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Protectiveness of Kleengard® LP and Tyvek®-Saranex® 23-P During Mixing/Loading and Airblast Application in Treefruits

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Dormant oil/organophosphate insecticide (OP) applications are important tools for integrated pest management in California. Airblast sprayers are generally used for this purpose. Engineering controls and/or personal protective equipment is required to mitigate potentially high worker exposure during mixing, loading, and application. Typically, normal pesticide product labeling required work clothing and personal protective equipment are augmented by gloves, boots, respiratory protection, and a chemical suit such as Tyvek-Saranex® (TVS) or a rainsuit.

Agricultural pest control normally results in low level pesticide contact and absorption. Exposures result from skin contact, inhalation, and even ingestion as a result of hand-to-mouth activity or the swallowing particles entrapped in upper airways. Since the vast majority of exposure occurs via the dermal route, gloves, and clothing are especially important mitigating factors. To test the effectiveness of two types of protective clothing to mitigate day-to-day exposure, Kleengard LP® (KGLP; now marketed as Kleengard XP®) and Tyvek-Saranex®, two crews wore test garments during routine airblast spraying of organophosphate tank mixes in California orchards during a 2-week period in January, 1996. The organophosphates used as dormant sprays in the Central Valley of California include chlorpyrifos (CP), diazinon (DZ), dibrom (DB), and methidathion (MT). Dialkyl phosphate metabolites in 24-hour daily urine specimens were used to monitor exposure. Measurements during non-spray periods would reflect aggregate exposures associated with the workplace, application equipment, and the personal environment (home, diet, drinking water, etc.).

MATERIALS AND METHODS

The dormant oil/OPs were selected by individual growers who contracted with private Pest Control Operators for spray service (Table 1). Local well water was used. Daily records of sprayed materials are filed with the County Commissioner.

The two independent work crews consisted of two subjects: Crew A-workers 1944 and 3181; and Crew B—2720 and 4856. Both applied spray mixes to orchards in the Fresno area during the 2-week study period. The crews consisted of two mixer/loader/applicators and a foreman. Informed consent to be a research subject was obtained from each worker. The crews used virtually identical work practices and equipment.

For the first week, one mixer/loader/applicator in each crew wore KGLP over

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Table 1. Organophosphate Insecticides Used In Dormant-Oil Sprays

Common Names	Product/ Formulation	Percent A.I.
Chlorpyrifos CAS[2921-88- 2]	Lorsban 4E	40.7%
Diazinon CAS [333-41-5]	Diazinon 50WP	50%
Dibrom CAS [300-76-5]	Legion	58%
Methidathion CAS [950-37-8]	Supracide 25WP Supracide 2E	25% 24.4%

standard work clothes (long pants, long sleeved shirt, socks, and shoes, sometimes augmented by gloves, baseball cap, and coat, sweatshirt, or coveralls); the other crew member wore the standard work clothes plus TVS. During the second week, workers who had worn KGLP switched to TVS and vice versa. Protective clothing was changed each day. In the early morning (0600 hours) and on particularly cold days, a windbreaker or jacket would sometimes be worn over the protective clothing. Gloves, rubber boots, and respirator were worn during mixing and loading. The total monitoring period was 14 days.

After OP exposures, we analyzed daily urine specimens for a suite of six dialkyl phosphates in 24-hour collections made in 2 L polypropylene bottles. Basic metabolic data for CP (Nolan et al., 1984), DZ (Muecke et al., 1970), and MT (Bull, 1968) were obtained from the literature. Collected complete daily urine specimens whether workers sprayed OPs that day. Workers were instructed to inform study staff of lost or incomplete samples. None were reported. Compliance was monitored by frequent discussions with workers and by measurement and evaluation of urinary creatinine (Bernard and Lauwerys 1987). A gram creatinine per liter urine guideline was used as a measure of compliance.

Urine specimens were chilled using frozen Blue Ice and held in either an insulated box or refrigerator until transport to the field laboratory. Volumes were measured and 20-30 ml portions were frozen for analysis at Pacific Toxicology Laboratories, Los Angeles, CA. Field fortifications were performed on alternate days. These were spiked to give solutions at three DAP levels to cover the expected range of analytes.

Statistical design was a 2 x 2 Latin square for each of the two crews. Rows and columns of the Latin squares were weeks and worker, respectively, and treatment was either TVS or KGLP. Analysis of variance appropriate for combining two Latin squares was done to compare the effect of the two types of clothing on ADD and on ADD per pound active ingredient applied (Snedecor and Cochran, 1967).

RESULTS AND DISCUSSION

Daily average urine volumes were 1.8 L and creatinine levels averaged 1.7 g, indicating good compliance (Elkins et al. 1974). DAP levels were measured (ug/L) or reported as less than 25 ug/L (LOQ). For example, the first day's specimen (subject 2720) contained evidence of previous spray activity with DZ (diethylphosphate @ 112 ug/L and diethylthiophosphate @ 102 ug/L. The calculated daily pesticide equivalent would be 1707 ug/day [((112 ug/L x 304/154) + (102 ug/L x 304/170)) x 4.23 L]. Specimens from the other subjects had AP levels below 25 ug/L. Because of differences in urine volume, the nondetectable DAP levels of 25 ug/L for subject 4856 yield an upper bound daily AP excretion estimate of 56 ug per day. This amount corresponds to a calculated level of 211 ug DZ per day [((25 ug/L x 304/154) + (25 x 304/170)) x 2.25 L]. The true value will be between 0 and the reported upper limit value of 211 ug DZ.

