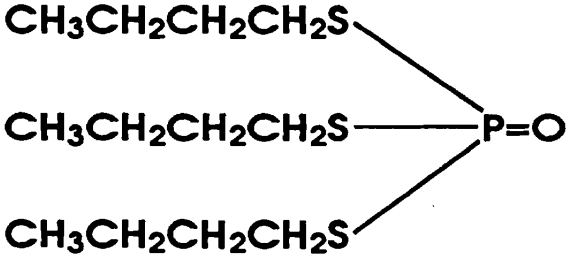
SRP DRAFT VERSION

Evaluation of S, S, S-Tributyl Phosphorotrithioate (DEF) as a Toxic Air Contaminant

Part A
Environmental Fate



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Department of Pesticide Regulation
California Environmental Protection Agency

October 1997

Report Number EH–96–05

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Acknowledgments

I would like to thank Heinz Biermann, Carolyn Lewis, Kevin Kelley, Pam Wales, David Duncan, Kathy Brunetti, Ruby Reed, Tareq Formoli, John Ross, Wynetta Kollman and David Supkoff for their review of or assistance with this document.

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I. OVERVIEW

In 1983, the California Legislature signed Assembly Bill 1807 into law, establishing criteria for the identification and control of toxic air contaminants (TACs). AB 1807 requires the Department of Pesticide Regulation (DPR) of the California Environmental Protection Agency, formerly part of the California Department of Food and Agriculture, to determine pesticides qualifying as TACs in their pesticidal use (Food and Agricultural Code, § 14021 et seq.). The passage of AB 3219 in September 1984 set specific timelines for investigation and review of registered pesticides as possible TACs, required public hearings in the TAC determination process, and enacted civil penalties for non-compliance of permit, use, and mitigation conditions set by DPR.

As part of the AB 1807/3219 process, DPR compiles a list of TAC candidates, identifying those pesticides posing a present or potential hazard to human health due to airborne emissions. DPR then reviews their physical properties, environmental fate, and human health effects. Air monitoring studies are arranged or contracted out by the Air Resources Board (ARB) (Food and Agricultural Code, §§ 14022–14023).

The active ingredient S,S,S-tributyl phosphorotrithioate is an organophosphate cotton defoliant used extensively in California. The two S,S,S-tributyl phosphorotrithioate-containing products registered in California, DEF® 6 (Miles Inc., Kansas City, MO) and Folex® 6 EC (Rhône-Poulenc Ag Company, Research Triangle Park, NC) underwent minor changes in formulation during the 1980s. Before 1986, Folex contained S,S,S-tributyl phosphorotrithioite instead of the oxidized phosphorotrithioate active ingredient. The phosphorotrithioite compound rapidly converted to phosphorotrithioate by oxidation in water, air, and on XAD-4 resin used for detection of both materials (Hermann and Seiber, 1981; Seiber et al., 1988). In this document, the use of either the phosphorotrithioite or phosphorotrithioate formulation of Folex in monitoring studies will be noted. **The reader can assume that the present S,S,S-tributyl phosphorotrithioate formulations of DEF and Folex are essentially equivalent, and unless otherwise indicated, DEF and Folex will be referred to collectively as DEF.**

DEF was added to the AB 1807/3219 candidate list in November 1986. The evaluation of DEF as a toxic air contaminant consists of three parts. Part A contains (a) the physical and chemical characteristics, patterns of use, and environmental fate representing DEF's potential as an air contaminant, and (b) the results of studies carried out by investigators from the Department of Environmental Toxicology at the University of California at Davis (UCD), who measured airborne levels of DEF in Central California. Part B, the exposure assessment, contains estimates of human exposure to airborne DEF. Part C reviews health effects, including: (a) an assessment of the availability and quality of data on health effects, and (b) the range of risk to humans resulting from current or anticipated exposure to DEF present in air where there is no threshold of significant adverse health effects.

II. BACKGROUND

DEF contains the formulation impurities and potential environmental conversion products n-butyl disulfide (n-dibutyl disulfide) and n-butyl mercaptan (1-butanethiol) (Figure 1). Both conversion products are highly volatile due to their high vapor pressures of 1 mm Hg @ 22°C (n-butyl disulfide) and 35 mm Hg @ 20°C (n-butyl mercaptan). Compounds with ambient vapor pressures greater than 10^{-3} mm Hg are considered fairly volatile, and are likely to be detected near the application source and downwind from it (Seiber and Woodrow, 1983).

Figure 1. Possible environmental fate of DEF according to Kilgore et al. (1984).

$$(CH_3CH_2CH_2CH_2S)_3P = O$$

S,S,S-tributyl phosphorotrithioate

$$\Downarrow$$

$$(CH_3CH_2CH_2CH_2SH)_3P = O$$

n-butyl mercaptan

$$\Downarrow$$

$$CH_3CH_2CH_2CH_2SSCH_2CH_2CH_2CH_3$$

n-butyl disulfide

$$\Downarrow$$

$$CH_3CH_2CH_2CH_2O{=}S{=}OCH_2CH_2CH_2CH_3$$

sulfone

$$\Downarrow$$

$$SO_4 \quad + \quad \text{alkyl chains}$$

n-Butyl mercaptan is exceptionally malodorous, and leads to complaints of influenza-like symptoms such as headache, nausea, and respiratory distress by mixer-loader-sprayers, flaggers, farm workers, bystanders, and nearby residents. Reports of strong, skunky odors are common several days following applications, suggesting that the defoliants (and/or their conversion products) may be volatilizing from the target.

Table 1 shows the physical and chemical characteristics of S,S,S-tributyl phosphorotrithioate that determine its environmental fate.

Table 1. Physical and chemical characteristics of S,S,S-tributyl phosphorotrithioate.

Common names	tribufos (proposed)[a], butifos
Trade names	DEF® 6, Folex® 6 EC
Percent active ingredient	70.5% (both products)
Other trade names	De-Green®, E-Z-Off D®[a]
Discontinued names	Ortho Phosphate Defoliant® (Chevron)
Formulation types	emulsifiable concentrate[a]
Manufacturers	Miles (DEF® 6), Rhône-Poulenc (Folex® 6 EC)
Molecular weight	314.52
CAS Registry No.	78–48–8
EPA Registration No.	3125–282 (DEF), 264–498 (Folex)
Molecular structure	$(CH_3CH_2CH_2CH_2S)_3P{=}O$
Physical form	colorless to pale yellow clear liquid
Boiling point	150°C @ 0.3 mm Hg[a]
Melting point	< –25°C[a]
Specific gravity	1.057 @ 20°C[b]
Vapor pressure	1.70×10^{-6} mm Hg @ 20°C[c]
Solubility	2.3×10^{-6} g/L @ 20°C (H_2O)[b] (Soluble in most organic solvents.)
Henry's law constant	2.88×10^{-4} atm · m^3/mol @ 20°C[d]
Ultraviolet absorbence	< 50 @ 300 nm
Photostability	$T^1/_2$ = weeks

[a] Royal Chemistry Society Agrichemicals Handbook, 1991.
[b] Farm Chemicals Handbook, 1994.
[c] CDFA Registration Data.
[d] Montgomery, J.H., 1993.
[e] Hermann, B.W., 1980.

A. Regulation of DEF and Folex

In 1978, California adopted a regulation establishing buffer zones for application of DEF and the pre-1986 form of Folex. DEF cannot be sprayed within one-half mile (≈ 804.5 m) of any area zoned as residential where people are actually residing, or other inhabited residential areas designated by the County Agricultural Commissioner, or any school in session or due to be in session within 24 hours (Calif. Code Regs., Title 3, § 6470). Applications cannot be made within one-eighth mile (≈ 201.1 m) of any school (Calif. Code Regs., Title 3, § 6470). DEF must be sprayed using specified jet nozzles and aircraft boom pressure to minimize drift problems (Calif. Code Regs., Title 3, § 6470).

In 1983, CDFA responded to public concern about the offensive odor of DEF and Folex by limiting n-butyl mercaptan content to less than 0.1% for products used within California (Calif. Code Regs., Title 3, § 6361). This prompted Rhône-Poulenc to introduce a low-odor formulation of Folex, switching from S,S,S-tributyl phosphorotrithioite as the active ingredient to the phosphorotrithioate formulation. Despite the use of only the more stable phosphorotrithioate compound, complaints by residents continue to be heard.

B. Application of DEF and Folex

1. Timing of application

From 1977 through 1995, data from the DPR Pesticide Use Report (PUR) have shown a steady use of DEF (Table 2). Rates of the products DEF and Folex specified by the label range from 0.75 to 2.25 lb/ac *(See Recommended rates of DEF and Folex, page 9 and Table 5, page 10).*

Note that in Tables 2 through 5 and throughout this report, standard measurements of pounds and acres are often used instead of metric conversions. These units are also used for pesticide product labels and DPR's Pesticide Use Reports.

For metric conversions, 1 pound = 0.4536 kilogram and 1 acre = 0.405 hectare.

Table 2. Reported uses[a] of DEF and Folex in California (1977–1995).

	S,S,S-tributyl phosphorotrithioate			S,S,S-tributyl phosphorotrithioite		
	pounds	acres	lb/ac[b]	pounds	acres	lb/ac
1977	817,865	499,749	1.64	438,482	266,281	1.65
1978	839,675	490,808	1.71	18,053	10,245	1.76
1979	1,278,528	732,790	1.74	431,384	238,079	1.81
1980	745,082	434,134	1.72	57,000	34,213	1.67
1981	887,923	465,875	1.91	208,374	114,438	1.82
1982	881,550	486,307	1.81	212,935	115,556	1.84
1983	643,606	372,077	1.73	596,843[c]	92,968	6.42
1984	838,552	472,745	1.77	281,589	155,696	1.81
1985	713,726	424,017	1.68	174,329	102,211	1.71
1986	558,045	307,634	1.81	198,002	117,390	1.69
1987[d]	979,240	574,628	1.70	—	—	—
1988	1,021,266	612,541	1.67	—	—	—
1989	973,521	605,856	1.61	—	—	—
1990	1,034,857	630,841	1.64	—	—	—
1991	861,241	594,687	1.45	—	—	—
1992	775,935	579,727	1.34	—	—	—
1993	998,332	659,152	1.50	—	—	—
1994	913,625	615,978	1.48	—	—	—
1995	883,567	605,188	1.46	—	—	—

[a] Figures reported in standard measures of pounds and acres. For metric conversions, 1 pound = 0.4536 kilogram and 1 acre = 0.405 hectare.

[b] Annual mean rate based on the Pesticide Use Report—actual rates during each year will vary according to specific use (i.e., amount used per application).

[c] Value from 1983 Pesticide Use Report is probably incorrect due to data entry error.

[d] Before 1987, the active ingredients for the products DEF and Folex were different (S,S,S-tributyl phosphorotrithioate and S,S,S-tributyl phosphorotrithioite, respectively). In 1987, both DEF and Folex products sold in California contained only the more stable phosphorotrithioate compound.

Most DEF is sprayed during September and October: in 1994, 98.8% was applied during these months, and in 1995, 97.8% (Table 3). From 1992 through 1995, over 80% of DEF was applied within three counties—Fresno, Kings, and Kern—with a combined population of over 1.3 million (Table 4). With the growth of communities surrounding the urban centers of Fresno and Bakersfield, residents often live, work, or attend school near agricultural land, increasing the possibility of exposure to volatilized DEF, despite the buffer zones surrounding schools and residences *(see page 4)*.

