# **Glove Permeation Tests Using Novel Microchemical Techniques for 2,4-Dichlorophenoxyacetic Acid (2,4-D) Derivatives**

Y.-W. Lin, S. S. Que Hee

Department of Environmental Health Sciences and UCLA Center for Occupational and Environmental Health, UCLA School of Public Health, 10833 Le Conte Ave., Los Angeles, California 90095-1772, USA

Received: 8 July 1998/Accepted: 13 December 1998

Abstract. The aim was to assess the permeation of different herbicide emulsion concentrate formulations of 2.4-dichlorophenoxyacetic acid (2,4-D) as 60.8 and 83.5% butoxyethyl ester (BEE) and 46.8% dimethyl amine salt (DMAS) through four types of glove materials (lined unsupported nitrile, unlined unsupported butyl, Silver Shield laminate, and Viton). This entailed the development of new microchemical techniques to allow sensitive capillary gas chromatography/mass spectrometry (GC/MS) of the permeated herbicide. The 2,4-D DMAS was esterified to the methyl ester by boron trifluoride-methanol complex with 99.2  $\pm$  3.7% efficiency using microwave heating to minimize reaction time and to process microsamples. The GC/MS detection limit was 5 ng/ml (ppb) of 2,4-D DMAS in the collection medium. The permeates from the ester formulations were analyzed directly for the ester above the detection limit of 9 ng/ml (ppb) BEE. The permeation investigations utilized the American Society for Testing Materials (ASTM)type permeation cells with liquid collection media. The results showed that these gloves could provide at least 6 h protection for these formulations.

Protective clothing is an essential personal protective equipment item for workers and for many others who require shielding from the adverse effects of chemical, physical, and biological agents. The transfer of a challenge agent through a protective clothing barrier without degradation of the barrier is permeation. Transfer through pinholes in the barrier present originally or after chemical degradation of the barrier is penetration. The time when the agent is detected in the collection medium by permeation, penetration, or both processes is termed the breakthrough time, t<sub>b</sub>, and is technique dependent. When the rate of appearance of agent in the collection medium is constant, the transfer process is said to be in steady state, characterized by both the steady state transfer rate,  $P_s$ , and the lag time,  $t_l$ , the latter being the hypothetical time when the steady state last shows zero transferred mass in the collection medium. Manufacturers of gloves and protective clothing offer only  $t_b$  and  $P_s$  for guidance for selection of chemically protective clothing. Gloves are also characterized by physical properties related to strength, flexibility, and wearer comfort in addition to protectiveness. The correct initial choice of gloves that are to be disposed of after the task is thus crucial. The influence of workshift manual manipulations on permeation properties requires separate study: if the gloves fail when no stress is on them, this needs to be known before donning them.

Although the permeation properties of commercially important solvents are well documented, those for pesticides in their formulations are not. A liquid pesticide like malathion can permeate without assistance (Lin and Que Hee 1998a). In fact, the presence of 12 xylene-fraction inert components moderated the permeating properties of pure malathion in a liquid emulsion concentrate, and this has been modeled for nitrile and butyl gloves (Lin and Que Hee 1998b, 1998c). The permeation of a solid pesticide is wholly dependent on the liquid inert ingredients of emulsifiable concentrates, an area of ongoing research for our research group. The permeation of solid organophosphates (Khan et al. 1997) and carbamates (Lu and Que Hee 1998) in their liquid emulsion concentrates has been already reported in addition to earlier work with an emulsion concentrate of isooctyl ester of 2,4-dichlorophenoxyacetic acid (2,4-D), the pure ester being a viscous, nonpolar liquid (Harville and Que Hee 1989). The present study extends the latter investigation for a different ester and a salt form of the organochlorine herbicide 2.4-D.

