Volatilization of *S*-Ethyl *N*,*N*-Dipropylthiocarbamate from Water and Wet Soil during and after Flood Irrigation of an Alfalfa Field

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The herbicide *S*-ethyl *N*,*N*-dipropylthiocarbamate (EPTC) was applied to alfalfa in irrigation water. The actual vapor loss rate was assessed using an aerodynamic technique to estimate the EPTC vapor flux from the field during and after 2.19 ppm EPTC was applied by flood irrigation. The EPTC vapor flux 59.5 cm above the field varied from 37 to 259 g ha^{-1} h^{-1} while surface water was present. The EPTC vapor flux values measured over wet soil after irrigation ranged from 2 to 103 g ha^{-1} h^{-1} and was highest at night. Of the 3.04 kg ha^{-1} EPTC applied, 7.0% was removed in tailwater runoff and 73.6% volatilized during the 52 hours of observation. This indicates that using surface irrigation water to apply EPTC to alfalfa is an inefficient method.

Measurement of loss of field applied pesticides by volatilization into the atmosphere has been an active area of agricultural research since Willis et al. (1971, 1972) first measured concentrations of pesticides in the air above treated soil plots. Actual vapor flux densities were measured above plots and fields of bare soil and corn (Caro et al., 1971; Parmele et al., 1972; Taylor et al., 1976), soybeans (Harper et al., 1976; White et al., 1977), and orchard grass (Taylor et al., 1977). These studies were recently summarized and evaluated by Taylor (1978).

In 1977, Soderquist et al. reported finding the thiolcarbamate herbicide molinate in the air above a flooded rice field and speculated that loss by volatilization from field water was "the major route of dissipation".

Applying *S*-ethyl *N*,*N*-dipropylthiocarbamate (EPTC) to alfalfa in flood-irrigation water (called herbigation) is often the preferred application method in California's Imperial Valley. Alfalfa is irrigated about 25 times annually and as many as six cuttings are removed each year. The soil is often treated with a preemergent herbicide, like EPTC, after each second or third cutting, by adding the herbicide to the irrigation water. EPTC is considered a volatile thiolcarbamate herbicide, moderately soluble in water [320 mg L^{-1} at 30 °C, Freed et al. (1967)] with a saturation vapor pressure of 2.97×10^{-2} mmHg at 30 °C (Hamaker, 1972). EPTC vapor flux densities in the atmosphere above an alfalfa field during flood herbigation were reported by Cliath in 1978. This report presents information on total volatilization losses during and after EPTC was applied.

METHODS AND MATERIALS

Experimental Site and Treatment. The experimental site was located at Brawley, CA, at the USDA Imperial Valley Conservation Research Center. The site was about 162 m long (N-S) and 126 m wide (E-W) and included a 2.04-ha area planted to alfalfa, as shown in Figure 1. Outside the west edge of the field, 24 12-m^2 basins with borders spaced 3.3 m apart were also planted to alfalfa and provided additional fetch from the windward direction. The soil was Holtville clay loam (Typic Torrifluvents). The field contained a poor-to-medium stand of alfalfa that had not been irrigated for 10–14 days. EPTC was applied to the alfalfa field by herbigation 7 days after cutting when the plants were approximately 15–25 cm high.

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A weighing lysimeter was located about 100 m W and 75 m S of the NE corner as shown in Figure 1. The meteorological equipment, which included radiometers, wind run anemometers, soil heat flux plates, air temperature and relative humidity sensors, and a wind direction indicator, were located near the lysimeter.

To measure irrigation water runoff from the field, two 10.2-cm Parshall flumes were installed 23 and 80 m W and 10 m S of the NE corner of the field.

A pesticide collection mast assembly was positioned on the expected downwind side of the field 85 m S and 25 m W of the NE corner of the field. The pesticide collection mast assembly was a modification of the setup reported by Turner and Glotfelty (1977). A detailed description was reported by Cliath (1978). Basically, the pesticide collection mast consisted of six polyurethane foam plug collectors attached to a vacuum source and positioned at 10, 18, 30, 45, 70, and 100 cm above the soil surface. The collectors positioned at 10 and 18 cm were within the crop canopy. Air was drawn through each of these collectors at 2 L min^{-1}.