Table 3. Monthly DEF use in pounds by county (1992–1995).

county	*lb*
1992	
March	
Fresno	118
June	
Fresno	1,574
July	
Imperial	41
Kern	175
Riverside	297
Total	*513*
August	
Fresno	333
Imperial	9,229
Kern	1
Kings	5
Riverside	7,059
San Bernardino	503
Total	*17,130*
September	
Fresno	308,488
Imperial	808
Kern	88,839
Kings	81,308
Madera	20,855
Merced	44,614
Riverside	3,676
Tulare	17,415
Total	*566,003*

county	*lb*
October	
Fresno	86,625
Kern	21,624
Kings	20,927
Madera	16,885
Merced	25,755
Riverside	570
Stanislaus	15
Tulare	10,917
Total	*183,318*
November	
county	*lb*
Fresno	9
Kern	287
Kings	355
Merced	210
Total	*861*
1993	
January	
Fresno	55
March	
Fresno	290
Tulare	58
Total	*348*
May	
Fresno	548

county	*lb*
June	
Fresno	148
Kern	81
Total	*229*
July	
Fresno	19
Imperial	167
Kern	290
Madera	218
Total	*694*
August	
Fresno	110
Imperial	6,164
Riverside	5,281
San Bernardino	462
Total	*12,017*
September	
county	*lb*
Fresno	190,026
Imperial	1,247
Kern	71,365
Kings	68,306
Madera	11,338
Merced	21,628
Riverside	4,447
Tulare	16,882
Total	*385,239*

county	lb
October	
Fresno	284,026
Kern	46739
Kings	131,558
Madera	33,002
Merced	57,138
Riverside	158
Tulare	21,825
Yolo	17
Total	*574,353*
November	
Fresno	2,624
Kern	1,635
Merced	1,173
Total	*5,432*

1994

May	
Fresno	178
July	
Fresno	63
Kern	272
Tulare	67
Total	*402*
August	
Fresno	626
Imperial	5,960
Kern	117
Kings	89
Riverside	1,850
San Bernardino	205
Total	*8,847*
September	
Fresno	226,449
Imperial	2,927
Kern	77,405
Kings	88,385
Madera	5,426
Merced	21,668
Riverside	6,656
San Bernardino	330
Tulare	8,548
Total	*437,794*

county	lb
October	
Colusa	462
Fresno	223,967
Imperial	65
Kern	40,444
Kings	110,420
Madera	27,760
Merced	50,768
Riverside	574
San Bernardino	115
Tulare	10,419
Total	*465,094*
November	
Kern	111
Madera	158
Merced	940
Total	*1,209*
December	
Fresno	101

1995

March	
Fresno	280
June	
Fresno	482
August	
Imperial	3,686
Riverside	568
San Bernardino	330
Total	*4,350*

county	lb
September	
Colusa	374
Fresno	56,055
Imperial	3,479
Kern	27,943
Kings	28,542
Madera	1,391
Merced	6,865
Riverside	6,650
San Bernardino	200
Tulare	3,316
Yolo	302
Total	*135,117*
October	
Colusa	1,954
Fresno	377,289
Glenn	83
Imperial	387
Kern	59,302
Kings	155,832
Madera	30,440
Merced	74,325
Riverside	3,762
San Bernardino	30
Tulare	28,824
Yolo	222
Total	*729,450*
November	
Colusa	207
Fresno	3,110
Imperial	70
Kern	3,180
Kings	980
Madera	2,725
Merced	3,394
Riverside	171
Stanislaus	102
Tulare	232
Total	*14,169*

Table 4. Counties applying DEF in 1992–1995 and their total populations in 1990.

County	1992 Amount applied, lb[a] (%)	1993 Amount applied, lb (%)	1994 Amount applied, lb (%)	1995 Amount applied, lb (%)	Total population[b]
Colusa	— (—)	— (—)	562 (< 0.1)	2,535 (< 0.1)	16,275
Fresno	397,147 (51.6)	477,844 (48.8)	451,384 (49.4)	436,936 (49.5)	667,490
Glenn	— (—)	— (—)	— (—)	83 (< 0.1)	24,798
Imperial	10,079 (1.3)	7,578 (0.7)	8,952 (< 0.1)	7,621 (< 0.1)	109,305
Kern	110,926 (14.4)	120,111 (12.3)	118,348 (13.0)	90,425 (10.2)	543,477
Kings	102,595 (13.3)	199,755 (20.4)	198,894 (21.8)	185,354 (21.0)	101,469
Madera	37,739 (4.9)	44,557 (4.6)	33,345 (3.7)	34,555 (3.9)	88,090
Merced	70,579 (9.2)	79,939 (8.2)	73,376 (8.0)	84,584 (9.6)	178,403
Riverside	11,602 (1.5)	9,886 (1.0)	9,080 (1.0)	11,151 (1.3)	1,170,413
San Bernardino	503 (< 0.1)	462 (< 0.1)	650 (< 0.1)	325 (< 0.1)	1,418,380
Stanislaus	15 (< 0.1)	— (—)	— (—)	102 (< 0.1)	370,522
Tulare	28,333 (3.7)	38,765 (4.0)	19,034 (2.1)	29,373 (3.3)	311,921
Yolo	— (—)	17 (< 0.1)	— (—)	524 (< 0.1)	141,092
Total	*769,518 (100.0)*	*978,914 (100.0)*	*913,625 (100.0)*	*883,567(100.0)*	

[a] 1 pound (lb) = 0.4535 kg
[b] Population totals from the 1990 U.S. Census

In the San Joaquin Valley, growers defoliate cotton during the autumn to meet the state-mandated early plowdown dates, intended to reduce infestation by the pink bollworm, *Pectinophora gossypiella*, and cotton boll weevil, *Anthonomus grandis* (Calif. Code Regs., Title 3, § 3595). Although pink bollworm moths are weak flyers, wind and storm fronts may transport them northward to the San Joaquin Valley from the Coachella Valley in southern California (U.C. IPM Project, 1984). Overwintering adults are destroyed by discing under crop debris immediately after harvest in fall to early winter, preventing their emergence the following spring. In the counties of Fresno, Kern, Kings, Madera, Merced, San Benito, and Tulare, all cotton plants must be destroyed during December; cotton cannot be replanted until March 20.

2. Use of defoliants for cotton

DEF induces defoliation by causing an abscission layer to form between the petiole and the stem, leading to leaf drop within 4 to 7 days. Defoliation permits earlier harvesting and results in higher grades of cotton because few green leaves remain to clog the picking equipment or stain cotton fibers (Ware, 1991). Plants dry quickly and thoroughly and the mature bolls open faster, reducing boll rots that damage fiber and seed. Defoliation also reduces populations of fiber-staining insects, particularly aphids and whiteflies, which deposit honeydew in the open bolls, leading to staining by sooty mold. Before applying a defoliant,

plant growth must be complete, and temperatures must exceed 80°F (26.7°C) during the day and 50°F (10.0°C) at night.

Growers generally defoliate cotton three different ways, depending on the desired result (Table 5). 1) *Bottom defoliation.* Removing bottom leaves up to the level of the highest mature bolls permits sunlight to penetrate and air to circulate, eliminating the environmental conditions favorable to the development of boll rot. An application using shielded drop nozzles directed toward the lower leaves allows the grower to machine harvest the top bolls (the picker's top 8 to 12 rows of spindles) as seed cotton. Because the plant is left green and flexible, the picker does not injure the untreated top leaves and immature bolls. Another defoliation treatment with DEF may be necessary for complete defoliation when top bolls are mature. 2) *Complete defoliation.* For complete removal of green leaves before machine harvesting, growers spray the mature plants when 50% or more of the bolls are open and 7–10 days before anticipated picking. Plants are considered mature if the youngest bolls cannot be dented by pressure between thumb and forefinger, or cannot be cut through easily with a sharp knife. 3) *Preconditioning.* Growers precondition or accelerate the aging of leaves of rank cotton (tall, dense, actively growing plants) by adding small quantities of defoliant to the last insecticide application or as a separate application 10–14 days before total defoliation is desired. When complete defoliation of rank cotton is necessary, a second application can be made 2–6 weeks after the first, but not later than seven days before harvesting. A tank mixture with the urea-based plant growth regulator, Dropp® (thidiazuron) is recommended for total defoliation when control of heavy regrowth is required. In 1991, 15,379 pounds of Dropp were applied to 900 acres of cotton in California (PUR, 1991). Growers often add ethylene generators such as ethephon (Prep®) to the tank mixture to hasten boll opening before harvest.

3. Recommended rates of DEF and Folex

Most (80%) defoliants are applied aerially by professional applicators or pest control operators, and approximately 20% by ground by professional pest control operators or ranch workers. Recommended rates of DEF and Folex (Table 5) are determined by type of spraying (ground or aerial), type of growth (normal or rank), type of harvest (hand-picked seed or mechanical lint) and cultivar ('Acala' or 'Pima').

Table 5. Recommended rates of DEF and Folex used on cotton.

Rate[a] (pints/acre)	*Application method* Air (Gallons water/acre)	Ground	*Directions*
Complete defoliation			
1⅓ to 2	5 to 10	15 to 25	DEF 6: apply specified dosage per acre to give thorough coverage of leaves when 50% or more of the bolls are open. For low volume (LV) or ultra low volume (ULV) application use not less than 1½ pints/A of once-refined vegetable oil.
1⅓ to 2	5 to 10	15 to 20	Folex 6 EC: apply when fiber quality of top bolls will not be damaged by loss of top leaves, or when top bolls are firm to thumb pressure. Application can be made up until first frost.
Bottom defoliation			
1 to 1½		10 to 15	DEF 6: apply specified dosage (the rate should be proportional to the fraction of the plant to be defoliated) per acre with spray directed only to the lower part of the plant where mature bolls are found.
1 to 1½		10 to 15	Folex 6 EC: apply when bottom bolls are mature or when youngest bolls cannot be dented by pressure between the thumb and forefinger or cut through with a sharp knife. Direct spray to thoroughly cover the leaves on the desired portions of plants to be defoliated.
Rank cotton defoliation			
2½	5 to 10	15 to 25	DEF 6: Apply specified dosage per acre to give thorough coverage of leaves when 50% or more bolls are open. Total rate may be applied in one or two applications (2–6 weeks apart) either alone or in an approved tank mix. For LV/ULV applications, a maximum of 2 pints/A of DEF 6 per use season may be applied in not less than 1½ pints per acre of once-refined vegetable oil. Do not apply more than 2½ pints of DEF 6/A in any crop season.

Table 5, continued

Rate[a] (pints/acre)	Gallons water/acre Air	Ground	Directions
2½	5 to 10	15 to 25	Folex 6 EC: Apply when 50% or more of the bolls are open. Treatment can consist of two applications but the total cannot exceed 2½ pints/A. Applications can be made until first frost. Do not apply more than 2½ pints of Folex 6 EC/A in any crop year.
'Pima' cotton defoliation			
2 to 2½	5 to 10	15 to 25	DEF 6: apply specified dosage to mature cotton plants with 50% or more open bolls. For best results on 'Pima' cotton, use a tank mix combination with 0.2 to 0.4 lb Dropp 50WP/A when 60% or more of the bolls are open.
2 to 2½	5 to 10	15 to 25	Folex 6 EC: see directions for DEF 6.

[a] For DEF and Folex, 1 pint ≈ 0.75 pounds ≈ 0.34 kg.
(1 pint per acre ≈ 0.84 kilograms per hectare.)

From 1977 through 1991, the amount of DEF applied annually ranged from 1.34 lb/ac (1992) to 1.91 lb/ac (1981) (Table 2). All annual mean applications (rate per year) of DEF fell within the minimum and maximum amounts for both DEF and Folex (0.75–2.25 lb/ac) specified by the label (Table 5). During the same years, all annual mean applications of Folex except one fell within the range recommended by the label (Table 2). The minimum rate applied was 1.15 lb/ac in 1992; the maximum was 6.42 lb/ac in 1983. The rate for 1983, approximately three times the rate recommended by the label, was probably listed as such due to an error in data entry.

4. Potential phytotoxicity

Studies have not shown damage to non-target crops planted near sprayed cotton fields. One study found air concentrations varying from 1.1 ppb 30 m downwind from a field to 73 ppt 400 m downwind, with no injury to lettuce growing in an adjacent field (Oshima et al., 1980). In 1985, Mobay Chemical Corporation compared the drift potential of ultra low volume (ULV) and suspended concentrate (dilute) formulations, finding that both shifted downwind about one hundred feet (Joe Vandepeute, memorandum to Tobi Jones, CDFA, Oct 1, 1985). The dilute application could potentially drift and affect sorghum for 25.3 m and alfalfa for 12.2 m, but the ULV application posed little hazard to any crops.

C. Environmental fate

DEF's low vapor pressure of 1.7 x 10^{-6} mm Hg @ 20°C *(see Table 1, page 3)* indicates that following an application, aerosol particles remain close to the source (Seiber and Woodrow, 1983). While an application is in progress, air currents transport the vapor created by evaporating aerosol particles. Following an application, vapors may continue to volatilize from treated foliage or soil for several days or weeks and move downwind (Seiber and Woodrow, 1983). The presence of DEF in the atmosphere may also result from adsorption of DEF particles onto airborne dust. Because DEF is applied during warm weather, the atmosphere is thought to be a major sink for vaporized and volatilized DEF during and following application (Seiber et al., 1983). The disturbance of cotton plants and soil during harvest also discharges DEF into the atmosphere (Seiber et al., 1983).

Both vapor pressure and air temperature play roles in the volatilization or dissipation of DEF. As air temperature rises, vapor pressure also increases, leading to faster volatilization from sprayed surfaces, which causes DEF to be released into the atmosphere more readily.