2,4-D is a phenoxy herbicide that on absorption ("systemic") is transported to its target sites ("translocated") (Audus 1976). It is usually applied as a salt or ester together with other inert components. 2,4-D amine salt, alkali salt, and low-volatile ester formulations are used to control broadleaf plants and weeds in orange groves, lawns, golf courses, forests, roadways, parks, playgrounds, playing fields, and agricultural land (Harris *et al.* 1992). 2,4-D butyl and octyl esters were the constituents of Agent Orange, the Vietnam War defoliant (Que Hee and Sutherland 1981). 2,4-D has been reported to cause convulsions, peripheral neuropathy, and brain damage in poisoning cases (Watterson 1988). Acute effects include skin and mucous membrane irritation. Workers have reported general weakness, headache, dizziness, stomach pains, and nausea after occupa-

Correspondence to: S. S. Que Hee

tional exposure (Hayes 1982; Stevens and Sumner 1991). Kansas farmers who used 2,4-D for more than 20 days per year reportedly had a risk of lymphatic cancer six times higher than a control group with no exposure to herbicides (Nadakavukaren 1990). Agricultural workers exposed to 2,4-D exhibited abnormal spermatozoa as tetraspermia (Lerda and Rizzi 1991). Suicides with 2,4-D dimethyl amine salt (DMAS) have been documented (Keller *et al.* 1994). The major route of human exposure to the semivolatile and nonvolatile forms of 2,4-D currently sprayed is through the skin (Hayes 1982). Thus, the wearing of personal protective equipment like gloves is necessary (Grover *et al.* 1988). Studies of permeation through glove materials are therefore essential.

Data on the permeation of some 2,4-D derivatives are available. 2,4-D DMAS permeated through cotton coveralls and a short-sleeved cotton T-shirt to farmers' skins (Grover et al. 1988). No breakthrough was observed when a 2,4-D Amine 96<sup>®</sup> formulation containing 2,4-D DMAS challenged neoprene, natural rubber, polyvinyl chloride, and nitrile butyl rubber for 8 h and 16 h using the ASTM and AIDA test methods, respectively, using a number of permeation cell types (Moody and Ritter 1990). Killex®, a 11.8% 2,4-D DMAS formulation, showed no detectable permeation against nitrile rubber gloves over a 24-h period (Moody and Nadeau 1994). The same challenge concentration of 2,4-D DMAS in acetone permeated through the same glove material during the 24-h testing period (Moody and Nadeau 1994). Thus, the type of carrier solvent was important. 2,4-D formulation emulsion concentrates and aqueous solutions of Esteron<sup>®</sup> 99 containing 2,4-D isooctyl ester had  $t_b < 10$  min for nitrile and neoprene glove materials (Harville and Que Hee 1989; Que Hee 1989). Tyvek (laminated Saranax) and unsupported nitrile protected up to 100 min. Permeation of 2,4-D free acid in acetone through natural rubber gloves was  $3.2 \pm 3.5\%$  after 48 h (Moody and Nadeau 1992).

The detection limits for the 2,4-D DMAS studies that did not use radiolabeling were high because high-performance liquid chromatography (HPLC) with ultraviolet (UV) detection was utilized as the analytical technique to define the herbicide  $t_b$ . Therefore, a more sensitive technique might reveal shorter  $t_b$ . The polarity of the active ingredient may also modify the permeation properties of the carrier solvent as evident for malathion (Lin and Que Hee 1998b, 1998c). Indeed the higher the concentration of the active ingredient, the more important should this effect be on inert components that do not permeate alone. The saline collection medium used to mimic sweat in some studies might cause a salt effect that would reduce solubility in the saline relative to water and keep a permeated organic from desorbing into the saline collection medium. This would cause long  $t_b$  and low  $P_s$ .

Though many methods are available for 2,4-D compounds to create volatile derivatives for sensitive (pg sensitivity) gas chromatography/mass spectrometry (GC/MS), there is still a need for methods that can determine small quantities of analytes without intensive sample preparation. In this study, an efficient and reliable microchemical GC/MS method for the esterification of 2,4-D DMAS microsamples was developed based on the BF<sub>3</sub>/methanol (BFM) method (Horner *et al.* 1974; Henshaw *et al.* 1975; Lee Choi *et al.* 1976). One DMAS salt and two butoxyethyl ester (BEE) low-volatile formulations

were investigated in the present study with methods of about equal sensitivity relative to 2,4-D acid equivalent.

