relatively high levels of STX as compared to the GTX's, but the present procedure did not detect neo-STX.

Although the toxicity of the scallops from Ofunato Bay in the northern part of Honshu Island was not associated with any visible dinoflagellate blooms, the responsible organism appeared to be *Gonyaulax* spp. (referred to as a *Protogonyaulax* spp.), possibly *tamarensis* (Ueda et al., 1981). The presence of a large proportion of the sulfated derivatives of 11-hydroxysaxitoxin indicated by the fluorescence profile would confirm the causative agent as a *Gonyaulax*. The presence of a relatively small sulfated 11-hydroxysaxitoxin peak in the crab toxin profile may also suggest a *Gonyaulax* origin. Shimizu and Yoshioka (1981) showed that, on incubation, these derivatives decreased and saxitoxin increased. This may account for their presence in relatively low amounts. Since these crabs were collected in the tropical waters of the southern-most islands of Japan, *Gonyaulax* has not been a suspect organism because of its apparent preference for colder waters.

The procedure in its present form thus offers a convenient method by which very small quantities of the STX family of PSP's (STX, GTX_2, and GTX_3) may be separated and identified in crude shellfish extracts. It would be highly desirable to be able to also separate and identify the neo-STX family of toxins (neo-STX, GTX_1, and GTX_4) by a sensitive fluorometric procedure rather than having to rely upon mouse toxicity tests, which require larger amounts of toxin and are more inconvenient to carry out.

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Operator Exposure Measurements during Application of the Herbicide Diallate

Samuel Dubelman,* Rudolf Lauer, Dennis D. Arras, and Stephen A. Adams

Measurements of dermal and inhalation exposure of field operators were made during application of the herbicide diallate preemergent to sugar beets. Each operation—tank fill, application, and incorporation—was measured individually in order to assess its relative contribution to the total exposure value. Inhalation exposure was measured by trapping the herbicide on polyurethane foam plugs while sampling the air around the operator's face. Dermal deposition, which was determined by attaching gauze pads to the operator's clothing and cotton gloves on the hands, was the main contributor to the total exposure. Dermal deposition on the hands during tank-fill operations exceeded all other dermal values by about 200-fold. The use of closed-system chemical transfer and neoprene gloves during tank fills reduced total exposure to diallate by about 2 orders of magnitude.

Diallate [*S*-(2,3-dichloroallyl) diisopropylthiocarbamate; the active ingredient in Avadex herbicide] is a preemergent, soil-incorporated herbicide marketed by Monsanto Co. for the control of wild oats in sugar beets and other crops. It has been estimated that yield and production losses due to wild oats exceed $300 million annually, with half of these losses occurring in North Dakota (USDA, 1977).

On May 31, 1977, the EPA issued an RPAR (Rebuttable Presumption Against Reregistration) notice on diallate for suspected oncogenicity and neurotoxic effects. Since diallate residues have not been detected in raw agricultural commodities (tolerances for "negligible residues" at the

Monsanto Agricultural Products Co., Research Department, Environmental Science Section, St. Louis, Missouri 63166.

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method sensitivity of 0.05 ppm are currently in effect for all labeled crops), the general population was not considered at risk. Applicator exposure to diallate had not been measured, and all risk assessments were arrived at by extrapolation from studies with unrelated pesticides and theoretical considerations. The studies reported here were designed to fill this data gap by providing direct measurements of dermal and inhallation exposure to diallate in each of the agricultural operations performed during herbicide application (tank fill, application, and incorporation). Knowledge of the degree of exposure associated with each operation would allow the development of additional label instructions (thus minimizing operator exposure). The total exposure value, which is needed for an accurate risk/benefit assessment, can be obtained by combining the values for the appropriate individual operations.

Because spray-tank filling and mixing operations were suspected of providing the highest contribution to potential applicator exposure, experiments were also conducted with "closed-system" transfer of chemicals into spray tanks. Results from these experiments are also summarized here and compared to conventional methods of tank filling.