1. Conversion to n-butyl disulfide and n-butyl mercaptan

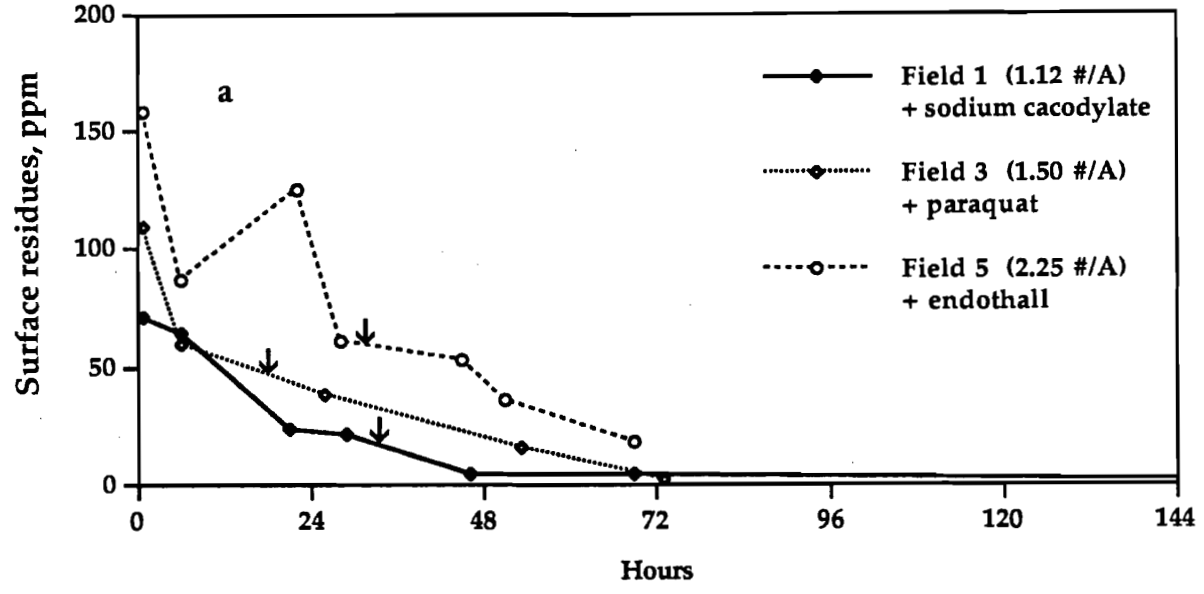
DEF is synthesized from the raw materials n-butyl mercaptan and phosphorus trichloride. These compounds react to form phosphorotrithioite, which is then air oxidized, yielding phosphorotrithioate (Monsanto Research Corp., 1977).

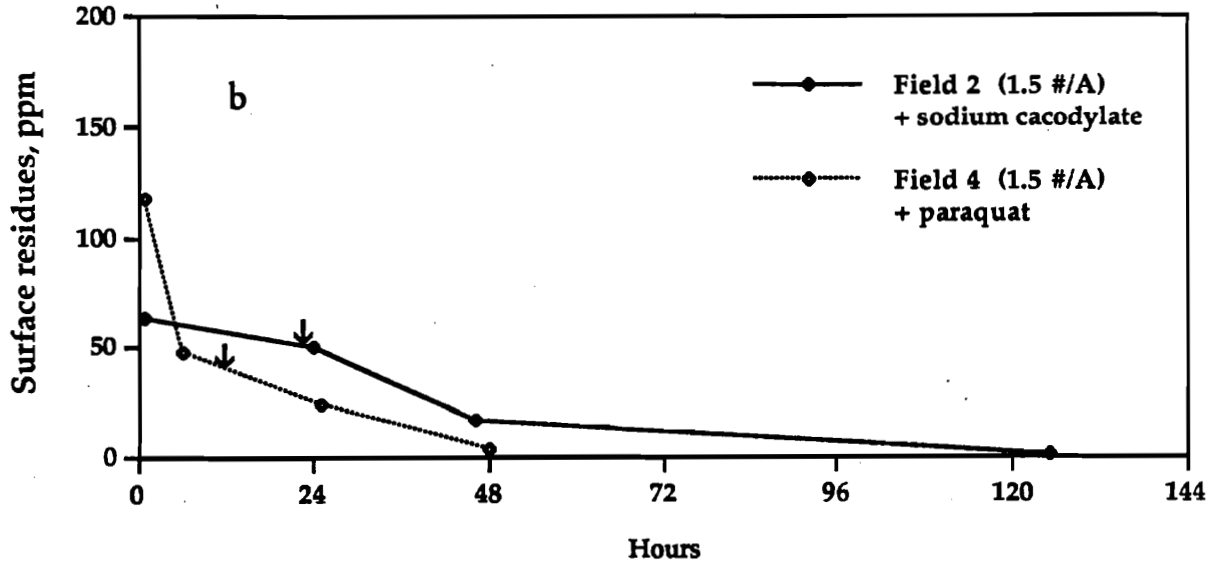
In a laboratory experiment, Hermann (1980) demonstrated the extent of photooxidation of phosphorotrithioite by exposing it to darkness and light. In the dark control phosphorotrithioite tank mixture, 8% of the phosphorotrithio*ite* was converted to phosphorotrithio*ate*, compared to 100% conversion when phosphorotrithioite was exposed to light. (Duration of this experiment was not mentioned.) When Hermann mixed phosphorotrithioite with water according to label directions and subjected it to light, the phosphorotrithioite photodegraded within 11 hours, yielding n-butyl mercaptan and n-butyl disulfide. Hermann also found that the level of mercaptan in a simulated phosphorotrithioite tank mix exposed to air increased from 0.08% to over 4.00%.

2. Persistence

According to Kilgore et al. (1984), airborne DEF residues from field applications dissipate rapidly once application is completed. Maddy et al. (1977) showed that at typical application rates for DEF and Folex (phosphorotrithioite) (1.0 to 2.5 lbs/A), over 60% of the material on foliar surfaces volatilized or degraded within 28 hours or less following application (Figure 2). All tank mixtures used in this study contained other defoliants, desiccants, and spreaders. Although the investigators applied DEF and Folex along with other active ingredients, these mixtures may give a more realistic picture of how DEF and Folex are actually used.

Figure 2. Surface (dislodgeable) residues of DEF (a) and Folex (b) from cotton leaves (Kern Co., 1975). Arrows (→) indicate the half-life for each combination of defoliant and desiccant. (From Maddy et al., 1977)





3. Effect of weather

Inversion layers often develop in the San Joaquin Valley when cool air traps warmer air below. In the southern San Joaquin Valley, inversions are common during September and October, when most DEF is applied (Seiber et al., 1983). Air quality problems also exist because fields are often surrounded by hills that limit air movement (Kilgore et al., 1984). Also, prevailing winds blow from the north, bringing air contaminants from the northern San Joaquin Valley south.

When defoliants are applied in the evening or night under calm atmospheric conditions, the vapors build up close to the ground and slowly disperse into the surrounding area (Seiber et al., 1983). According to the researchers, mercaptan odor would possibly be reduced by limiting applications to morning or early afternoon because morning breezes would disperse the mercaptan odor before it built up to an unpleasant level.

In one study by Kilgore et al. (1984), DEF was applied during a period of air temperatures averaging 24°C and wind speed ranged between 4 to 6 mph (1.8 to 2.7 m/s). DEF-contaminated particles and vaporized DEF were carried several kilometers from the original application site. The investigators propose that mild weather conditions (temperatures well below the average for that time of year) at the application site may have contributed to the diffusion of DEF-contaminated air masses toward warmer, more populated areas. *(See section D.2.e.—Kilgore et al., 1984, page 28.)*

D. Airborne levels reported in the literature

Many of the following studies quantifying airborne levels of DEF were set up as drift studies to document off-target movement of pesticide applications. Knowing how much DEF actually reaches the target may help to predict eventual volatilization of DEF and n-butyl mercaptan. Collecting and evaluating temperature, relative humidity, and wind speed and direction may also help predict distance and rate of travel from the target into non-target areas.

1. Airborne levels of DEF at site of and off-site downwind from the application (application monitoring)

a. Kilgore et al., 1984

Two cotton fields were monitored for DEF during aerial application periods using high volume (HiVol) air samplers set up 300 ft (91.5 m) downwind from the edge of the fields (Kilgore et al., 1984). (Note: The fields were located in Kern County, but dates of DEF application and sampling are not given.) The first study showed that DEF drifted at least 91.5 m downwind following treatment of a 106-acre field. After DEF was sprayed on the second field (240 A), almost three times more drift residue was collected by two collocated air samplers placed 91.5 m downwind. Most of the drift residue was found on the glass fiber filter of the sampling apparatus, the layer that the residue would contact before seeping into the XAD-4 resin. This suggests that the residue adhered to particulate matter, rather than

existing in a liquid or gaseous state. Concentrations of DEF residues on the filters were 3,200 ng/m^3 for the single sampler in the first field, and 6,500 and 6,000 ng/m^3 for the two samplers in the second field.

The researchers estimated that half or less of the spray material reached the cotton plants. Mylar sheets placed at the edges of both fields showed similar amounts of deposition, as did the sheets placed downwind from both fields at 91.5 m. The researchers estimate that one-tenth to one-half of the sprayed DEF missed the cotton plants and reached the ground.

b. Oshima et al., 1980

Oshima et al. (1980) assessed at- and off-site post-application movement of DEF in Fresno County following aerial applications of DEF on September 17 and Folex on October 1, 1979. Fallout samplers (XAD-4 resin-filled glass jars and glass fiber filters) to measure field coverage were placed at positions surrounding the application area, and high volume (HiVol) samplers operating at a flow of 0.93 m^3/min to measure DEF concentration placed at two downwind vectors. An analysis of variance was performed on the data to evaluate the effect of distance of the HiVol samplers from the application area (0 m, 30 m, 200 m, and 400 m) and fallout medium (glass fiber fallout filters and fallout jars) on DEF concentration. The investigators monitored DEF during the application and several hours after the application was completed. They also recorded air temperature, relative humidity, barometric pressure, and wind speed and direction using a Weather Measure mobile weather station.

The background level of DEF at the first site (September 17) was 606 ng/m^3. The investigators subtracted this value from subsequent levels of DEF (Table 6). The average wind direction during application was from the west, and following application, southeast. HiVol samplers were placed south of the field, and fallout samplers to the south and west. The resin fallout jars collected significantly more DEF than the glass fiber filters. Results from the drift design using two downwind vectors of four samplers per vector indicated that there was a significant DEF drift downwind of the applied field. Fallout levels ranged from 14,500 ng/m^3 30 m downwind to 953 ng/m^3 400 m downwind. Post-application monitoring at six to eight hours showed low levels of DEF (1 ng/m^3); samples collected on the field one day after application showed much higher concentrations (1,137 ng/m^3 at 30 h). Because only average values for wind direction are presented here (west at time of application, southeast following application), and HiVol samplers were placed south of the field, collection of DEF may not have been entirely representative. The north-south direction of the aerial swath may have also resulted in drift away from the sampling location. In the San Joaquin Valley, prevailing winds are usually from the north (the assumption for this study), with east–west winds also common; to accommodate variability in wind direction and local air currents, air samplers should be placed at all four directions of the field.

Table 6. Airborne levels of DEF at site and off-site downwind of application. (From Oshima et al., 1980).

Time after application, hr (day)	Position of sampler[a]	Concentration of DEF, ng/m^3	Comments
Sept. 17, 1979			
Background[b]	F	606.0	Aerial application (272 kg DEF), 8:46–10:46 AM;
0	F	trace	remaining samples collected for two-hour durations.
6	F	≈ 1.0	No temperature or relative humidity data. Average
	200 m	≈ 1.0	wind speed during application = 1.25 m/s; Min/max
	400 m	≈ 1.0	wind speed = 0.89–1.81 m/s. Wind direction: following
24 (1)	F	761.0	application = 114.4° (SE); average = 250.0° (W).
30	F	1,137.0	
Oct. 1, 1979			
Background[b]	F	missing	Aerial application (286 kg Folex), 11:00 AM–2:10 PM;
0	F	trace	remaining samples collected for two-hour durations.
4	F	4,020.0	All Folex converted to DEF before analysis. Average
	45 m	1,750.0	temperature during application = 31.0°C; RH = 27.3%;
	210 m	691.0	average wind speed = 4.08 m/s; Min/max wind speed =
	350 m	635.0	2.69–5.39 m/s. Wind direction: following applica-
23	F	1,085.0	tion = 345.6° (N); average = 294.6° (NW).

[a] F = samplers located in field; other samplers located downwind.
[b] Background levels for 10/17/79 eliminated from subsequent calculated drift levels. No background data for 10/1/79 because of equipment malfunction; data are relative to the unknown background level and cannot be compared directly with data of other sites or studies.

For the October 1, 1979 Folex (phosphorotrithioite) study, background levels of DEF or Folex were not determined due to an equipment malfunction. During the monitoring period, the average temperature was 31°C and relative humidity was 27.3%. Following application, Folex immediately oxidized to DEF (phosphorotrithioate). Drift levels ranged from 3,180 ng/m^3 downwind to 433 ng/m^3 350 m downwind. Four hours after application, 4,020 ng/m^3 DEF was collected within the field; 635 ng/m^3 was collected 350 m downwind. The researchers suggest that this off-site level appears to be present as the normal background level in cotton-growing areas in Fresno County during September and October.

c. Hermann, 1980

Hermann (1980) monitored two fields in Kings County for DEF (299 ac; Devil's Den; October 12, 1978) and Folex (phosphorotrithioite) (148 ac; Southlake/Tulare Lake Basin; November 1, 1978) (Tables 7a and 7b). Low volume (LoVol) samplers monitored concentrations of DEF, n-butyl disulfide, and n-butyl mercaptan at approximately 30 L/min in and adjacent to the application sites; HiVol (1 m^3/min) samplers were positioned at upwind sites and at further distances downwind, and moved at different sampling times according to wind conditions.

In the Devil's Den study, most DEF and n-butyl mercaptan were collected downwind by the HiVol samplers immediately following application. Levels of n-butyl mercaptan higher than trace amounts were recovered by the LoVol samplers at 24 h (upwind) and 96 h (downwind) following application. In the Southlake/Tulare Lake Basin study, most n-butyl mercaptan was collected two hours after application by the HiVol samplers placed 10 m downwind. The LoVol samplers positioned at both the upper and lower field also collected n-butyl mercaptan 24 h following application.

