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Permeation of Malathion Through Glove Materials

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The aims of this study were to recommend gloves (lined, unsupported Solvex nitrile, Viton, or Silver Shield laminate) to protect against malathion skin exposure, and to investigate how the carrier (water, hexane, or *m*-xylene) modified the permeation of the malathion of two commercial emulsion concentrate formulations. An I-PTC 600 American Society for Testing and Materials-type permeation cell at 30°C allowed hexane collection of malathion, with samples taken every 10 minutes for gas chromatography/mass spectrometry analysis. Malathion did not permeate Silver Shield or Viton up to 8 hours at 30°C whether it was pure or formulated. Of all the formulation and mixture experiments, pure malathion had the shortest breakthrough time (t_b), shortest lag time (t_l), and highest steady-state permeation rate (P_s) through nitrile. Malathion did not permeate within 8 hours when the formulation of low alkylbenzene content was diluted to the same malathion concentration in water as malathion/*m*-xylene was with hexane. In contrast, the formulation of high alkylbenzene content at this aqueous dilution allowed malathion permeation, with a t_b of 4 to 5 hours and a long t_l. Viton and Silver Shield gloves are recommended for handling technical/pure-grade malathion and malathion emulsifiable concentrate formulations. Nitrile gloves should be replaced every 60 minutes when handling these two formulations because of the malathion t_b of 1 hour, but they will not protect against pure/technical malathion. Nitrile can be used for at least 4 hours to protect against diluted formulations and diluted pure/technical malathion. LIN, Y.-W.; QUE HEE, S.S.: PERMEATION OF MALATHION THROUGH GLOVE MATERIALS. APPL. OCCUP. ENVIRON. HYG. 13(3):158–165; 1998. © 1998 AIH.

Malathion {$(MeO)_2$-(P=S)-S-CH[-(CH_2COOEt)-(COOEt)], where Me is methyl and Et is ethyl; S-1, 2-*bis*(ethoxycarbonyl)ethyl-O,O-dimethylphosphorodithoate}$^{(1)}$ is an organophosphate pesticide also called malathon, carbofos, mercaptothion, maldison, mercaptotion, OMS 1, and ENT 17034. It was introduced by American Cyanamid in 1950. Malathion is a liquid with a melting point of 2.85°C, a boiling point of 156 to 157°C at 760 mmHg, a vapor pressure of 5.3 mPa at 30°C, a specific gravity of 1.23 at 25°C, and a water solubility of 145 mg/L at 25°C. It is an irreversible cholinesterase inhibitor. The World Health Organization allowable daily intake is 20 μg/kg; the rat acute oral LD_{50} is 1400 to 2800 mg/kg body weight.$^{(1)}$ The human lethal dose is about 857 mg/kg body weight.$^{(2)}$ The workplace air threshold limit value time-weighted average is$^{(3)}$ 10 mg/m^3 (skin). Malathion is a contact insecticide/acaricide that is also used as an ectoparasiticide for humans and animals. It has contact, stomach, and respiratory action.$^{(1,2)}$

Mixtures that contain the pesticide and other compounds to aid field spraying are formulations. Some common ones for malathion are:$^{(1)}$ Celthion™, Cythion™, Dielathion™, EI4049™, Emmatos™, Exathion™, Fyfanon™, Hilthion™, Karbofos™, Kypfos™, Lucacathion™, Malamar™, Malaphele™, Malatol™, Malatox™, Malixol™, Maltox™, MLT™, Sumitox™, Vegfru™, and Zithiol™. Liquid formulations that form emulsions on mixing with water contain petroleum distillate inert components to adjust surface tension to produce the correct target droplet size on spraying, and surfactants to promote emulsion formation in water. Malathion formulations exert broad-spectrum control of sucking and chewing insects and spider mites on fruits, vegetables, trees, and ornamentals. Insect vectors like mosquitoes, flies, and those in poultry and animal houses are controlled. Malathion spraying against the Mediterranean fruit fly *Ceratitis capitata* (Wiedemann) has attracted attention.$^{(4)}$ Skin absorption is the major route of human exposure.$^{(5-7)}$

Few garment permeation data exist for malathion formulations and none for pure malathion. When challenged with formulations of 30 to 70 percent malathion, a Teflon™ Chemfab Challenge garment of 1-mm thickness had a malathion breakthrough time (t_b) of >186 minutes.$^{(8)}$ A fluorescent tracer study of pesticide workers who applied a wettable powder malathion formulation at an aqueous concentration of 0.75 mg/ml reported exposure through garments.$^{(9)}$ An *in vitro* cholinesterase and skin patch investigation showed 100 percent cotton knit gloves protected against 50 μL of 0.3 percent Cynthion™ malathion/ethanol.$^{(10)}$ The present laboratory study investigated malathion permeation through several rubber glove materials using an American Society for Testing and Materials (ASTM)-type permeation cell.