EXPERIMENTAL SECTION

Location. The exposure studies were performed in the Red River Valley near Grandin (about 30 miles north of Fargo) and Kindred (35 miles southwest of Fargo), ND. Specifically, large amounts of barley and sugar beets are grown in this area, for which Avadex EC is used as a fall-applied wild oat herbicide. The area provided large plot sizes and good separation distances between fields treated, thereby eliminating cross contamination problems.

Application Equipment. The spray/harrow apparatus consisted of a modified 30-ft Melroe multiweeder fitted with a fiberglass tank and a 30-ft spray boom. The spray boom was mounted 12 in. above the ground and was equipped with nine 5-gal flood jet nozzles. Spray solutions were delivered from the tank to the spray boom by a direct-drive pump driven by a ground wheel. The tank was filled with 225 gal of water to which was added 5 gal of Avadex EC formulation. With this mixture and a dilivery rate of 15 gal/acre, 1.25 lb of diallate was applied per acre. Treatment plots were approximately 20 acres in size and required about 1 h for application. A second incorporation was done at a 90° angle, within 24 h, on the fields where the spray/harrow applications were made. The same multiweeder used for the initial application (pump disengaged and tank empty) was used for the second incorporation.

For the boom spray plots, a McGregor sprayer was used. Equipment consisted of a 20-ft boom using 13-80015T jet tips, 18-in. boom height, 30 $lb/in.^2$ operating pressure, and a ground speed of 5 miles/h. The tank was filled with 100 gal of water and 3.5 gal of Avadex EC formulation. With this mixture and a delivery rate of 10 gal/acre, 1.25 lb of diallate was applied per acre. Treatment plots were approximately 10 acres in size and required about 1 h for application. Immediately after application the plots were incorporated to a depth of about 2 in. by using a 30-ft Melroe multiweeder.

For tank fills using closed-system chemical transfer, three commercially available units were used: the Protect-O-Loader (Protect-O-Manufacturing Co., Redmond, OR), the Chemprobe (Cherlor Manufacturing Co., Salinas, CA), and the Chemductor (Hollingsworth Co, Boone, IA). A Sears portable utility pump, Model No. 390.26000 (Sears, Roebuck & Co., Chicago, IL) was used to transfer the chemical form the closed-system probe or canister to the sprayer. A McGregor plot sprayer equipped with a 20-ft boom and TK-2 flood jet nozzles was used. The closed system was connected via heavy wall tygon (1-in. i.d.) or rubber hose provided by the closed-system manufacturer to the inlet of the Sears pump. The outlet of the Sears pump was connected through heavy wall, 1-in. i.d., tygon tubing to a tee installed between the pressure regulator and the bypass valves of the sprayer. A Worcester stainless steel, 0.5-in. NPT, ball valve was connected to the inlet of the tee to facilitate chemical transfer. The sprayer's bypass valves were kept open during chemical transfer to the sprayer tank.

In each case, the sprayer tank was half-filled with water (75 gal), and a 5-gal can of Avadex EC was then transferred. Following several rinses of the closed system, the sprayer tank was filled to the 150-gal mark with water.

Treatments were performed by using Ford 9600 and John Deere Model 4430, 4630, and 8630 tractors with cab and comfort control systems.

Sampling Techniques. For determination of the potential inhalation exposure, air samples were collected by using Bendix Model 500 high-volume air samplers, fitted with 11.8 cm diameter × 5.0 thick polyurethane foam (PUF) plugs. The effectiveness of PUF plugs as a sampling media for collection of airborne pesticides, PCB's, and other environmental contaminants has been described elsewhere (Turner and Glotfelty, 1977; Louis et al., 1977; Simon and Bidleman, 1979).

The polyurethane foam was obtained in 5 cm thick sheets from a local hardware store. Cylindrical 11.8 cm diameter plugs were cut from the foam sheet with a sharpened metal template. Extractable impurities were removed prior to use by successive washings with pesticide-grade acetone and hexane on a Büchner funnel, vacuum applied.

Air was sampled at the rate of 51 m^3/h, representing about 25 times the rate of air inhalation by humans (Webb, 1964).