Originally, the investigators intended to monitor residue levels before, during, and following the application with the downwind samplers, while monitoring the background levels with the upwind samplers. Because wind direction constantly shifted and multidirectional eddies often blew through the fields, positioning of samplers did not always correspond with actual wind direction. To correct for shifts in the wind direction, the investigators developed the Effective Sampling Volume (ESV), which represents the volume of air processed by the sampler while downwind from the field. *(For a thorough explanation of downwind flux and the ESV, see Appendix 3.)*

Table 7a. Airborne levels of DEF, n-butyl mercaptan, and n-butyl disulfide collected following application of DEF (Devil's Den (Kings County); application — October 12, 1978). (From Hermann, 1980)

Time after application, hr (day)	Position of sampler[a]	Concentration[b] of DEF (ng/m^3)	Concentration of n-butyl disulfide (ng/m^3)	Concentration of n-butyl mercaptan (ng/m^3)
HiVol samplers				
0	50 m NW	1,189.0	2.2	14.5
0	50 m S	115.0	0.2	1.8
0	350 m SW	1,243.0	0.5	4.2
4	50 m NW	575.0	2.2	14.9
4	350 m SW	174.0	tr	tr
16	50 m NW	4.0	0.7	4.8
16	350 m N	70.0	0.1	1.0
24 (1)	50 m NW	450.0	0.5	3.5
24	350 m N	10.0	2.5	27.0
24	350 m SW	2.0	0.0	0.0
42	50 m NW	167.0	0.4	3.0
42	350 m N	160.0	0.0	0.0
42	350 m SW	37.0	tr	tr
48 (2)	50 m NW	13.0	0.0	0.0
48	350 m N	8.0	0.0	0.0
48	350 m SW	0.3	tr	tr
66	50 m NW	44.0	0.0	0.0
66	350 m N	12.0	tr	tr
66	350 m SW	37.0	tr	tr
72 (3)	50 m NW	24.0	0.0	0.0
72	350 m SW	30.0	0.0	0.0
90	50 m NW	0.1	tr	tr
90	350 m SW	12.0	0.0	0.0
96 (4)	350 m N	30.0	tr	tr
LoVol samplers				
0	10 m NW	1,019.0	tr	tr
0	100 m N	19.0	tr	tr
0	250 m E	187.0	tr	tr
4	10 m NW	711.0	tr	tr
4	100 m N	387.0	tr	tr
4	250 m E	264.0	1.5	20.0
16	100 m N	59.0	0.0	0.0
16	250 m E	77.0	0.0	0.0

(continued on next page)

Table 7a, continued

Time after application, hr (day)	Position of sampler[a]	Concentration[b] of DEF (ng/m^3)	Concentration of n-butyl disulfide (ng/m^3)	Concentration of n-butyl mercaptan (ng/m^3)
LoVol samplers (continued)				
24 (1)	10 m NW	483.0	0.0	0.0
24	100 m N	75.0	0.6	167.0
24	250 m E	41.0	0.0	0.0
24	5 m SW	337.0	tr	tr
42	10 m NW	368.0	0.0	0.0
42	100 m N	341.0	0.0	0.0
42	250 m E	21.0	0.0	0.0
42	5 m SW	20.0	0.0	0.0
48 (2)	10 m NW	96.0	0.0	0.0
48	100 m N	tr	0.0	0.0
48	250 m E	tr	0.0	0.0
66	10 m NW	59.0	0.0	0.0
66	250 m E	165.0	0.0	0.0
66	5 m SW	260.0	0.8	•
72 (3)	100 m N	76.0	tr	•
72	250 m E	136.0	0.0	0.0
72	5 m SW	69.0	0.0	0.0
90	10 m NW	•	tr	tr
90	250 m E	36.0	0.0	0.0
90	5 m SW	19.0	0.0	0.0
96 (4)	10 m NW	546.0	0.0	0.0
96	100 m N	21.0	0.0	•
96	250 m E	8.0	0.0	0.0
96	5 m SW	118.0	0.1	72.0

[a] Maximum wind speed = 0.19 m/s; wind direction = N and E.

[b] tr = trace (> 0.05 ng/m^3, < 0.1 ng/m^3); • = sample not taken or lost during extraction

Table 7b. Airborne levels of DEF[a], n-butyl mercaptan, and butyl disulfide collected following application of Folex (phosphorotrithioite) (Tulare Lake Basin, Southlake (Kings County); application — November 1, 1978). (From Hermann, 1980)

Time after application, hr (day)	Position of sampler[b]	Concentration[c] of DEF (ng/m^3)	Concentration of n-butyl disulfide (ng/m^3)	Concentration of n-butyl mercaptan (ng/m^3)
HiVol samplers				
0	10 m S	1,321.0	0.0	27.5
0	50 m N	457.0	0.0	10.1
0	804 m var.	182.0	0.0	1.6
0	804 m var.	201.0	0.0	0.0
2	10 m S	1,047.0	2.7	1,576.0
2	50 m N	34.0	0.0	12.2
2	804 m var.	4.0	0.0	1.5
2	804 m var.	4.0	0.0	0.0
18	10 m S	67.0	0.4	0.8
18	50 m N	22.0	•	1.6
18	804 m var.	12.0	0.0	tr
18	804 m var.	3.0	0.0	0.0
24 (1)	10 m S	•	•	•
24	50 m N	•	•	•
24	804 m var.	•	•	tr
24	804 m var.	•	•	0.0
42	10 m S	•	•	•
42	50 m N	54.0	0.4	1.5
42	804 m var.	16.0	0.0	1.4
42	804 m var.	•	•	1.2
48 (2)	10 m S	47.0	0.0	1.0
48	50 m N	157.0	0.0	•
48	804 m var.	40.0	0.0	2.0
48	804 m var.	33.0	0.0	•
66	10 m S	63.0	0.0	1.0
66	50 m N	190.0	0.0	3.6
66	804 m var.	2.0	0.0	0.0
66	804 m var.	2.0	0.0	0.0
72 (3)	10 m S	•	•	•
72	50 m N	46.0	0.0	0.0
72	804 m var.	8.0	0.0	0.0
72	804 m var.	39.0	0.0	0.0
90	10 m S	171.0	0.0	0.8
90	50 m N	86.0	0.0	0.0
90	804 m var.	56.0	0.0	0.0
90	804 m var.	41.0	0.0	0.0

(continued on next page)

Table 7b, continued

Time after application, hr (day)	Position of sampler[b]	Concentration[c] of DEF (ng/m^3)	Concentration of n-butyl disulfide (ng/m^3)	Concentration of n-butyl mercaptan (ng/m^3)
HiVol samplers (continued)				
96 (4)	10 m S	30.0	0.0	0.0
96	50 m N	26.0	0.0	0.0
96	804 m var.	9.0	0.0	0.0
96	804 m var.	•	•	0.0
LoVol samplers				
0	5 m S	•	•	•
0	10 m N	669.0	0.0	tr
0	10 m W	6,080.0	tr	•
0	upper field	•	•	•
0	lower field	•	•	•
2	5 m S	•	•	•
2	10 m N	258.0	0.0	tr
2	10 m W	•	•	•
2	upper field	•	•	•
2	lower field	•	•	•
18	5 m S	1,019.0	tr	tr
18	10 m N	19.0	tr	tr
18	10 m W	•	•	•
18	upper field	•	•	•
18	lower field	•	•	•
24 (1)	5 m S	•	•	•
24	10 m N	•	•	•
24	10 m W	•	•	•
24	upper field	602.0	•	32.0
24	lower field	411.0	tr	36.1
42	5 m S	208.0	tr	•
42	10 m N	421.0	0.0	tr
42	10 m W	•	•	•
42	upper field	•	•	•
42	lower field	•	•	•
48 (2)	5 m S	•	•	•
48	10 m N	•	•	•
48	10 m W	•	•	•
48	upper field	253.0	tr	•
48	lower field	110.0	0.0	0.0

(continued on next page)

Table 7b, continued

Time after application, hr (day)	Position of sampler[b]	Concentration[c] of DEF (ng/m^3)	Concentration of n-butyl disulfide (ng/m^3)	Concentration of n-butyl mercaptan (ng/m^3)
LoVol samplers (continued)				
66	5 m S	130.0	0.0	•
66	10 m N	•	•	•
66	10 m W	•	•	•
66	upper field	•	•	0.0
66	lower field	•	•	•
72 (3)	5 m S	18.0	0.0	•
72	10 m N	•	•	•
72	10 m W	•	•	•
72	upper field	160.0	0.0	tr
72	lower field	151.0	0.0	0.0
90	5 m S	135.0	0.0	•
90	10 m N	123.0	0.0	0.0
90	10 m W	•	•	•
90	upper field	301.0	0.0	0.0
90	lower field	5,497.0	tr	tr
96 (4)	5 m S	780.0	0.0	•
96	10 m N	18.0	0.0	0.0
96	10 m W	•	•	•
96	upper field	131.0	0.0	0.0
96	lower field	108.0	0.0	0.0

[a] Folex oxidizes to DEF when exposed to air and light.

[b] Maximum wind speed = 0.19 m/s; wind direction = N and E

[c] tr = trace (> 0.05 ng/m^3, < 0.1 ng/m^3); • = sample not taken or lost during extraction

2. Ambient airborne levels of DEF

The following summaries focus on airborne levels of DEF in communities close to the application area. Section III (page 31) describes a study on ambient airborne levels of DEF in the southern San Joaquin Valley. This study was contracted to investigators at the University of California, Davis by the Air Resources Board to monitor ambient airborne levels of DEF to fulfill the mandate of AB 1807.

a. Stanley et al., 1971

In one of the earliest detailed studies to assess levels of pesticides in ambient air, DEF was detected in Stoneville, Mississippi, one of nine urban and rural sites monitored throughout the United States (Stanley et al., 1971). The investigators studied aerosol and vapor phases of 19 specific pesticides—16 chlorinated hydrocarbons and three organophosphates. Although DEF was not on the original list of pesticides, it was detected at the rural Stoneville site in 12 of 98 samples at an average concentration of 16.0 ng/m^3. Monitoring in Stoneville extended for two weeks per month for six months (May through October, 1967) during expected pesticide spraying and periods of rainfall. The investigators correlated the highest concentrations of pesticides with reported spraying and the lowest concentrations with several days of rain. Records of spraying and rainfall were not available in Stoneville for the weeks of October 2 and October 16, when the samples of DEF were collected. DEF was not detected at the two urban sites monitored in California, Fresno and Riverside, although the investigators did not specify the dates of monitoring, and air samples may not have been collected during the cotton defoliation season.

b. Arthur et al., 1976

Arthur et al. (1976) also examined ambient airborne pesticide levels around Stoneville, Mississippi. Weekly air samples were taken from 1972 to 1974 using a MISCO model 88 air pesticide sampler collecting 7 m^3 air per week for approximately 12 h/wk for a total of 156 weeks. The investigators detected 13 chlorinated hydrocarbons and six organophosphates. DEF was detected only during the months of September and October, at a maximum level of 16.0 ng/m^3 (year unspecified).

Table 8. Concentrations of DEF (parts per trillion)[a] and n-butyl mercaptan (μg silver) collected in the San Joaquin Valley October–November, 1980. Dashes (—) indicate no sample taken; bullets (•) indicate sampling period extended for two or more twelve-hour periods. (Data from CDFA executive summary of 1980 DEF and n-butyl mercaptan monitoring study, 1981.)

