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Exposure to Guthion During Spraying and Formulating

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The exposure of spray operators and formulating plant workers to Guthion * was determined in connection with a field survey of the hazards which may result from the formulation and use of the more highly toxic insecticides in the province of Quebec. The survey was made during the 1962 spraying season in apple orchards in the Rougemont district of the province and in a local formulating plant.

At the time of the survey, apple trees were being sprayed by an air-blast machine utilizing concentrations of Guthion ranging from 0.5 to 6.0 lb of 25% wettable powder per 100 gallons of water. The duration of any one spraying operation varied from 15 to 45 minutes, there being 3 to 15 such applications per day depending on the size of the orchard. The number of spraying days throughout the season also varied from 3 to 15. The investigations which were made in the formulating plant were conducted during the formulation of Guthion 25% wettable powder (WP).

Measurements were made of the respiratory and dermal exposures of spray operators to Guthion by means of air concentration determinations, by the technique of attaching filter pads to respirators and by strapping absorbent materials to the forehead and wrists of observers sitting on tractors beside spray operators. Similar methods of determining the exposure of formulating plant workers were used in the areas of the plant under consideration, ie, the blending and general work areas, with the exception that dermal exposures and respirator exposures by the pad technique were determined on the actual workers rather than on observers.

Experimental Procedure

Air samples taken in the tractor operator's breathing zone were collected in all-glass fritted absorbers by means of portable electric or hand-operated suction pumps. Similar sampling procedures were used for the collection of air samples from the breathing zone of spray operators during tank filling and of formulating plant workers during the formulation of Guthion 25 WP. Air flow rate through the absorbers was 90 liters per hour.

Respiratory exposure was determined directly from the quantities of Guthion deposited on filter pads attached to double-unit respirators and indirectly by calculation using the determined values for concentrations of Guthion in the air. Measurements of respiratory exposure by means of air concentration values require an assumed tidal volume and respiratory rate. In calculations of these exposures an assumed lung ventilation of 444 liters per hour [1] for spray operators during spraying and tank filling operations was used.

Direct measurement of dermal exposure was made, by means of three-layer α-cellulose absorbent pads † attached by pressure-sensitive adhesive tape to the forehead and wrists, on observers seated beside spray operators during spraying operations and on workers in the formulating plant. The size of the pads used on the forehead was 2×10 inches and on the wrist 2×6 inches. The results for dermal exposure were obtained by calculation using Berkow's method [2] from the means of the determinations of forehead and wrist exposures and an assumed total exposed surface area of unclothed body parts of 3.16 sq ft.

The colorimetric method of Meagher et al [3] was used for analysis of Guthion from air samples,

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* *O,O*-dimethyl-*S*-(4-oxobenzotriazino-3-methyl) phosphorodithioate.

† Johnson & Johnson Limited, Montreal.

respiratory pads, and skin pads. This method is based on the alkaline hydrolysis of Guthion to anthranilic acid, diazotization, and coupling with *N*-(1-naphthyl) ethylenediamine dihydrochloride which produces a color having maximum absorption at 555 mμ.

Serum cholinesterase was measured by the method of Main et al.[4]

Results

The results of determinations of Guthion in the air at the breathing zone of spray operators during spraying and tank filling and in the air at the breathing zone of workers in the formulating plant are given in Table 1. It may be seen from the Table that during spraying operations, air concentrations of Guthion ranged between 0.05 and 2.55 mg per cubic meter with a mean of 0.64 mg per cubic meter. During tank filling, concentrations of Guthion were considerably higher, ranging from 0.26 to 6.20 mg per cubic meter with a mean of 2.76 mg per cubic meter. During formulation, concentrations were even higher with a maximum of 9.64 mg per cubic meter being recorded in the blending area of the formulating plant.

TABLE 1.—*Respiratory Exposure of Workers to Guthion Based on Concentrations of Guthion in Air and on Quantities of Guthion Collected on Filter Pads Attached to Respirators*

Subject No.	Activity	Duration of Spraying (Min)	No. of Sprayings (Per Da)	Air Conc (Mg/Cu Meter)	Exposure		
					Air (Mg/Hr)	Pads (Mg/Hr)	Pads (Mg/Da)
10	Spraying of orchards	40	4	0.44	0.20	0.53	1.41
20	" " "	30	6	0.62	0.28	0.14	0.42
40	" " "	35	4	0.16	0.07	0.24	0.56
60	" " "	15	8	0.35	0.16	0.45	0.90
70	" " "	40	10	0.43	0.19	0.12	0.80
80	" " "	25	10	0.98	0.44	0.09	0.38
90	" " "	45	10	0.30	0.13	0.18	1.35
110	" " "	20	5	0.25	0.11	0.09	0.15
120	" " "	35	13	0.12	0.05	0.12	0.91
130	" " "	20	6	0.13	0.06	0.10	0.20
140	" " "	40	5	0.05	0.02	0.07	0.23
150	" " "	25	6	0.72	0.32	0.09	0.23
160	" " "	45	3	0.99	0.44	0.16	0.36
180	" " "	30	9	0.98	0.44	1.60	7.20
190	" " "	45	4	0.26	0.12	0.12	0.36
210	" " "	30	10	1.38	0.61	0.16	0.80
220	" " "	45	5	0.80	0.36	0.14	0.53
240	" " "	35	15	2.55	1.13	0.39	3.42
250	" " "	35	15	0.44	0.20	0.15	1.32
300	" " "	25	9	1.36	0.60	0.21	0.79
			Range:	0.05 to 2.55	0.20 to 1.13	0.07 to 1.60	0.15 to 7.20
			Mean:	0.64	0.30	0.26	1.12
430	Tank filling			0.98	0.44	0.81	0.61
460	" "			0.26	0.12	0.10	0.08
530	" "			3.08	1.37	1.04	0.78
540	" "			6.20	2.75	3.12	2.34
550	" "			3.31	1.47	1.27	0.95
			Range:	0.26 to 6.20	0.12 to 2.75	0.10 to 3.12	0.08 to 2.34
			Mean:	2.76	1.23	1.27	0.95
	Formulating 25% WP						
	General work area			1.07		0.09	0.72
				2.10			
	Blending area			9.64		1.03	8.24
				4.14			