Sampling of the air during tank-filling operations was accomplished by holding the air sampler adjacent to the operator's face, from the time the herbicide container was opened until the entire contents had been emptied into the spray tank and the tank capped. During applications and incorporations, two air samplers were used. One air sampler was located inside the tractor cab near the operator's head; the second was mounted outside the cab on the fender to simulate a tractor without a cab. The air samplers were run from start to finish of each respective operation, thereby providing a time weighted average exposure measurement.

Measurement of dermal exposure was accomplished by attaching 4 × 4 in. Johnson & Johnson sterile gauze pads to various parts of the operator's body. Five body locations were used for sampling: head, forehead, shoulder, chest, and back. For "closed-system" tank filling, a total of 12 gauze pads were used in order to measure deposition in additional body locations such as arms, thighs, and ankles. During application and incorporation, one gauze pad was attached to the tractor fender outside the cab, in order to acquire data representing use of a tractor with no cab. So that change-over time is kept to a minimum between operations, the gauze pads were stapled to a hat for the head and forehead samples, while the torso samples were attached to jackets or to disposable paper coveralls changed after each operation to avoid cross contamination between operations.

Dermal exposure to the hands was measured by using white cotton gloves. This technique would exaggerate

Table I. Diallate Recovery Studies

	polyurethane foam plugs	gauze pads	cotton gloves	soil
fortificn range, μg	1.0–2000	0.3–100	2.5–5000	5.0–50
no. of expt	25	27	28	10
recovery range, %	72–116	79–98	68–96	62–72
av recovery, %	92.3	86.2	83.5	68.2
SD	10.9	6.0	9.4	4.5
coeff of variation, %	11.8	6.9	11.2	6.6

exposure levels as the gloves absorbed any spills which could normally be washed or wiped off the hands (Davies, 1980). Hence, the purpose of this experiment was to evaluate the level of dermal exposure for an operator that, contrary to label directions, would handle the chemical with bare hands (in the case of closed-system tank fill, neoprene gloves were worn on top of the cotton gloves, as per label instructions). The cotton gloves were prewashed by using nanograde acetone followed by nanograde hexane.

Soil samples were taken immediately after each herbicide application. The samples were taken by using a 2 in. diameter metal cylinder inserted into the soil to a depth of 2 in. These core samples were taken randomly throughout the treatment plot until enough soil had been collected to fill a 0.5-gal metal can.

Collection, retention, and desorption efficiencies were determined by injection of microliter volumes of diallate in hexane onto the surface of PUF plugs, gauze pads, gloves, and soil (Table I). The fortified samples were carried through tank fill, application, and incorporation operation (air was being drawn through PUF plugs). Control experiments were similarly carried out with unfortified collection media. No diallate was sprayed during these "dry" runs.

Collected samples (PUF plugs, gauze pads, and gloves) were wrapped in aluminum foil and stored individually in metal cans. All cans (including soil) were stored in dry ice packed, insulated shipping boxes for transfer to the analytical laboratory where they were stored frozen (−20 °C) until analyzed.

Field Operations. Measured field operations include six conventional tank fills, nine closed-system tank fills (three repetitions × three types of closed-system transfer), six applications, and six incorporations. Additionally, field control and fortification experiments for measurement of analytical recovery and field stability of samples were conducted immediately preceding the actual "exposure" measurements. Appropriate "validation" experiments were conducted in the laboratory prior to field use of the techniques to ensure trapping and retention of diallate on the collection media. All experiments were done during the fall season, prior to soil freeze-up, with air temperatures ranging from 39 to 72 °F, soil temperatures of 45–56 °F, relative humidities of 40–92%, and winds 0–20 miles/h mainly from the north and northwest. During one of the conventional tank-fill replicates, winds of 28 miles/h from the northwest were experienced and the chemical was splashed over implements and measuring equipment. This replicate was excluded from the analytical presentation since the farmer would not spray under these windy conditions (research personnel had decided to work that day, against the farmer's advice).