Beginning at 0730 h on May 25, 1977, 3.04 kg/ha EPTC was applied at an average concentration of 2.17 ppm by adding about 14 mL min^{-1} of a 0.84 kg L^{-1} (7 lb gal^{-1}) EC formulation through a Dripolator to irrigation water in the head ditch flowing at 0.056 m^3 s^{-1} (2 cfs). The herbigation of the alfalfa progressed from west to east across the field until the equivalent of 13 cm (5.2 in.) of irrigation water was applied to the field surface. Herbigation ceased when the head flume was closed at 1630 h.

Beginning at 0930 h on May 25, 1977, we measured wind speed ($\bar{u}$), temperature ($\bar{T}$), and atmospheric temperature lapse rate ($\overline{\Delta T}$) every 30 min until 1900 h on May 27. The wind speed was measured with six calibrated Casella rotating cup anemometers located at 40, 60, 80, 100, 130, and 200 cm above the soil surface. Temperatures were measured with Bowen temperature sensors spaced 35 cm apart and located 45 and 80 cm above the soil surface. Details of the meteorological instrumentation were reported by Cliath (1978).

Runoff from irrigation water began at 1300 h and continued until about 0100 h the next day. We obtained 3.8-L grab samples of runoff each hour until 1504 h and every 2 h afterward until 0144 h on May 26 when runoff ceased. Staff gauge records were made at each sampling to calculate total pesticide runoff from flow volumes and herbicide concentrations in the irrigation tailwater.

Vaporized EPTC was sampled beginning at 1445 h on May 25, when the irrigation water passed the sampling

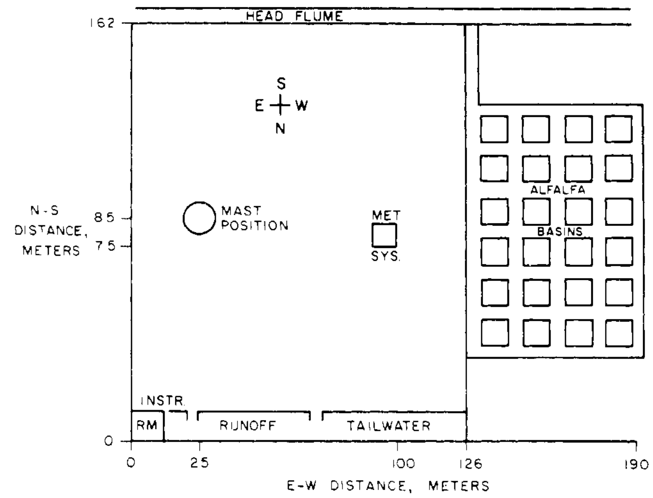

Figure 1. Map of experimental site located at Brawley, CA.

mast. The polyurethane foam plugs were replaced every 2 h and air flow rates were also readjusted to 2 L min^{-1}. Pesticide vapor collection continued without interruption from 1445 h on May 25 to 1845 h on May 27.

Field soil samples from 0–15 cm depth were taken on 24, 26 May and 2, 7 June 1977. Using an Oakfield probe, three samples containing three cores per sample were taken on 24 May, and nine soil samples containing six cores per sample were taken on 2, 7 June 1977. On 26 May 1977, one day after flooding, 10 soil samples were obtained with a trowel and spatula, as the Oakfield probe would not work in wet clay loam.

The water samples, soil samples, and air sampling plugs were stored at 5, −10, and −10 °C, respectively, until analyzed. The water samples were extracted by hexane partition. The soil samples and air sampling plugs were Soxhlet extracted for 4 and 2 h, respectively, with an azeotropic mixture of hexane and acetone. All samples were concentrated to appropriate volumes and quantitated using a gas–liquid chromatograph equipped with a flame-photometric detector in the sulfur mode.

