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Drift from a Commercial, Aerial Application of Methyl and Ethyl Parathion: An Estimation of Potential Human Exposure

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In the summer of 1979 there was considerable public concern in certain areas of Utah regarding the impact which aerial pesticide applications might have on the health of nearby residents. Public reaction was particularly intense in Uintah county in northeastern Utah, partly due to the large interface between agricultural and residential property. Attention was focused on aerial spraying of methyl and ethyl parathion for control of insect pests on alfalfa, although other organophosphorus and carbamate insecticides were being applied by airplane in this area.

The objective of this study was to estimate potential exposure to nearby residents during a typical spraying operation on alfalfa. Spray drift was quantitated by determining surface residues of the active materials, methyl and ethyl parathion, within and adjacent to a target field. Human dermal exposure was estimated by extrapolation of the surface pesticide concentrations found. The persistence of the phosphorothionate residues was also monitored as further human exposure could result from dermal contact with contaminated foliage.

EXPERIMENTAL

Pesticide Application. On 2 July 1979, 73 acres of alfalfa at the Ashley Maeser Stake Farm, Vernal, UT were sprayed. The pesticide formulation utilized was an emulsifiable concentrate containing 6 lb/gal of ethyl parathion and 3 lb/gal of methyl parathion (Parathion 6-3, Clean Crop$^{(R)}$). The material was applied at the recommended rate of 1/3 pint/acre with a Cessna 188 Ag Plane. The plane flew in a north-south orientation while spraying and, as in common in this area, no flaggers were used. Application took place at 7:30 am, at which time wind conditions were negligable.

Sampling. The test plot (Figure 1.) consisted of a treated alfalfa field and an adjoining non-target pasture. The alfalfa was approximately 15 cm in height. Quackgrass (Agropyron repens), the predominate species in the adjoining pasture, was approximately 75 cm in height, but only the uppermost 15 cm were collected.

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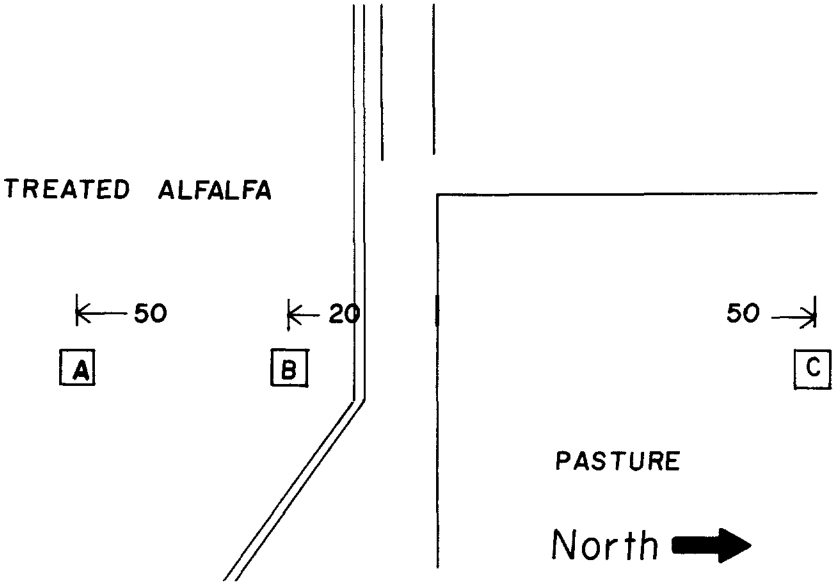

FIGURE 1.: The test plot.

Staked sampling sites were located along a north-south transect. Alfalfa sampling Sites A and B were 50 and 20 yards, respectively, from the fence bordering the fields. Non-target samples were collected at location C, 50 yards north of the perimeter. Foliage samples were collected at each location 96 h prior to spraying (Prespray) and 4, 28, and 72 h after treatment. In order to prevent cross contamination, gloves were changed prior to sampling at each location. Plant material was transported in sealed polyethylene bags, stored in foam chests, and held below 0° C prior to analysis.

Extraction and Cleanup. Plant material (10.0 g) was chopped into lengths approximately one cm or less and added to a Soxhlet extractor; no thimble was used and a plug of glass wool retained the sample. The hexane solvent was allowed to reflux for 60 min. The extract was cooled, dried by passage through sodium sulfate, and the volume was adjusted to 30 mL on a rotary evaporator. Pesticides were extracted from the nonpolar solvent by partitioning with an equal volume of hexane-saturated acetonitrile; the mixture was shaken vigorously for 5 min. The polar layer was taken just to dryness on a rotary evaporator and resuspended in 10 mL petroleum ether.

The sample was fractionated on a 12.5 cm, 60-100 mesh, activated Florisil column. Residues were transferred to the column quantitatively by rinsing the flask with 5 x 10 mL of petroleum ether. The column was eluted with 50 mL each of petroleum ether, 6% diethyl ether, 15% diethyl ether, 50% diethyl ether, and 60 mL of diethyl ether. The last 2 fractions were combined, concentrated on a rotary evaporator, transferred to a graduated, tapered test tube, concentrated under a stream of nitrogen, and adjusted to 2.0 mL with acetone.

