Drift from and Transport Subsequent to a Commercial, Aerial Application of Carbofuran: An Estimation of Potential Human Exposure*

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Aerial pesticide spraying in Uintah Basin, UT continued to be an issue of public concern in the summer of 1980. A number of developments occurred in the Vernal-Maeser area, and Utah in general, regarding aerial spraying near residential communities: (1) the extension pesticide coordinator for the state issued a memorandum recommending the use of less toxic pesticides than the parathions, (2) a community meeting, organized by the Federal Aviation Agency, was conducted in the Uintah Basin, (3) this laboratory agreed to share the results of a spray monitoring study under way with the public, and (4) one aerial applicator in the Uintah Basin closed his operation.

The present report describes a spray drift study conducted in Maeser, UT on 5 and 6 June 1980. This study employed high-volume air sampling equipment and meteorological instruments not available in an earlier study of parathion spraying (DRAPER & STREET 1981); only foliar residues were measured in the previous investigation. The pesticide applied in 1980 was carbofuran, possibly as a result of the University's recommendation.

The objective, as with the previous year's study, was to obtain an estimate of the extraneous exposure that a bystander might be subjected to. Specifically, inhalation and dermal exposure during and immediately subsequent to aerial spraying were to be estimated. The experimental format and assumptions made in the data treatment were oriented toward obtaining a "worst-case" estimate.

EXPERIMENTAL

Pesticide Application. On 5 June (Site A, 20 acres) and 6 June 1980 (Site B, 40 acres) alfalfa fields located in Maeser, UT were treated aerially with Furadan 4-Flowable at the rate of 0.5 lb a.i./acre. The fields are depicted in Figure 1. The adjuvent Bond Super Sticker (Loveland Industries, 1 pint/100 gal) was used. In each case the applicator plane, a Grumman Ag Cat equipped with an automatic flagging device, flew in an east-west orientation. At Site A application took place at 7:20 am at which time the wind speed averaged 2.9 mph out of the WSW and remained relatively constant throughout sampling. During the 20 min spraying the temperature and relative humidity (R.H.) were 15° C

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and 49%, respectively. At the completion of sampling, 11:20 am, the temperature was 21° C and the R.H. was 49%. At Site B spraying took place at 6 am with no wind initially, but by 7 am, when the application was completed, the wind averaged 0.5 mph out of the north. Wind was predominantly out of the WSW at 1.5 mph during collection of "volatilization" samples. The temperature and R.H. were 4° C and 52% at 6 am and by 9 am, at the termination of sampling, 18° C and 41%, respectively.

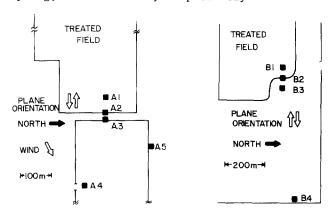


FIGURE 1.: Pesticide application sites.

Sampling. At Site A air samplers were stationed at 3 locations to monitor during application (so-called drift samples) and one station for the subsequent 2 h volatilization sample. Site B utilized only 2 stations for drift measurement. At Site A.3 2 samplers were operated, one being 20 m north of the other; at Station B.3 2 high-volume samplers were 10 m apart on a north-south line. Foliage samples were collected before and after treatment at locations within and on the periphery of the alfalfa field; nontarget foliage samples were quackgrass. Foliage samples from 2 fields treated approximately 30 h previously by the same applicator were taken in an analogous fashion: 50 m within the field, the perimeter, and 50 m out of the field. These samples were used to validate the applicator's performance.

Apparatus. Staplex Model TFTA high-volume air samplers were equipped with a glass fiber filter (outermost) and approximately 120 mL of XAD-4 macroreticular resin in a 1.8 cm bed (Rohm and Haas). Particulates were entrapped on the glass filter and vapors were absorbed on the resin. Air sampler flow rates were calibrated with equipment supplied by the manufacturer.