Experimental

Rationale for Selection of Formulations and Glove Materials in the Present Study

Potential malathion exposures are highest when handling pure and technical-grade materials and emulsifiable concentrates. Most commercial emulsion concentrate formulations contain 30 to 91 percent (w/w) malathion nominal content.$^{(11)}$ One selected formulation was Aqua Malathion 8™ (FMC, Philadelphia, Pennsylvania) of 80.5 percent malathion. The second, Prentox Malathion 50 percent Emulsifiable Insecticide™ (Prentiss Drug and Chemical Co. Inc., Sandersville, Georgia), was of 50 percent (w/w) malathion content. The inert components of the latter were stated on the label and material safety data sheet to be "xylene range aromatic solvent" of 50 percent total formulation content. The constituent alkylbenzenes (branched and straight-chain alkyl groups attached to a benzene ring) were not specified. The xylene range fraction is that petroleum distillation fraction (cut) above the boiling point at 760 mmHg of toluene (>111°C) up to 205°C in crude oil or straight-run naphtha distillation, in heavy gas oil cracking, and in catalytic reforming of heavy naphtha at oil refineries.(12) It may therefore include such aromatic hydrocarbons as xylenes, ethylbenzene, trimethylbenzenes, ethyltoluenes, cumene, *n*-propylbenzene, and higher molecular weight branched and straight-chain alkylbenzene congeners and isomers up to C_{11} in chain length.(12)

There are no glove manufacturer recommendations for pure malathion based on chemical degradation or permeation. If a formulation contains xylene range aromatic solvent, the most polar compounds would be the xylene isomers (referenced under xylene) and ethylbenzene. Ansell Edmont(13) recommends nitrile (t_b of 75 minutes; steady-state permeation rate P_s 9–90 $\mu g/cm^2/min$) and supported polyvinyl alcohol for protection against xylene. The latter does not protect against aqueous solutions and was not investigated further. Nitrile's potential to protect was then assessed by examining the permeation data for the lower molecular weight members of the alkylbenzene homologous series, namely, toluene and benzene. Toluene has a t_b of 10 minutes, and nitrile is degraded chemically by benzene.(13) Only Ansell Edmont data were consulted since the permeation data were obtained under uniform conditions of permeation and analytical chemical detection as xylene. Thus nitrile may not protect against formulations containing appreciable benzene and toluene, but should protect against alkylbenzenes of higher molecular weight than xylene.

Another glove assignment method is through the method of chemical surrogates.(14) Malathion is an organophosphate ester. The Ansell Edmont catalog(13) contains few ester data. In the acetate ester homologous series,(13) ethyl acetate degrades nitrile, but the less polar propyl acetate (t_b 20 minutes), butyl acetate (t_b 75 minutes), and amyl acetate (t_b 60 minutes) do not. Tricresyl phosphate, a nonpolar phosphoric acid ester, has a P_s of <0.9 $\mu g/cm^2/min$ and a t_b of >6 hours, but the presence of two sulfurs instead of oxygens and alkyl groups instead of aromatic groups in malathion is expected to increase reactivity. Nevertheless, nitrile should protect against malathion–xylene mixtures. The question to be answered is, how good is that protection?

Laboratory challenge experiments should simulate worst-case field exposure situations as described elsewhere.(15) Formulation challenge of a glove maximizes the interactions of the pesticide and inert components and reflects worker exposure potential during the handling and preparation of formulations. Pure malathion and pure inert component challenges reflect maximum sequential exposure potentials during separate exposures. Pure pesticide permeation also represents when all the more volatile inert components have disappeared after field spraying, a situation linked to crop/orchard/restaurant worker reentry exposure potentials. The highest concentrations of a sprayed formulation occur at the smallest dilution recommended for spraying.

Since malathion vapor pressure is low and malathion has a low flame ionization detector (FID) response factor, malathion is not detected sensitively by air collection/gas chromatography (GC)-FID, the major permeation analytical method used by glove manufacturers. Instead, a liquid collection(15) system in an ASTM-type permeation cell was used. Hexane was chosen as the collection solvent since malathion was miscible and Ansell Edmont data(13) showed that hexane did not degrade or permeate nitrile ($P_s < 0.9$ $\mu g/cm^2/min$ and $t_b > 6$ hours at 25°C). It could also be resolved from xylene-range inert components and malathion on GC/mass spectrometry (MS). However, no hexane back permeation must occur. Hexane was thus analyzed in samples of the challenge side liquid and headspace just after placing the hexane solvent in the collection side and after permeation experiments.

An aqueous collection solvent simulates sweaty conditions at high worker physical activity and hot conditions, but prevents transfer of already-permeated malathion on the inner glove because of low water solubility.(1) Malathion transfer to the gloved hand can still occur when conditions dry out. An unsuitable collection medium may show little or no compound collection even though the latter has permeated the material. The availability of the permeated compound to the collection medium must be maximized to ensure that the permeation step through the material is the dominant process.(16) Mixing of aqueous challenge and collection solutions must therefore be optimized as well. The temperature chosen was 30°C, since this was the average surface temperature of the glove surface when worn at an ambient temperature of 25°C.