Only OPs handled by the crews were assumed to contribute to DAP reported. A common set of DAPs are cleared and can be analyzed. These assumptions are imperfect, but they would not result in an underestimate of exposure. Because the DAPs reported are common metabolites OPs, our assignment of parent compound is not absolute. The calculated insecticide equivalents cleared in urine were based on which OP was sprayed and the sum of the calculated equivalents of each of the six DAP (ug/L) attributable to the parent insecticide. Most were less than the limit of quantitation (LOQ) of 25 ug/L. When that occurred the LOQ was conservatively assumed to be the upper limit and the potential urine level was calculated (<25 ug/L x urine volume, L). This absolute value is a function of urine volume; hence, it varies from sample to sample. If measurable amounts of APs were not present, the urinary level was assumed to be between 0 and the LOQ.

There were 10 OP spray days, which were unevenly divided between the crews. Crew A sprayed OPs 4 days. Data are given in Table 2 for Crew B that sprayed OPs on 6 days. Urinary DAP levels were 980 ug/day or less. ADDs were remarkably similar regardless of whether KGLP or TVS was worn. This observation is in accord with physical rather than chemical factors governing potential dermal exposure to pesticides of similar dermal absorption.

After use of an OP, without additional spraying, measurable DAPs clearance occurred from 2 to 7 days. Exposures on days 2 through 8 (0-356 ug) were near or below the LOQ (Crew A). Prolonged, low-level clearance could reflect the reservoir effect of skin, repeated low-level exposures from contaminated equipment or clothing, or uncertain sources of non-occupational exposure.

Exposure estimates divided by measured body weights (Table 3) are calculated absorbed dosages (CAD). In Crew A, handler 1944 consistently registered urine DAP levels at < LOQ. His average CADs ranged 0-3.2 ug/kg/day. Handler 3181 who performed identical work had a measured CAD of 3.0 ug/kg/day. This observation informally indicates that the exposures may have been similar. CADs and amounts of OP used per application are listed in Table 4.

The workers had similar OP exposures in each test garment (Table 4). Daily DAP clearance measurements resulted in a CAD of 0.12 to 0.22 ug/kg bw/pound a.i. applied. The lowest value occurred on the last day of the study and is only a fraction of the total CP equivalents that would have been excreted following the largest CP application (105 pounds) of the study period.

Table 2. Spray schedule of spray crew – "Fresno B"

Date Study Day	Product	Product per Load	# of Loads	Lbs a.i. per Acre	Lbs a.i. per Day	Start/ Stop	Notes
1 (Sat)	Asana	20 oz.	19			7:30a.m./ 3:00 p.m.	None
2	None	None	None	None	None	None	None
3	Asana	20 oz.	15			8 a.m./ 3:30 p.m.	None
4	Diazinon 50 WP	12.5 lbs	2	4.2	12.5	8 a.m./ 9:30 a.m.	None
5	Diazinon 50 WP	12.5 lbs.	6	4.2	37.5	6 a.m./ 9:30 a.m.	split day
5	Supracide 25 WP	12 lbs.	16	2.0	48	12:45pm/ 6:10 p.m	split day
6	Supracide 25 WP	12 lbs.	2	2.0	6	6:30pm/ 8:15 p.m.	split day
6	DZ 50 WP	15 lbs.	6	5.0	45	10 a.m./ 12 p.m.	split day
7	None	None	None	None		None	None
8	Legion	1 gal.	6	4.8	43.2	7:15a.m./ 10:45a.m	Champ 1.67 gal
9	None	None	None	None		None	None
10	None	None	None	None		None	Rain
11	Lorsban 4E	1.25 gal.	10	3.3	50	9 a.m./ 2:30 p.m.	None
12	Bond	0.5 gal.	22			9 a.m./ 4:50 p.m.	None
13	None	None	None	None		None	None
14	Lorsban 4E	1.25 gal.	21	3.3	105	8 a.m./ 5 p.m.	2 tank mixes

Total exposures (ug absorbed per kg body weight) for number of applications shown in parentheses. An application is one day of work, which varied as shown in Table 4. The dosage and dosage per pound were not significantly different between TVS and KGLP ($P > 0.05$).

The garments were new each day and were large enough to comfortably fit each worker. In preliminary trials workers frequently had complained about "small sizes." All garments were ample and all workers were satisfied with the fit. There was a strong preference for the softer material of the KGLP garments. Several workers commented that they fit as well as a "jump suit" and that unused garments could be comfortably worn "around town."

