Exposure of Workers to Carbaryl

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Since the carbamate pesticide, carbaryl (1-Naphthyl N-methylcarbamate), was first registered for agricultural use in 1958 it has enjoyed a reputation as one of the safest compounds as far as hazard to man is concerned. While conducting exposure studies on pesticide applicators and formulating plant workers during the last several years our observations have led us to believe that workers pay very little attention to prevention of excess human exposure when working with this compound which they consider practically nonhazardous. This has been more apparent with formulating plant workers than with spraymen. We have also noticed that these same workers become more cautious and provide more protection to themselves when working with compounds which they consider to be highly toxic. Apparently their safety education has impressed them with the need for protection when exposed to highly toxic compounds but with little respect for any potential effects long-term exposure to less acutely toxic compounds may produce.

Exposure values for orchard spraymen in Australia obtained by SIMPSON (1965) indicated that the amount of carbaryl deposited on dermal test areas was nearly four times more than for the more acutely toxic pesticide, azinphosmethyl, in the same experiment. Spray concentrations were not given, but it is doubtful that the carbaryl spray concentration was four times as great as for azinphosmethyl considering that the concentrations used in orchards in the United States for carbaryl are usually no more than twice that for azinphosmethyl. However, in Canada JEGIER (1964), studying exposure of seven orchard spraymen, found exposure to carbaryl about the same in relation to spray concentration as for azinphosmethyl.

In a study of workers engaged in the production, handling, and shipping of carbaryl shortly after the compound was first finding widespread use, BEST and MURRAY (1962) measured air concentrations at various work stations and also analyzed urine samples of workers in an effort to determine degree of exposure. They did not find air concentrations at levels above the 5 mg/M^3 threshold limit established for carbaryl by the AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (1972) except in the air separator house and in the breathing zone of the "bagger" during abnormal conditions. However, they found that 41% of urine samples collected contained in excess of 10 ppm total 1-naphthol, which they considered to be high.

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The present paper reports results of studies of potential dermal and respiratory exposure of formulating plant workers and spraymen to carbaryl, as well as urinary excretion of 1-naphthol by certain formulating plant workers.

Materials and Methods

Tests were conducted on workers in three pesticide formulating plants during formulation of 4% and 5% carbaryl dust and on spraymen operating tractor-drawn power air-blast equipment as they applied 0.045% to 0.06% carbaryl spray to fruit orchards. Workers studied at the formulating plants were at the bagging or mixing stations which are generally considered to be the areas of greatest potential contamination.

Estimation of the amounts of dermal and respiratory exposure that workers would potentially incur followed the techniques and procedures described in detail by DURHAM and WOLFE (1962). Potential dermal contamination was measured primarily by attaching absorbent a-cellulose pads for spray exposure, or layered gauze pads for dust exposure, to various parts of the worker's body or clothing and allowing them to be exposed during a timed period of work. The amount of pesticide entering the body via the respiratory route was estimated from the contamination of special filter pads used in place of the usual outer absorbent filter pads which cover the filter cartridges of the respirators worn by the subjects. The filter pads were covered with inverted plastic funnels modified to a specific aperture size to reproduce as nearly as possible the aerodynamics of air flow through the nostrils. The funnels also prevented direct impingement of droplets or particles onto the pad except for those carried through the apertures by respiratory action. This technique renders it unnecessary to measure total air volume because all inhaled air passes through the filter pads.

Exposure pads were extracted with nanograde benzene in a soxhlet extractor. A total of 480 analyses of dermal exposure pads and 73 respirator pads was carried out in the present study representing 32 different exposure situations for spraymen and 48 for formulating plant workers. Analysis of pad samples was carried out using a spectrofluorometric method. Evaluation of current spectrofluorometric methods, such as that published by ARGAUER *et al*. (1970), yielded some problems with respect to our samples which were overcome by employing a nonaqueous, basic hydrolyzing medium (isopropanol saturated with sodium methylate), to convert the carbaryl to 1-naphthol. The fluorescence of the 1-naphthol was then read in a Perkin Elmer Hitachi, MPF-2A fluorescence spectrophotometer.[1] The values were converted to carbaryl equivalent and reported as such. The method was found to be both rapid and accurate.