Materials

The two malathion formulations used were described above. Malathion (95% nominal purity from Pfaltz and Bauer, Waterbury, Connecticut), Optima-grade hexanes and sodium dichromate (Fisher Scientific, New Lawn, New Jersey), and *m*-xylene (Kodak, Rochester, New York) were pure chemicals also utilized. Lined, unsupported Sol-Vex™ nitrile gloves (37-165, 22 mil, 38 cm in length) were from Ansell Edmont (Coshocton, Ohio). Silver Shield™ laminate (SS104M, 3 mil) and Viton (F124, 9 mil) were both from North Hand Protection (Charleston, South Carolina).

The permeation cell was an ASTM-type I-PTC 600 from Pesce Lab Sales (Kennett Square, Pennsylvania). Vernier calipers allowed measurement of nitrile diameters cut for permeation studies. A micrometer screw gauge (L.S. Starrett Co., Athol, Massachusetts) facilitated nitrile thickness measurements before and after permeation experiments. A torque wrench (Mechanics Products, Kent, Washington) ensured equal permeation cell nut tightness and no leaks. A moving tray shaker water bath from Fisher Scientific (model 125 No. 129) allowed temperature control (30.0° ± 0.5°C) with sufficient horizontal shaking to ensure homogeneous solutions on both sides of the permeation cell (8.42 ± 0.04 cm/s for formulation and organic solution challenges; 14.3 ± 0.3 cm/s for aqueous challenges as shown from GC/MS malathion measurements in the challenge side over time). The velocities were measured from knowing the horizontal tray travel distance (pitch) and the time for one pitch as measured by stopwatch. A clamp on a fixed supporting rail facilitated permeation cell immersion. Eppendorf micropipets (Brinkman Instruments, Westbury, New York), Hamilton gas 10-μL chromatographic and 10-ml gas-tight syringes, 2-ml TFE Teflon-lined silicone septum screw cap Pyrex vials, and Teflon tape to stop volatilization (Fisher Scientific) were also used.

Permeation Experiments

The complete method has been described elsewhere.(15) There were two types of experiments: screening (malathion permeation after 2 and 8 hours of challenge) and kinetic (samples taken from the collection side every 10 minutes). The initial and final volumes of the challenge and collection sides were measured to check evaporation; challenge side samples and their headspaces were analyzed for hexane by having no GC/MS solvent delay.

In summary, the glove was equilibrated at least 24 hours at 65 ± 1 percent relative humidity in a desiccator containing saturated aqueous sodium dichromate at room temperature (21.1° ± 0.3°C). Diameters of 3.80 ± 0.09 cm were cut from the glove palm and thicknesses measured at three different places to determine an average and standard deviation (SD) for each specimen. 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 inch-pound. The cell was immersed in the water bath to assess external leakage. A volume of 10 ml of hexane collection medium was added, followed by 15 ml of challenge solution; the initial 0.100-ml samples were then taken from both sides and the tray was set shaking. Precooled (−20°C), acid-washed 2-ml vials received the 0.100-ml hexane samples from the collection side at known times to prevent hexane evaporation. After permeation runs, the glove material was placed overnight in a desiccator containing indicating Drierite under vacuum. The glove thickness was remeasured, and the glove was examined microscopically. All experiments were at least in triplicate. Cleaning of the permeation cells and gaskets was through brush scrubbing with neutral detergent in hot water, rinsing with acetone and then with hexane, and then repetitively filling both sides of the permeation cell with hexane until no malathion could be detected. The cell was then emptied and dried.

The challenges, each of 15-ml volume, were: malathion (Mala); 12.8 g malathion in *m*-xylene (Mala-Xyl); Mala-Xyl diluted in hexane to contain 183 mg malathion (Mala-Xyl-Hex); Prentox formulation containing 7.64 g malathion (Prent); Aqua malathion in *m*-xylene to contain 7.99 g malathion (Aqua-Xyl); 0.36 ml Prentox in distilled water to contain 183 mg malathion (Prent-Aq); and 0.20 ml Aqua Malathion 8 in water to contain 200 mg malathion (Aqua-Aq).

Analysis of Samples

A 2-μL aliquot of thawed collection solution was injected into a Hewlett-Packard 5890A gas chromatograph/5988A quadrupole mass spectrometer (Hewlett-Packard, Palo Alto, California). The column was a chemically bonded, fused-silica DB-1701 capillary column 30 m long, 0.32 mm i.d., and 1-μm film thickness (J&W/Alltech, Deerfield, Illinois). The ion source was in the positive ion electron impact mode at 70 eV and of m/z range 50 to 500. The constant temperature zones were: injector 250°C, transfer line 250°C, and ion source 250°C. The initial column temperature was 50°C for 6 minutes (solvent delay) and 15°C/min to a final temperature of 250°C until all peaks eluted. The helium carrier flow rate was 3.0 ± 0.3 ml/min. The total ion current mode was used for identifications. Quantifications were made by determining abundances on selective ion monitoring at m/z 125 for malathion, m/z 105 for molecular weight 120.19 alkylbenzenes, and m/z 91 for molecular weight 106 alkylbenzenes and interpolating on external standard curves. Breakthrough times were obtained from samples taken at a time which yielded data with a signal/noise ratio of 2 for the specific m/z ion. External standards of malathion in hexane defined linear dynamic ranges. Sample dilution with hexane was performed into the linear range as appropriate. Hexane back-permeation analysis occurred at the solvent delay temperature without solvent delay. The cumulative permeated mass m_t was calculated by interpolation of the mass in the injected aliquot corrected for any zero time background and for fraction of collection side injected. Correction of total collection volume was also done for previous aliquots removed.

