C. Furlow
FIB/FOD

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

APR 13 1990

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: California Study of Unintentional Residues of Diazinon, Methidathion, Chlorpyrifos and Ethyl Parathion. MRID No. None. DEB No. 6216. HED Project # 0-0491.

FROM: Martha J. Bradley, Chemist MJ Bradley
Dietary Exposure Branch
Health Effects Division (H7509C)

TO: Hoyt Jamerson, PM 43
Registration Support Branch
Registration Division (H7505C)

and

Toxicology Branch
Health Effects Division (H7509C)

THRU: Richard D. Schmitt, PhD., Chief
Dietary Exposure Branch
Health Effects Division (H7509C) Richard D Schmitt

The California Department of Food and Agriculture (CDFA) has submitted a study entitled "A Field Study of Fog and Dry Deposition As Sources of Inadvertent Pesticide Residues on Row Crops" November, 1989, by B. Turner, S. Posell, N. Miller and J. Melvin.

The month long study was conducted in January 1989, and monitored air, crop, fog and fall-out cards for the pesticides diazinon, methidathion, chlorpyrifos and parathion during and between fog events occurring during normal application of the subject pesticides to nearby orchard crops.

Background

The State of California, during the winters of 1985-1986 and 1987-1988, sampled and analyzed a number of crops grown in Stanislaus County. Low levels of methidathion, chlorpyrifos, diazinon, and parathion were found on leafy type vegetables. Levels found on the leafy type vegetables were methidathion, non-detected (ND) to 0.15 ppm; chlorpyrifos, ND to 0.24 ppm with one value of 7.9 ppm; diazinon, ND to 0.4 ppm; and parathion, ND to

0.55 ppm. The (CDFA) determined that the illegal residues were not from deliberate application to the crops but had been applied to vineyards and orchards in the area.

Technology Services Group Inc. on behalf of Ratto Bros., Inc., requested (July, 1988) crop group tolerances of 0.4 ppm each for inadvertent residues of diazinon, methidathion, chlorpyrifos and ethyl parathion on leaves of root and tuber vegetables, leafy vegetables, brassica leafy vegetables, fruiting vegetables and herbs and spices. (PP#8E3690, PP#8E3691, PP#8E3692, PP#8E3693.)

Tolerances have already been established for many members of the requested crop groups except herbs and spices for chlorpyrifos (180.342 from 0.5 to 2 ppm), diazinon (180.153 from 0.5 to 0.75 ppm) and ethyl parathion (180.121 at 1 ppm). There are no tolerances on members of the requested crop groups for methidathion (180.298).

The **Conclusions** and **Recommendations** of this Branch (M.Bradley, 11/5/88) in response to the pesticide petitions were not to establish the proposed tolerances because the data submitted were not sufficient to show that the residue was inadvertent and was caused by "atmospheric transport", better information is needed, i. e. what residues can be expected of what pesticides on what crops and that the residues are truly inadvertent. For further consideration, the results of the proposed CDFA study of the situation was requested to be submitted.

Conclusions

1. The CDFA study represents 1 crop (dill) grown in one month in one area of Stanislaus County, California. The 3 sites in that county are surrounded by orchards on at least two sides. It is neither representative for California or nationally for the country as an indicator of unintentional residues which can be expected on crops.

2. The limited data submitted indicate that unavoidable residues are occurring but these data do not allow us to determine the residue levels to be expected.

3. Post-application movement occurred from local spraying (within 400 meters of row crop fields) i.e. the higher residues on dill of parathion and diazinon at Site 3.

4. Regional transport also occurred from outside the 400 meter distance i.e. the presence of methidathion which was not applied within the 400 meter zone and the presence of the other three at sites where they were not applied within the 400 meter zone.

5. Fog plays some role in the transport of the pesticides from

orchards into the cultivated fields for example, the pesticides were in the fog water and generally there were greater increases of the pesticide residues in the crop during intervals containing fog events.