Location	Dos Palos (Merced Co.)		Mendota (Madera Co.)		Lemoore (Kings Co.)		Coalinga (Fresno Co.)	
Assay	DEF	silver	DEF	silver	DEF	silver	DEF	silver
Oct 1 PM	0.001	—	0.013	100	0.018	120	0.015	140
Oct 2 AM	0.001	100	0.002	170	0.002	—	0.000	68
Oct 2 PM	0.002	650	0.020	130	—	270	—	260
Oct 3 AM	0.000	140	0.006	180	0.001	340	0.001	150
Oct 3 PM	0.003	170	0.024	—	—	230	0.001	490
Oct 4 AM	—	170	—	260	0.002	240	0.000	260
Oct 4 PM	0.002	190	0.034	230	0.013	340	0.001	—
Oct 5 AM	0.001	48	0.003	240	0.015	56	0.000	380
Oct 5 PM	0.001	140	0.004	72	0.014	140	0.000	96
Oct 6 AM	0.004	220	0.004	220	0.007	160	0.001	—
Oct 6 PM	0.003	620	0.003	430	—	240	—	250
Oct 7 AM	0.004	65	0.003	110	—	57	—	32
Oct 7 PM	0.005	77	0.021	94	0.014	140	0.000	130
Oct 8 AM	0.002	90	0.003	30	0.002	130	0.000	30
Oct 8 PM	0.003	23	—	160	0.019	•	—	•
Oct 9 AM	0.001	•	0.003	•	0.018	95	0.001	45
Oct 9 PM	0.003	29	0.019	42	0.008	•	0.001	•
Oct 10 AM	0.001	•	0.002	•	0.010	25	0.001	34
Oct 10 PM	0.001	—	0.000	130	0.012	•	0.001	•
Oct 11 AM	0.001	—	0.004	•	0.003	130	0.000	130
Oct 11 PM	0.003	—	0.008	•	0.014	16	0.002	110
Oct 12 AM	0.001	44	0.002	28	0.006	•	0.001	•
Oct 12 PM	0.002	•	0.011	•	0.008	•	0.000	•
Oct 13 AM	0.003	130	0.006	37	0.025	230	0.000	48
Oct 13 PM	0.001	•	0.009	•	0.009	•	0.001	•
Oct 14 AM	0.000	95	0.002	200	0.001	150	0.000	130
Oct 14 PM	0.002	•	0.008	•	0.007	•	0.000	•
Oct 15 AM	0.001	170	0.002	47	0.002	130	0.000	40
Oct 15 PM	0.002	43	0.004	72	0.007	•	0.000	•
Oct 16 AM	0.001	•	0.001	•	0.002	140	0.000	180
Oct 16 PM	0.000	60	0.001	100	0.003	•	0.001	•

(continued on next page)

Table 8, continued

Location	Dos Palos (Merced Co.)		Mendota (Madera Co.)		Lemoore (Kings Co.)		Coalinga (Fresno Co.)	
Assay	DEF	silver	DEF	silver	DEF	silver	DEF	silver
Oct 17 AM	0.001	•	0.002	•	0.001	40	0.000	21
Oct 17 PM	0.002	55	0.004	70	0.004	•	0.000	•
Oct 18 AM	0.001	•	0.005	•	0.002	38	0.001	25
Oct 18 PM	0.002	—	0.005	60	0.006	•	0.001	•
Oct 19 AM	0.001	—	0.001	•	0.001	—	0.000	—
Oct 19 PM	0.001	—	0.004	•	—	—	0.000	—
Oct 20 AM	0.002	—	0.005	—	0.001	—	0.000	—
Oct 20 PM	0.002	—	0.004	—	0.002	—	0.000	—
Oct 21 AM	0.001	—	0.002	41	0.001	31	0.000	39
Oct 21 PM	0.002	33	0.001	•	0.004	•	0.000	•
Oct 22 AM	0.001	45	0.002	46	0.002	55	0.003	41
Oct 22 PM	0.003	•	0.004	•	0.003	•	0.001	•
Oct 23 AM	0.001	—	0.001	210	0.001	120	0.000	93
Oct 23 PM	0.003	180	0.003	•	0.003	•	0.001	•
Oct 24 AM	0.002	12	0.002	17	0.001	22	0.000	110
Oct 24 PM	0.002	•	0.009	•	0.005	•	0.000	•
Oct 25 AM	0.000	180	0.004	140	0.002	110	0.000	140
Oct 25 PM	0.000	•	0.000	•	—	•	—	—
Oct 26 AM	0.000	12	0.001	—	0.001	100	0.000	19
Oct 26 PM	0.001	—	0.002	—	0.001	•	0.000	•
Oct 27 AM	0.000	30	0.001	68	0.001	83	0.000	140
Oct 27 PM	0.001	•	0.002	•	0.001	•	0.001	•
Oct 28 AM	0.000	—	0.000	42	0.000	80	0.000	—
Oct 28 PM	0.000	—	0.001	•	0.001	•	0.000	—
Oct 29 AM	0.000	—	0.000	—	0.000	140	0.000	51
Oct 29 PM	0.001	—	0.002	—	0.001	•	0.000	•
Oct 30 AM	0.001	69	0.000	—	0.000	110	0.000	98
Oct 30 PM	0.000	•	0.001	—	0.001	•	0.000	•
Oct 31 AM	0.000	80	0.000	100	0.000	—	0.000	210
Oct 31 PM	0.000	•	0.001	•	0.001	—	0.000	•
Nov 1 AM	—	140	0.001	130	0.000	16	0.000	—
Nov 1 PM	—	—	0.001	•	0.000	•	0.000	—
Nov 2 AM	0.000	46	0.000	88	0.000	120	0.000	190

[a] DEF concentrations averaged over the 12-hr collection period.

c. CDFA, 1981

In 1980, the Environmental Hazards Assessment Program of CDFA (now of DPR) monitored DEF and n-butyl mercaptan at Coalinga (Fresno County), Dos Palos (Merced County), Lemoore (Kings County), and Mendota (Madera County) in the San Joaquin Valley to determine airborne levels during the defoliation season. At each of the sites, investigators set up permanent monitoring equipment (HiVol samplers and silver-precipitating bubblers), and a mobile laboratory (gas chromatograph calibrated for n-butyl mercaptan) designed to rotate among the four towns (Table 8). During the cotton defoliation season (October 1 to November 2, 1980), air monitors at the permanent sites sampled continuously every 12 hours, and the mobile lab sampled air hourly. At each location, an experimental bubbler system extrapolated the quantity of available sulfur (provided from a source of sulfur, such as n-butyl mercaptan) by measuring any silver/sulfur salt precipitate. The investigators recorded aerial applications of DEF and Folex (phosphorotrithioite) adjacent to Mendota, but all applications within a one-mile radius of the other monitoring sites were made by ground.

DEF was collected by the HiVol samplers at each of the permanent monitoring sites: levels averaged for 12-hour increments ranged from zero to 0.034 ppt (Table 8). The highest values were recorded in Mendota. Precipitated silver was found in the bubbler systems at all four permanent sites.

The investigators assumed that the sulfur source was n-butyl mercaptan, but levels of precipitated silver did not correlate well with instantaneous readings from the gas chromatograph from the mobile laboratory, where readings were specific for n-butyl mercaptan (Table 9). At these latter sites, only 29/480 (≈ 6%) of all samples resulted in positive readings for n-butyl mercaptan, ranging from 0.29 ppb to 9.93 ppb. Most of the samples were collected on three days out of 33 total days of sampling, although sampling rotated among sites.

Table 9. Positive n-butyl mercaptan concentrations sampled by gas chromatography in the San Joaquin Valley October–November, 1980. (Data from CDFA executive summary of 1980 DEF and n-butyl mercaptan monitoring study, 1981.)

Location	Date (1980)	Time	ppb of n-butyl mercaptan[a]	μg/m³
Coalinga (Fresno Co.)	Oct. 3	2230	5.86	23.6
Dos Palos (Merced Co.)	Oct. 4	0501	1.39	5.6
		2200	1.12	4.5
	Oct. 5	2400	0.74	3.0
		0200	0.42	1.7
		0400	0.29	1.2
		1120	1.06	4.3
		1300	0.99	4.0
		1410	0.42	1.7
		1530	0.42	1.7
		1700	1.06	4.3
	Oct. 26	1400	1.79	7.2
	Oct. 29	0915	3.92	15.8
		1001	7.45	30.0
		1100	6.45	26.0
		1157	8.94	36.0
		1447	5.86	23.6
		1746	9.93	99.3
Lemoore (Kings Co.)	Oct. 7	0100	0.42	1.7
		0500	3.58	14.4
	Oct. 8	0100	0.59	2.4
		0258	0.42	1.7
		0507	0.42	1.7
Mendota (Madera Co.)	Oct. 23	1040	4.87	19.6
		1140	9.70	39.0
		1240	7.45	30.0
		1340	4.17	16.8
		1550	1.98	8.0
		1715	5.36	21.6

[a] Instantaneous values at time of measurement averaged over 12-hour collection period.

Despite sensitive tests to detect DEF and n-butyl mercaptan, the CDFA/EHAP study may have overlooked potential short-term exposure levels. Although the gas chromatographic readings from the mobile laboratory were specific for levels of n-butyl mercaptan, these results may be uncharacteristic of short-term exposure because the time of defoliant application, the relative distance to sprayed fields, and meteorological data were not recorded. The investigators conclude that a study is needed that documents actual short-term exposure values from a sprayed cotton field.

d. Oshima et al., 1980

In 1979, airborne levels of DEF were monitored at two schools: one in Mendota (Madera County) from September 25 to October 23, and one in Dos Palos (Merced County) from October 1 to October 23 (Oshima et al., 1980). The investigators collected samples using LoVol samplers, and used a Meloy Industries Total Sulfur Analyzer to detect gas-phase sulfur compounds. DEF was not detected in samples collected at either school during the entire monitoring period. The Meloy analyzer recorded spikes of sulfur-containing compounds, but because these readings were not compound-specific, actual levels of DEF or its breakdown products could not be inferred. The investigators advise that including a chromatographic column to separate compounds is necessary for positive detection of n-butyl disulfide or n-butyl mercaptan.

e. Kilgore et al., 1984

Ten rural and urban sites in Kern County (Delano, Wasco, Shafter, Lerdo Prison, Taft, Arvin, and east, south, west, and central Bakersfield) were monitored for DEF from September to November, 1979 (Table 10). High-volume samples were taken twice daily for three-hour periods at times of maximum wind speed (7 AM–10 AM and 4 PM–7 PM). The investigators collected four sets of morning and evening samples at all ten sites: 1) background (mid-September), 2) peak application (early October), 3) one week following peak application (mid-October), and 4) several weeks following peak application (early November). The actual application dates were not specified, but the investigators assumed peak application occurred during early October.

Background samples showed no residues of DEF, except for low quantities detected at Delano and Shafter, which were linked to early trial applications by two growers in northwestern Kern County. Gas chromatographic analysis of sampler glass fiber filters and XAD-4 resin did not suggest other pre-application sources of DEF. During peak application, DEF was detected at all sites. Samples collected one week later contained lower concentrations of DEF, except for those from Shafter where the evening sampler filter concentration was 87.4 ng/m^3, but had been detectable at 2.7 ng/m^3 (the minimum concentration recorded) during peak application. Several weeks following peak application, only one sample taken from Taft showed detectable DEF residues (2.7 ng/m^3).

Table 10. Concentrations of DEF (ng/m^3) collected in the San Joaquin Valley (Kern County), October –November, 1979. Bullets (•) indicate no DEF detected.[a] (Data from Kilgore et al., 1984.)

		Application period			
Sampling site	Sampling time/type[bc]	Pre-application	During application	1 week after application	Several weeks after application
Delano	AM/F	3.6	4.5	11.6	•
	AM/R	•	10.7	•	•
	PM/F	•	24.1	5.6	•
	PM/R	•	16.1	•	•
Wasco	AM/F	•	45.5	16.1	•
	AM/R	•	4.5	5.4	•
	PM/F	•	17.8	14.3	•
	PM/R	•	•	•	•
Shafter	AM/F	•	7.1	22.3	•
	AM/R	5.4	42.8	6.2	•
	PM/F	•	2.7	87.4	•
	PM/R	•	16.9	15.2	•
Lerdo Prison	AM/F	•	19.6	π[d]	•
	AM/R	•	16.1	π	•
	PM/F	•	51.7	π	•
	PM/R	•	5.4	π	•
Taft	AM/F	•	3.6	10.7	•
	AM/R	•	3.6	•	2.7
	PM/F	*f*[d]	8.0	25.9	•
	PM/R	*f*	3.6	•	•
Arvin	AM/F	•	3.6	§[d]	•
	AM/R	•	3.6	§	•
	PM/F	•	4.5	7.1	•
	PM/R	•	12.5	3.6	•
Bakersfield east area	AM/F	•	25.0	16.1	•
	AM/R	•	14.3	•	•
	PM/F	•	7.1	2.7	•
	PM/R	•	3.6	•	•
Bakersfield central area	AM/F	•	5.4	9.8	•
	AM/R	•	36.6	12.5	•
	PM/F	•	12.5	2.7	•
	PM/R	•	•	3.6	•

Table 10, continued

Sampling site	Sampling time/type[bc]	Application period: Pre-application	During application	1 week after application	Several weeks after application
Bakersfield south area	AM/F	•	48.2	23.2	•
	AM/R	•	6.2	19.6	•
	PM/F	•	2.7	7.1	•
	PM/R	•	•	•	•
Bakersfield west area	AM/F	•	22.3	18.7	•
	AM/R	•	6.2	6.2	•
	PM/F	•	2.7	4.5	•
	PM/R	•	•	•	•

[a] Limit of detectability = 300 ng or 2.7 ng/m^3

[b] Sampling times: 7 AM–10 AM and 4 PM–7 PM; part of air sampler analyzed: F = glass fiber filter, R = XAD-4 resin

[c] Pre-application period = mid-September; during application = early October, and post application = late October to early November. (These dates are estimated from text describing the experimental set up.)

[d] π = interfering peak; *f* = air sampler malfunction; § = sample lost

For most samples collected during and following peak application, DEF concentrations recovered on filters were approximately twice those on the resin, indicating that DEF was adsorbed to particulates 0.3 µm or larger in size. Throughout the sampling period the filters accumulated dust created by farming activity, which, according to the investigators, did not interfere with recovery of DEF residues. During peak application, DEF was detected on all filters and 6 out of 10 evening resin samples at all sites. One week later, filter concentrations of DEF were highest in Shafter, Wasco, and Taft, while DEF was not detected on many resin samples. In the Bakersfield area, filter and resin concentrations were lower, and were generally higher in the morning. Evening samples in Shafter and Taft showed slightly higher concentrations than did morning samples. During harvest approximately 20 days later, airborne DEF concentrations were undetectable.