Permeation Data Analyses

Linear regression of m_t versus contact time t (Equation 1) was used to describe the steady-state section parameters with the steady-state mass transfer rate dm_s/dt being the slope and $m_t = 0$ being the lag time t_l. P_s is the regression slope dm_s/dt divided by the exposed surface area A, with A here being 4.34 cm².

$$m_t = (dm_s/dt)\ t + m_o = (P_sA)\ t + m_o \quad (1)$$

The diffusion coefficient D_p is defined from Fick's second law and assumes a constant glove thickness of 1 during the experiment (Equation 2):

$$t_l = 1^2/(6D_p) \quad (2)$$

Results

GC/MS Analyses

GC/MS showed that the major alkylbenzene inert components in both Prent and Aqua were xylenes, trimethylbenzenes, ethyl toluenes, and propyl benzenes. The alkylbenzenes were 45.9 percent (w/w) in Prent and 0.027 percent (w/w) in Aqua. The exact composition of the inert components and their permeation kinetics is the subject of another article.(22) *m*-Xylene, the most abundant xylene isomer, was 1.50 ± 0.12 percent in Prent and 0.00200 ± 0.00019 percent in Aqua. The bulk of the alkylbenzenes (>98%) in both formulations were molecular weight 120. The actual malathion concentrations were 52 ± 2 and 88.4 ± 3.7 percent, respectively, the latter being significantly above nominal content. The linear range lower limit for malathion was 4.6 ng. Pure malathion (retention time 17 minutes) was 93.0 ± 0.5 percent pure with isomalathion (retention time 13 minutes) <1 percent. Isomalathion was not detected in Aqua, but Prent had a trace. Hexane did not back-permeate.

Permeation Studies

The screening results (Table 1) show that malathion permeated for all nitrile challenges except the low concentration Mala-Xyl-Hex and Aqua-Aq. Malathion did not permeate Viton and Silver Shield under any conditions (Table 1). Silver Shield

TABLE 1. Results of Screening Experiments with Different Glove Materials at Different Challenge Times in Hours (CT), Initial Material Thickness (T_i) and Final Thickness (T_f) in Millimeters ($n = 3$), and 15-ml Challenges (Ch) at Different Malathion Mass in Milligrams (Mal)

Material	T_i(SD)	T_f(SD)	Ch(Mal)	CT	t_b	P(%)
Nitrile	0.62 (0.14)	0.70 (0.02)	Mala 1 (18,150)	2	<2	116 (0.64)
	0.71 (0.03)	0.78 (0.06)	Mala 2 (18,150)	2	<2	166 (0.91)
	0.78 (0.08)	0.82 (0.03)	Mala 3 (18,150)	2	<2	283 (1.6)
	0.72 (0.04)	0.77 (0.09)	Mala-Xyl 1 (12,800)	2	<2	17 (0.13)
	0.72 (0.04)	0.87 (0.03)^A	Mala-Xyl 2 (7260)	2	<2	3.5 (0.048)
	0.82 (0.02)	0.86 (0.05)	Mala-Xyl 3 (7260)	2	<2	3.0 (0.041)
	0.78 (0.09)	0.83 (0.04)	Mala-Xyl 4 (7260)	2	<2	3.4 (0.047)
	0.81 (0.03)	0.84 (0.03)	Mala-Xyl-Hex (183)	8	>8	<0.02 (<0.01)
	0.88 (0.04)	0.91 (0.03)^A	Prent 1 (7640)	8	<4	25.4 (0.33)
	0.90 (0.02)	1.00 (0.04)^A	Prent 2 (7640)	8	<4	8.30 (0.11)
	0.92 (0.05)	1.00 (0.03)	Prent 3 (7640)	8	<4	10.20 (0.13)
	0.88 (0.06)	1.00 (0.01)	Prent 4 (7640)	8	<4	2.100 (0.027)
	0.88 (0.04)	0.91 (0.05)	Prent-Aq 1 (183)	8	<8	8.3 (4.5)
	0.85 (0.01)	0.88 (0.02)	Prent-Aq 2 (183)	8	<8	3.0 (1.6)
	0.86 (0.03)	0.90 (0.01)	Prent-Aq 3 (183)	8	<8	1.6 (0.87)
	0.75 (0.01)	0.78 (0.09)	Aqua-Xyl 1 (7990)	2	<2	6.8 (0.085)
	0.81 (0.02)	0.82 (0.02)	Aqua-Xyl 2 (7990)	2	<2	7.6 (0.095)
	0.78 (0.01)	0.83 (0.02)^A	Aqua-Xyl 3 (7990)	2	<2	4.1 (0.051)
	0.77 (0.02)	0.79 (0.04)	Aqua-Aq (200)	8	>8	<0.02 (<0.01)
Viton	1.1 (0.1)	1.2 (0.1)	Mala	8	>8	<0.02 (<10^{-3})
	1.0 (0.04)	1.0 (0.1)	Prent	8	>8	<0.02 (<0.01)
	1.0 (0.05)	1.0 (0.1)	Prent-Aq (183)	8	>8	<0.02 (<0.01)
	1.1 (0.1)	1.1 (0.1)	Aqua (14,980)	8	>8	<0.02 (<0.01)
Silver Shield	0.82 (0.04)	0.85 (0.01)	Mala (18,500)	8	>8	<0.02 (<0.01)
	0.89 (0.01)	0.88 (0.03)	Prent (7640)	8	>8^B	<0.02 (<0.01)
	0.84 (0.02)	0.84 (0.05)	Prent-Aq (183)	8	>8	<0.02 (<0.01)
	0.83 (0.02)	0.85 (0.02)	Aqua (14,980)	8	>8	<0.02 (<0.01)