## **Materials and Methods**

#### Gloves and Reagents

Four types of glove barriers were tested: lined unsupported Sol-vex nitrile from Ansell Edmont (Coschocton, OH, catalog No. 37-165, 0.56 mm thickness, 38 cm in length), unlined unsupported butyl (B131, light weight, 0.36-0.38 mm thickness, 28 cm in length), Silver Shield laminate (SS104M, 0.76 mm), and Viton (F124, 2.3 mm) from North Hand Protection (Charleston, SC). The more expensive Silver Shield and Viton gloves should be protective to 2,4-D ester formulations, and the much less expensive nitrile gloves should be less protective (Harville and Que Hee 1989). The inexpensive butyl gloves were expected to offer about the same protection as nitrile, based on solvent protection characteristics relative to nitrile. Weedone Brand LV4 (60.8% nominal weight percentage of 2,4-D BEE), Weedone Brand LV6 (83.5% nominal weight percentage of 2,4-D BEE), and Weedar Brand 64 (46.8% nominal weight percentage of 2,4-D DMAS) were provided by Rhone-Poulenc (Research Triangle Park, NC). 2,4-D (Kodak, Rochester, NY), 2,4-D BEE, 2,4-D DMAS, and 2,4-D methyl ester (ME) (Chem Service, Westchester, PA) were used as the primary standards. Methanol MeOH (Optima, Fisher Scientific, Fair Lawn, NJ), anhydrous diethyl ether (Reagent A.C.S., Fisher Scientific), and boron trifluoride (BF<sub>3</sub>)-MeOH complex BFM  $\sim$ 50% wt BF<sub>3</sub> (Aldrich, Milwaukee, WI) were used in 2,4-D DMAS esterification. Hydrochloric acid HCl (trace metal grade, 30.5-38.0 % w/w) and sodium hydroxide NaOH (Fisher Scientific) facilitated pH adjustment.

Nitrogen (99.995%) from Alphagaz (Walnut Creek, CA) was passed through a charcoal tube (20/40 mesh, Aldrich) before use in evaporative concentrations. Optima grade hexane and 2-propanol from Fisher Scientific were the collection media for permeation and dilution purposes as appropriate (Table 1). American Society for Testing and Materials (ASTM)-Type I distilled water was generated by a Millipore Super-Q water filter system (Bedford, MA). Sodium dichromate (Fisher Scientific) was used to produce an atmosphere of known relative humidity (RH).

## Apparatus

ASTM-type I-PTC-600 permeation cells (Figure 1) were from Pesce Lab Sales (Kennett Square, PA). The moving tray shaker water bath used for simultaneous immersion of three permeation cells was a Fisher Scientific model 125 series No. 429 (Lin and Que Hee 1998a–c). A torque wrench (Mechanics Products, Kent, WA) ensured equal tightness of permeation cell nuts. A vortex mixer (Thermolyne type 16700 mixer, Dubuque, IA) facilitated liquid-liquid extraction. Kimax test tubes of 15 ml and 10 ml with Teflon-septum screw caps contained permeates for processing. An 850-W microwave oven (Gold Star, model 1080M, Seoul, Korea) heated the samples.

The analysis utilized a Hewlett-Packard 5890A gas chromatograph equipped with a Hewlett-Packard 5988A quadrupole mass spectrometer in 70 eV positive ion electron impact mode. The fused silica capillary column was a 30-m long  $\times$  0.32-mm ID DB-1701 with 1.0  $\mu$ m chemically bonded 14% cyanopropylphenyl film from J&W Scientific (Alltech, Deerfield, IL). Carrier gas helium of 99.9999% purity at flow rate 3.0  $\pm$  0.3 ml/min was from Alphagaz.