Analysis. Methyl and ethyl parathion were quantitated on a gas chromatograph fitted with a flame photometric detector and a 2 m x 4 mm i.d. glass column containing 60/80 mesh Gas Chrom Q coated with 5% OV-210. Operational parameters used were: column temperature, 190° C; detector block, 195° C; inlet, 280° C; carrier gas flow, 70 cc/min. Injections were 6 uL with an attenuator setting of 32 x 10^3.

RESULTS AND DISCUSSION

Analytical Procedure. The analytical scheme developed quantitated only surface residues of the parent phosphorothionates. Hexane was the preferred extraction solvent as more polar solvents destroyed the integrity of plant tissues and resulted in coextraction of large amounts of water and pigments. No interferences were detected in untreated plant samples (Figure 2).

The recovery "through-the-method" for both residues from alfalfa ranged from 70 to 85% for fortifications at 0.10 and 1.0 mg/kg (duplicate analyses). Vigorous shaking and adequate contact time at the solvent partitioning step was essential for high recoveries. Limits of detection for methyl and ethyl parathion on alfalfa were 23 and 16 µg/kg, respectively, well below the established tolerance levels for alfalfa hay (FEDERAL REGISTER 1972); 1.25 mg/kg (wet wt) or 5 mg/kg (dry wt).

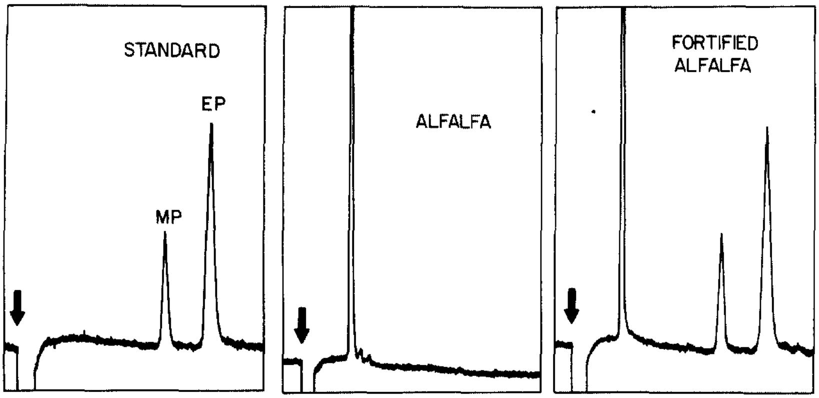

FIGURE 2.: Chromatograms of methyl parathion (MP) and ethyl parathion (EP) mixed standard, an untreated alfalfa sample, and untreated alfalfa fortified with 0.1 mg/kg of each insecticide.

Foliar Residues. Residue levels of ethyl parathion and methyl parathion are in TABLE 1. Parathion was not detectable at any location prior to the aerial application. Four h subsequent to the pesticide spraying, 7.0 mg/kg of ethyl parathion and 2.8 mg/kg of methyl parathion were present as foliar residues at Site A. At this time, parathion residues were approximately 0.1 as great 50 yards from the fence, in the untreated, nontarget pasture (Site C). The data indicate that a continuum of values existed between Sites A and C; a single sample collected at 72 h at the fence line bordering the fields indicated residue levels similar to Site B.

TABLE 1. Foliar Pesticide Residues

Insecticide	Time	A	B	C
MP	Prespray	nd[a]	nd[a]	nd[a]
	4 h	2.8 ± 1.1	1.4 ± 0.89	0.26 ± 0.20
	28 h	0.71 ± 0.29	0.49 ± 0.12	0.14 ± 0.13
	72 h	0.32 ± 0.37	0.42 ± 0.27	0.034 ± 0.014
EP	Prespray	nd[b]	nd[b]	nd[b]
	4 h	7.0 ± 3.1	3.8 ± 2.0	0.72 ± 0.50
	28 h	2.5 ± 1.3	1.5 ± 0.4	0.50 ± 0.33
	72 h	0.69 ± 0.41	1.4 ± 1.2	0.14 ± 0.05

[a] Not detected = below 23 µg/kg [b] Not detected = below 16 µg/kg

Immediately after treatment, methyl parathion residues averaged 40% of ethyl parathion levels at the 3 sampling stations; the formulated mixture was stated to contain ethyl and methyl parathion in a 2:1 ratio. Three discrete analyses were performed on each sample--samples were not mixed and subsampled--and the relatively large standard deviations reported presumably reflect real variation in the nonhomogenous samples and not low analytical precision. A portion of the sample collected at Site C 4 h after spraying exceeded the tolerance for ethyl parathion on alfalfa hay. The average, however, was below the specified 1.25 mg/kg and it is certain that parathion residues on the entire mass of foliage were well below the tolerance; only the uppermost, exposed portions of the grass were sampled.