The EPTC vertical flux ($P\uparrow$) were calculated from gradients of EPTC vapor density (ΔC) and wind speed ($\overline{\Delta \mu}$) by the aerodynamic equation

$$P\uparrow = k^2 \overline{\Delta C}\,\overline{\Delta u}/\varphi^2[\ln (z_2 - z_0)/z_1 - z_0)]^2 \qquad (1)$$

at heights z_1 and z_2 above the surface, where z_0 is the "roughness length" or the height above the soil where $\bar{u}$ extrapolates to 0 m s^{-1} when plotted against ln z, and k is the von Karman constant, whose value is usually 0.4. A stability correction term (Φ) is necessary to correct for the effect of atmospheric instability on the vertical flux, and reflects changes in atmospheric lapse rate. Under inversion conditions where $\overline{\Delta T}$ is positive, $\Phi^2 > 1$ and the apparent EPTC flux is decreased because of reduced atmospheric diffusivity. Likewise, under a lapse condition when $\overline{\Delta T}$ is negative, $\Phi^2 < 1$, and the apparent EPTC flux is increased. The form used for (Φ) was developed by Pruitt et al. (1973) and was calculated from

$$\Phi = (1 \pm 16Ri)^{\pm 0.33} \qquad (2)$$

where Ri is the Richardson gradient number, which is calculated from

$$Ri = g(\overline{\Delta T}/\Delta z)/\bar{T}(\Delta u/\Delta z)^2 \qquad (3)$$

where g is the acceleration of gravity in centimeters per second squared, $\bar{T}$ is the average air temperature in degrees Celsius, and $\overline{\Delta T}$ is the difference in air temperature between z_2 and z_1.

Table I. EPTC Concentrations in Air over an Alfalfa Field during and after Flood Irrigation

day and sampling periods (h PDT)	concentration, μg m^{-3}, heights above the soil (cm): 10	18	30	45	75	100
25 May 1977						
1445-1645	91.7	*a*	83.1	71.9	44.2	29.1
1645-1845	81.0	95.2	76.0	49.2	38.9	30.1
1845-2045	106.3	82.8	62.8	44.1	33.3	19.3
2045-2245	28.5	19.5	19.5	13.3	10.1	7.2
2245-0045	27.1	*a*	16.2	13.9	10.8	7.4
26 May 1977						
0045-0245	24.3	12.0	16.1	9.7	9.0	7.8
0245-0445	63.4	41.1	41.1	31.4	17.3	8.2
0445-0645	71.3	41.7	42.7	25.6	19.5	9.5
0645-0845	21.0	18.9	14.1	11.2	5.5	5.6
0745-1045	20.4	*a*	13.2	10.4	7.1	7.8
1045-1245	*a*	*a*	9.2	8.4	7.8	4.5
1245-1445	14.8	10.2	8.8	8.5	5.1	4.0
1445-1645	10.3	7.2	5.5	7.7	7.0	3.6
1645-1845	9.5	4.2	4.9	4.0	3.7	*b*
1845-2045	7.6	*b*	3.0	7.0	2.5	*b*
2045-2245	7.2	2.4	2.9	3.7	3.5	*b*
2245-0045	25.5	19.2	15.2	12.0	5.1	3.4
27 May 1977						
0045-0245	13.1	14.3	10.0	14.1	4.8	*a*
0245-0445	26.8	16.3	12.4	10.1	3.7	2.1
0445-0645	18.5	13.8	10.8	7.1	8.6	4.0
0645-0845	5.3	2.7	3.2	3.1	2.6	2.8
0845-1045	5.0	4.2	3.4	3.0	2.8	2.8
1045-1245	5.3	3.9	3.4	3.3	2.8	1.5
1245-1445	7.0	*a*	4.8	*a*	4.2	*b*
1445-1645	6.2	*a*	*a*	6.7	*b*	*b*
1645-1845	8.7	5.7	5.2	4.9	*a*	*a*

[a] Sampling problem or sample lost. [b] Sample concentration less than detection limits (2× base line noise).