 Table 1. Challenge formulations, glove materials, and collection media used in the permeation tests

	Weedone	Weedone	Weedar
	Brand LV4	Brand LV6	Brand 64
Sol-vex Nitrile <sup>a</sup>	Hexane	Hexane	Water
Butyl <sup>b</sup>	2-Propanol	2-Propanol	Water
Viton	Hexane	Hexane	Water
Silver Shield	Hexane	Hexane	Water

<sup>a</sup> Average measured thickness was  $0.80 \pm 0.08$  mm, n = 9

 $^{\rm b}$  Average measured thickness was 0.39  $\pm$  0.03 mm, n = 9

 $^{\rm c}$  Average measured thickness was 1.05  $\pm$  0.06 mm, n = 9

 $^{d}$  Average measured thickness was 0.85  $\pm$  0.03 mm, n = 9



Fig. 1. ASTM type I-PTC 600 permeation cell

## Esterification of 2,4-D Dimethyl Amine Salt

A mass of 0.1211 g 2,4-D DMAS was dissolved in 25 ml of Milli-Q water to generate 4.84 mg/ml stock solution. 530 µl 10% (w/w) NaOH aqueous solution was added to a 0.1-ml aliquot of the 2,4-D DMAS stock solution to ensure a pH > 14. The aqueous alkaline solution was then heated in the microwave oven at the lowest power level until bubbles first appeared (about 90-120 s for a solution temperature of about 80°C starting from room temperature). The solution was cooled at room temperature. The pH of the solution was adjusted by HCl (530  $\mu$ l) to ensure a pH < 2. 2,4-D was extracted by diethyl ether (0.5  $ml \times 5$ ) with vortexing for 1 min/extraction. The supernatants were collected in Kimax test tubes. Excess diethyl ether was then evaporated under a gentle stream of nitrogen. One milliliter MeOH and 0.5 ml BFM (0.2 g/ml) were added to the concentrated solution. The solution was then heated in the microwave oven at its lowest power level for about 90-120 s and cooled. A 1-ml aliquot of Milli-Q water was added and vortexed for 3 min. Hexane  $(2 \text{ ml} \times 5)$  was added and the solution was vortexed for 1 min/extraction to extract 2,4-D ME. The combined extracts were concentrated using nitrogen to fit into the linear dynamic range of 2,4-D ME. A 0.1-ml Milli-Q water reagent blank in triplicate was processed in parallel.

To esterify the 2,4-D DMAS from Weedar 64 formulation, 20-µl aliquots of the formulation were diluted to 25 ml by Milli-Q water. A volume of 0.1 ml of this aqueous solution was taken and an equal volume of hexane was used to extract the neutral organics three times each by vortexing for 1 min. The aqueous phase was then hydrolyzed and esterified as described above. The same equal-volume-hexane extraction for the neutral organics was also performed after the alkaline

hydrolysis. All the hexane extraction samples were analyzed by GC/MS to investigate nonpolar components. Concurrent sample processing of water blank and 2,4-D DMAS aqueous solutions provided reagent blanks and positive controls, respectively.

## Permeation Experiments

The complete method has been described elsewhere (Harville and Que Hee 1989; Lin and Que Hee 1998a-c). In summary, the glove was equilibrated at least 24 h at RH 65  $\pm$  1% in a desiccator containing saturated aqueous sodium dichromate at room temperature  $(21.1 \pm 0.3^{\circ}\text{C})$ . The material was placed between the two Teflon gaskets of the permeation cell. The two Pyrex chambers were inserted into the aluminum flanges, and the nuts were tightened to a torque of 16 in-lb. A volume of 10 ml of collection medium was added. The collection media were selected depending on the types of challenge solutions and glove materials (Table 1). After placing 15 ml of challenge solution into the challenge chamber, the initial 100-µl samples were taken from both sides, and the tray set to shake at 8.42  $\pm$ 0.04 cm/s at 30.0  $\pm$  0.5°C. Precooled (-20°C) vials received the 100-µl samples from the collection side (Table 1). The initial and final volumes of the challenge and collection sides were measured to assess evaporation. The challenge headspaces were analyzed for hexane and 2-propanol as appropriate by deleting the GC/MS solvent delay. All experiments were in triplicate.