Analytical Methodology. Polyurethane foam (PUF) plugs were extracted with pesticide-grade hexane. The plug was placed in an 85-mm Büchner funnel and rinsed twice with hexane (250 and 50 mL). Plugs were com-

Table II. Inhalation Exposure Measurements (Air Sampling with Polyurethane Foam Plugs)

field operation	no. of replicate fields	av exposure time, min	av concn of diallate, μg/m³
tank fill and mix (conventional)	6	2.8	4.6
tank fill, closed system (Protect-O-Loader)	3	17.3	0.22
tank fill, closed system (Chemprobe)	3	17.0	0.50
tank fill, closed system (Chemductor)	3	16.3	0.20
boom spray application			
closed cab tractor	3	42.6	5.0
open tractor[a]	3	42.6	3.8
spray/harrow application			
closed cab tractor	3	69.3	15.8
open tractor[a]	3	69.3	12.7
disc incorporation			
closed cab tractor	3	27.6	18.6
open tractor[a]	3	27.6	4.2
harrow incorporation			
closed cab tractor	3	42.3	24.4
open tractor[a]	3	42.3	1.8

[a] Sampling pumps outside of tractor cab simulate open tractor. Samples inside and outside of cab were taken simultaneously.

pressed after each extraction with the aid of a beaker to ensure complete recovery of the extracting solvent. The combined extracts were concentrated to a 5-mL volume by rotary evaporation at room temperature. The concentrated extract was applied to a column (1 × 10 cm) of polyethylene-coated alumina (Kensco No. K-3209) topped with 1 cm of anhydrous sodium sulfate, and the column was rinsed sequentially with 200 mL of hexane and 80 mL of 0.05% ethyl acetate in hexane (these rinses were discarded). Diallate was eluted from the column with 200 mL of 0.1% ethyl acetate in hexane. This eluate was concentrated to 5 mL and quantitated by gas chromatography with ^{63}Ni electron capture detection on a glass column (1.8 m × 4 mm i.d.) of 3% XE-60 on 100–120-mesh Gas-Chrom Q, at 175 °C with a flow rate of 30 cm^3/min nitrogen.

Gauze pads were extracted by placing in an 8-oz bottle with 150 mL of hexane and shaking on a mechanical shaker for 30 min. After the hexane extract was decanted, the gauze pad was further rinsed with two 25-mL aliquots of hexane. The combined extracts were concentrated to 5 mL. Column cleanup and quantitation were as described for PUF plugs.

Cotton gloves were extracted with several hexane aliquots totaling 600 mL. The combined extracts were concentrated to 10 mL and applied to a column, 1 × 12 cm, aluminum oxide (grade III activity; prepared from Woelm alumina W-200 basic according to manufacturer specifications). Following sample application the column was rinsed with 25 mL of hexane (discarded). Diallate was eluted with 100 mL of hexane, concentrated to 5 mL, and quantitated as described above. Soil samples were extracted with 100 mL of isooctane–2-propanol (2:1). After filtration an aliquot of the extract was injected to the gas chromatograph under the conditions described above. Concentration and cleanup were not necessary. The moisture content of the soil was determined by drying in an oven at 110 °C for 24 h.

Analytical sensitivity of the methodology was 1 μg of diallate/PUF plug (0.02 μg/m^3), 0.3 μg/gauze pad (0.003 μg/cm^2), 2.5 μg/glove (0.003 μg/cm^2), and 0.2 ppm in a 25-g sample of soil.

Table III. Dermal Exposure Measurements Using Gauze Pads and Cotton Gloves

field operation	field replicates	dermal deposition of diallate on gauze pads and gloves, $\mu g/cm^2$ [a] head	forehead	shoulder	chest	back	other body[b]	fender[c]	hands
tank fill and mix (conventional)	6	0.15	0.67	0.06	0.19	0.07	NS	NS	71.2
tank fill, Protect-O-Loader, closed system	3	<0.005	<0.005	<0.005	<0.005	<0.005	0.013	NS	<0.06
tank fill, Chemprobe, closed system	3	<0.005	<0.005	<0.005	<0.005	<0.005	0.005	NS	<0.06
tank fill, Chemductor, closed system	3	<0.005	<0.005	<0.005	<0.005	<0.005	0.009	NS	<0.06
boom spray application	3	0.03	0.05	0.06	0.04	0.03	NS	0.06	0.11
spray/harrow application/ incorporation	3	0.06	0.10	0.16	0.20	0.16	NS	0.10	0.60
incorporation (disc)	3	0.04	0.09	0.10	0.09	0.09	NS	0.03	0.11
incorporation (harrow)	3	0.05	0.13	0.16	0.14	0.09	NS	0.03	0.24

[a] Numbers are average of field replicate samples. NS = no sample taken. [b] Other body numbers are average of samples from thigh, forearm, bicep, and ankle. [c] Gauze pad on tractor fender simulates deposition with "open" tractor. All other values are for closed (cab) tractor.