Mala, 93 percent malathion; Mala-Xyl, malathion in *m*-xylene; Prent, Prentox formulation; Prent-Aq, Prentox formulation in distilled water solution; Aqua, Aqua malathion 8 formulation; Aqua-Xyl, Aqua malathion 8 formulation in *m*-xylene; Aqua-Aq, Aqua malathion 8 formulation in distilled water; t_b, breakthrough time in hours; P (%), mass permeated in milligram with the percentage of malathion mass permeated relative to challenge mass specified in brackets.

[A] Statistically different thickness from initial at $p < 0.025$.

[B] 1,2,4-Trimethylbenzene, but not other inert components or malathion, broke through.

with Prent showed 1,2,4-trimethylbenzene breakthrough, but not other inert components or malathion. The most protective glove, therefore, is Viton, closely followed by Silver Shield, and then nitrile.

Only 4 of 19 individual runs showed significant nitrile swelling at $p < 0.025$ (Student's *t* test): one Mala-Xyl, two Prent, and one Aqua-Xyl (Table 1). These all involved high malathion challenge mass in undiluted formulation or in *m*-xylene. There was no correlation ($p < 0.025$) of glove initial thickness to the corresponding final thickness, implying no permanent swelling. Glove initial thickness for all experiments (Table 1) varied most for nitrile (average thicknesses 0.62 to 0.92 mm), followed by Silver Shield (average thickness 0.82 to 0.89 mm), and least for Viton (1.0 to 1.1 mm average thickness). Similarly, after permeation (Table 1), the final average thicknesses were: nitrile, 0.70 to 1.00 mm; Silver Shield, 0.84 to 0.88 mm; and Viton, 1.0 to 1.2 mm. These average final ranges did not differ from average initial ranges at $p < 0.025$, also implying no permanent swelling.

The permeated malathion mass through nitrile was highest for pure malathion challenges, and declined with decreasing challenge mass. For malathion challenge masses between 7260 and 7990 mg, 2.1 to 25.4 mg permeated in 2 to 8 hours for Prent, 4.1 to 7.6 mg in 2 hours for Aqua-Xyl, and 3.0 to 3.5 mg in 2 hours for Mala-Xyl. For Prent-Aq, malathion permeated 1.6 to 8.3 mg in 8 hours, while it was not detected for Aqua-Aq or Mala-Xyl-Hex for the same low challenge mass of malathion.

Table 2 summarizes all the nitrile kinetic run data for malathion. Figures 1 to 3 present average permeation data for pure malathion, malathion from Aqua-Xyl/Mala-Xyl, and malathion from Prent, respectively. P_s values were highest for Mala (370 to 1270 $\mu g/cm^2/min$), followed by Aqua-Xyl (12 to 37 $\mu g/cm^2/min$), Mala-Xyl (16 to 18 $\mu g/cm^2/min$), Prent (2.2 to 8.3 $\mu g/cm^2/min$), and Prent-Aq (1.3 to 20 $\mu g/cm^2/min$). The t_l values were shortest for Mala (48 to 81 minutes), followed by Mala-Xyl (73 to 75 minutes) and Aqua-Xyl (74 to 88 minutes), but were much longer for Prent (190 to 240 minutes) and Prent-Aq (290 to 390 minutes). The variations for Aqua-Xyl and Mala-Xyl were caused by differing initial glove thicknesses, since when this was factored into Equation 2 for t_l, all of the D_p for malathion challenge masses >7260 mg (excluding Prent) were not statistically different, and ranged from 1.0×10^{-3} mm^2/min to 1.5×10^{-3} mm^2/min. This confirms that a steady state of saturated diffusion of malathion occurred at these conditions. Prent-Aq had a malathion D_p of

TABLE 2. Malathion Kinetic Data for Lined Sol-Vex Nitrile Gloves for 15-ml Challenge Volumes (Mean Initial Thickness 0.819 mm and Standard Deviation 0.086 mm)