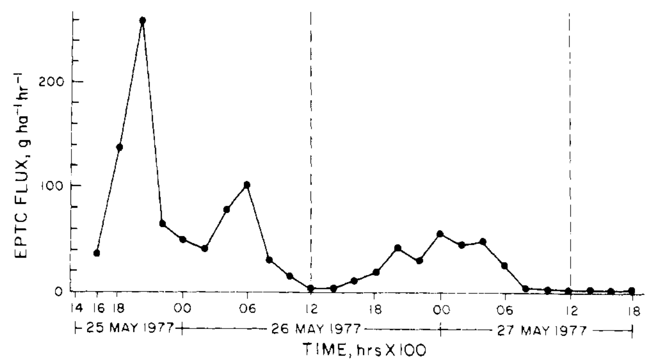

Figure 2. Calculated EPTC vapor flux during and after EPTC was applied by flood irrigation to an alfalfa field.

RESULTS AND DISCUSSION

Table I shows the EPTC concentrations in air above the field for 52 h after the irrigation-applied herbicide treatment. The EPTC vapor concentrations at each collector height were generally highest when water flowed across the field between 1445 and 2045 h on day 1. The EPTC vapor concentration in air did not decrease to zero during the night, but began to increase at 0245 and 0445 h on day 2 and at 0245 h on day 3. Diurnal EPTC vapor concentrations were lowest between 1845 and 2245 h on day 2 and between 0645 and 1645 h on day 3.

Figure 2 is a plot of the vertical EPTC flux during the 52-h field run. The EPTC flux was highest between 1845 and 2045 h on day 1, which coincided with the highest EPTC vapor concentrations in the air above the field. We observed direct correlations between EPTC vapor con-

Table II. EPTC Concentrations in Irrigation Water at the Head Ditch and in Tailwater at the Runoff Flume on Day 1

location	time, h	EPTC concn, ppm
head ditch	0840	2.14
	1300	2.30
	1450	2.08
tailwater	1504	1.92
	1711	1.97
	1915	1.76
	2100	1.44

Table III. EPTC Residues in Soil before and after Flood Irrigation

sample	EPTC concn (0-15 cm),[a] ppm
24 May 1977, preapplication	0.38 ± 0.08
26 May 1977, postapplication (1st day)	0.60 ± 0.10
2 June 1977, postapplication (8th day)	0.11 ± 0.03
7 June 1977, postapplication (13th day)	0.17 ± 0.01

[a] The 95% confidence limit or two times standard error of the mean, S_m, calculated with the equation $2S_m = 2SD/\sqrt{n}$, where SD = standard deviation and n = number of determinations.

centration gradients measured between 45 and 80 cm above the soil surface and the calculated EPTC flux intensities for the remainder of the run.

Table II presents the EPTC concentrations in irrigation and runoff water during the flood irrigation. Samples of herbicide-treated irrigation water taken 10 m below the mixing point in the head ditch and 120 m before the release gates averaged 2.17 ppm during the application period. Tailwater EPTC concentrations obtained from the runoff flume nearest to the pesticide mast decreased from 1.92 to 1.44 ppm on day 1 during the periods when EPTC vapor flux was greatest.

Table III shows EPTC soil residues at the 0–15-cm soil depth before and after the EPTC application. The high pretreatment soil residue values were caused by a pilot study application on April 6, 1977, and the effect of intervening cool weather. Data are also included for soil residues on June 2 and 7 to show soil residue levels expected after 1 and 2 weeks of hot weather.