6. Dry deposition of the pesticides was also occurring during non-fog periods in the row crop fields. There was an increase in accumulation of diazinon in dill at Site 3 during non-fog events. The predicted increased accumulation of residues in dill due to fog accounted for some but not all of the measured accumulation and parathion was detected on the fallout cards exposed during non-fog intervals.

7. Many factors may influence the deposition of pesticides on crops including the chemical and physical characteristics of the chemical, the application equipment, the quantity and location of the pesticide applications, drift, meteorological factors and vegetative characteristics.

Recommendations

Although the CDFA study is limited, it appears that the contamination of the row crops is due to a number of variables as listed above. Because of the many variables, and the fact that the pesticide applications are not under the control of the row crop growers, it would be difficult to plan residue field trials to adequately cover all of the various situations in this California valley. We feel that CDFA is going in the right direction to solve the present problem in planning additional studies to determine ways to decrease the contamination of untargeted areas. For example, something as simple as labeling restrictions or closer adherence to labeling restrictions may solve the problem.

The CDFA should:

1. Submit a map of the Stanislaus County study designating treatment areas and times relative to the sites.

2. Investigate ways of avoiding this pesticide contamination.

Details of CDFA Study

Organophosphate pesticides are applied to the orchard-growing areas of Stanislaus County, Ca. as dormant sprays applied in solution using high volume spray equipment at rates of one to several kg active ingredient per hectare. The dormant spray period, from December 1 through January 31 coincides with the fog season. The organophosphate pesticide residues were found on row crops in January and February. The study was conducted to examine

possible transport mechanisms for movement of pesticides from orchards to cultivated fields. The stated objectives were (1) to determine whether the residues found on the crops were the result of post-application movement from local spraying (within 400 meters of row crop fields) or were due to regional transport from outside the 400 meter distance; (2) to determine whether fog was responsible for the transport of the pesticides from orchards into the cultivated fields; and (3) to determine whether dry deposition of the pesticides was occurring during non-fog periods in the row crop fields.

Three experimental sites were chosen with orchards on at least two sides; were similar in size; had not been treated with the subject pesticides the previous year; and were at least 2.4 but no more than 4.8 km apart. Sites 1 and 2 had a buffer zone of 400 meters within which no parathion was to be used. Site 3 (the "control" site) had no buffer zone for parathion.

Replicate fog water samples were collected at each site during fog events, with sampling periods of 5 hours. Dill plants were used over the 30 day study period to measure cumulative pesticide deposition. Composite samples were collected every three days during the month. Composite fallout card samples for parathion analysis were collected during fog and non-fog days from each site. The fallout cards were exposed for 5 hours during fog and for 4 hours during non-fog days. The fog water was refrigerated until analysis and the dill and fallout cards were frozen until analysis.

Pesticide applications reports for the four subject pesticides within the 400 meter site and for methidathion for approximately 200 square miles surrounding the study sites were conducted. The reports consisted of the type of pesticide, quantity applied, equipment used, commodity, hectares treated and location of the application. Meteorological data, average wind speed, wind direction, average temperature and average relative humidity were constantly measured at the three study sites. Windroses showing wind velocity and direction were created for each day at each site. However, no maps or drawings are submitted to allow visual representation of the study sites, their adjacent orchards and areas of spraying.

Analytical Methodology

CDFA developed the methods and conducted the analysis for parathion, diazinon, chlorpyrifos and methidathion in water, dill and fallout card samples. The method for water, "the Sampling and Analysis of Water for Pesticides" is published in the EPA Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, 1979. The water is extracted with methylene chloride and analyzed by GC using a flame photometric detector. Recoveries of the four subject pesticides from water fortified with