A gas chromatograph fitted with a nitrogen-phosphorus detector and 1.5 m x 4 mm i.d. glass column packed with 3% OV-1 on 80-100 mesh Gas Chrom Q was used. Operating parameters were: oven, 170° C; inlet, 220° C; detector, 270° C; carrier, 60 mL/min $\rm N_2$.

Analysis. Foliar carbofuran residues were determined using the following scheme: 10 g of crop were added to a 125-mL separatory funnel without cutting or chopping. This minimized the

the disruption of cell walls and the extraction of intracellular components. The plant material was extracted with 5 x 50 mL of dichloromethane which was combined, dried by passage through sodium sulfate, and collected in a 500-mL flask. The extract was reduced to 5 mL on a rotary evaporator and transferred quantitatively with dichloromethane to a 10-mL graduated test tube. The volume was reduced to 1 mL under a stream of nitrogen and made to 5 mL with acetone. Some samples required filtration. Glass fiber filters were subjected to the same extraction procedure. A small plug of glass wool was inserted in the separator to retain the filters which fragmented during extraction.

Each resin sample was extracted with 200 mL of acetone in a Soxhlet apparatus for 1 h after the initial cycle. Solvent was dried by passage through sodium sulfate and the sample was reduced to 2 mL on a rotary evaporator. Quantitative extraction was achieved; 107% recovery was obtained with a 2.0 mg fortification. The resin extract was highly contaminated as evidenced by the pungent odor of resin, the glc profile, and the recovery of 0.8 mL of yellow oil. For low level detection of carbofuran, the sample required clean up by adsorption chromatography. A Florisil fractionation, previously used on crop samples, was employed (NELSON & COOK 1980). The odiferous contaminant(s) eluted in the first fraction, carbofuran in the second, and colored contaminants were retained at the salt-Florisil interface. In spite of the purification, detection limits were considerably higher than in the other matrices due to the detector response found for the procedural blank. Recovery of carbofuran from the column was quantitative.

Quantitative analysis was accomplished by injecting 6 uL aliquots of the 4.0 mL sample. Quantitation was by absolute calibration against a 1.0 ng/uL or 30 ng/uL carbofuran standard.

<u>Trapping efficiency</u>. To test the trapping efficiency of the macroreticular resin, the following experiment was conducted. A glass fiber filter was treated with 30 mg of carbofuran in acetone. The air-dried filter was mounted on 2 resin cartridges in series and air was drawn through the adsorption train for 2 h. Chemical analyses of the resin samples indicated that 98% of the pesticide was trapped in the front cartridge and 2% in the second. Previous investigations have likewise shown XAD-4 macroreticular resin to trap carbofuran vapors efficiently; $78 \pm 8\%$ recovery was found with air flow rates of 30 L/min (FERREIRA 1979).

RESULTS AND DISCUSSION

<u>Foliar Residues</u>. Foliar carbofuran levels indicated some spray drift at Sites A and B (TABLE 1.). There was considerable variability in residue levels among subsamples at each station due to the nature of the sampling; grass or alfalfa samples were only 0.1 kg and representative samples were difficult to obtain.

TABLE 1. Foliar Carbofuran Residues at Sites A and B.

Time	Residue (mg/kg)	
Prespray .	nd ^a	
Postsprayb	4.7 + 2.7	
Postspray	nd	
Postspray	0.9 + 0.5	
Prespray	nd —	
Postspray	3.5 + 1.2	
Postspray	nd	
	Prespray Postspray Postspray Postspray Prespray Prespray Postspray	Prespray nd^a Postspray $\operatorname{4.7} \pm 2.7$ Postspray nd Postspray nd Postspray $\operatorname{0.9} \pm 0.5$ Prespray nd Postspray $\operatorname{3.5} \pm 1.2$

aNot detected (< 0.05 mg/kg)

There was a disparity between pesticide residue levels in these experiments and those in two sprayings occurring the previous day (4 June 1980, TABLE 2.). The residue levels were higher at each corresponding location in spite of a 24-30 h weathering period.

