is the vegetative stage of the fungus growing on cereal grain, had been mixed into the compost layer. After that layer was fully grown with mycelium, the casing layer was added. The casing consisted of a mixture of top soil and spent compost that had been raised to a pH of about 7.6 by the addition of ground limestone. This layer, although it provides little or no nutrients, does provide water and is essential for fruiting to occur. As the mycelium completes the colonization of the casing, the threads begin to anastomose forming "pins" which become "buttons", which grow into mature fruiting bodies. During the early button stage mushroom growing sections were placed in the desiccators that were held in an environmental chamber at 15 °C for the sporophore to develop. At the time when pins began their formation, known amounts of water diluted diazinon EC were applied to 9 cm × 17 cm cedar boards and the boards were suspended by wires about 5 cm over the surface of the casing. The glass lid was separated from the desiccator body by the wires holding the boards. The separation provides a degree of ventilation required for mushroom growth. The concentration of diazinon vapor above the growing mushrooms though not measured, was expected nevertheless to be greater than in a ventilated growth facility such as a mushroom house.

To analyze for diazinon, the mushrooms (10–50-g samples) were blended with 200 mL of methylene chloride and 10 mL of 2 N sulfuric acid for 5 min. The blend was filtered and anhydrous sodium sulfate was added to the filtrate to remove residual water. Next an aliquot between 150 and 175 mL of the filtrate was concentrated to near dryness with the use of a Rinco evaporator. The residue was dissolved in 5.0 mL of ethyl acetate and a 5-μL aliquot was injected into a Model 500 Tracor gas chromatograph with a flame photometric detector that contained a 526-nm interference filter and was equipped with a 180 cm, 4 mm ID glass column containing 3% (wt/wt) SP-2100 on 80/100 mesh Suplecoport and operated at 160 °C. The flow rates (mL/min) were nitrogen 160, oxygen 40, and hydrogen 200. Chromatographic peaks for the samples were compared with 1–10-ng injections of standard solutions of diazinon. Recoveries of diazinon at 0.01 mg/kg were nearly 100%.

Diazinon Sorption on Various Substrates in Sealed Glass Desiccators. A 9-cm diameter glass petri dish that contained 10 g of technical diazinon or an equivalent of an emulsifiable concentrate was used as the primary source of diazinon vapors in those tests involving substrates other than mushrooms. Directly above this primary source, and

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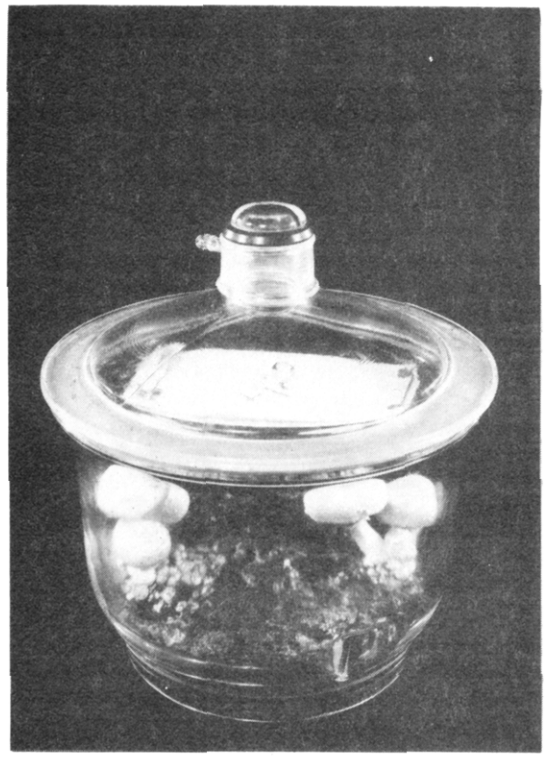

Figure 1. Mushrooms growing in a glass desiccator that contains a diazinon treated cedar board.