3, 5, 20, 100 and 500 ppb ranged from 80 to 125%. The detection limit is 1.0 ppb. The method used for dill analyses is a CDFA multi-residue method in which residues are extracted with acetonitrile, the extract is filtered, and the aqueous layer is salted out with sodium chloride. An aliquot of the organic layer is evaporated and the residue is made to volume with acetone and analyzed by GC using a flame photometric detector. Recoveries of the four subject pesticides from dill fortified at 0.03, 0.05, 0.2, 1.0, and 5.0 ppm ranged from 63 to 146%. The detection limit is given as 0.01 ppm. The method used for parathion in the fallout cards (Kimbies) was extraction by shaking with ethyl acetate, concentration of the extract, cleanup through a Florisil sep-pak and detection by GC with a flame photometric detector. Recoveries of parathion at levels of 1, 5 and 25 micro grams was 70 to 100%. The detection level was 1 micro gram per one sample (10 kimbies).

The methods used are standard organophosphate analytical methods, similar to the FDA multiresidue methods.

Residues

A storage dissipation study was conducted on water and dill samples. Samples fortified with all four compounds were analyzed at weekly intervals for 56 days with no apparent breakdown of the four subject pesticides.

Residues in fog water expressed as micro grams per kilogram ranged from 2 to 33.7 for parathion, 1.1 to 237.1 for diazinon, non-detected to 9.6 for chlorpyrifos and non-detected to 11.3 for methidathion.

Residues in dill in ppm at Sites 1 and 2 range from non-detected at the beginning of the month to a maximum at the end of the month of .123 for parathion, 0.255 for diazinon, 0.453 for chlorpyrifos and 0.048 for methidathion. Residues in dill at Site 3 range from non-detected at the beginning of the month to a maximum of 0.265 ppm parathion, 5 ppm diazinon, 0.24 ppm chlorpyrifos and 0.062 ppm methidathion at the end of the month. Applications occurring within the 400 meter zone of the sites were chlorpyrifos at 31 kg ai on 14 ha the middle of the month at Site 1, two applications of diazinon at 16 kg ai on 8 ha and 8 kg on 4 ha near the end of the month at Site 2 and three applications of parathion and two applications of diazinon on Site 3 in the middle of the month. At Site 3, parathion was applied at 17 kg on 11 ha, 3 kg on 2 ha and 17 kg on 10 ha while diazinon was applied at 11 kg on 5 ha and 90 kg on 32 ha.

In general, incremental residues in dill were greater during intervals that contained fog events than in intervals without fog with the exception of Site 3 where diazinon incremental residues were greater during dry periods. From an estimate of water holding

capacity of the dill, a predicted concentration increase in dill residues due to fog was calculated for each 3-day sampling interval. A comparison of the actual deposition and the predicted concentration increase show that generally, the actual residue increase was much greater than that predicted from fog alone. While fog may be responsible for some of the residue in dill, other sources must be involved.

Of twenty seven fallout cards exposed to five hours of fog ten were positive for residues of parathion while of 35 samples exposed in non fog times, ten were positive for parathion. Site 3 contained three times the number of positive samples found at the other sites and had the highest dry deposition value, 8.8 micro grams which occurred immediately after or during application of parathion within the 400 meter zone.

DEB concurs with the CDFA report that the residues found on the dill were the result of post-application movement from local spraying (within 400 meters of row crop fields) and were due to regional transport from outside the 400 meter distance; that fog plays some role in the transport of the pesticides from orchards into the cultivated fields; and dry deposition of the pesticides was also occurring during non-fog periods in the row crop fields. Many factors may influence the deposition of pesticides on crops including the chemical and physical characteristics of the chemical, the application equipment, the quantity and location of the pesticide applications, drift, meteorological factors and vegetation characteristics.

Although the CDFA study is limited, it appears that the contamination of the row crops is due to a number of variables as listed above. Because of the many variables, and the fact that the pesticide applications are <u>not</u> under the control of the row crop growers, it would be difficult to plan residue field trials to adequately cover all of the various situations in this California valley. We feel that CDFA is going in the right direction to solve the present problem in planning additional studies to determine ways to decrease the contamination of untargeted areas. For example, something as simple as labeling restrictions or closer adherence to labeling restrictions may solve the problem.