A total of 102 urine samples was collected from formulating plant workers during and following exposure to determine the amount of excretion of the carbaryl metabolite, 1-naphthol, in persons who appeared to be subjected to relatively high exposure. These samples were also analyzed by the spectrofluorometric method noted above. An advantage of this procedure with urine samples is the ability to read the major metabolite, 1-naphthol, directly in the presence of other urinary compounds without cleanup. These results were confirmed using the method of SHAFIK *et al.* (1971). This procedure employs an acid reflux hydrolysis of carbaryl to 1-naphthol. This phenol is then reacted with chloroacetic anhydride to form the chloroacetate derivative of 1-naphthol which is analyzed by electron capture gas chromatography.

Results and Comments

As can be seen in Table 1, pesticide formulating plant workers mixing and bagging 4% and 5% carbaryl dust were subjected to greater potential dermal and respiratory exposure than were field workers applying 0.045% to 0.06% carbaryl spray by power air-blast machines in orchards. Mean values for potential exposure of formulating plant workers was 73.9 mg/hr of work activity dermally and 1.1 mg/hr respiratorily. For spraymen the mean values were 59.0 mg/hr dermally and 0.09 mg/hr respiratorily. Considerable variation can be seen in the range of exposure values for each work activity. Each exposure situation seems to involve a different combination of factors that affect exposure. One of the factors observed as causing occasional high values for formulating plant workers during the study was malfunctioning of the bag filler spout mechanism, resulting in excess billowing of dust formulation into the work area. One of the factors causing higher than average exposure values for spraymen was thought to be wind. We believe that, in either operation, another factor may be laxity in taking precautions to prevent exposure when working with carbaryl. In a check of 15 formulating plant workers and 15 spraymen working with carbaryl, approximately one-half of the formulating plant workers, and none of the spraymen wore respirators.

The higher potential respiratory values for formulating plant workers reflected the frontal exposure to the more

[1]Use of trade names is for identification purposes only and does not constitute endorsement by the U.S. Environmental Protection Agency.

TABLE 1

Potential Dermal and Respiratory Exposure of Formulating Plant Workers and Field Spraymen to Carbaryl[a]

Subject	Route of exposure	Exposure situations studied	Exposure (mg/hr)	
			Range	Mean
Formulating plant workers[b]	Dermal	48	0.80 - 1209.30	73.90
	Respiratory	48	0.03 - 4.10	1.10
Field spraymen[c]	Dermal	32	1.70 - 211.80	59.00
	Respiratory	25	0.01 - 1.08	0.09

[a]Calculated on the basis of the worker wearing a short-sleeved, open-necked shirt, no gloves or hat, with his clothing giving protection of the areas covered.
[b]Workers on mixing and bagging operations (4% and 5% dust).
[c]Operating power air-blast spray machines in fruit orchards (0.045% to 0.06% spray).

concentrated dry carbaryl dust formulation. The very low potential respiratory exposure of spraymen indicated that most of the dilute spray droplets emitted from the air-blast machines used were too large to be easily drawn into the nasal orifice.

Data for exposure of different body areas, as shown in Table 2, indicates that for the formulating plant workers the highest potential exposure was on the hands, forearms, and the front of the body areas; whereas, in spraymen the downward drift of spray droplets appeared to produce highest exposure values for the shoulder areas and back of the neck.

The determination of blood cholinesterase activity was not included in this study. However, tests on other formulating plant workers have not shown detectable blood cholinesterase inhibition due to carbaryl exposure. It should be noted that the carbaryl cholinesterase complex is unstable and samples must be specially handled and processed in order to demonstrate a carbaryl-induced inhibition.