Table IV. Analysis of Soil after Herbicide Application

type of application	lb/acre diallate[a] applied	found
control	0	0
spray/harrow	1.25	0.60
boom spray	1.25	1.07

[a] Each number is an average of six field replicates.

RESULTS AND DISCUSSION

The two primary pathways for human exposure during herbicide application are direct inhalation and dermal deposition. Data for inhalation exposure were obtained by sampling air through polyurethane foam plugs held next to the operator's face (Table II). Note that for applications and incorporations diallate concentrations inside the tractor cab were slightly higher than outside. This was probably due to contamination of the air inside the cab (dirt carried on shoes, gloves soaked with spray during nozzle cleaning, etc.).

Dermal deposition was measured by the use of cotton gloves on the hands and absorbent gauze pads attached to various parts of the operator's clothing (Table III). Soil samples were taken after application to verify the application rate (Table IV).

The primary purpose of this study was to determine the magnitude of the exposure associated with each of the agricultural operations shown in Tables II and III, in order to develop additional label instructions for minimizing exposure. Table V shows the total operator exposure due to inhalation and dermal deposition for an operator weighing 60 kg. The values are arrived at by using eq 1 and 2:

$$\text{inhalation exposure } (\mu g/kg) = [\text{measured } \mu g/m^3 \times \text{time (h)} \times 1.8 \text{ m}^3/\text{h}]/60 \text{ kg of body weight} \quad (1)$$

$$\text{dermal deposition } (\mu g/kg) = [\text{measured } \mu g/cm^2 \times \text{exposed skin } (cm^2)]/60 \text{ kg of body weight} \quad (2)$$

where "measured $\mu g/m^3$" is the diallate concentrations found in Table II, time (h) is the amount of time spent by the operator in performing the operation for a 20-acre plot (Table II), and 1.8 m^3/h is the breathing rate of an average human being (*Fed. Regist.*, 1977); measured $\mu g/cm^2$ are the values given for deposition on the hands and deposition on the face/neck area (the average of the values for the head, forehead, and shoulder pads) in Table III. The surface area of "exposed skin" is 910 cm^2 for the face and neck and 820 cm^2 for the hands (Durham and Wolfe, 1962; Davies, 1980).

Table V. Total Operator Exposure in Each Application Operation[a]

field operation	inhalation exposure, $\mu g/kg$	dermal deposition, $\mu g/kg$ face/neck	hands
tank fill, conventional	0.006	4.5	973
tank fill, closed systems			
Protect-O-Loader	0.001	<0.07	<0.8
Chemprobe	0.004	<0.07	<0.8
Chemductor	0.001	<0.07	<0.8
boom spray application	0.106	0.70	1.50
spray/harrow combination	0.547	1.61	8.20
disc incorporation	0.256	1.16	1.50
harrow incorporation	0.516	1.71	3.28

[a] All exposure values are based on application to 20-acre plots.

Comparison of inhalation and dermal exposures (Table V) indicates that dermal deposition is the main contributor to the total operator exposure. In the case of a conventional tank fill, and without using rubber gloves (contrary to label instructions), dermal deposition on the hands contributes >99% of the total exposure. In contrast, the use of neoprene gloves and closed systems for tank fills reduced the dermal deposition during tank filling to negligible levels. Dermal deposition was 4–15-fold higher than inhalation exposure for application and incorporation operations. Inhalation exposures during application and incorporation operations were 17–91-fold higher than during tank fills, probably a result of longer exposure times and generation of herbicide-carrying particles by the agricultural implements.