The design of the permeation sampling time followed our previously published protocol (Harville and Que Hee 1989; Lin and Que Hee 1998a). The initial testing was a 0-h and a 8-h screening test in triplicate with samples taken in 1-h increments. The samples were then analyzed in reverse time order. For kinetic permeation curves to be defined at every 10 min as reported in the other publications of our permeation research group (Mikatavage *et al.* 1984; Harville and Que Hee 1989; Khan *et al.* 1997; Lin and Que Hee 1998a, 1998b, 1998c; Lu and Que Hee 1998), a t<sub>b</sub> of at least 6 h was the cut-off to ensure enough data points to define the steady state permeation period.

#### GC/MS Analysis

A 1- $\mu$ l aliquot from the 100  $\mu$ l of thawed collection solution was injected for GC/MS analysis. The MS was operated in the total ion current (TIC) mode to acquire mass spectra. The selected ion monitoring (SIM) mode was used at m/z 199 for the 2,4-D ME and at m/z 220 for 2,4-D BEE quantitations. The constant temperature zones were: injector 250°C, transfer line 250°C, and ion source 250°C.

For analysis of the permeation samples for Weedone<sup>®</sup> LV4 and LV6, the initial column temperature was  $55^{\circ}$ C for 2 min, then  $25^{\circ}$ C/min to  $80^{\circ}$ C and held there for 27 min, followed by  $10^{\circ}$ C/min to  $100^{\circ}$ C, and then  $30^{\circ}$ C/min to the final temperature of  $250^{\circ}$ C until all peaks eluted. The solvent delay time was 3 min.

The permeation samples of the Weedar 64 formulation were analyzed as 2,4-D ME in hexane and neutral organics in hexane after the alkaline hydrolysis. 2,4-D ME was determined with the following temperature program: initial column temperature of  $60^{\circ}$ C for 2 min, ramped at 25°C/min to 250°C, and then held for 5 min. The program for the nonpolar inert components was: initial column temperature of  $60^{\circ}$ C for 2 min, ramped at 5°C/min to 250°C, and held for 10 min.

Breakthrough times ( $t_b$ ) were obtained from samples taken at a time that yielded data with signal/noise (S/N) ratio of 2 for the specific m/z ion. External standards of 2,4-D ME and 2,4-D BEE in hexane were used in their defined linear dynamic ranges. The method detection limits of 2,4-D ME and 2,4-D BEE were 5 ng/ml (ppb) and 9 ng/ml (ppb), respectively, in the collection solution.

## **Results and Discussion**

## Esterification

Five replicates for 2,4-D DMAS esterification showed 99.2  $\pm$  3.7% recovery. There was no significant difference at p  $\leq$  0.05 relative to a reflux method of recovery 96.0  $\pm$  1.5% (Horner *et al.* 1974). The sample processing time was only 20 min.