Air temperatures during the sampling period averaged 75°F (24°C) and wind speed ranged between 4 to 6 mph (1.8 to 2.7 m/s). Despite relatively mild weather conditions, DEF-contaminated particulates and DEF vapor dispersed several kilometers from the application site to residential areas.

III. DOCUMENTATION OF AIRBORNE LEVELS: AMBIENT AIR MONITORING OF DEF

A. Southern San Joaquin Valley Study, August 31 to November 4, 1987

Investigators in the Department of Environmental Toxicology at the University of California, Davis (UCD) monitored ambient airborne levels of DEF in the southern San Joaquin Valley from August 31 to November 4, 1987, during the recorded period of peak application (Seiber et al., 1988). Records on DEF applications to nearby cotton fields were not kept. Mean 24-hour values for the study period at each of six sites ranged from below the minimum detection limit (MDL) of 1.1 ng/m^3 (0.1 ppt) to a maximum of 340.0 ng/m^3 (26.4 ppt or 0.026 ppb) at the University of California West Side Research and Extension Center in Five Points (Fresno County). The overall mean of all 24-hour samples positive for DEF collected at this site was 110.0 ng/m^3 (8.7 ppt).

1. Introduction

On November 4, 1986, CDFA requested that the Air Resources Board (ARB) monitor ambient airborne levels of DEF to fulfill the mandate of AB 1807. ARB staff met with representatives of the Fresno County Agricultural Commissioner's Office on July 15, 1987 regarding DEF use and sampling locations. On August 3, plans were submitted by UCD, with whom ARB contracted for DEF sampling, and by ARB for DEF analysis. Sampling of five Fresno County sites continued four days each week from August 31 to November 4, 1987 to coincide with peak application time based on historical use. UCD submitted the DEF draft report in March 1988 and the final report in November.

2. Methods

Four rural sites in Fresno County were selected for air monitoring: Tranquility Fire Department, Tranquility; San Joaquin School, San Joaquin; UC West Side Research and Extension Center, Five Points; and Huron Day Care Center, Huron. To serve as background sampling sites the investigators chose two urban ARB monitoring sites in Fresno (Fresno County) and Bakersfield (Kern County).

The Tranquility site, surrounded on three sides by cotton fields, provided a potential high-exposure situation. Although the other rural sites were situated near cotton fields (San Joaquin and the West Side field station within 25 m, Huron approximately 402 m), no information on the distance of the monitoring sites to actual DEF applications existed. Each of the rural monitoring sites was sampled at a distance of less than one-half mile (≈ 804.5 m), or within the regulated application buffer zone. For logistical reasons, airborne DEF was not concurrently monitored at nearby application sites; the investigators suggest evaluation of data from the application studies of Hermann, 1980; Oshima et al., 1980; and Wilson et al., 1980. The sampling method used in this study does not discriminate between DEF and Folex

(S,S,S-tributyl phosphorotrithioite), but because Folex oxidizes rapidly in air and on XAD-4 resin to form DEF, a separate method was unnecessary.

Samplers were connected to high-volume air sampling pumps by 1-cm diameter Tygon™ tubing. Each sampler consisted of a 4-cm by 12-cm Teflon™ cup connected to latex tubing. To set up the apparatus, the investigators rinsed each sampling tube with acetone, charged each with 30 mL of XAD-4 resin, and turned on the pump. They measured air flow with a calibrated flow meter by attaching the meter to the open end of each sampler. Starting time for the sampling period was noted and the air flow of the sampler measured in liters per minute (L/m). They again noted air flow once sampling was completed, and averaged beginning and ending flows for the 24-hour period. When sampling was completed, the resin was transferred to bottles with Teflon-lined lids, labeled, and placed on dry ice until transported to UC Davis, where they were kept at –20°C. Samples delivered to ARB were also kept on dry ice.

Before beginning field sampling, the investigators established that the maximum sampling period without breakthrough was 24 h with a flow rate of 65 L/m, although approximately half of the field samples were collected at rates higher than that. The investigators collected three replicates at Five Points, and two at the other sites. At each site, one of the replicates was designated the primary sample, and the other sample (or samples at Five Points) considered replicates.

3. Results and discussion

Tables 11a and 11b show the ambient air concentrations for the rural sites (Tranquility, San Joaquin, Five Points, and Huron) in ng/m^3 and ppt, respectively. Because of the variations in flow rates, the minimum detection limit (MDL) ranged from 0.78 ng/m^3 (0.06 ppt) to 3.00 ng/m^3 (0.24 ppt), with an average of 1.10 ng/m^3 (0.09 ppt).

Table 12 shows ambient air concentrations for the urban sites, Fresno and Bakersfield. Fresno was sampled a total of 19 days and Bakersfield 17 days; DEF was detected on only four and two days, respectively.

Table 11a. Ambient air concentrations of DEF (ng/m^3) collected at four rural sites in Fresno County, California, August 31 to November 4, 1987.[a]

Date	Tranquility		San Joaquin		Five Points			Huron	
	A	B	A	B	A	B	C	A	B
Aug. 31	L[b]	8.4	22.4	17.5	20.6	20.9	20.8	13.1	14.7
Sept. 1	7.0	8.4	16.0	16.6	10.8	12.7	14.5	17.8	16.8
Sept. 2	13.0	11.1	M[c]	M	9.3	10.4	11.3	7.6	9.9
Sept. 3	5.0	4.3	7.6	5.6	3.2	2.4	2.4	4.7	4.9
Sept. 8	3.7	2.7	15.1	17.9	21.6	23.2	9.8	1.1	1.2
Sept. 9	<[d]	<	1.6	1.7	1.8	1.8	1.8	12.9	11.6
Sept. 10	<	<	<	<	110.0	117.0	175.0	9.9	7.4
Sept. 14	3.8	6.9	4.4	4.5	248.0	204.0	203.0	61.4	61.6
Sept. 15	10.0	9.8	14.5	13.3	64.2	68.5	79.0	52.7	56.6
Sept. 16	10.0	9.8	23.6	20.4	23.3	22.6	35.1	13.7	16.9
Sept. 17	13.7	10.0	20.7	16.7	16.9	18.6	15.3	14.2	14.7
Sept. 21	61.1	90.5	<	27.8	107.0	139.0	110.0	3.0	<
Sept. 22	64.8	74.7	M	M	111.0	129.0	135.0	13.1	16.9
Sept. 23	52.7	60.6	79.3	68.8	290.0	271.0	238.0	42.9	41.8
Sept. 24	120.0	75.9	84.2	49.6	358.0	375.0	287.0	102.0	119.0
Sept. 28	59.0	51.1	26.7	40.2	N[e]	N	N	36.2	49.6
Sept. 29	131.0	155.0	M	M	208.0	168.0	229.0	25.1	29.8
Sept. 30	158.0	157.0	158.0	190.0	271.0	236.0	312.0	41.3	53.6
Oct. 1	193.0	219.0	N	N	244.0	312.0	294.0	46.2	54.9
Oct. 5	157.0	184.0	244.0	149.0	69.1	118.0	71.9	7.5	6.3
Oct. 6	116.0	136.0	N	N	143.0	153.0	N	35.5	27.0
Oct. 7	111.0	147.0	71.4	82.2	135.0	116.0	141.0	93.4	94.0
Oct. 8	152.0	150.0	79.7	70.8	226.0	209.0	197.0	41.3	49.3
Oct. 12	203.0	198.0	105.0	128.0	294.0	271.0	326.0	52.0	49.2
Oct. 13	135.0	L	80.2	65.2	78.7	80.4	74.7	67.5	69.2
Oct. 14	147.0	133.0	68.4	65.6	46.5	55.5	62.9	6.7	7.1
Oct. 15	79.4	82.2	14.4	13.6	37.5	27.8	27.3	3.2	2.3
Oct. 19	82.1	90.0	89.4	70.6	38.7	51.9	43.9	8.5	7.8
Oct. 20	61.8	62.4	35.1	42.8	78.7	75.3	72.4	14.0	20.8
Oct. 21	49.0	60.3	15.0	9.0	M	M	M	2.0	2.0
Oct. 26	4.1	2.8	<	<	21.8	39.9	29.2	5.2	5.5
Oct. 27	46.7	51.0	35.0	36.1	54.6	41.5	47.2	6.6	4.7
Nov. 2	23.1	28.9	20.5	19.8	N	N	N	4.0	2.8
Nov. 3	18.9	23.8	M	M	N	N	N	N	N
Nov. 4	N	N	N	N	N	N	N	—[f]	—

[a] Data from Seiber et al., 1988. Final report to the Air Resources Board: pilot analysis of DEF in air. (A, B, and C [Five Points only] refer to replicated samples.)

[b] L indicates that sample was lost.

[c] M indicates equipment malfunction.

[d] < indicates concentration is below the average minimum detection limit (MDL) of 1.1 ng/m^3.

[e] N indicates that sample was collected but not analyzed.

[f] Dash (—) indicates no sample taken.

Table 11b. Ambient air concentrations of DEF (ppt) collected at four rural sites in Fresno County, California, August 31 to November 4, 1987.

Date	Tranquility		San Joaquin		Five Points			Huron	
	A	B	A	B	A	B	C	A	B
Aug. 31	L	0.6	1.8	1.4	1.6	1.6	1.6	1.0	1.1
Sept. 1	0.5	0.6	1.2	1.3	0.8	1.0	1.1	1.4	1.3
Sept. 2	1.0	0.9	M	M	0.7	0.8	0.9	0.6	0.8
Sept. 3	0.4	0.3	0.6	0.4	0.4	0.2	0.2	0.4	0.4
Sept. 8	0.3	0.2	1.2	1.4	1.7	1.8	0.8	0.1	0.1
Sept. 9	<	<	0.1	0.1	0.1	0.1	0.4	1.0	0.9
Sept. 10	<	<	<	<	8.6	9.2	13.7	0.8	0.6
Sept. 14	0.3	0.5	0.3	0.4	19.3	15.9	15.8	4.8	4.8
Sept. 15	0.8	0.8	1.1	1.0	5.0	5.3	6.2	4.1	4.4
Sept. 16	0.8	0.8	1.3	1.6	1.8	1.8	2.7	1.1	1.3
Sept. 17	1.1	0.8	1.6	1.3	1.3	1.4	1.2	1.1	1.2
Sept. 21	4.8	7.0	<	2.2	8.3	10.9	8.6	0.2	>
Sept. 22	5.0	5.8	M	M	8.7	10.1	10.5	1.0	1.3
Sept. 23	4.1	4.7	6.2	5.4	22.6	21.1	18.5	3.3	3.2
Sept. 24	9.4	5.9	6.6	3.9	27.8	29.2	22.3	8.0	9.3
Sept. 28	4.6	4.0	2.1	3.1	N	N	N	2.8	3.9
Sept. 29	10.2	12.1	M	M	16.2	13.1	17.8	2.0	2.3
Sept. 30	12.3	12.2	12.3	12.2	21.1	18.4	24.3	3.2	4.2
Oct. 1	15.0	17.1	N	N	19.1	24.4	23.0	3.6	4.3
Oct. 5	12.3	14.4	19.1	11.6	5.4	9.2	5.6	0.6	0.5
Oct. 6	9.0	10.6	N	N	11.2	12.0	N	2.8	2.1
Oct. 7	8.7	11.5	5.6	6.4	10.5	9.1	10.0	7.3	7.3
Oct. 8	11.9	11.8	6.2	5.5	17.6	16.3	15.3	3.2	3.8
Oct. 12	15.8	15.4	8.2	10.0	22.9	21.2	25.4	4.0	3.8
Oct. 13	10.5	L	L	L	6.1	6.3	5.8	5.3	5.4
Oct. 14	11.5	10.3	5.3	5.1	3.6	4.3	4.9	0.5	0.6
Oct. 15	6.2	6.4	1.1	1.1	2.9	2.2	2.1	0.2	0.2
Oct. 19	6.4	7.0	7.0	5.5	3.0	4.0	3.4	0.7	0.6
Oct. 20	4.8	4.9	2.7	3.3	6.1	5.9	5.6	1.1	1.6
Oct. 21	3.8	4.7	1.2	0.7	M	M	M	0.2	0.2
Oct. 26	0.3	0.2	<	<	1.7	3.1	2.2	0.4	0.4
Oct. 27	3.6	4.0	2.7	2.8	4.2	3.2	3.7	0.5	0.4
Nov. 2	1.8	2.2	1.6	1.5	N	N	N	0.3	0.2
Nov. 3	1.5	1.8	M	M	N	N	N	N	N
Nov. 4	N	N	N	N	N	N	N	—	—

[a] Data from Seiber et al., 1988. Final report to the Air Resources Board: pilot analysis of DEF in air. (A, B, and C [Five Points only] refer to replicated samples.)

[b] L indicates that sample was lost.

[c] M indicates equipment malfunction.

[d] < indicates concentration is below the average minimum detection limit (MDL) of 0.09 ppt.

[e] N indicates that sample was collected but not analyzed.

[f] Dash (—) indicates no sample taken.