TABLE 2. Foliar Carbofuran Residues at Reference Sites Treated 4 June 1980.

Time	Residue (mg/kg)
Postspray ^a	10.3 + 2.2
Postspray	$\frac{2.6}{100}$ $\frac{\pm}{100}$ 3.0
Postspray	nd ^D
Postspray	5.4 ± 5
Postspray	3.8 + 4
Postspray	2.8 ± 4
	Postspray Postspray Postspray Postspray Postspray Postspray

^aApproximately 30 h after spraying ^bNot detected (< 0.02 mg/kg)

Carbofuran in Air. At Site A carbofuran was detectable in air samples only at Station A.3, immediately adjacent the target field. During application the average concentration of carbofuran over the 17 min sampling interval was 2 ug/m. A considerable difference was noted between the 2 air samples taken 20 m apart at this station (TABLE 3). The aircraft applied 6 swaths of pesticide in each direction on the east boundary of the field. The passes were, therefore, approximately 20 m apart. The data suggest that drift was considerably different for east and west approaches. At Site A carbofuran was only detectable in the glass filters indicating that the majority of the pesticide was in particulate form. The filters used trap 1 µm particles with 90% efficiency and reportedly exhibit "good efficiency" for trapping particles in the range of 0.01 to 10 µm (Staplex Co. product literature).

bone hour after spraying

TABLE 3. Carbofuran Levels in Air at Site A.

Station	Sampling Interval (min)	Flow Rate (m³/min)	Total Residue (ug)	Time-Average Concentration (ug/m ³)
A.3 Drift A.3 Drift A.4 Drift A.5 Drift A.5 Volatilization	17	0.71	8.0	0.7
	17	0.51	29	3.3
	17	0.40	nda	< 0.3
	27	0.23	ndb	< 0.6
	120	0.51	6.4	0.1

^aNot detected (< 2 ug)

The exposed surface area of the glass filters was 62 cm² although samplers were oriented poorly for maximum interception of fallout; sampler units generally faced downward. Using the same assumptions employed to estimate potential dermal exposure at Site A.3, it is estimated that 66 ug of carbofuran would undergo deposition on the exposed filter surface. By instrumental analysis between 12 and 44% of this amount was detected—reasonable agreement in view of the random orientation of sampling units. These data suggest that the majority of the insecticide considered here as airborne was actually fallout, not suspended aerosol or vapor.

At Site B carbofuran drift was detected as adsorbate on glass filters and in the macroreticular resin (TABLE 4). It is likely that the pesticide was initially trapped on the filter in large particulates, but underwent partial volatilization during the large sampling interval. Filters are often inefficient at trapping airborne pesticides for this reason (LEE 1976). The total residue trapped at Site B.3 was slightly lower than that observed at Site A.3. Comparisons are difficult, however, due to differences in sampling interval, climatic conditions, and sampling locations relative to the target fields.

TABLE 4. Carbofuran Levels in Air at Site B.

Station/Sample Type	Sampling Interval (min)		Total Residue (ug)	Time Average Concentration (ug/m ³)
B.3 Drift-Filter	55	0.57	5.3	0.17
B.3 Drift-Filter	55	0.40	4.8	0.22
B.4 Drift-Filter	55	0.23	nd^2	< 0.0071
B.3 Volatilization-Filter	110	0.52	0.20	0.0035
B.3 Volatilization-Filter	110	0.42	0.22	0.0048
B.3 Drift-Resin	55	0.57	5.3	0.17
B.3 Drift-Resin	55	0.40	4.1	0.19
B.4 Drift-Resin	55	0.23	nd	< 0.067
B.3 Volatilization-Resin	110	0.52	nd	< 0.015
B.3 Volatilization-Resin	110	0.42	nd	< 0.018

^aNot detected (< 90 ng for glass fiber filters, < 850 ng for resins)

b_{Not detected} (< 3.6 ug)

Drift was not detected by air sampling at any of the distant stations (A.4, A.5, and B.4). Carbofuran showed some transport subsequent to the spraying operation (TABLE 3 and 4) although the kinetics of the process are invisible due to the long sampling interval. The term volatilization may not be accurate as the material was trapped as particulate matter greater than 0.01 μm ; the transport mechanism may involve small particle suspensions or resuspension of the pesticide sorbed to dust. Flow rates varied between 0.23 and 0.71 m^3/min depending on the sampler unit.