Szmigielska and Schoenau (1995) reported the esterification of 1-ml aliquots of 2,4-D DMAS in a water bath heating step of 15 min. 2,4-D DMAS was extracted by diethyl ether and esterified overnight by 2-chloroethanol/BCl3 with recovery of 98.5  $\pm$  4.8% for rat serum and 93.3  $\pm$  7.5% for rat brain tissue (Oliveira and Palermo-Neto 1995). The sensitivity was about 250 ng/ml for serum and 300 ng/g for brain tissue. Mierzwa and Witek (1977) reported the recovery of 2,4-D 2,2,2-trichloroethanol ester formed after overnight reaction to be 92.1  $\pm$  3.4% with detection limit of 96 ng/ml using GC/electron capture detection (ECD). Roseboom et al. (1986) utilized 2,4-D esterification by pentafluorobenzyl bromide (PFBBr), 2-naphthacyl bromide, and 4-bromomethyl-7-methoxycoumarin for 2,4-D esterification with recoveries of 91%, 99%, and 84%, respectively. The esters were purified on a silica gel column after the esterification to eliminate interferences. 2,4-D in sediments and natural waters were also esterified by PFBBr by 3-h reaction followed by silica gel column cleanup (Lee and Chau 1983; Lee et al. 1986). The recoveries were from 71% to 108% for sediments and from 73% to 108% for natural waters. The GC/ECD detection limits were 10 µg/kg and 1.0 µg/L, respectively. Fuming sulfuric acid-ethanol (1:20, v/v) was utilized for 2,4-D esterification with a detection limit of 20 ng/ml by GC/ECD (Siltanen and Mutanen 1985). The reagent had to be prepared daily. The limit of detection was 10 ng/ml by GC/ECD. 2,4-D in water samples was esterified by 2,2,2trifluoroethanol (TFE) at 70°C for 60 min with 85.0  $\pm$  3.2% recovery (Adolfsson-Erici and Renberg 1991). Lee et al. (1995), who esterified 2,4-D by H<sub>2</sub>SO<sub>4</sub>/TFE at 60°C for 60 min, reported 107.1  $\pm$  0.5% recovery and 50 ng/ml detection limit by GC/MSD and GC/ECD. 2,4-D in acetone was also esterified by H<sub>2</sub>SO<sub>4</sub>/TFE at 60°C for 120 min with 99.56  $\pm$  0.63% recovery (Hong et al. 1996). All literature esterifications took longer than the technique of the present study, which also had acceptable sensitivity, but used commercially available reagents.

Microwave heating potentially allows quick and efficient processing of many microsamples. GC/MS with SIM eliminates background interferences should GC/ECD have interferences.

Weedar 64 formulation contained an average 2,4-D acid equivalent of 42.7  $\pm$  1.5 µg or 48.7  $\pm$  1.7% (w/w). Compared with the nominal content of 46.8% (w/w), this was not significantly different at p  $\leq$  0.05. No neutral organic peaks of boiling point greater than hexane were detected by GC/MS after alkaline hydrolysis. However, the major inert component for this DMAS formulation should be water.

#### Permeation Studies

The results of the permeation experiments are summarized in Table 2. No breakthrough of the four gloves was observed

Fable 2.	Summary of the permeation results of the systems
defined in	n Table 1

Formulations	Glove Material	<i>t</i> <sub>b</sub> (h)	m <sub>g</sub> (ng)
Weedone Brand LV4 (60.8%	Sol-vex Nitrile	7-8	<60
2,4-D butoxyethyl ester)	Butyl	>8	<60
	Viton	>8	<60
	Silver shield	>8	<60
Weedone Brand LV6 (83.5%	Sol-vex Nitrile	>8	<60
2,4-D butoxyethyl ester)	Butyl	>8	<60
	Viton	>8	<60
	Silver Shield	>8	<60
Weedar Brand 64 (46.8%	Sol-vex Nitrile	7-8	$62.0 \pm 6.3$
2,4-D DMAS)	Butyl	6–7	$86 \pm 18$
	Viton	7-8	51 ± 13
	Silver Shield	> 8	<50

Breakthrough at a trace level in one of the nitrile triplicates was observed between 7 h and 8 h, with the other two at >8 h for LV4  $t_b$ : breakthrough time in h (S/N = 2 for analyte);  $m_g$ : cumulative permeated mass of 2,4-D acid equivalent in ng for the active ingredient at 8 h;  $m_g$  is expressed as the arithmetic mean  $\pm$  standard deviation when permeation was observed, and detection limits are denoted as < quantities

within 8 h for Weedones LV6 and LV4. One run of Weedone LV4 through nitrile did show permeation between 7–8 h, suggestive of quality control variation for nitrile gloves. Silver Shield showed no permeation of Weedar 64 within 8 h, but butyl and nitrile showed respective  $t_b$  of 6–7 h and 7–8 h.