The results of determinations of respiratory exposures by both direct and indirect methods are compared also in Table 1. The respiratory exposures are given in terms of milligrams per hour and milligrams per day, the latter being derived from the results of the direct method using the filter pad technique and the duration and number of spray applications per day. Table 1 shows respiratory exposures during spraying operations of 0.02 to 1.13 and 0.07 to 1.60 mg per hour and means of 0.30 and 0.26 mg per hour by the indirect and direct methods, respectively. The maximum daily respiratory exposure during spraying operations was 7.20 mg. The results of the determinations of daily respiratory exposures during tank filling are based on an average tank filling time of three minutes and a maximum of 15 tank fillings per day, and it may be seen from the Table

TABLE 2.—*Dermal Exposure of Workers to Guthion Based on Quantities of Guthion Collected on Cellulose Pads Attached to Forehead and Wrist*

Subject No.	Activity	Duration of Spraying (Hr)	Dermal Exposure: Measured (Mg/Sq Ft/Hr) Forehead	Wrist	Mean	Total (Calc) (Mg/Hr)	(Mg/Da)
10	Spraying of orchards	2.67	2.46	4.36	3.41	10.8	28.1
20	" " "	3.00	1.33	2.00	1.66	5.3	15.9
40	" " "	2.33	1.45	1.39	1.41	4.5	9.9
60	" " "	2.00	19.50	20.72	20.11	63.5	127.2
70	" " "	6.67	1.07	0.63	0.85	2.7	17.8
80	" " "	4.17	0.38	0.29	0.34	1.1	4.5
90	" " "	7.50	0.87	1.38	1.12	3.5	26.3
110	" " "	1.67	0.62	1.04	1.66	5.3	8.5
120	" " "	7.58	0.67	2.00	2.67	8.4	63.0
130	" " "	2.00	1.82	4.32	3.07	9.7	19.4
140	" " "	3.33	0.67	0.87	0.77	2.4	7.9
150	" " "	2.50	1.00	1.04	1.02	3.2	8.0
160	" " "	2.25	1.93	2.73	2.33	7.4	16.3
180	" " "	4.50	27.97	10.65	19.31	69.7	313.7
190	" " "	3.00	1.24	0.83	1.03	3.3	9.9
210	" " "	5.00	2.27	1.93	2.10	6.6	33.0
220	" " "	3.75	3.65	2.85	3.25	10.3	38.1
240	" " "	8.75	8.28	2.90	5.59	17.7	153.9
250	" " "	8.75	1.74	2.25	1.99	6.3	54.8
300	" " "	3.75	2.65	3.40	3.02	9.5	35.1
					Range:	1.1 to 69.7	4.5 to 313.7
					Mean:	12.5	49.5
430	Tank filling		4.14	28.73	16.43	52.9	39.6
460	" "		2.23	4.14	3.18	10.1	7.5
530	" "		29.21	20.72	24.96	78.9	59.1
540	" "		22.38	27.62	25.00	79.0	59.3
550	" "		9.12	18.41	13.76	43.5	32.7
					Range:	10.1 to 79.0	7.5 to 59.3
					Mean:	52.9	39.6
	Formulating						
1	Blending area		2.07			6.5	52.0
2	" "		2.59			8.2	65.6
1	" "		6.60			20.9	167.2
2	" "		3.20			10.1	80.8
3	" "		1.56			4.9	39.2
					Range:	4.9 to 20.9	39.2 to 167.2
					Mean:	10.1	80.9

that, although air concentration values were considerably higher during tank filling than during spraying, the actual respiratory exposures were appreciably less. Calculations of daily respiratory exposures in the formulating plant are based on an eight-hour working day. Table 1 shows also that the daily respiratory exposure in the blending area during formulating reached a slightly higher figure than the maximum recorded value during spraying operations. In the general work area of the formulating plant the daily respiratory exposure reached 0.72 mg per day, or only one tenth of the maximum value recorded during spraying.

