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Alkyl Phosphate Residue Values in the Urine of Florida Citrus Fieldworkers Compared to the National Health and Nutrition Examination Survey (HANES) Sample

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In a 1981 Florida citrus pesticide usage survey, it was found that substantial quantities of ethion, carbophenothion, malathion, and dioxathion are used on Florida citrus crops. Ethion is used for Snow scale and Rust mites; carbophenothion is used on Rust and Spider mites, Snow scale and other scale insects; malathion is used on Snow, Glover, and Yellow scale; and dioxathion on Rust mites. In Florida most spraying takes place from May through October, and again in February through March. In addition, diseases such as scab and melanose are controlled in Florida with oil/Benlate in June and July, depending on the time of bloom, with another spraying on dormant plants in February (Knapp, 1979).

Re-entry poisonings among fieldworkers have frequently been attributed to dislodgeable foliar residues. In fact, the Task Group on Occupational Exposure To Pesticides in a 1974 report to The Federal Working Group on Pest Management made the following statement:

> It has been recognized that the chemical pesticides remaining as residues on treated plant surfaces may constitute a hazard to the health of the workers who must, in the course of their work, come into substantial contact with these surfaces. The Task Group went on to identify citrus as the crop that "presents the greatest potential hazard for reentry poisoning".

This study was designed to monitor citrus fieldworkers during the course of their normal work activity. Urine from 597 fieldworkers employed in the Florida citrus industry as pesticide applicators, mixers, loaders, tractor drivers, scouts, general combination workers (fieldhands), and pickers were monitored for alkyl phosphate residues. The alkyl phosphate residue mean values found in the fieldworkers were compared to mean values found in the HANES population.

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METHODS AND MATERIALS

To determine the population at risk among Florida citrus fieldworkers (FCFW), a sampling frame of the 16,399 Florida citrus growers was constructed using computer tapes of county tax rolls. A stratified random sample of growers was selected and a list of fieldworkers employed by selected growers was developed by job category: mixers, loaders, applicators, tractor drivers, scouts, general combination workers (fieldhands), and pickers. Fieldworkers were then randomly sampled from each job category. A total of 436 growers and 1,811 fieldworkers were included in the study. A random sub-sample of growers was selected to identify workers for blood and urine collection. Informed consent forms were signed by each participant and a small payment was provided for serum and urine donors.

From those workers participating, a urine sample was collected at the workplace at the end of the work day. Workers were asked to urinate in washed and hexane rinsed laboratory specimen bottles. Each bottle contained a blank label securely attached so as not to come off during transportation in dry ice (Avery S-2448 labels 1" x 3" size). Bottle caps were lined with teflon or aluminum foil. Each worker was handed a specimen bottle and at that time the subject's name was written indelibly on the bottle label. After the subject returned the specimen bottle with urine, it was immediately frozen. All urine samples collected from the workers at the work site were transported immediately in dry ice for shipping to the University of Miami laboratory for analysis, or stored in a freezer for no more than a few hours until shipment could be arranged.

Samples were shipped in a styrofoam container with 25-35 lbs of dry ice. The entire insulated container was packed in a cardboard container to protect the insulated container from damage. The laboratory was notified in advance that a shipment was underway and an expected time of arrival. Actual shipping was by air freight or overnight bus freight to ensure that samples arrived at the laboratory without thawing. Sample labels contained the following information: Full Name, Time of sample collection, Grower Number, and Worker Number.

Samples were received at the laboratory by a member of the staff of the Division of Chemical Epidemiology, University of Miami School of Medicine. Laboratory personnel then assigned a laboratory number to each sample and entered it into a permanent, bound record. The laboratory number, worker number, individual identification number, grove name where worker employed, date and time collected, date and time sample was received at the laboratory and the responsible field coordinator were recorded.

Urine samples were defrosted. A 15-cc aliquot of shaken urine was centrifuged and used to determine creatinine and osmolality. Two 20-cc aliquots were placed in prelabeled, clean vials pending analysis. Storage was at -12 to -18°C and never with standards. An aliquot of every tenth urine was shipped to a cooperating laboratory for quality control. Detectors were calibrated daily using approved methods (U.S. EPA) Alkyl phosphates were determined by the method of Lores and

Bradway (1977). Spiked urine samples and reagent blanks were used to monitor for interfering components daily. Detection limits were usually 0.02 ppm but occasionally rose higher with a few at 0.03 ppm and a very few at .04 ppm.

RESULTS AND DISCUSSION

A total of 597 urine samples were analyzed for the presence of dimethyl phosphate (DMP), dimethyl thiophosphate (DMTP), dimethyl dithiophosphate (DMDTP), diethyl phosphate (DEP), diethyl thiophosphate (DETP), and diethyl dithiophosphate (DEDTP). The study covered the spraying season when mostly permanent and semi-permanent workers are employed in grove maintenance (including pesticides application) and the harvest season when pickers (including migrants) are the most numerous workers in the groves. The sample numbers, percent above detection limits, and means and standard errors of the alkyl phosphate residues among the FCFW are shown in Table 1.

