Bull. Environ. Contam. Toxicol. (1987) 38:793–797

Environmental Contamination and Toxicology

Sulfotepp in Diazinon and Other Organophosphorus Pesticides

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The presence of the toxic impurity, sulfotepp (O,O,O',O'-tetraethyl dithiopyrophosphate), in technical diazinon has been known since the introduction of diazinon in the marketplace as a broad spectrum insecticide (Martgot and Gysin 1957). Because of its toxicity, sulfotepp as an impurity has been implicated in cases of human poisoning (Sovocool et al. 1981). Sulfotepp is also resistant to hydrolysis and therefore is a concern in disposal of waste or spilled diazinon (Dennis et al. 1980). Recently, levels of sulfotepp in micro-encapsulated formulations of diazinon manufactured in the U.S.A. have been determined (Karr 1985). It was therefore felt useful to examine other types of formulations, as well as technical diazinon, used in Canada to determine if regulatory action may be required. Since sulfotepp has been shown to be formed during the manufacturing process (Karr 1985) and is not a hydrolysis product (Margot & Gysin 1957, Sovocool 1981) it was decided to examine other technical organophosphorus pesticides for its presence. Wilkins et al. (1985) recently reported the presence of sulfotepp in demeton. Parathion has been shown to contain sulfotepp (Diggory et al. 1977, Greenhalgh et al. 1983).

The most likely precursor of sulfotepp in organophosphorus pesticides is diethyl thiophosphoryl chloride (Toy 1951). Eight pesticides registered in Canada as active ingredients may use this precursor (Sittig 1980) or alternatively possess the diethyl thiophosphoryl moiety. Technical samples for all eight were analyzed for sulfotepp.

Various approaches to the analysis of sulfotepp as an impurity are recorded. The HPLC method of Nicol et al. (1982) suffers from the fact that sulfotepp lacks a strong chromophore and is not readily detected at the short wavelength required for analysis. Impurities in commercial HPLC solvents make the situation worse. Phosphorus-31 NMR has been proposed as a technique for examining impurities in technical organophosphorus pesticides (Wayne et

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al. 1982). There has been one attempt to examine sulfotepp in diazinon by this technique (Greenhalgh et al. 1983), but the equipment is expensive and, whilst suitable for technical pesticides, does not lend itself to formulated products. Furthermore, it requires very experienced personnel.

Gas chromatographic methods which use packed columns (Meir et al. 1979), in our hands, lacked the resolution to separate sulfotepp from other impurities. Capillary gas chromatography with 0.2-mm i.d. columns and flame photometric detection (Karr 1985) requires more specialized equipment than is generally available in the pesticide formulation laboratory. In this work, a packed column gas chromatograph was modified by using low-cost readily available equipment to accept 0.53 mm i.d. fused silica capillary columns. Both flame ionization and nitrogen-phosphorus detectors were employed for the detection of sulfotepp in diazinon and other organophosphorus compounds.

MATERIALS AND METHODS

Analytical standards and technical grade pesticides from manufacturers were obtained through the Canadian Centre for Pesticide Analytical Standards, Agriculture Canada, Ottawa. Such materials are required for registration of pesticides in Canada. Formulated products were obtained as part of Agriculture Canada's regular monitoring program for verifying manufacturer's level of active ingredient.

Standards, technical grade pesticides and liquid formulations were prepared for analysis by dissolving known quantities in hexane such that the level of active ingredient was between 4 and 12 mg/mL. Granular formulations were suspended in hexane and shaken and then the hexane was filtered.

Two microliter aliquots were injected into a Hewlett-Packard 5710 gas chromatograph equipped with flame ionization and nitrogen phosphorus detectors. The instrument was modified to accept 0.53 mm i.d. fused silica columns by using a Megabore conversion kit (J&W Scientific Inc.). Make-up gas was supplied to the detector base from the unused flow controller and injection port. A 30 m x 0.53 mm i.d. Durabond-17 column (J&W) was found suitable for all determinations. Chromatographic conditions were as follows: injector 250°; detector 300°; initial oven temperature 100° for 4 min, then programmed at 4°/min to 250°. Column flow was 7.8 mL/min, make-up 30 mL/min. Chromatograms were recorded on a Varian Vista 402 chromatographic data system. Retention times of sulfotepp and diazinon were 21.6 and 23.7 min, respectively. The linearity of the system for both detectors was found to be excellent over the range 0.2 to 20 ng of sulfotepp/uL.