No previous data are available in the literature for the permeation of 2,4-D BEE formulations. Two herbicide formulations containing 2,4-D DMAS have been reported as "no permeation" when nitrile gloves were challenged for 16 h using a less sensitive HPLC analytical technique (Moody and Ritter 1990). However, the formulations differed from the one tested in the present study, though the glove types were the same.

The observation of no breakthrough in an 8-h test implies potentially complete protection should workers have a continuous 8-h shift, subject to work practices. This is so for all Silver Shield challenges, and also for the other three glove types when challenged with the butoxyethyl ester formulations Weedone Brand LV4 and LV6. Workers usually change their gloves during the midshift or 2-h interval breaks without washing them. For the challenge to the 2,4-D DMAS formulation Weedar Brand 64, Sol-vex nitrile, butyl, and Viton gloves could be redonned at 7 h in exposure time if little contact with the formulation has occurred, as determined by an industrial hygienist.

Acknowledgments. This work was supported by Grant RO1 OH02951 from the National Institute for Occupational Safety and Health of the Centers for Disease Control and Prevention and by the UCLA Center for Occupational and Environmental Health.

## References

Adolfsson-Erici M, Renberg L (1991) Gas chromatographic determination of phenoxyacetic acids and phenoxypropionic acids as their 2,2,2-trifluoroethyl esters. Chemosphere 23:845–854

- Audus LJ (ed) (1976) Herbicides: Physiology, biochemistry, ecology, 2nd ed. Academic Press, New York, vols 1 and 2
- Grover R, Cessna AJ, Muir NI, Riedel D, Franklin CA (1988) Pattern of dermal deposition resulting from mixing/loading and ground application of 2,4-D dimethylamine salt. In: Mansdorf SZ, Sager R, Nielsen AP (eds) Performance of protective clothing: second symposium. ASTM STP 989, ASTM, Philadelphia, PA, pp 625– 629
- Harris SA, Solomon KR, Stephenson GR (1992) Exposure of homeowners and bystanders to 2,4-dichlorophenoxyacetic acid (2,4-D). J Environ Sci Health 27B:23–28
- Harville J, Que Hee SS (1989) Permeation of a 2,4-D isooctyl ester formulation through neoprene, nitrile, and tyvek protection materials. Am Ind Hyg Assoc J 50:438–446
- Hayes WJ (1982) Pesticide studies in man. Williams and Wilkins, Baltimore, MD
- Henshaw B, Que Hee SS, Sutherland RG, Lee CC (1975) Gas-liquid chromatography and gas-liquid chromatography combined with mass spectrometry of a butyl ester formulation of (2,4-dichlorophenoxy)acetic acid. J Chromatogr 106:33–39
- Horner J, Que Hee SS, Sutherland RG (1974) Esterification of (2,4-dichlorophenoxy)acetic acid—a quantitative comparison of esterification techniques. Anal Chem 46:110–112
- Hong M, Kim M, Smith AE (1996) Simultaneous determination of 2,4-D, dicamba, and mecoprop in soil leachates by gas chromatography with electron capture detection. J Assoc Off Anal Chem Int 79:988–1004
- Keller T, Skopp G, Wu M, Aderjan R (1994) Fatal overdose of 2,4-dichlorophenoxyacetic acid (2,4-D). Foren Sci Int 65:13–18
- Khan AA, Chen X, Que Hee SS (1997) Permeation of chlorpyrifos and endosulfan formulations through protective materials. Appl Occup Environ Hyg 12:413–417
- Lee AS, Hong M, Smith AE (1995) Analysis of 2,2,2-trifluoroethyl derivatives of carboxylic acid herbicides by gas chromatography with mass-selective and electron capture detection. J Assoc Off Anal Chem Int 78:1459–1464
- Lee Choi K, Que Hee SS, Sutherland RG (1976) 2,4-D levels in the south Saskatchewan River in 1973 as determined by a GLC method. J Environ Sci Health 11B:175–183
- Lee H, Chau ASY (1983) Analysis of pesticide residues by chemical derivatization. VI. Analysis of ten acid herbicides in sediment. J Assoc Off Anal Chem 66:1023–1028
- Lee H, Stokker YD, Chau ASY (1986) Chemical derivatization analysis of pesticide residues. X. Analysis of ten acid herbicides in natural waters. J Assoc Off Anal Chem 69:557–560
- Lerda D, Rizzi R (1991) Study of reproductive function in persons occupationally exposed to 2,4-dichlorophenoxyacetic acid (2,4-D). Mutation Res 262:47–50
- Lin Y-W, Que Hee SS (1998a) Permeation of malathion through glove materials. Appl Occup Environ Hyg 13:158–165