Also included in Table 1 are data from the Health and Nutrition Examination Survey (HANES) carried out by the National Center for Health Statistics (NCHS). These data were provided to the authors in the form of a computer printout prior to publication by NCHS.

As is shown in Table 2A, the spray season FCFW had a much larger percentage of detectable levels of all alkyl phosphates monitored than did the HANES sample. The harvest season FCFW had a higher proportion of values above the detection limits than did HANES subjects except for DMP and DMTP. The spray season FCFW had higher proportions above trace than did the harvest season FCFW except for DMDTP and DETP.

A comparison of mean residue levels for observations above detection limits is shown in Table 2B. The FCFW (both spray and harvest) are consistently above the HANES sample only for DEP and DETP. One noteworthy feature is that for DEDTP, the HANES sample mean is not different from the spray season FCFW mean and is actually higher than that for the harvest season FCFW.

Clothing worn by the fieldworkers was fairly standardized. Spray season workers wore leather shoes or boots, long pants, short sleeved or no shirts, while the harvest season workers wore essentially the same articles of clothing, except that pickers wore long sleeved shirts with protective padding surrounding the arm from wrist to elbow, with heavy leather/cotton gloves. Franklin, et al (1981) found in a study of mixers, loaders, and applicators that all workers had quantifiable levels of alkyl phosphates following exposure even though each worker wore long-sleeved coveralls, half-face respirators, gloves, boots, and hats. The authors also concluded that measuring urinary metabolites appeared to be more sensitive than either air or patch monitoring. A screening method for rapid assessment of exposure to organophosphates through analysis of urinary alkyl phosphates has been described by Reid and Watts (1981).

Table 1. Urinary Alkyl Phosphate Residues (ppm) Among Florida Citrus Fieldworkers and the HANES National Sample (Non-Detectable and Trace * Values Excluded From Calculations of Means and Standard Errors)

		DMP	DMTP	DMDTP	DEP	DETP	DEDTP
Spray	Number in Sample	332	323	331	332	331	331
	% Above Trace	48.2	17.6	6.9	68.7	33.2	23.0
	Mean (SE)	.16 (.035)	.08 (.017)	.11 (.019)	.41 (.068)	.37 (.079)	.24 (.057)
Harvest	Number in Sample	264	262	265	265	262	262
	% Above Trace	6.1	3.8	6.8	43.0	26.3	5.3
	Mean (SE)	.39 (.198)	.15 (.083)	.25 (.106)	.09 (.007)	.07 (.006)	.06 (.006)
TOTAL	Number in Sample	596	585	596	597	593	593
	% Above Trace	29.5	11.5	6.9	57.3	30.2	15.2
	Mean (SE)	.18 (.037)	.09 (.019)	.17 (.049)	.30 (.046)	.25 (.050)	.21 (.049)
HANES	Number in Sample	6894	6895	6895	6894	6895	6895
	% Above Trace	10.2	5.3	0.3	6.2	5.2	0.1
	Mean	.05	.06	.05	.04	.04	.11

* - See text for a discussion of detection limits.

Table 2. Statistical Analysis of Urinary Alkyl Phosphate Residues Among Florida Citrus Fieldworkers and the HANES National Sample

A. Comparison[a] of Frequency of Observations Above Detection Limits

	DMP	DMTP	DMDTP	DEP	DETP	DEDTP
Spray Season vs. HANES	*	*	*	*	*	*
Harvest Season vs. HANES	n.s.	n.s.	*	*	*	*
All Workers vs. HANES	*	*	*	*	*	*
Spray vs. Harvest Season	*	*	n.s.	*	n.s.	*

B. Comparison[b] of Mean Values for Observations Above Detection Limits

	DMP	DMTP	DMDTP	DEP	DETP	DEDTP
Spray Season vs. HANES	*	n.s.	n.s.	*	*	n.s.
Harvest Season vs. HANES	n.s.	n.s.	n.s.	*	*	*
Spray Season vs. Harvest Season	n.s.	n.s.	n.s.	*	*	n.s.

a - Chi-square analysis with continuity correction. Each comparison at $\alpha/24 = .002$ using the Bonferroni procedure.
b - Student-t test. Each comparison at $\alpha/18 = .003$ using the Bonferroni procedure.
* - Statistically significant at the stated probability level.

With one exception there is a gradient of urinary alkyl phosphate residues from higher values among the FCFW to lower values among the HANES sample. The harvest season FCFW have higher (although not statistically significant) values of the methyl metabolites while the spray season FCFW have higher ethyl metabolites. However, the frequency of values above detection limits is highest among the spray season FCFW compared to the harvest season FCFW and HANES. These findings are consistent with the use of demeton, diazinon, and ethion which were found to be frequently applied (particularly ethion) to citrus during this study.

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