The presence of sulfotepp was confirmed in technical pesticides by GC-MS (Wilkens et al. 1985) by using a Kratos MS-50 interfaced with an INCOS data system and Perkin-Elmer Sigma 2 gas chromatograph equipped with an on-column injector and a 30 m x

0.32 Durabond-5 capillary column. MS operating conditions were: ionization 70 eV, ion source 250°; accelerating voltage 800 eV; SIM mode at 322.023; resolution 10,000 (10% valley). GC conditions were head pressure 7 psig; oven 110° initial, programmed 10°/min to 260°.

RESULTS AND DISCUSSION

Table 1 represents the results obtained for sulfotepp in technical and formulated diazinon obtained in Canada between 1984 and 1986. The highest level was 0.53 g/100 g a.i. The levels are similar to those reported by Karr (1985). Samples 096 and 097 represent different lots of the same registered products, and sample 096, which has a significantly higher level of sulfotepp, is known to have been manufactured prior to 1983. Sample 097 was from 1986 production. No conclusions can be drawn, however, regarding the effect of products aging on sulfotepp formation, since different sources of diazinon may have been used and some recent samples had similar or higher levels.

Table 1. Sulfotepp in Technical and Formulated Diazinon Products

Sample	g/100 g a.i. Sulfotepp(1)	% Diazinon(2)
Tech A	0.02	92
Tech B	0.21	87
Tech C	0.10	97.7
022	0.05	13.3 LC
024	0.09	12.4 LC
034	0.01	51.2 EC
035	0.02	51.3 EC
039	0.02	53.0 EC
044	0.10	53.3 EC
055	0.05	50.6 EC
077	0.08	12.9 LC
078	0.01	1.9 Dust
079	0.05	4.8 Gran
096	0.39	12.2 LC
097	0.04	12.2 LC
101	0.53	1.0 Dust
102	0.25	47.5 EC
103	0.22	48.6 EC
128	0.05	12.7 LC
130	< 0.01	12.8 LC
150	0.05	12.8 LC
166	0.11	52.3 EC
187	0.04	12.2 LC
235	0.05	12.2 LC
247	0.02	12.0 LC
250	< 0.01	51.2 EC
270	0.03	51.2 EC
333	0.20	53.3 EC
373	0.14	54.8 EC
488	0.10	52.2 EC
508	0.11	11.9 EC
509	0.02	14.7 EC
911	0.15	2.0 Dust
968	0.26	51.7 EC

(1) Based on content of actual diazinon level.

(2) Procedure for % diazinon in formulations (Lee & Hindle 1985). LC = liquid concentrate, EC = emulsifiable concentrate.

The other organophosphorus pesticides other than demeton contain little sulfotepp as shown in Table 2. The levels of sulfotepp in demeton are not of regulatory concern since the acute oral LD_{50}

for rats, which ranges from 2.5 to 12 mg a.i./kg (Worthing & Walker 1983), causes this pesticide to be restricted to commercial use.

These results confirm those obtained by using P-31 NMR (Greenhalgh et al. 1983) and GC-MS (Wilkins, 1985).

Table 2. Sulfotepp in Technical Organophosphorus Pesticides

Pesticide(1)	g/100 g a.i. Sulfotepp	Pesticide(1)	g/100 g a.i. Sulfotepp
parathion	0.07	demeton (F)	3.6
chlorpyrifos	0.01	demeton (G)	3.1
fensulfothion	0.01	disulfoton (H)	0.01
phosalone	0.01	disulfoton (J)	0.01
coumaphos (D)	0.06	terbufos	0.03
coumaphos (E)	0.04		

(1)Suffix letters indicate different sources of technical product.

Acknowledgments. We thank Greg Malis and Narine Gurprasad for providing the GC-MS confirmations.

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Received October 10, 1986; accepted December 5, 1986.