Figure 3 shows the micrometeorological conditions observed during the field study. Uniformity of meteorological conditions for the entire field study were evident from the uniformity of the curves. Taylor et al. (1977) concluded from their work that pesticide flux intensities are directly responsive to R_N, as is water loss (ET) from soil and vegetation. One might expect, then, a proportional decrease in EPTC vapor flux between 1445 and 2045 h on day 1 with the decrease in R_N. However, EPTC flux values did not decrease because of changes in $\overline{\Delta T}$ and $\overline{\Delta u}$ that denoted atmospheric instability. Ordinarily, under intense insolation, over a dry soil surface air temperatures are higher at the field surface which causes a period of maximum instability or mixing just after solar noon; with reduction of R_N during the evening, air near the soil surface becomes cooler than that above and the mixing of the air due to temperature gradients is dampened out.

During our field study over water or moist soil, a typical "oasis effect" was observed, where advective energy from outside the site, in the form of sensible heat, caused water evaporation in excess of available R_N and G. During periods of positive R_N, mild temperature inversions in the

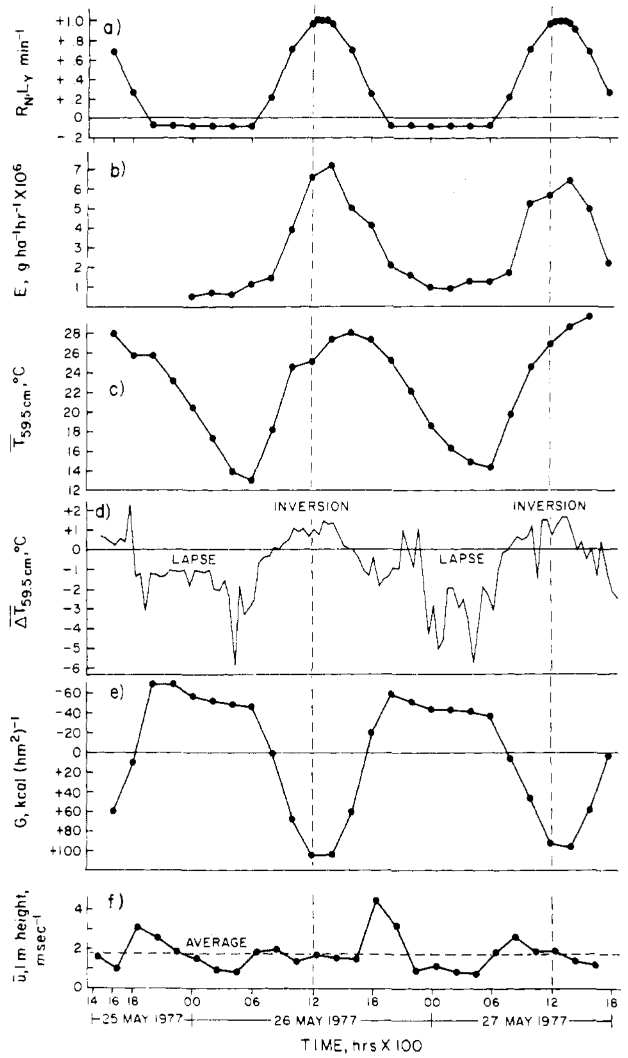

Figure 3. Micrometeorological conditions observed during the field study on May 25, 26, and 27, 1977, at Brawley, CA, where R_N is solar net radiation, E is water flux from a weighing lysimeter, T is the average temperature at the 59.5-cm height. T is the temperature difference between 80- and 45-cm height, G is the surface soil heat flux, and u is the average wind speed at the 1-m height.

air above the field were noted when the air temperatures nearer the field surface were lowered by the cooling effect of evaporating water. This increase in stability occurred between 1445 and 1715 h on day 1 and between 0800 and 1600 h on days 2 and 3. During periods of negative R_N, temperature lapse conditions were observed when the air nearer the soil surface was heated by stored heat in the soil and water and was warmer than the advected air from outside the site. This decrease in stability occurred between 1715 and 2130 h on day 1, between 0000 and 0630, and 1600 and 2000 h on day 2, from 2330 h on day 2 to 0145 h on day 3, and between 0445 and 0630 h on day 3. These nighttime temperature conditions agreed with studies by Fritschen and van Bavel (1962), who concluded that in an arid climate when the average air temperature above wet soil is increasing, as it does in the spring, heat stored in the soil is given off to the air during the evening.