As indicated by Davies (1980), the use of cotton gloves for measurement of dermal exposure to the hands would lead to overestimation of exposure because "... the glove might absorb more liquid than could be expected to adhere to flesh". We agree with the view that cotton gloves may produce overestimation of dermal deposition, but simplification of the field operations and providing some degree of safety for the operators in the study were major factors in our decision to use gloves. Alternate methods of direct measurements would have involved washing or swabbing herbicide deposited on bare hands (Durham and Wolfe, 1962). Hence, we consider the values shown in Table V for hand exposure to be higher than can be ex-

Table VI. Total Operator Exposure for Complete Herbicide Application Sequence[a]

application system	inhalation exposure, μg/kg	dermal deposition, μg/kg	total exposure, μg/kg
conventional tank fill + boom spray + disc incorporation	0.37	982.3	982.7
conventional tank fill + spray/harrow combination	0.55	987.3	987.8
closed system (Chemprobe) + spray/harrow combination	0.55	10.6	11.2

[a] Exposure values based on application to 20-acre plots.

pected during normal use of this herbicide.

The total exposure for any application system can be calculated by adding the values for individual operations. Several possibilities are shown in Table VI. Note that the use of the closed-system tank fill does not reduce the total inhalation exposure but significantly reduces the dermal deposition. The later result is believed to be mainly due to the use of neoprene gloves (as specified in label instructions) on top of the cotton gloves. Therefore, the most important conclusion derived from this study is that the total operator exposure to diallate during herbicide applications can be reduced by almost 2 orders of magnitude by the use of neoprene gloves and a closed system for tank-fill operations.

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Fall Armyworm Control and Residues of Methomyl on Coastal Bermuda Grass

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Methomyl, monocrotophos, and acephate effectively controlled fall armyworm larvae in stands of Coastal Bermuda grass, but carbaryl and trichlorfon were ineffective. Residues of methomyl, the compound selected for detailed studies, declined rapidly with time after application, and by 7 days about 7% of the initial deposit remained regardless of the rate of application. Methomyl loss during dehydration in a natural gas dryer was about 54%. The pelletizing process caused an additional loss of about 14%. Thus, the total loss of methomyl during processing of green hay to pellets amounted to about 68%. Losses of residues during air curing of hay in the field amounted to about 37%.

Coastal Bermuda grass [*Cynodon dactylon* (L.) Pers.] is a warm-season forage grass of major importance in the southeastern United States. With good management practices 2 to 4 times as much dry matter per unit area can be produced with Coastal than with common Bermuda grass (Dobson et al., 1974). It is grazed by cattle, cut and cured for hay, or cut, dehydrated, and ground for use in feed mixes for cattle, hogs, and poultry; the meal is also pelletized for animal feed.

A devastating infestation of fall armyworm (*Spodoptera frugiperda* J. E. Smith) developed on Coastal Bermuda grass in southeastern North Carolina in Aug and Sept 1975. The population of larvae was so great that severe defoliation and losses in yield occurred. There were moderate outbreaks in at least 2 years since 1975. Other southern states frequently have such infestations.

Reports of ineffectiveness of carbaryl (1-naphthyl *N*-methylcarbamate) and trichlorfon [dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate], commercial products which are registered for control of fall armyworms on Bermuda grass, and the need for control prompted us to initiate field studies on the comparative effectiveness of carbaryl, trichlorfon, methomyl [*S*-methyl *N*-[(methylcarbamoyl)oxy]thioacetimidate], and monocrotophos [dimethyl phosphate ester with (*E*)-3-hydroxy-*N*-methylcrotonamide] in the fall of 1975. The studies were designed to evaluate control of fall armyworm larvae by ground and aerial applications and to supply samples of green, cured, and pelletized Coastal Bermuda grass for residue analyses. Portions of this work were reported briefly in abstract form (Campbell and Sheets, 1976).

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EXPERIMENTAL SECTION

The study consisted of small-plot experiments in 1975, 1976, and 1977, which were treated with ground equipment, and large plots in 1975, which received aerial applications. Samples from all experiments were analyzed for residues of methomyl.

Small-Plot Experiments. In 1975, plots 7.5 by 15 m were laid out in Scotland County, NC, on a dense, well-established stand of Coastal Bermuda grass showing moderate to severe fall armyworm damage. Treatments were methomyl at 0.28, 0.56, and 1.1 kg/ha, monocrotophos

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