Challenge		MM	t_b	P_s (SD)	t_l (SD)	D_p
Pure		18.15	0–10	370 (15)	48.0	1.3
			0–10	880 (110)	80.6	1.0
			0–10	1270 (100)	68.8	1.5
	Mean (SD)		5	840 (450)	66 (17)	1.3 (0.3)
Prent		7.64	60–80	8.29 (1.0)	190	0.68
			160–180	5.30 (0.39)	240	0.63
			140–160	7.14 (0.35)	200	0.71
			80–100	2.21 (0.23)	230	0.64
	Mean (SD)		120 (48)	5.74 (2.65)	215 (24)	0.670 (0.037)
Aqua-Xyl		7.99	50–60	37 (4)	81.8	1.1
			60–70	12 (1)	73.6	1.5
			60–70	30 (4)	87.5	1.2
	Mean (SD)		62.0 (5.8)	26 (13)	81.0 (7.0)	1.30 (0.20)
Mala-Xyl		7.26	60–70	18 (1)	75.1	1.4
			60–70	16 (1)	74.7	1.5
			60–70	18 (1)	73.2	1.4
	Mean (SD)		65	17 (1)	74.3 (1.0)	1.40 (0.10)
Prent-Aq		0.183	250–260	19.8 (1.4)	385	0.34
			260–270	3.82 (0.20)	287	0.42
			270–280	1.33 (0.14)	296	0.42
	Mean (SD)		265 (10)	8.3 (10)	323 (54)	0.39 (0.046)

MM, malathion challenge mass in grams; t_b, breakthrough time in minutes; P_s, steady-state permeation rate μg/cm²/min; t_1, lag time in minutes; D_p, diffusion coefficient of permeation multipled by 10^3 in square millimeters per minute calculated from individual t_l and thickness (l) by $D_p = 1^2/6t_l$; pure, 93 percent malathion; Prent, Prentox malathion 50 percent emulsifiable insecticide; Aqua, FMC Aqua malathion 8; Mala-Xyl, 6 ml of pure malathion diluted with *m*-xylene to 15 ml; Prent-Aq, 0.36 ml Prentox formulation in aqueous solution; Aqua-Aq, 0.2 ml FMC Aqua malathion 8 in aqueous solution; Mal-Xyl-Hex, pure malathion with 183 mg *m*-xylene in hexane solution; mean, arithmetic mean.

58 percent of that for Prent itself, while that for the latter was 52 percent of the Mala data. The individual t_l's were always longer than the corresponding t_b's. Paired mean t_b/t_l ratios were: Mala, 0.080 ± 0.022; Prent, 0.55 ± 0.20; Aqua-Xyl, 0.77 ± 0.11; Prent-Aq, 0.84 ± 0.15; and Mala-Xyl, 0.875 ± 0.012. Only Mala differs drastically from the rest of the data.

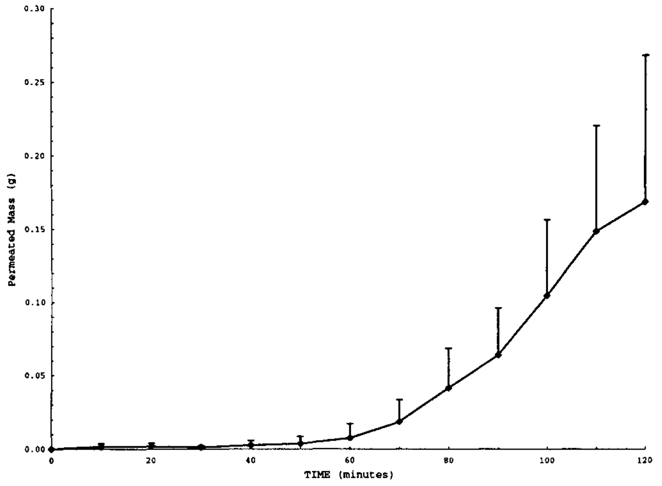

FIGURE 1. Average permeation of malathion as pure liquid through Sol-Vex nitrile gloves from three experiments where malathion challenge mass was 18.15 g. The vertical bars represent 1 SD.

Discussion

These data are the first published to show that a pure, moderately volatile organophosphate pesticide can permeate glove materials. Solid pesticides need the aid of solvents. All malathion permeation curves showed just one steady-state section and thus obeyed type A permeation.$^{(17)}$ Solvent interactions

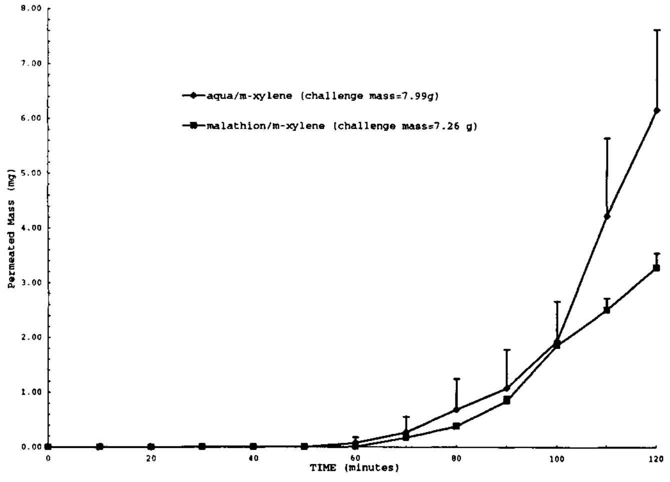

FIGURE 2. Average permeation of malathion through Sol-Vex nitrile gloves from three experiments each for malathion/*m*-xylene (malathion challenge mass 7.26 g) and for Aqua/*m*-xylene (malathion challenge mass 7.99 g). The vertical bars represent 1 SD.