The CDFA should submit a map of the Stanislaus County study designating treatment areas and times relative to the sites and investigate ways of avoiding this pesticide contamination.

cc: M. Bradley, RF, Circu, PP8E3690, PP8E3691, PP8E3692, PP8E3693 PMSD/ISB
H7509C:DEB:M Bradley:mb:CM#2:Rm810:557-7324:03/21/90
RDI:RSQuick:03/11/90:RALoranger:03/ /90

1/18/90 mb

Use this form for individual studies & to submit pesticide applications.

EPA

United States Environmental Protection Agency
Office of Pesticide Programs
Washington, DC 20460

Data Review Record

Confidential Business Information - Does not contain National Security Information (E.O. 12065)

Pack Number: 0-0491

Date Received: 1/18/90

1. Product Name: none

Chemical Name: none

2. Identifying Number	3. Record Number	4. Action Code	5. MRID/ Accession Number	6. Study Guideline or Narrative
Inadvertant Residues	257691	268		
(INADVERTANT)				

7. Reference No.	8. Date Rec'd (EPA)	9. Prod/Review Mgr/DCI	10. PM/RM Team No.	11. Date to HED/ EFED/RD/BEAD	12. Proj Return Date	13. Date Returned to RD/SRRD
-1-	01-02-90	JAmerson	43	01-09-90	4/15/90	

Instructions

Jameson-Quick on 7/23/90

Review of CDFA's study of the deposition of inadvertent pesticide residues on row crops is requested. Does the study provide information useful to the Agency's consideration of inadvertent residues. (See Victor Kimm's letter of 05-22-89). Does CDFA's study provide information useful to the review of PP's 8E3690, 8E3691, 8E3692, 8E3692? See M. Bradley's review of 11-25-88.

This Section Applies to Review of Studies Only

14. Check Applicable Box
- ☐ Adverse 6(a)(2) Data (405)
- ☐ Special Review Data (870)
- ☐ Generic Data (Reregistration) (660)
- ☐ Product Specific Data (Reregistration) (655)

15. No. of Individual Studies Submitted

16. Have any of the above studies *(in whole or in part)* been previously submitted for review?
☐ Yes *(Please identify the study(ies))* ☐ No

17. Related Actions

18.	To	Type of Review
HED		Science Analysis & Coordination
		Toxicology/HFA
		Toxicology/IR
	✓	Dietary Exposure
		Nondietary Exposure
EFED		Ecological Effects
		Environmental Fate & Groundwater
SRRD		Special Review
		Reregistration
		Generic Chemical Support
RD		Insecticide-Rodenticide
		Fungicide-Herbicide
		Antimicrobial
		Product Chemistry
		Precautionary Labeling
BEAD		Economic Analysis
		Analytical Chemistry
		Biological Analysis

19. Reviews Also Sent to
- ☐ SAC ☐ PC
- ☐ TOX/HFA ☐ PL
- ☐ TOX/IR
- ☐ DEB ☐ EA
- ☐ NDE ☐ AC
- ☐ BA
- ☐ EEB
- ☐ EFGWB
- ☐ SR
- ☐ RER
- ☐ GSC
- ☐ IR
- ☐ FH
- ☐ AM

20. Data Review Criteria

A. Policy Note No. 31
- ☐ 1 = data which meet 6(a)(2) or meet 3(c)(2)(B) flagging criteria
- ☐ 2 = data of particular concern from registration standard
- ☐ 3 = data necessary to determine tiered testing requirements

B. Section 18
- ☐ 1 = data in support of section 3 in lieu of section 18

C. Inert Ingredients
- ☐ 1 = data in support of continued use of List 1 inert

☐ Confidential Statement of Formula (EPA Form 8570-4) Attached *(Trade Secrets)*

☐ Label Attached