While water was on the field the increase in EPTC flux between 1445 and 2045 h was the result of change from stable to unstable air conditions at 1845 h coupled with a 2.5× increase in $\overline{\Delta u}$ between 1845 and 2045 h. $\overline{\Delta T}$ was positive between 1445 and 1715 h and negative from 1715 to 2145 h. Between 1445 and 1845 h $\overline{\Delta u}$ was 0.19 m s^{-1} and

Table IV. Amounts of EPTC in Runoff, and Volatilized from Water and Wet Soil, during and after a Flood Irrigation Application to Alfalfa

EPTC	kg/ha	% of total applied
applied in irrigation water (av 2.17 ppm)	3.04	100.0
runoff in tailwater (av 1.70 ppm)[a]	0.21	7.0
volatilized from water[b]	0.86	28.4
volatilized from wet soil[c]	1.38	45.2
total volatilized	2.24	73.6
total lost	2.45	80.6

[a] EPTC concentration in runoff varied from 1.97 to 1.44 ppm during volatilization measurements. [b] Volatilized between 1445 and 2045 h on 25 May. [c] Volatilized between 2045 h on 25 May and 1845 h on 27 May.

0.5 m s^{-1} between 1845 and 2045 h, during the period of peak EPTC flux.

During the night between 0045 an 0645 h on day 2 and between 2330 and 0630 h on day 3, atmospheric lapse or unstable conditions predominated even though we observed no strong changes in $\bar{u}$ or $\overline{\Delta u}$. During these periods both EPTC vapor density and vapor flux (Table I and Figure 2) significantly increased. This indicates that under field condition, direct insolation was not necessary for production of EPTC flux. Soil-heat-flux measurements (Figure 3e) and temperature lapse conditions at night (Figure 3d) indicated that the main source of energy for flux production was heat stored in the wet soil. Probably under these conditions of warm wet soil and cold night air, convective energy from the soil overshadowed the advective energy from the wind, resulting in EPTC flux greater than expected for conditions generally occurring at night.

The EPTC vapor concentrations in the air and EPTC vapor flux values were lowest between 0700 and 1800 h on days 2 and 3. The mild temperature inversions above the field during part of these intervals can reduce the vapor flux, but cannot account for the low concentrations of EPTC vapor. Reductions in overall vapor concentration are directly correlated with conditions at the soil surface (Spencer at al., 1973). Measurements of downward flow of water and soil moisture content of the soil surface were outside the scope of this study; however, the effects of bulk water flow and changes in surface soil moisture content on pesticide movement are well documented (Spencer et al., 1973; Harper et al., 1976; Turner et al., 1978).

The amounts of EPTC loss measured in water and air during and after the flood-irrigation application are shown in Table IV. Of the 3.04 kg ha^{-1} EPTC applied, 7.0% was removed in tailwater runoff and 73.6% volatilized into the atmosphere for a total loss of 80.6% during the 52 h of observation. The remaining unaccounted for EPTC was probably in the soil. The increase in soil residues between 24 May and 26 May 1977 in the 0–15-cm depth was equivalent to 16.0 ± 13% of the applied EPTC. During the first 24 h of the study, 55% of the applied EPTC was lost by volatilization. These data indicate that using surface irrigation water to apply highly volatile herbicides is an extremely inefficient method of application. Losses could be substantially decreased by using less volatile herbicides and by irrigating so as to decrease the percentage of the irrigation water lost as tailwater.

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Received for review September 14, 1979. Accepted January 11, 1980. Contribution of Agricultural Research, SEA, USDA, the California Agriculture Experiment Station, Riverside, California, and Agriculture Canada, Research Branch, Regina, Sask., Canada. Mention of commercial products is solely to identify equipment and materials used and does not constitute endorsement by the USDA.