Potential Human Exposure. The following assumptions were utilized to estimate potential inhalation exposure: the hypothetical subject was a 70 kg male, the breathing rate was 1.8 m $^3/h$, and airborne residues were considered to undergo quantitative deposition in the upper respiratory tract and were equivalent to oral exposure. These assumptions have recently been described by JENSEN (1980). The maximum inhaled dose of carbofuran at Site A.3 during the aerial application and the subsequent volatilization period was 2.0 μg ; respiratory exposure at Site B.3 was estimated to be 0.7 μg . These estimates are, apparently, in good agreement as Site A.3 was approximately one half the distance from the target than Site B.3.

Potential dermal exposure was estimated using calculations and assumptions described previously (DRAPER & STREET 1981). Foliar residue concentrations at various locations and the assumption that the concentration at Site A.1 represented the intended rate of application, 227 g/acre, provided deposition data. The exposed skin area of a 70 kg male was composed of the normally unclothed body surfaces (face, hands, forearms, back and front of the neck, and "V" of the chest), the total area of which has been estimated using Berkow's method to be 2930 cm (BATCHELOR & WALKER 1954).

The dermal dosage incurred by an individual at Site A.3 totals 3.1 mg of carbofuran (TABLE 5). Assuming a continuum of values between Site A.1 and A.3, the maximum dermal dose receivable outside the treated field was 100 $\mu g/kg$; the dermal dose at Site A.3 on a per wt basis was approximately 44 $\mu g/kg$. Dermal exposure was estimated to exceed that due to respiratory exposure by a very large margin. This was concluded in spite of calculations based on extraordinarily large tidal volumes, respiration rates, and the assumption of complete pulmonary deposition. These data support the conclusions of an earlier investigation of human exposure to parathion spray drift (DRAPER & STREET 1981) in which similar dermal exposures were estimated while exposure by inhalation was not considered.

TABLE 5. Estimated Maximal Off-site Potential Exposure to Carbofuran in a Single Spraying Episode.

- a) Intended application rate; assumed equivalent to A.1 (227 g/acre)
- b) Conversion factor (acre/4047 m²)
- c) Residue concentration at A.3/Residue concentration at A.1 (0.9/4.7)
- d) Exposed skin surface of a 70 kg male (0.293 m²)
- e) Standard body weight (70 kg)

Estimate: (a) x (b) x (c) x (d) x (e) $^{-1}$ = 0.044 mg/kg

The established Threshold Limit Value (TLV) for carbofuran is 50 μg/m³. During aerial sprayings carbofuran levels did not exceed 3.3 $\mu g/m^3$ at any location; this peak concentration was measured over a 17 min sampling interval 20 m from the target field. The TLV is a time-weighted concentration for a 40 h work week that nearly all workers can be exposed to without adverse effect; eye and skin irritation and other minor conditions are considered adverse effects.

The acute dermal toxicity of carbofuran is considerably lower than that of ethyl or methyl parathion (TABLE 6). A large margin exists between the greatest potential bystander exposure and published dermal toxicities. In the present study the potential hazard to human health is probably minor due to the small, single dose incurred and the relatively low dermal toxicity of the insecticide.

TABLE 6. Dermal Toxicities.

Compound	Acute Dermal LD ₅₀			
	Rat (mg/kg) Rabbit (mg/kg)		
Carbofuran	120	885		
Ethyl parathion	7	40		
Methyl parathion	67	300		

au.s. DEPARTMENT OF HEW (1976)

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