separated by a wire mesh shelf, were placed 9-cm petri dishes containing known amounts of various substrates as sorbents. The system was sealed with the desiccator lid. The vapor pressure of diazinon at 25 °C was calculated to be 1.9×10^{-4} torr based on literature values of 1.4×10^{-4} torr at 20 °C and 2.8×10^{-4} torr at 30 °C. We estimated that the rate of evaporation for diazinon, based on the near linear relationship between vapor pressures and evaporation rates as described by Guckel et al. (1982) for several insecticides, at less than 1600 μg/day from the surface of the 9-cm petri dish. Appropriate volumes of ethyl acetate (10–150 mL) were used to extract the diazinon from the sorbents and a 5-μL aliquot injected into the gas chromatograph which was operated at a reduced column temperature of 120 °C when dichlorvos was analyzed. For those tests in which silica gel was the sorbent extraction was accomplished by passing ethyl acetate through the sorbent in a glass column. Carbaryl likewise was extracted with methylene chloride, the solvent evaporated, and the fluorescence measured after addition of aqueous sodium hydroxide.

RESULTS AND DISCUSSION

Data in Table I show that mushrooms growing under conditions of minimum ventilation can sorb diazinon vapor at detectable levels. In only one case was the tolerance for diazinon of 0.75 ppm (mg/kg) exceeded even though the cedar boards had been impregnated with diazinon at levels greater than would normally be applied per unit area of treated mushroom house surface. Several variables affect the data. The compost growth media undoubtedly competes with the growing mushrooms for the available diazinon vapor. The amount of compost was not the same in all desiccators. Futhermore, compost is a nonhomogeneous mixture whose properties are known to change continuously during growth of the mushrooms. In addition, biological and chemical degradation of diazinon is expected to occur after sorption. We conclude that it is reasonable to account for the trace amounts of diazinon residues found in untreated mushrooms as being due to sorption of diazinon vapor. The values of 0.004 ppm and less originally found reflect the amount of ventilation known to occur in a mushroom house.

Table I. Diazinon Residues in Mushrooms Grown in Glass Desiccators[a]

diazinon,[b] mg	harvest time,[c] days	diazinon, mg/kg (found in mushrooms)
1.2	6	0.004
2.4	6	0.02
24.0	6	0.11
24.0	14	0.56
240.0	14	0.69
24.0	34	0.33
24.0	78	1.8
120.0	78	0.60
24.0	87	0.21
120.0	87	0.74
24.0	97	0.15
120.0	97	0.54

[a] Untreated mushrooms contained <0.002 mg/kg of diazinon. [b] The amount of diazinon brushed onto 9 cm × 7 cm cedar boards. [c] The mushrooms were grown at 15 °C in glass desiccators.

Table II. Diazinon Vapors Sorbed by Various Substrates in Glass Desiccators

test	sorbent (6 g) in petri dish	diazinon sorbed, mg/kg
	Nonpreequilibrated Desiccators	
		after 18 h
1	casein 80	0.4
2	white flour	0.6
3	granulated sugar	1.1
4	cotton	5.0
5	silica gel	7.2
6	white bread	8.4
7	whatman #3 filter paper	9.3
8	glass wool	10.0
9	kimwipes	10.2

test	sorbent coated on petri dish	diazinon sorbed, μg
	Nonpreequilibrated Desiccators	
		after 122 h
10	soybean/cottonseed (10 mg)	52
	wheat germ (10 mg)	60
	butter (10 mg)	63
	butter (30 mg)	85
	Preequilibrated Desiccator	
		after 72 h
11	no coating	4.6
	1-octadecanol (10 mg)	9.4
	steric acid (10 mg)	14
	beeswax (10 mg)	44
	wheat germ oil (10 mg)	75
		after 120 h
12	1-octadecanol (50 mg)	17
	steric acid (50 mg)	25
	wheat germ oil (50 mg)	104
	beeswax (50 mg)	108
	paraffin oil (50 mg)	115
	soybean/cottonseed oil (50 mg)	131
13	calcium chloride (6 g)	14
	granulated sugar (6 g)	35
	silica gel (6 g)	94
	wheat flour (6 g)	106
	cotton (6 g)	146
		after 144 h
14	wheat germ oil (10 mg)	69
	kimwipes (1.61 g)	73
	filter paper (3.2 g)	308