Foliar residues of the parent phosphorothionates dissipated rapidly with time (Figure 3). At Site A residues had dropped below 1.25 mg/kg within 72 h for ethyl parathion and within 28 h for methyl parathion. The first order half-lives of methyl and ethyl parathion were 12 and 16 h, respectively, based on initial slopes of semi-logarithmic plots; dissipation kinetics, however, appeared to be greater than first order. The dissipation curves depicted do not reflect (exactly) the loss of potential toxicity of the applied insecticides; residue levels of the relatively more toxic oxygen analogs, environmental transformation products of the phosphorothionates, were not determined in this study. Paraoxon and methylparaoxon, however, are known to be less persistent than their precursors.

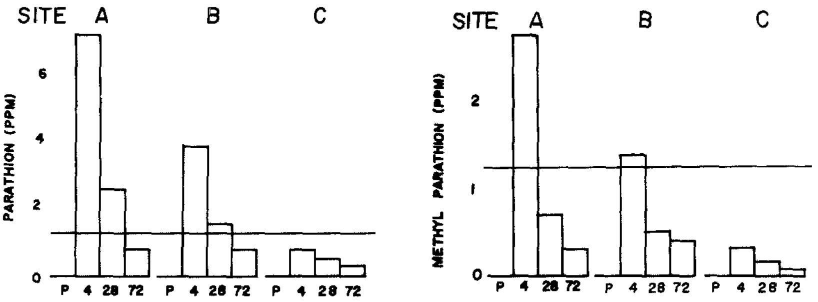

FIGURE 3.: Dissipation of ethyl and methyl parathion residues with time. Horizontal line indicates legal tolerance levels for residues on alfalfa hay.

The aerial pesticide application studied may represent a favorable case for the following reasons: meteorological conditions were good (negligable wind or temperature inversion), label instructions and regulations were adhered to, and the applicator exhibited maximum attention and concern.

Potential Human Exposure. During the pesticide application the surface deposition of parathion at Site C was between 9.2 and 10.3 percent of that at Site A; human dermal exposure due to spray drift would have been in proportion to these values. It was assumed that residue levels at Site A represented the intended rate of application, 113 g ethyl parathion/A and 57 g methyl parathion/A. Finally, human exposure at Site C was estimated to occur dermally and only across the normally unclothed body surfaces; face, hands, forearms, back and front of the neck, and "V" of the chest. The total area of these exposed surfaces for a 70 kg human male has been previously estimated to be 2,930 cm^2 (BATCHELOR & WALKER 1954). Exposure calculations appear in TABLE 2.

TABLE 2. Estimation of Potential Human Exposure.

Dermal Exposure to Ethyl Parathion:

$$(113\ \mathrm{g/acre})^{a}(\mathrm{acre}/4047\ \mathrm{m}^{2})^{b}(0.10)^{c}(0.293\ \mathrm{m}^{2})^{d} = 0.82\ \mathrm{mg}$$

Dermal Exposure to Methyl Parathion:

$$(56\ \mathrm{g/acre})^{a}(\mathrm{acre}/4047\ \mathrm{m}^{2})^{b}(0.093)^{c}(0.293\ \mathrm{m}^{2})^{d} = 0.38\ \mathrm{mg}$$

[a] Intended application rate; assumed equivalent to Site A
[b] Conversion factor
[c] Ratio of residues at Site C/residues at Site A
[d] Exposed skin of a 70 kg male

A dermal dose of 0.82 mg of ethyl parathion and 0.38 mg of methyl parathion would have been incurred by a bystander at Site C during the aerial spraying. Dosing was assumed to be a single instantaneous event as deposition probably occurred rapidly. Assuming a continuum of residue values between Site B and C, the exposure is estimated to have been 4 times greater at the fence line separating the treated and non-target fields. The combined exposure to both organophosphates equals 17 μg/kg for a 70 kg male or up to 70 μg/kg on the immediate perimeter of the treated field.

Previous studies of orchard spray operators exposed to parathion have indicated that potential hazard is much greater from dermal exposure than from inhalation (BATCHELOR & WALKER 1954). The predominant importance of dermal exposure was demonstrated more recently in a study of carbofuran drift from aerial applications (DRAPER, GIBSON & STREET 1981). Dermal exposure is usually the major component of the total dose received in various exposure situations (WOLFE 1976).

Methyl parathion and ethyl parathion are highly toxic pesticides by both oral and dermal routes. The mammalian dermal toxicities of these compounds vary between 7 and 600 mg/kg depending on the laboratory animal tested (U.S. DEPARTMENT OF HEW 1976). Even on the immediate boundary of the field being sprayed, it is not likely that the dose incurred in a "typical" aerial spraying event would reach 70 μg/kg. A factor of 100 would exist between the median lethal toxicity in the most sensitive test species and estimated human dermal exposure derived by worst-case analysis. The use of microencapsulated malathion formulations, due to their decreased dermal toxicity, would lower significantly the potential hazard associated with aerial spraying near highly populated areas. Deposition data indicate that a rapid decline in dermal exposures would be expected over distances of tens of meters.

The human health effects of low level exposures to toxic chemicals are poorly understood. It is important to note, however, that incidents of this type are infrequent or even single events, not chronic. Previous studies, summarized by WOLFE (1976), have shown that persons exposed incidently to pesticides in situations of this type do not contact sufficient material to cause serious injury.

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