Aqueous sprays containing CP, DZ, DB, or MT were applied using airblast sprayers in combination with dormant oils during these studies in the winter of 1996 in the San Joaquin Valley of California. Small amounts, which produced no adverse effects, were absorbed by handlers during full work days during which routine work practices were followed. Phosphatases catalyzed hydrolysis of the

Table 3: Calculated absorbed dosage (CAD) per pound a.i. applied

Crew-Week	Handler/Garment	Insecticide pounds a.i.	CAD ug/kg	ug/kg/lb. a.i.
A-1	1944/K	Methidathion	8	0.18
	3181/T	45.5	6	0.13
	1944/K	Chlorpyrifos	8	0.12
	3181/T	66	7	0.11
B-1	4856/K	Diazinon	4	0.32
	2720/T	12.5	4	0.32
	4856/K	Diazinon	5	0.13
	2720/T	37.5	6	0.16
	4856/K	Diazinon	10	0.22
	2720/T	45	10	0.22
	4856/K[a]	Methidathion	12	0.22
	2720/T[a]	54	9	0.17
A-2	3181/K	Methidathion	6	0.17
	1944/T	33	8	0.24
	3181/K[a]	Methidathion	5	0.15
	1944/T[a]	33.75	3	0.09
B-2	2720/K	Naled	14	0.32
	4856/T	43.2	7	0.16
	2720/K	Chlorpyrifos	12	0.24
	4856/T	50	7	0.14
	2720/K[a]	Chlorpyrifos	4	0.04
	4856/T[a]	105	5	0.05

[a] One day urine would yield low metabolites
[b] Applied over a 2-day period

organophosphate insecticides to yield diethyl- or dimethylphosphates or corresponding dithiophosphates as stable biomarkers that were rapidly cleared in urine in microgram amounts. The insecticides have similar physical and chemical properties and disposition in animal models and exposed persons. For example, CP has been studied in humans and a variety of animals with similar results (Bull 1968; Nolan et al. 1984). DZ yields diethylthiophosphate (DETP) and diethylphosphate (DEP) whose first-order urine clearance as DZ equivalents account for about 75% of the administered dose after 24 hours (Mucke, et al. 1970). Rapid metabolism to stable biomarkers and extensive clearance in urine make the organophosphate insecticides valuable tools for characterization of workplace exposures and for evaluation of personal protective equipment such as the garments used in this work.

The determination of creatinine provided an informal measure of the completeness of urine collection. Creatinine distributes into total body water, is negligibly bound to plasma constituents, is eliminated entirely by renal excretion, and has a clearance equal to glomerular filtration rate (Rowland and Tozer 1980). Adult humans

Table 4. Total organophosphate clearance of handlers wearing either Tyvek-Saranex or Kleengard LP during airblast spraying

		TVS			KGLP		
Crew	Worker	ug/kg (appl.)	avg./ appl	per lb. a.i.	ug/kg (appl.)	avg./ (appl.)	per lb. a.i.
A	3181	13 (2)	6.50	0.120	11 (2)	5.50	0.120
	1944	11 (2)	5.50	0.165	16 (2)	8.00	0.150
B	2720	29(4)	7.25	0.218	30 (3)	10.00	0.200
	4856	19 (3)	6.33	0.117	31 (4)	7.75	0.222
	average		6.40	0.155		7.81	0.183

excrete an average of 1.8 g (1.1 to 2.5 g) creatinine/24 hr (Elkins et al. 1974). In this study the ratio of creatinine:urine (ml) was 1.7:1.8, providing strong evidence of the completeness of the 24-hour specimens which were provided.

Workers who mixed/loaded and applied organophosphate/dormant oil sprays wearing work attire plus either KGLP or TVS absorbed very small amounts of insecticide during a 14-day trial employing continuous urine biomonitoring. In every respect the garments met the workers' needs for protection and comfort. Pesticide exposures were equivalent ($P > 0.05$) regardless of whether KGLP or TVS were worn.

Protective clothing recommendations on the safe handling of products are important parts of pesticide manufacturer's guidance to customers. To maximize compliance the protective garment must be comfortable and deliver the degree of protection required to mitigate the risk of excessive exposure. In this case KGLP provided superior comfort and equivalent protectiveness against pesticide exposure. Dormant oil spraying using air blast equipment can present a significant challenge to protective clothing. When typical work practices of mixer/ioader/applicators were performed, the garments each provided full body chemical resistant protection. During 2 weeks of work, calculated excreted dosages of organophosphate insecticides were from 0.12 to 0.22 ug/kg bw/pound active ingredient (0.26-0.48 ug/kg bw/kg ai.).

Urine biomonitoring of mixer/loader/applicators of dormant oil/OPs who wore TVS or KGLP revealed equivalent levels of pesticide exposure. Worker comfort is a significant compliance issue with respect to clothing in the workplace, and should be considered in risk management. KGLP was strongly preferred with respect to pliability and the dissipation of body heat. It is also significant that levels of applicator OP exposure are significantly less than those predicted by available models. The findings warrant consideration for risk assessment and risk management when exposure reduction is an important concern.

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