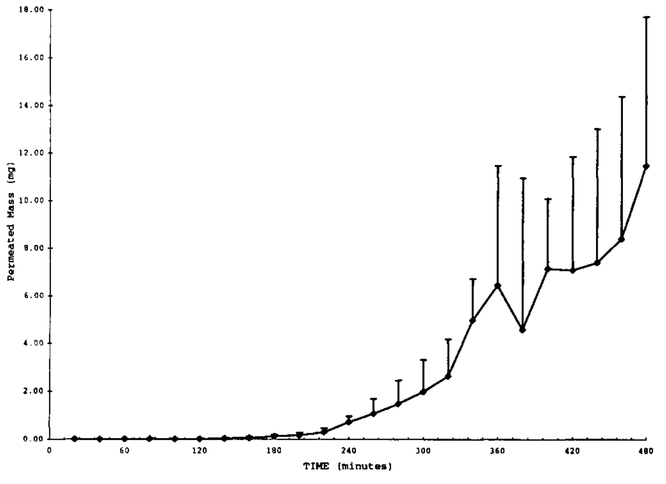

FIGURE 3. Average permeation of malathion through Sol-Vex nitrile gloves from four experiments for Prentox formulation (malathion challenge mass 7.64 g). The vertical bars represent 1 SD.

are still important since the t_b and t_l are much longer for malathion in Prent, where less polar alkylbenzenes than *m*-xylene predominate relative to Aqua-Xyl and Mala-Xyl even though malathion challenge concentrations are about the same for all three. This demonstrates that the different physical properties of alkylbenzenes can modify permeation behavior of a pure, more permeating component like malathion. The permeation of Prent-Aq relative to Aqua-Aq and Mala-Xyl-Hex, which all contained about the same malathion concentration, implied that the organic phase of Prent-Aq preferentially partitioned into the nitrile barrier. The lack of malathion permeation in the hexane carrier confirmed that nitrile was impermeable to hexane at these permeation conditions. The permeation of 1,2,4-trimethylbenzene without that of malathion after 8-hour challenges of Silver Shield glove material demonstrated that differential permeation of formulation components can occur. The relationships of the permeation characteristics of the alkylbenzene inert components to those of malathion in the formulations will be explored elsewhere.(22)

When mid-range t_b's (malathion did not permeate at zero time) were correlated to corresponding t_l's for each run in Table 2, the following regression equation was obtained for $n = 16$ for $v = n - 2$ degrees of freedom for Student t_v:

$$t_b = 0.785\ t_l - 17.8 \qquad r = 0.906,$$

$$\text{Student } t_{14} = 8.01, \qquad p < 0.025 \tag{3}$$

Each t_b is related linearly to its corresponding t_l at $p < 0.0005$. Individual t_l and t_b pairs are also correlated at $p < 0.025$ for the eight alkylbenzene isomers of molecular weight 120,(18) and for the four xylene positional and skeletal isomers of molecular weight 106.(19) Since these alkylbenzene isomers are the dominant alkylbenzenes in this formulation, there is consistency between studies. Averaged t_b's were also correlated with averaged t_l's for malathion but at lower p (<0.005) for $n = 5$:

$$t_b = 0.833\ t_l - 23.1 \qquad r = 0.956,$$

$$\text{Student } t_3 = 5.64, \qquad p < 0.025 \tag{4}$$

This correlation was not observed for molecular weight 120 and 106 alkylbenzenes(17,18) because of greater scatter of data there, and because two steady-state periods were often observed for the former.(18) Equations 3 and 4 are important since glove manufacturers do not provide t_l data. The t_b's are dependent on the detection method, whereas t_l's are not, and relationships like Equations 3 and 4 may allow t_b data to be translated into t_l data for a given permeation and analytical chemistry method. Many manufacturers also list the shortest t_b rather than the average t_b, necessitating use of equations like Equation 3 for a given sensitivity to determine t_l.

The only other significant ($p < 0.025$) correlation for the average data was:

$$P_s = -1{,}038\ t_b/t_l + 826 \qquad r = -0.922,$$

$$\text{Student } t_3 = 4.12 \tag{5}$$

When Equation 4 was substituted into Equation 5 for t_b:

$$P_s = 23{,}978/t_l - 39 \tag{6}$$

The correlation of P_s with $1/t_l$ was not significant at $p < 0.025$, showing that Equation 5 does not have sufficient statistical power.

The only other significant correlation ($p < 0.025$) for the individual data was:

$$\ln P_s = 2.55\ D_p + 0.554 \qquad r = 0.551,$$

$$\text{Student } t_{14} = 2.47 \tag{7}$$

Substituting from Equation 2 for D_p:

$$\ln P_s = 0.425\ l^2/t_l + 0.554 \tag{8}$$

That is, ln P_s will not correlate to $1/t_l$ without accounting for initial glove thickness, or the correlation is to D_p rather than $1/t_l$. Glove manufacturers do not provide D_p data. Model building would be facilitated if they did.