Table 12. Ambient air concentrations of DEF collected in Fresno (Fresno County) and Bakersfield (Kern County), California, September 3 to October 27, 1987.[a]

Date	Fresno (ng/m^3)		Bakersfield (ng/m^3)		Fresno (ppt)		Bakersfield (ppt)	
	A	B	A	B	A	B	A	B
Sept. 3	<[b]	<	—[c]	—	<	<	—	—
Sept. 8	<	<	<	<	<	<	<	<
Sept. 9	<	<	<	<	<	<	<	<
Sept. 10	<	<	<	<	<	<	<	<
Sept. 14	<	<	<	<	<	<	<	<
Sept. 15	<	<	—	—	<	<	—	—
Sept. 16	<	<	<	<	<	<	<	<
Sept. 21	<	<	<	<	<	<	<	<
Sept. 22	<	<	—	—	<	<	—	—
Sept. 23	—	—	1.4	5.6	—	—	0.1	0.4
Sept. 28	<	<	<	<	<	<	<	<
Sept. 29	—	—	9.7	14.0	—	—	0.8	1.1
Oct. 1	6.3	4.5	—	—	0.5	0.4	—	—
Oct. 5	—	—	<	<	—	—	<	<
Oct. 7	4.7	2.4	<	<	0.4	0.2	<	<
Oct. 8	3.6	3.6	—	—	0.3	0.3	—	—
Oct. 13	<	<	<	<	<	<	<	<
Oct. 14	<	<	<	<	<	<	<	<
Oct. 15	<	<	—	—	<	<	—	—
Oct. 19	<	<	<	<	<	<	<	<
Oct. 20	2.7	1.8	—	—	0.2	0.1	—	—
Oct. 21	<	<	<	<	<	<	<	<
Oct. 26	—	—	<	<	—	—	<	<
Oct. 27	—	—	<	<	—	—	<	<

[a] Data from Seiber et al., 1988. Final report to the Air Resources Board: pilot analysis of DEF in air. (A and B refer to replicated samples.)

[b] < indicates concentration is below the average minimum detection limit (MDL) (1.1 ng/m^3 or 0.09 ppt).

[c] Dash (—) indicates no sample taken.

Table 13 summarizes the field samples collected, totaling 161 primary samples and 190 replicates (352 samples total). Equipment malfunctions prevented collection of data at Five Points (October 21) and San Joaquin (September 2, 22, 29). For each 24-hour period, all samplers malfunctioned: all three at Five Points, and both at San Joaquin. At Tranquility, one out of two samples were lost during collection on August 31 and October 13. Samples were collected but not analyzed by the laboratory at Huron (November 3), Five Points (September 28, November 2, November 4), San Joaquin (October 1, October 6, November 4), and Tranquility (November 4). Sampling became difficult during the first week of November due to rain; most of the scheduled sampling periods were not completed.

Table 13. Summary of ambient air concentrations of DEF for samples collected August 31–November 4, 1987 (southern San Joaquin Valley).

	Maximum positive conc.[a] (ppt)	Second highest positive conc. (ppt)	Average of all samples[b] (ppt ± SE)	Average of all samples[b] (ng/m^3 ± SE)	Total number samples analyzed[c]	Number (percentage) above MDL (%)
Tranquility	16.0	15.6	5.4 ± 0.86	69.7 ± 11.02	66	62 (94%)
San Joaquin	15.4	13.6	3.6 ± 0.74	46.0 ± 9.47	56	51 (91%)
Five Points	26.4	23.4	8.4 ± 1.44	107.3 ± 18.41	92	89 (97%)
Huron	8.6	7.3	2.1 ± 0.38	27.2 ± 4.85	66	65 (98%)
Fresno	0.4	0.3	0.1 ± 0.03	0.7 ± 0.36	38	8 (20%)
Bakersfield	0.9	0.3	1.0 ± 0.80	0.1 ± 0.10	34	4 (13%)
					Σ = 352	279 79.3%

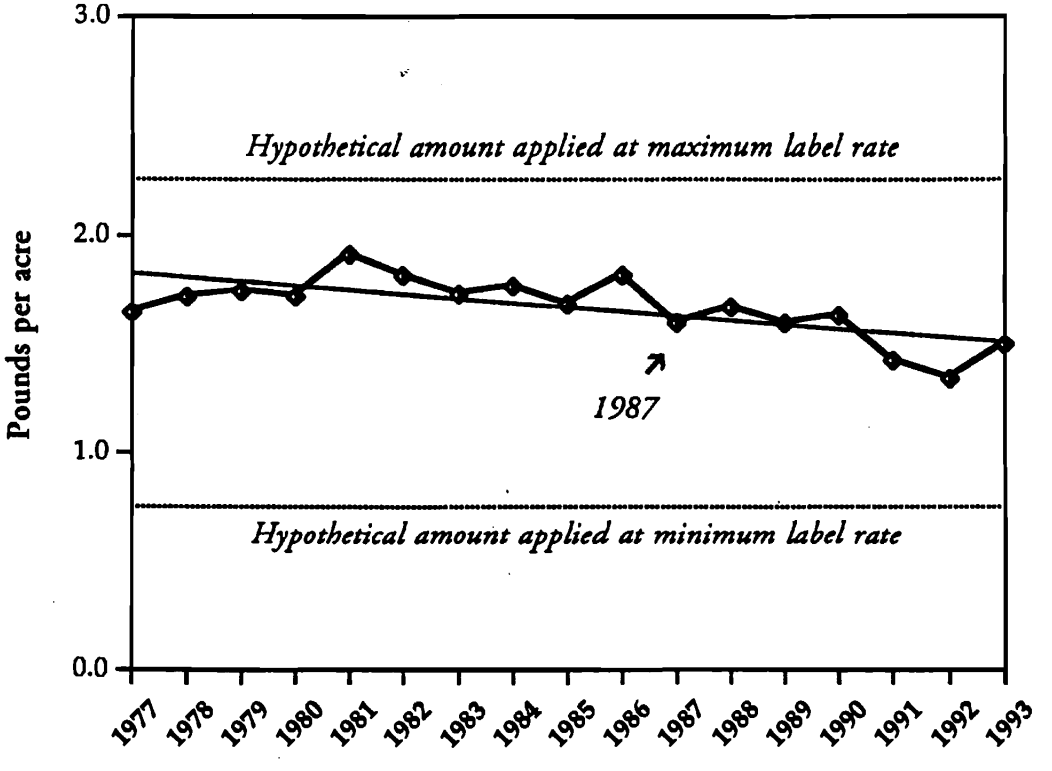
[a] Determined from three (Five Points) or two (all other sites) collated replicates.

[b] MDL = Minimum detection limit (0.09 ppt) based on 100 ng detection limit per sample and an average total air volume of 88.3 m^3.

[c] Number of primary samples for each site: Tranquility = 33, San Joaquin = 28, Five Points = 31, Huron = 33, Fresno = 19, and Bakersfield = 17. (Total primary samples = 161; total replicates = 191; total samples = 352.)

Figure 3 shows the year-by-year rate of DEF applied and acreage covered based on annual use reports. This figure is included to 1) verify that reported rates have consistently fallen within specified minimum and maximum label rates since at least 1977, and 2) show that 1987—the year of the contracted ambient monitoring—was about average for the rate of DEF applied. However, air concentrations reported in monitored sites may have been higher or lower than normal.

Figure 3. Use of DEF (pounds per acre) for California, 1977–1993. Note use of DEF in 1987.



B. Methods of analysis

1. Study of DEF trapping efficiency

The investigators completed a trapping efficiency study before the field sampling began. Glass tube inlets to air sampling cups containing 30 mL of XAD-4 resin were spiked with 10 µg of DEF. Samplers ran for 24 h with a total air volume of 76 m^3. Two experiments of three replicates each were run. The glass tube was rinsed with ethyl acetate and analyzed for DEF along with the glass wool and resin.

The UCD investigators analyzed the samples spiked during the trapping efficiency study. Resin samples were extracted three times with 45 mL of ethyl acetate, which was concentrated using rotary and nitrogen evaporators. Samples were analyzed by gas chromatography using a Varian 2100 with an alkali-flame ionization detector and 1.83 m x 0.32 cm packed column. The column packing consisted of 1.5% SP 2250 and 1.95% SP 2401 liquid phase on 100/120 mesh SupelcoPort. Flow rates for the hydrogen, air, and nitrogen carrier gases were 40, 250, and 28 mL/min, respectively. Temperatures for the injector, detector, and column were 230, 230, and 200°C, respectively.

Averages (in micrograms) with standard deviations (S.D.) and trapping efficiency are given below in Table 14. Backup resin was also run during Experiment Two to check for breakthrough. DEF was detected in only one of three replicate backup traps (0.11 µg).

Table 14. Trapping efficiency of DEF in 24-hour spikes.

Expt	Spike Level (µg)	Found ($\bar{x} \pm$ S.D.)			Percent Trapped
		Glass Tube	Glass Wool	Resin	
1	10	1.10 ± 0.805	0.060 ± 0.011	5.47 ± 0.874	62%
2	10	0.644 ± 0.147	0.042 ± 0.016	5.74 ± 0.653	62%

2. Sampling precision

The investigators calculated precision using the following equation:

$$P = \frac{Y - \frac{(Y + X)}{2}}{X} \times 100$$

where P is the calculated data precision, Y is the concentration from the duplicate sampler of the collocated pair, and X is the concentration from the primary sampler of the collocated pair. Precision for the data ranged from –26% to +43%. Note that the formula conventionally used is:

$$P = \frac{|Y - X|}{\frac{(X + Y)}{2}} \times 100$$

Completeness for the entire data set was greater than 90% for the ambient samples, based on the number of valid samples analyzed, divided by the total number of samples taken.

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Appendix 1 — Equations Used for Conversions

1. ng/m^3

$$ng/m^3 = \frac{\text{amount of pesticide (ng)}}{[\text{flow rate (L/min)}]\ [\text{sampling period (min)}]/1000\ L/m^3}$$

2. $ng/m^3 \rightarrow ppt$

(Use PV = nRT)

$$n = \frac{PV}{RT}$$

$$ng/m^3 = \frac{ppt \times 314.52}{24.5}$$

314.52 is the molecular weight of DEF and 24.5 is the volume in liters at 25°C and 760 mm Hg (one atmosphere).

$$n = \frac{1\ atm \cdot 1000\ L}{0.082\ L \cdot atm\ /\ mole \cdot K}$$

$$n = 40.65\ \text{moles air}/m^3\ @\ 27°C\ (80°F)$$

$$\frac{\text{ng DEF}}{\text{mw DEF}} = \text{ng moles DEF}$$

$$\frac{\text{ng moles DEF}}{\text{n(moles air)}} = \text{ppt DEF}$$

$$= \frac{\text{ng DEF}/m^3/\text{mw of DEF}}{\text{moles air}} \qquad = \frac{\text{ng DEF}/m^3/314.52\ g/mole}{40.65\ \text{moles air}/m^3}$$

$$= \frac{\text{ng DEF}/m^3}{40.65 \times 314.52} \qquad = \frac{\text{ng DEF}/m^3}{12785.238} = ppb$$

$$1\ ppt = \frac{\text{ng DEF}/m^3}{\frac{12785.238}{1000}} = 12.785\ ng/m^3$$

Note: The 12.785 conversion factor assumes an average temperature during the sampling period of 300 K (27°C or 80°F). When average temperatures were not provided, any values expressed in ng/m^3 were converted to ppt using 12.785. When values were expressed both in ng/m^3 and ppt, we extrapolated average temperatures to check for seasonal consistency. The relationship between temperature and the ng/m^3-to-ppt conversion factor is shown below in Figure A1. Conversion factors were used to convert data expressed in ng/m^3 to ppt when average temperatures were reported.

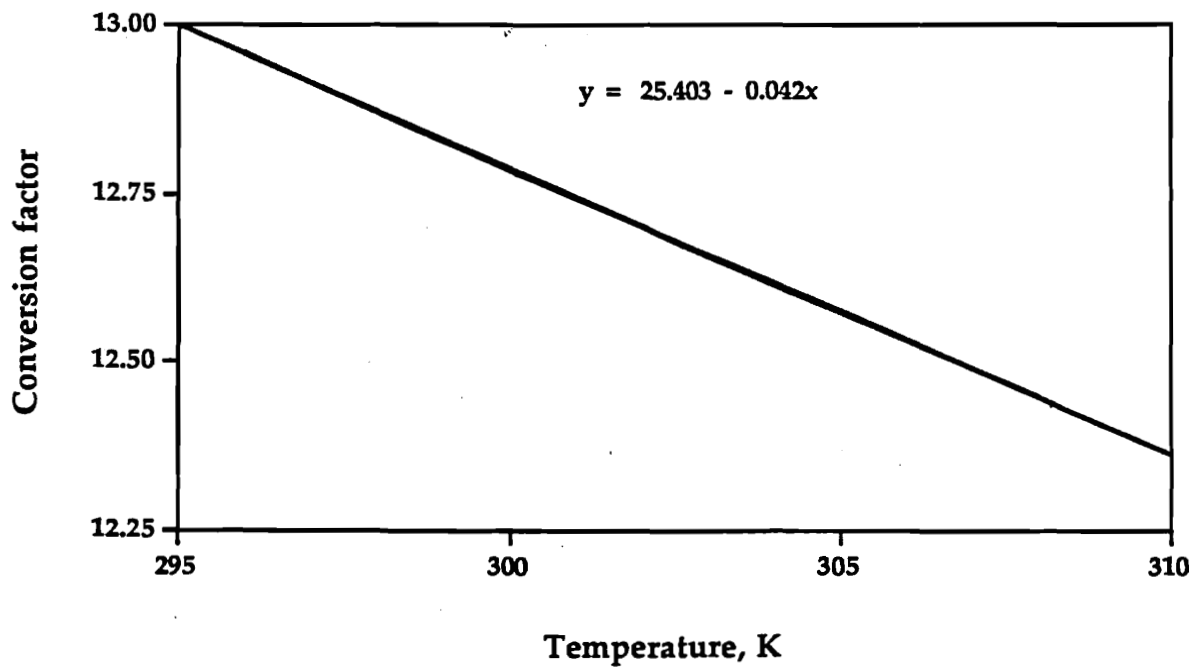


Figure A1. The relationship between temperature and the ng/m^3-to-parts per trillion conversion factor; 12.785 is the conversion factor at 300 K.

