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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 9 1986

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Diazinon (057801) Analysis of Public Comments in Response to PD 1/2/3 (RCB No. 764)

FROM: Susan V. Hummel, Chemist
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Susan V. Hummel

THRU: Charles. L. Trichilo, Branch Chief
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TO: Ingrid Sunzenauer, PM#78
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SRB has requested that RCB provide an analysis of the public comments on the diazinon PD1/2/3. One comment was attached to the request, and two comments were provided to RCB by SRB subsequent to their request. Public comments included in this review are those from the Susquehanna Group Sierra Club, USDA, and Ciba-Geigy.

Comment

The Susquehanna Group Sierra Club comments that diazinon formulations contain sulfotep (O,O,O,O-tetraethyl dithio-pyrophosphate) as a major impurity. An American Chemical Society press release dated April, 1976 is cited. The ACS press release is a summary of a paper presented at the 12th Middle Atlantic Regional Meeting of the American Chemical Society by Dr. E. P. Meier, et. al., U. S. Army, Fort Detrick, MD. The press release states that sulfotep (sic) is a pesticide 30 to 120 times more toxic than diazinon, and considerably more stable than diazinon.

EPA Response

(SRB may want to include only parts of this in the formal response.)

EPA is aware of the sulfotepp impurity in diazinon and in other organophosphate pesticides. Information on the levels of sulfotepp in diazinon products and analytical methods to

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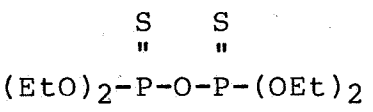
detect the sulfotepp impurities will be required as part of the reregistration process. The registration standard for diazinon is currently in preparation and the Product Chemistry and Residue Chemistry Chapters for the Registration Standard are due 7/3/86 (W. Hazel, personal communication, 4/4/86). Several other published references are available on sulfotepp impurities in diazinon, as well.

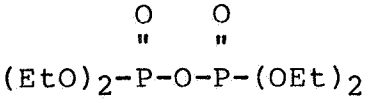
Sulfotepp is itself a pesticide, marketed by BAYER AG under the trade name BLADAFUM as a greenhouse fumigant. It is not used in the United States. Sulfotepp is the dithio homolog of TEPP. (See Figure 1 for structures.)

FIGURE 1

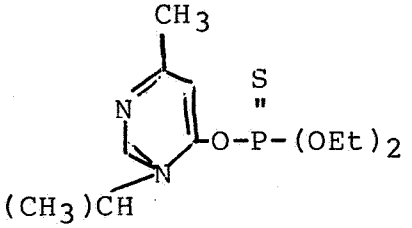
Sulfotepp (O,O,O,O-tetraethyl-dithiopyrophosphate)



TEPP (tetraethylpyrophosphate)



Diazinon (O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate)



Dr. E. P. Meier, et al, published a paper entitled, "Sulfotepp, a Toxic Impurity in Formulations of Diazinon," Bull. Environm. Contam. Toxic. 23, 158-164 (1979). This paper indicated that sulfotepp is an impurity in diazinon formulations, and is also an impurity in parathion formulations (present at a sulfotepp/parathion ratio of 1.3%). The Army was interested in chemical degradation and disposal of pesticide wastes. They reported that acid hydrolysis destroyed >99.9% of the diazinon, but that the toxicity of the reaction mixture was reduced by <50%. The sulfotepp content of the mixture was unchanged by the acid hydrolysis. The age of the formulations were not a factor in the amount of sulfotepp present. We note that the Army appeared to be using Ciba-Geigy formulations of diazinon.

R. Greenhalgh (Agriculture Canada), et. al., published results of ^{31}P-NMR analysis of organophosphates ("Phosphorus-31 Nuclear Magnetic Resonance Analysis of Technical Organophosphorus Insecticides for Toxic Contaminants," J.

Agric. Food Chem., 31(4), 710-713 (1983)). Dialkyl aryl phosphates (diazinon, fenchlorphos, fensulfothion, fenitrothion, methyl parathion, and parathion), trialkyl phosphorodithioates (dimethoate, ethion, malathion), and dialkyl aryl phosphorodithioates (methidathion and phosalone) were analyzed. Sulfotepp and other impurities were identified. Sulfotepp was found in diazinon (0.34%) and parathion (0.11%), but not in fensulfothion. Sulfotmpp (the methyl homolog of sulfotepp) was found in fenitrothion (0.21%), but not in fenchlorfos or methyl parathion.

A paper presented by James Karr of Pennwalt Corporation at the Fall, 1984 meeting of the Association of Official Analytical Chemists (AOAC) reported levels of sulfotepp in technical diazinon. The following levels were reported:

Diazinon Source	Concentration of Sulfotepp
Ciba Geigy (U.S.)	260 ppm
Ciba Geigy (France)	200-300 ppm
Nippon-Kayaku (Japan)	3500-5500 ppm
Makhteshim (Israel)	1900-2300 ppm

This paper was summarized in a memo from D. F. Hill (EPA Enforcement, Denver, CO) to J. Seitz (OPTS Compliance Monitoring Staff), 12/7/84. D. F. Hill also reported that his laboratory had seen elevated sulfotepp levels in chlorpyrifos samples.

Dr. Robert Zendzian, Toxicology Branch, has concluded that these levels of sulfotepp impurity in diazinon technical are not of toxicological significance (memo of R. Zendzian to J. Melone, 4/1/85). However, Dr. Zendzian notes that the Ciba-Geigy Diazinon technical is stabilized to prevent further conversion of the diazinon to sulfotepp. We recommend that Dr. Zendzian or another representative from Toxicology Branch be present at the SAP meeting to answer questions on this subject.

Comment

The USDA commented that EPA indicated that there is a lack of residue data on grasses. However, residue data should be available since diazinon is registered for use on pasture grass at similar label dosage rates and has a tolerance on those grasses of up to 60 ppm on fresh grass.

EPA Response

USDA is correct in stating that diazinon is registered for use on pasture grasses and that there is a tolerance of 60 ppm on fresh grasses. However, the registered rate for use

on pasture grasses is 0.5 lb ai/A. (Residue data have been submitted in support of the tolerance at this rate.) The rate of 0.5 lb ai/A is far less than the registered rate of 11 lb ai/A, and less than the proposed rate of 4 lb ai/A, as well. RCB does not feel that it is possible to extrapolate the available residue data to these higher application rates.

Ciba-Geigy Comments

The response to the PD 1/2/3 by Ciba Geigy contained no comments pertinent to RCB concerns.

cc: R.F., circu, Diazinon S.F., Diazinon S.R.F. (Hummel), S. Hummel, Diazinon Reg. Std. File (Hazel), Parathion S.F., Chlorpyrifos S. F., PM#15, PM#12 (E. Allen), SIS, PMSD/ISB
RDI:EZ:4/8/86:RDS:4/8/86
TS-769:RCB:SVH:svh:RM810:CM#2:4/9/86