TABLE 2

Potential Dermal Exposure of Body Areas to Carbaryl per Hour of Work Activity During Mixing and Bagging Operations in Formulating Plants and During Application of Dilute Spray in Orchards

Body area	Total calculated exposure (μg/sq cm/hr)	
	In formulating plant[a]	During spray application[b]
Face	15.6	12.7
Shoulders	9.7	24.1
Front of neck and chest	26.5	13.4
Back of neck	5.5	15.3
Forearms and hands	15.6	9.9

[a]Mean values for 48 exposure situations.
[b]Mean values for 32 exposure situations.

Results of analyses of urine samples for the carbaryl metabolite, 1-naphthol, indicated that in certain instances relatively high levels of carbaryl had been absorbed by the formulating plant workers. Of 102 samples analyzed, concentrations of 1-naphthol varied from 0.2 to 65 ppm with a mean of 8.9 ppm. Twenty-six of these samples contained more than the 10 ppm of 1-naphthol which BEST and MURRAY (1962) reported as being in the high concentration range. The rate of excretion varied from 0.004 to 3.4 mg/hr, with a mean value of 0.5 mg/hr. Following exposure to carbaryl at the start of the work day the excretory level of 1-naphthol increased, reaching its maximum level during the late afternoon and evening hours, then dropped off to a lower level before the start of the next day's work. One of the higher rates of excretion (3.2 mg/hr) occurred in a worker who was practically engulfed in carbaryl dust for a short period of time as a result of a bag filler spout malfunction. He was not wearing a respirator. Peak excretion occurred approximately 6 hours after the excess exposure.

The 0.5 mg/hr mean value for excretion of 1-naphthol is equivalent to approximately 0.7 mg/hr excretion of carbaryl. This would indicate that absorption during an 8-hour work day would be 5.6 mg of carbaryl. If the mean potential dermal and respiratory exposure values for formulating plant workers, as noted above, are added together the calculated total potential exposure is 75.0 mg/hr, or 600 mg for an 8-hour work day. The wide difference between this potential exposure and the known absorption, based on excretion, indicates that absorption from dermal contact with the carbaryl dust is probably not very complete. MAIBACH and co-workers (1971) using ^{14}C-labeled pesticides found that carbaryl was almost a complete penetrant when applied in acetone to the skin of human subjects. However, WEIL and co-workers (1971) using different formulations of pesticide compounds on rats and rabbits, found that the solid forms were generally less toxic than the liquid forms, indicating that there is less dermal absorption from solids. Since dry wettable powder and dust formulations are classed as solids the indication of relatively low dermal absorption of carbaryl in formulating plants, based on excretion of 1-naphthol, leads us to conclude that absorption of carbaryl from dry formulations in formulating plants may be only a small fraction of the total potential calculated exposure.

Using the combined mean dermal and respiratory potential exposure values obtained in the present study of formulating plant workers and spraymen, the calculated percent of toxic dose per hour of exposure would be only 0.03% for formulating plant workers and 0.02% for spraymen. Even the highest exposure value obtained represents only 0.4% of a toxic dose per hour of work. These exceptionally low calculated values, of course, reflect a wide margin of safety to workers exposed to carbaryl considering the relatively low toxicity of the compound. At these dosage levels concern about acute toxic effects in workers would be minimal; however, in this study our interest is in the fact that quantity-wise the body is subjected to relatively high levels of the compound.

When no great additional effort is involved in providing protection from excess exposure over that which is normally practised when working with more toxic pesticide compounds, it seems wise to put forth that effort even when working with a compound of low acute toxicity. As much of the skin area as possible should be covered with protective clothing in order to avoid excess absorption of the compound, whether spraying in the field or working in the formulating plant. Where exposure is to dry formulations of carbaryl the respiratory route takes on increased significance and warrants the use of tight-fitting cartridge-type respirators, especially when working at the mixing or bagging stations in the formulating plant.

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