Values obtained for dermal exposures are given in Table 2. The exposures are given in terms of milligrams per hour and milligrams per day, the latter being derived from the results of determinations of the quantities of Guthion collected hourly on α-cellulose absorbent pads and the precise daily working period. Table 2 shows ranges of dermal exposures during spraying operations of 1.10 to 69.7 mg per hour with a mean of 12.5 mg per hour. Daily exposures ranged from 4.5 to 313.7 mg with a mean of 49.5 mg.

Exposures during tank filling are based on an average filling time of three minutes and a maximum of 15 tank fillings per day, and it may be seen from Table 2 that, although the mean hourly exposure of 52.9 mg is considerably greater than that obtained during spraying, the over-all daily exposure was slightly less, with a mean of 39.6 mg. Determinations of dermal exposure in the formulating plant during the formulation of Guthion 25 WP showed a mean hourly dermal exposure of 10.1 mg which is less than the mean hourly exposure during both tank filling and spraying operations. Calculations of daily dermal exposure during formulating are based on an eight-hour working day, and Table 2 shows that the mean daily exposure in the blending area of the plant was 80.9 mg. This value exceeds the corresponding value obtained during tank filling and approaches twice the value obtained during spraying.

Comment

At the present time there is no accepted threshold limit value for the concentration of Guthion in the air; nevertheless an examination of Table 1 reveals that the majority of the air concentration values recorded during the operations of spraying, tank filling, and formulating exceed any feasible limit for continuous exposure which might be adopted in the future, cf parathion, 0.1 mg per cubic meter.[5]

Notwithstanding the exposure of spray operators to the above air concentrations, due to the comparatively short duration of spraying and tank filling operations, measurements of actual respiratory and dermal exposures showed them to be of a very low order. It is pointed out in reference to respiratory exposure that several spraymen used respirators and that one operator used a respirator during tank filling; however, the respiratory exposures given in Table 1 are the respiratory exposures which would have occurred had no respirators been used. Similarly in the case of dermal exposure, while the minimum clothing worn by some spray operators consisted of shoes, socks, long trousers, and short-sleeved open-necked shirts, others had more protection; but here again the dermal exposures given in Table 2 represent the exposures which would have occurred with the minimum clothing.

Respiratory exposures were found to be much less than dermal exposures. The mean respiratory exposure during spraying was found to be 0.26 mg per hour and during tank filling 1.27 mg per hour. The mean dermal exposure on the other hand was 12.57 mg per hour during spraying and 52.9 mg per hour (although as previously mentioned the mean daily exposure was 39.6 mg) during tank filling. Dermal exposures up to at least 8 mg per hour have been shown to have no effect on blood cholinesterase levels.[6] The maximum combined respiratory and dermal exposures obtained, ie, 3.12 mg per hour respiratory and 79.0 mg per hour dermal exposures, expressed as "percentage of toxic dose" [7] and based on dermal median lethal

TABLE 3.—*Cholinesterase in Blood Serum of Workers Before and After Formulating Guthion 25 WP*

Subject	A Reference Activity *	B Actual Activity †	Ratio B/A in %
1	6.34	4.93	77.7
2	7.26	6.43	88.4
3	5.02	4.32	86.0
4	7.20	6.24	86.6
5	7.42	6.75	90.9
6	7.30	6.53	89.4
7	5.86	4.61	78.6
8	7.20	6.14	85.2

Data provided by the Industrial Health Division of the Provincial Department of Health.

* Reference activity refers to the cholinesterase activity determined on blood samples obtained before exposure.

† Actual activity refers to the cholinesterase activity determined on blood samples obtained after exposure.

dose, (LD_{50}) values for male white rats show a percentage toxic dose absorbed per hour of 0.7. This value may be compared with values of 0.004 quoted for Guthion in checking cotton and 5.4 for parathion in apple spraying.[5]

Also shown in Table 2 are the respiratory and dermal exposures to which formulating plant workers may be subjected in the absence of protection from respirators or special clothing. In the formulating plant under investigation the workers were well protected by respirators and suitable protective clothing, and the exposures did not result in any appreciable depression of the blood cholinesterase levels, as may be seen from Table 3.

Summary and Conclusion

During the formulation of Guthion 25% wettable powder and the spraying of apple orchards with sprays containing 0.5 to 6.0 lb of 25% wettable powder per 100 gallons of water the following air concentrations and exposures were found:

A. Average air concentrations in the operators' breathing zone during spraying, tank filling, and formulating were found to be 0.64, 2.76, and 4.24 mg per cubic meter of air, respectively.

B. In the absence of chemical cartridge type respirators, the average daily respiratory exposures during spraying, tank filling, and formulating were found to be 1.12, 0.95, and 4.48 mg when determined by the direct method using the filter pad technique.

C. In the absence of protective clothing, average dermal exposures during spraying, tank filling, and formulating were found to be 49.5, 39.6, and 80.9 mg per day when determined by the direct method using the absorbent pad technique.

The results of measured respiratory and dermal exposures indicate that, under conditions such as obtained during the above survey, workers in apple orchards and formulating plants are unlikely to exhibit symptoms of acute Guthion poisoning.

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