Appendix 2 — Standard Operating Procedure for the Determination of DEF in Ambient Air: ARB Method NLS019

1. Scope

This document describes a method for the analysis of DEF at concentrations normally found in ambient air. The method was developed from procedures tested by the California Department of Food and Agriculture and the University of California Davis Department of Environmental Toxicology.

2. Summary of Method

After sampling, the exposed XAD-4 sorbant is extracted in duplicate with 50 mL portions of ethyl acetate. The resulting extract is concentrated to a volume of 5.0 mL. Two microliters are injected into a gas chromatographic system equipped with a 12-meter DB–1 fused silica capillary column, N-P thermionic detector (TSD), and data system. The resulting peak is identified by characteristic retention time and quantitated in reference to external standards. The identity of the compound can be confirmed by use of a column of different characteristics, a detector of different selectivity, or by GC/MS.

3. Interferences/Limitations

3.1 *For sampling, see Section III. Documentation Of Airborne Levels, page 25.*

3.2 Compounds responding to the TSD detector and having similar GC retention times may interfere, causing misidentification or erroneous quantification.

3.3 All samples received by the laboratory are placed immediately in a freezer operating at –4°C or lower. Samples are not stored longer than two weeks before analysis to prevent degradation.

4. Apparatus

4.1 Varian Model 3400 Gas Chromatographic system equipped with a thermionic detector (TSD), split/splitless capillary injector, and Model 402 data system.

4.2 DB–1 fused silica capillary column, 12 m x 0.25 mm i.d., 0.5 mm film thickness.

4.3 Erlenmeyer flasks, 250 mL, with ground glass stoppers.

4.4 Sample agitating table with holders for 250-mL flasks.

4.5 Explosion-proof hot plate with continuously adjustable heating controls.

5. Reagents and Chemicals

5.1 Ethyl acetate, pesticide grade. CAUTION: THIS SOLVENT IS VERY VOLATILE AND VERY FLAMMABLE. DO NOT EXPOSE TO OPEN FLAME OR HEAT SOURCES!

5.2 Stock Standard: Commercially available certified solution of 1000 µg/mL in methanol (Nanogens, Inc.).

5.3 Calibration Standards: Dilute 100 µL, 40 µL, and 10 µL of the Stock Standard into 100 mL of ethyl acetate. This corresponds to 1.0, 0.4, and 0.1 µg/mL, respectively.

5.4 Control Standard: Dilute 200 µL of the Stock Standard into 10.0 mL ethyl acetate. This corresponds to 20 µg/mL, or 50 µL = 1.0 µg.

6. Instrument Conditions

Column: 12 m x 0.25 mm i.d. DB-1 fused silica capillary

Temperatures:

Injector	250°C
Detector	300°C
Oven	50°C, initial; hold for 1 min; ramp at 50°C/min to 150°C; hold 4 min; ramp at 8°C/min to 220°C; hold for 4 min.
Flow rates	Carrier: helium, 30 cc/min at splitter; 0.8 min splitless hold; 25 cm/s carrier velocity
Detector	TSD-Range 11, Attenuation x 1

7. Instrument Calibration Procedure

7.1 Before proceeding with the instrument calibration, a solvent blank must be analyzed. Inject 2.0 µL of blank solvent. If the analysis indicates interferences or contamination, the solvent must be replaced and the problem solved.

7.2 A method blank must be analyzed for every 12 samples analyzed. Select 30 cc of unused XAD-4 and carry the sorbant through the entire extraction and analysis process. If interferences are noted, the source must be found and eliminated.

7.3 Instrument calibration is performed by the injection of 2.0 µL of the 1.0 µg/mL standard. The resulting chromatogram is used to calibrate the retention time and response factor of DEF under the conditions of the analysis. Additional standards (0.4 and 0.1 µg/mL) are then analyzed to demonstrate method linearity and precision. This calibration procedure must be performed for every 12 samples analyzed.

7.4 To ensure that the procedure is in statistical control, a matrix spike (control sample) must be analyzed with each batch of samples. Thirty mL of XAD-4 is spiked with 50 mL of the control standard and carried through the entire procedure. The results of this analysis must fall within the upper and lower warning limits of the method. If the results continue to fall outside the proscribed limits, the method must be discontinued and the problem solved.

8. Analysis of Samples

8.1 Remove the exposed XAD-4 resin from the sample container, place the resin in a 250-mL stoppered Erlenmeyer flask, rinse the sample container either 50 mL ethyl

acetate, and add to the flask. Place the flask on a shaker table and agitate for 45 minutes. After extraction, let the resin settle and filter the supernatant through glass wool into a clean concentrator flask. Add an additional 50 mL ethyl acetate to the resin, re-extract, and add entire contents to the filter funnel. After the extract has drained into the concentrator, rinse the extraction flask with 20 mL of solvent and add to the filtered resin. Let drain completely.

8.2 Add a Teflon boiling chip to the concentrator flask and evaporate the solvent to approximately 1 mL. CAUTION: ETHYL ACETATE IS VERY FLAMMABLE. USE A FUME HOOD AND EXTREME CARE! With careful rinsing, dilute the extract to 5.0 mL with solvent. Place the extract in properly labeled amber screw-capped vial and store for analysis.

8.3 Inject 2.0 µL of each extract into the chromatographic system for analysis. Record all pertinent information in the instrument analysis book and on the resulting chromatograms.

8.4 The results are recorded in micrograms per sample and are calculated as follows:

Micrograms (µg) = µg/mL (found) x 5 mL (sample volume)

9. **Method sensitivity**

The method sensitivity is shown in Table A1. The data were generated using standards. Note that the MDL is presented in µg/mL and in µg/sample assuming a final extract volume of 5.0 µL.

10. **Desorption Efficiency and Sample Stability**

The sorbant used by the UCD personnel for sampling was spiked with 2.0 and 1.0 µg of DEF and analyzed according to the above procedure. The average recovery was found to be 92% with a variation of 8.5%. Two portions of sorbant were spiked with 1.0 µg DEF and stored at –4°C for 2 weeks. The sorbant was then analyzed with an average recovery of 96%.

Table A1. DEF calibration curve.

Conc, mg/mL	Area count x 10^4	Relative S.D., %
2.00	14.36	4.1 (n = 5)
1.00	7.460	6.3 (n = 4)
0.40	2.630	5.2 (n = 5)
0.08	0.454	5.0 (n = 5)
0.04	0.199	6.7 (n = 5)

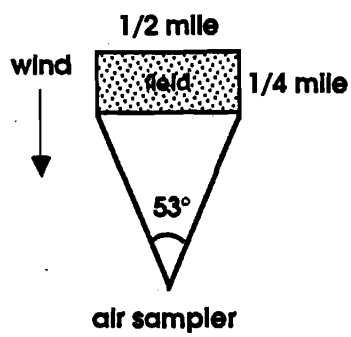
Linear Regression Analysis Data (see Table A1, page A5)

Correlation coefficient = 0.9996
Intercept = -0.11×10^4 counts (0.015 μg/mL)
Slope = 7.29×10^4 counts/μg/mL DEF
Minimum detection limit = intercept + 3(RSDX intercept)
= 0.02 μg/mL or 0.1 μg/sample

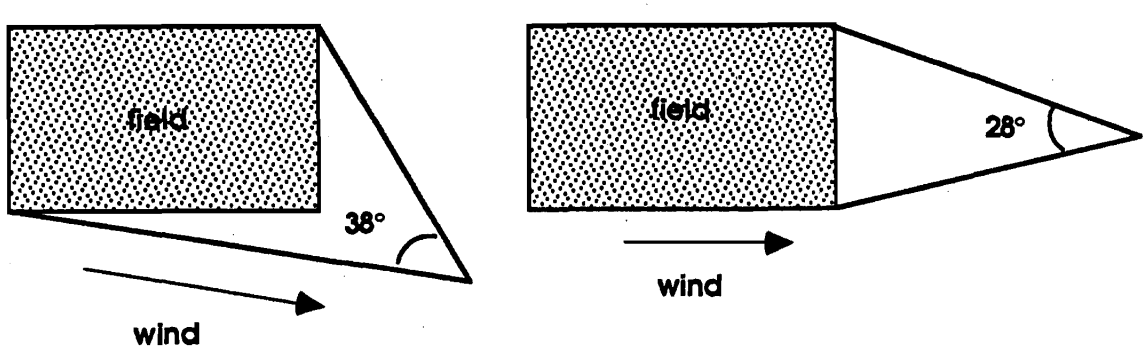
Appendix 3—Calculating wind direction according to the downwind flux

When sampling a field for airborne pesticide levels, wind speed and direction are important meteorological considerations. In an idealized experiment, downwind samplers monitor pesticide levels before, during, and following an application; upwind samplers monitor background levels. Shifting wind direction is typical of most fields; the wind often blows unpredictably, and upwind samplers may periodically sample downwind and vice versa.

Hermann and Seiber (1979) corrected wind speed and direction for ½-mile downwind sampling stations by developing the Effective Sampling Value (ESV), the actual volume of the air processed by the sampler while downwind from the field. The ESV is calculated by multiplying the actual time the wind blows within a specific angle (defined by the field's geometry) by the sampling rate. For example, a typical half-mile station might include all wind within a 53° arc.



Rather than placing the air sampler directly north or south of the field, it would be placed along the half-mile edge of the field appearing to be downwind during the sampling interval. The downwind angle would change in response to the placement of the sampler.



The geometry of the monitored fields also complicate measurements. While monitoring two cotton fields for DEF, Hermann and Seiber (1979) found that samplers placed directly

south or north measured air traveling over 1/4 mile of treated cotton plants, but when placed directly east or west, this distance increased to 1/2 mile. So, even though the downwind angle was less for the east–west samplers, the amount of cotton plants within their downwind angle was equal to that of the north–south downwind angle.

To reconcile this problem, the investigators used an average downwind angle (40°) for all placements of the air samplers. They used a somewhat smaller ESV for the N–S stations, and a slightly larger ESV for the E–W stations, which helped eliminate the concentration differences in the samples due to field geometry.

To calculate the downwind flux, the sample concentration is divided by wind speed in m/min, since wind speed is directly proportional to the sample volume. For example, a 10 m/min wind creates a sample volume half as large as a 20 m/min wind. By dividing by the wind speed, the sample volume is eliminated as a variable, allowing calculation of the amount of chemical that passes through a m^2 area of air each minute (= the downwind flux).

The formula for downwind flux is:

$$\underset{\textit{total sample}}{\mu g} \times \underset{\textit{inverse sample volume}}{\frac{1}{m^3}} \times \underset{\textit{wind speed}}{\frac{m}{min}} = \underset{\textit{downward flux}}{\frac{\mu g}{m^2\ min}}$$

Table A2. Downwind flux of DEF on cotton leaves. (Hermann & Seiber, 1979)

Day	Sample (µg)	ESV, m^3	µg/m^3	wind speed, m/min	downwind flux, µg/m^2 · min	leaf residues (ppm, dry)
0	13.80	15.75	0.87	51.76	45.13	——
1	1.37	59.25	0.23	32.19	7.44	208.7
2	4.81	56.62	0.08	13.41	1.14	139.5
3	0.94	2.26	0.42	2.68	1.11	124.6
4	1.72	69.15	0.02	59.01	1.47	138.3

Table A2 uses data of DEF collected from a Folex (phosphorotrithioite) application site at Tulare Lake Basin, Southlake (Kings County) *(see Table 7b, page 20)*. Folex was applied November 1, 1978, and the researchers monitored concentrations of DEF, n-butyl disulfide, and n-butyl mercaptan in and adjacent to the application sites using HiVol and LoVol samplers. (Folex oxidizes to DEF—more than half converts to DEF in the spray tank before

dispersal—and subsequently to the two other breakdown products.) To compensate for changing wind speed and direction, the data were transformed using the equation for downwind flux. According to Table A2, the amount of defoliant drifting from the treated area declined rapidly from the day of application (Day 0) onward. The concentration (in $\mu g/m^3$) on Day 0 was twice that of Day 3. Immediately following application, concentration combined volatilization and drift during spray. However, downwind flux was almost 50 times greater during application than on Day 3. This demonstrates how accounting for wind speed and direction can change the way chemicals are measured.