One author has previously shown that log t_b of a homologous series analyzed at the same detection conditions is correlated significantly to the change in Snyder eluent strength ($E°$)(20) relative to the $E°$ of the lowest molecular weight member of the series.(16) Unfortunately, $E°$ values for alkylbenzene congeners and isomers beyond toluene (except for *p*-xylene) and for malathion are not known. The next best correlate(16) to log t_b was the logarithm of the heptane/water partition coefficient. Again there are insufficient data. The next significant correlate with log t_b was log K_{ow}, the logarithm of the octanol/water partition coefficient. The log K_{ow} for malathion is 2.89 at 20°C.(20) The log K_{ow}'s for benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene are:(19) 2.13, 2.69, 2.77, 3.20, 3.15, and 3.15, respectively, at 20°C.

If malathion is as reactive with nitrile as xylenes, malathion should have permeation characteristics close to those for the three xylenes and toluene under the same permeation and analytical conditions according to these log K_{ow} values. In the present study, pure malathion shows a t_b of 0 to 10 minutes, a P_s of 370 to 1270 μg/cm^2/min, and a t_l of 48 to 81 minutes, the average P_s being in the Fair 90 to 900 μg/cm^2/min classification range.(13) The equivalent data for the pure molecular weight 106 alkylbenzenes for a thinner (0.41 ± 0.05

mm) Sol-Vex nitrile glove are:(18) *o*-xylene, t_b 20 to 30 minutes, P_s 160 to 250 $\mu g/cm^2/min$, and t_l 44 to 61 minutes; *m*-xylene, t_b 10 to 20 minutes, P_s 330 to 370 $\mu g/cm^2/min$, and t_l, 20 to 29 minutes; *p*-xylene, t_b 10 to 20 minutes, P_s 720 to 1000 $\mu g/cm^2/min$, and t_l 31 to 48 minutes; and ethylbenzene, t_b 20 to 30 minutes, P_s 130 to 300 $\mu g/cm^2/min$, and t_l 36 to 39 minutes. The corresponding data for *p*-xylene permeation through gloves of the same thickness as the present experiment(18) were: t_b, 10 to 20 minutes, P_s, 510 to 840 $\mu g/cm^2/min$, and t_l, 36 to 45 minutes, not very different relative to the characteristics for the thinner glove. Pure malathion permeation, therefore, most resembles that of pure *p*-xylene ($E° = 0.26$)(21) relative to P_s, but acts more like toluene ($E° = 0.29$)(21) relative to t_b. The E° for malathion is tentatively assigned to be about their average, namely, 0.275, the uncertainty being ±0.015 from the relative errors of the two log K_{ow}'s.

The correlation between log K_{ow} and E° found elsewhere is just significant at $p < 0.025$(16) (Equation 9):

$$\log K_{ow} = -4.49\, E° + 3.3 \tag{9}$$

Assuming a log K_{ow} of 2.89 for malathion,(20) E° is 0.091, and near the $E° = 0.08$ of isopentane,(21) a value that makes malathion much too nonpolar. Equation 9 does not have sufficient statistical power, as discussed elsewhere.(16) When log K_{ow}'s are regressed linearly against the corresponding E°'s for benzene, toluene, and *p*-xylene (E° of 0.32 for benzene and 0.29 for toluene(21)), Equation 10 is obtained instead:

$$\log K_{ow} = -17.0\, E° + 7.59 \qquad r = -0.9984 \text{ with } p < 0.025 \tag{10}$$

Substituting a log K_{ow} of 2.89 for malathion into Equation 10 yields an E° of 0.28, more in agreement with the qualitative treatment discussed above. It is expected(16) that interpolations within homologous series through equations like Equation 10 should be better than utilizing generalist equations like Equation 9. Since malathion is a nonpolar ester that is only reactive under alkaline conditions,(1) the partitioning behavior of pure malathion appears intermediate between toluene and *p*-xylene. The carrier results with hexane ($E° = 0.01$)(21) and water ($E° = >1.1$)(21) are explained in terms of E° and dilution effects of the carrier.(22)

Conclusions

Pure malathion, undiluted malathion formulations, and 50 percent malathion/*m*-xylene permeated through nitrile within 8 hours, but not through Viton or Silver Shield gloves. Malathion in a commercial formulation, in *m*-xylene mixtures, and in a formulation mixed with *m*-xylene permeated through nitrile with slower steady-state permeation rates, longer breakthrough times, and longer lag times than pure liquid malathion due to dilution and the modulating effects of the more nonpolar inert components. The influence of the carrier, whether *m*-xylene or water, was also evident. This suggested that the bulk properties of the challenge solutions determined the permeation of individual mixture components as well as dilution effects.

Recommendations

Viton and Silver Shield gloves are recommended for handling technical/pure-grade malathion and undiluted malathion emulsifiable concentrate formulations. When used for handling the same formulations, nitrile gloves can be used safely for 60 minutes, since malathion breaks through in 1 hour, but they will not protect against pure/technical malathion. Nitrile can be used for longer times of at least 4 hours to protect against diluted solutions of formulations in water carrier, such as when sprayed in the field.

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