- Lin Y-W, Que Hee SS (1998b) Permeation of a malathion formulation through nitrile gloves. Appl Occup Environ Hyg 13:286–298
- Lin Y-W, Que Hee SS (1998c) Permeation of a malathion formulation through butyl gloves. J Haz Mat 60:143–158
- Lu X, Que Hee SS (1998) Permeation of methomyl in Lannate L through nitrile gloves. J Haz Mat 59:279–285
- Mierzwa S, Witek S (1977) Gas-liquid chromatographic method with electron-capture detection for the determination of residues of some phenoxyacetic acid herbicides in water as their 2,2,2trichloroethyl esters. J Chromatogr 136:105–111
- Mikatavage M, Que Hee SS, Ayer HE (1984) Permeation of chlorinated aromatic compounds through Viton and Acrylonitrile polymer glove materials. Am Ind Hyg Assoc J 45:617–621
- Moody RP, Nadeau B (1992) Effect of the mosquito repellent DEET and long-wave ultraviolet radiation of the herbicide 2,4-D and the insecticide DDT in natural rubber gloves. Am Ind Hyg Assoc J 53:436–441
- Moody RP, Nadeau B (1994) Nitrile butyl rubber glove permeation of pesticide formulations containing 2,4-D-amine, DDT, DEET, and Diazinon. Bull Environ Contam Toxicol 52:125–130
- Moody RP, Ritter L (1990) Pesticide glove permeation analysis: comparison of the ASTM F739 test method with an automated flow-through reverse-phase liquid chromatography procedure. Am Ind Hyg Assoc J 51:79–83
- Nadakavukaren A (1990) Man and environment: a health perspective, 3d ed. Waveland Press, Prospect Heights, IL
- Oliveira GH, Palermo-Neto J (1995) Toxicology of 2,4-dichlorophenoxyacetic acid (2,4-D) and its determination in serum and brain tissue using gas chromatography-electron-capture detection. J Anal Toxicol 19:251–255
- Que Hee SS (1989) Permeation of some pesticidal formulations through glove materials. In: Perkins JL, Stull JO (eds) Chemical protective clothing performance in chemical emergency response. ASTM STP 1037, ASTM, Philadelphia, PA, pp 157–164
- Que Hee SS, Sutherland RG (1981) The phenoxyalkanoic herbicides, vol 1. CRC Press, Boca Raton, FL
- Roseboom H, Herbold HA, Berkhoff CJ (1986) Determination of phenoxy carboxylic acid pesticides by gas and liquid chromatography. J Chromatogr 249:323–331
- Siltanen H, Mutanen R (1985) Formation of derivatives of chlorophenoxy acids and some other herbicides. Chromatographia 20:685– 688
- Stevens JT, Sumner DD (1991) Herbicides. In: Hayes WJ Jr, Laws ER Jr (eds) Handbook of pesticide toxicology, vol. 3. Academic Press, San Diego, CA, pp 1319–1325
- Szmigielska AM, Schoenau JJ (1995) Determination of 2,4-D amine in soils using anion exchange membranes. J Agric Food Chem 43:151–156
- Watterson A (1988) Pesticide users' health and safety handbook: an international guide. Van Nostrand Reinhold, New York, NY, pp 162–163