Diazinon Sorption on Various Substrates and on Walls of Glass Desiccators. The Sink–Mobile Reservoir Effect. The amounts of diazinon vapor sorbed by various substrates in sealed glass desiccators are summa-

Table III. Effect of Time and Vapor Pressure on Amount Sorbed in a Sealed Glass Detector

sorbate	vapor pressure, torr at 25 °C	sorption time	μg sorbed/6 g of sorbent	
			cotton	silica gel
carbaryl		9 days		30
diazinon	0.0003	6 days	100	80
dichlorvos	0.012	6 days	2000	14000
water	23.0	hours	600000	1500000
hexane	148.5	hours	200000	3800000

rized in Table II. The data reflect the complex nature of the sorption process which depends on variables such as the available surface area of the sorbent, as controlled by pore sizes of the amorphous or crystalline sorbent, and the diffusion or solubility characteristics at the sorbate/sorbent interface.

In several trials in which we measured the amount of diazinon sorbed in 18 h by various substrates, the size of the desiccators affected the amounts of diazinon sorbed. Lower values were observed for sorbents placed into larger desiccators. This we term the sink effect since the glass inside surface of the desiccator was competing with the sorbent for vapors emitted by the primary source in the petri dish. Higher values were observed consistently for sorbents placed into desiccators preconditioned 72 h with diazinon. This we term the mobile reservoir effect. The glass surface of the desiccator sorbs vapors during preconditioning, and in effect, becomes a secondary source providing the surface area from which molecules are free to desorb and transfer to a more competitive sorbent that subsequently is introduced. Ethyl acetate rinsings taken of the inside wall surfaces of the glass desiccator after 72 h of preconditioning gave values for diazinon of about 700 μg, or about 0.3 μg of vapor deposited per cm^2 of glass surface. Given the 9-cm diameter petri dish as the primary source of vapor in the desiccator, for pesticides with higher vapor pressures than diazinon, such as dichlorvos or naphthalene, the sink effect would have been masked by the speed by which equilibrium between source and sink is established. For pesticides with a vapor pressure much less than diazinon, such as parathion and DDT, as examples, the mobile reservoir effect would become noticeable only if the time allowed for preequilibration was extended to weeks or months thus permitting the mobile reservoir surface to be coated.

Vapor Pressure and Time in Enclosed Systems. Data in Table III illustrate the effect of vapor pressure and time on the amount of sorbate that may be expected to be found sorbed on cotton or silica gel placed in an enclosed system such as a desiccator. Other chemicals with vapor pressures lower than diazinon, such as dursban and the 3-phenoxybenzyl synthetic pyrethroids, should transfer lessor amounts to awaiting sorbents based on their relative vapor pressures in an enclosed system at the same temperature. Corresponding chemicals with high vapor pressures, such as 1,2-dibromoethane (vapor pressure 11 torr at 25 °C) and carbon tetrachloride (vapor pressure 116 torr at 25 °C), produced initial residues of 160 ppm and 800 ppm on cereal grains in sealed silos, the amounts limited only by the quantity of the fumigants actually used in the tests (Jagielski et al., 1978).

The sealed desiccator illustrates the situation where ventilation in an enclosed system is kept at a minimum thereby maximizing the amount of chemical vapor presented per unit time per unit area at the sorbent surface. Kitchen cabinets, automobiles, refrigerators, clothes closets, warehouses, greenhouses, honey bee colonies, mushroom houses, and chemical storage areas exhibit varying degrees of ventilation with subsequent decreases expected in the relative amounts of chemicals sorbed whenever sorbents and sorbates are introduced. Implications as those regarding safety and health in the sorption and desorption of chemical vapors in various enclosed environments as a function of increased temperature and decreased ventilation may deserve additional study.

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