

Organophosphorus pesticide exposure in agriculture: effects of temperature, ultraviolet light and abrasion on PVC gloves

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Abstract: Elbow length PVC gloves are often recommended for protection against organophosphorus pesticide (OP) exposure in agriculture. However, performance may be reduced due to high temperature, UV exposure and abrasion. We sought to assess these impacts for two OPs under normal use and reasonable worst-case scenarios. Glove permeation tests were conducted using ASTM cells with two PVC glove brands at 23°C and 45°C for up to 8 h. Technical grade dichlorvos and formulated diazinon were used undiluted and at application strength. Breakthrough of undiluted dichlorvos occurred at both 23°C and 45°C, but only at 45°C for application strength. Breakthrough of diazinon was not achieved, except when undiluted at 45°C. UV-exposed and abraded gloves showed reduced performance, with the effect being approximately two-fold for dichlorvos. Only small differences were noted between glove brands. Extra precautions should be taken when handling concentrated OPs at high temperature, or when using abraded or sunlight-exposed gloves.

Key words: Abrasion, Glove permeation, Organophosphorus pesticides, Temperature, UV

Agricultural workers are a large identifiable occupational group at risk of exposure to organophosphorus pesticides (OPs). The activities of pesticide mixing, loading and spraying, put them at risk for chemical uptake and intoxication¹. Usually, thick PVC gloves are worn for handling OPs as they are relatively inexpensive and often recommended in product Safety Data Sheets (SDSs). However, no gloves are suitable for all chemicals and it has not been feasible to mathematically model the performance for various product formulation containing solvents². There are limited data on glove permeation for formulated OPs, especially on permeation of concentrated pesticide formulations containing active ingredients and carrier solvents³.

While tests with low concentration OPs are relevant for sprayers, glove permeation data for high concentrations (full strength, undiluted concentrate) OPs are necessary for the workers involved in mixing and loading of OPs or for splash or spillage incidents.

Much agricultural work is conducted outdoors where UV exposure, high temperature and abrasion may degrade glove performance. Significant exposures are possible depending on the task, chemical properties and environmental conditions. However, there are few studies of the influence of temperature, UV or abrasion, especially with regard to PVC gloves^{4–7}.

Dichlorvos and diazinon are OPs commonly used in Australia in the domestic, agricultural, pest control and veterinary sectors. Dichlorvos is a synthetic organic fumigant that is moderately lipophilic (log K_{ow} 1.16) with a molecular weight of 221.0 and molecular volume of 156

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Å³. Diazinon, on the other hand, is relatively insoluble in water (log K_{ow} 3.81) with a molecular weight of 304.3 and molecular volume of 273 Å³. This study was conducted to examine the performance of PVC gloves (unused, exposed to UV light or abraded) against contact with two OPs of different physicochemical properties, in various conditions, with the assumptions that:

- (i) agricultural workers could be dealing with a range of chemicals with varying properties,
- (ii) concentrations of OPs used may be undiluted (for mixing) and diluted products (ready for spraying)
- (iii) exposure time may vary and the daily maximum duration is typically 8 h, and
- (iv) exposure could occur at various temperatures (temperate to hot summer days).

Glove preparation

Glove permeation resistance tests were conducted using one inch American Society for Testing and Materials (ASTM) permeation test cells and two brands of elbow-length PVC gloves recommended in SDSs for use in OP handling. The first brand was *Excalibur* gloves (RN No. #48583, Style W6218R, FTY11371110) sourced from Protector AlSafe, Regency Park, South Australia. The second was *ProChoice* gloves (106M-3-SFC-14014) purchased from SafetyQuip, Dry Creek, South Australia. In this study, glove swatches were cut out of the palm area of the gloves and the thickness was measured at several points with a digital thickness gage (547–301, 0.01 mm–10 mm, Mitutoyo). Thickness of *Excalibur* gloves were 1.05 to 1.26 mm, and *ProChoice* gloves had thickness ranging from 1.07 to 1.28 mm. To mimic exposure to UV radiation in real life, gloves were exposed to UV radiation in a UV exposure box with UV-A lamps (FL6BL 6 W 350 nm) and UV-B lamps (FL8E 8 W 302 nm) supplied by Ultra-Violet Products Pty Ltd (Australia) for 48 h. This irradiance was approximately equal to seven days of exposure to the extreme midday sun⁸). For abraded PVC gloves, palm section of the glove was mounted on a foam-backed hand sander and carefully abraded by using a horizontal belt sander (Ryobi, RBDS4601G, 370 W) until the thickness of the gloves was reduced by 5%, corresponding to a PVC top layer reduction of approximately 10% (0.06 mm). Then, the surfaces of the abraded gloves were vacuumed and wiped with a wet sponge to remove small particles produced during the abrasion process.

Chemicals

In order to mimic a real-life use scenario, the gloves were

tested with two concentrations of OP solution; full strength (undiluted) and application strength. Dichlorvos was 1,398 g/L technical grade DDVP (Lot No. 212002AX0028) of 97% purity without co-solvent from Amvac Chemical Corporation (Australia) - used for making formulated dichlorvos products. *Barmac* Diazinon Insecticide (804 g/L diazinon and 80 g/L hydrocarbon liquid as the carrier solvent) was formulated by Accensi and was obtained from Barmac (Queensland, Australia). Application strength OPs (6 g/L dichlorvos, 0.5 g/L diazinon) were prepared by diluting the full strength OP with purified water. Analytical grade standards (Fluka-45428 for diazinon, Fluka-45441 for dichlorvos) from Sigma-Aldrich were used for preparing standard solutions prior to analysis.

Permeation cell set-up

OP permeation was determined by sandwiching the glove swatches between the donor chamber and the receptor chamber of the ASTM cell. Cells exhibited a diffusion-available surface area of 5.31 cm² and a receptor compartment volume of 16.4 ml. Based on suitability and chemical solubility, receptor fluids were purified water (for dichlorvos) and 50% (v/v) ethanol in water (for diazinon). Receptor fluid was continuously stirred with a modified stirrer at 350 rpm⁹). Samples (200 µL) were taken from the receptor chamber at appropriate intervals (every 15 min for the first hour, and hourly for the remaining duration up to 8 h) throughout the experiment and replaced with fresh receptor fluid of the same volume. The experiments were repeated four times, either set-up in ambient conditions (23°C) for exposure in normal temperate conditions or in an oven at 45°C to resemble the worst case scenario extreme hot conditions.

Analytical detection

All samples were analysed by High Performance Liquid Chromatography-UV (HPLC-UV) with the operating conditions adapted from previous studies¹⁰) with GBC LC 1120 HPLC Pump connected to a PE Nelson 900 Series Interface and Shimadzu SPD-20A Prominence UV/Vis detector. A volume of 20 µL sample was directly injected into the Alltech Alltima (C18, 5 micron, length 150 mm, I.D 4.6 mm) separation column. The mobile phases were aqueous acetonitrile 40:60 at 220 nm wavelength (dichlorvos) and 70:30 v/v with 250 nm (diazinon).

Descriptors of permeation

The following variables were used as descriptors for the ability of OPs to permeate through the gloves into the

Table 1. Summary of PVC glove test outcomes for dichlorvos and diazinon under various exposure temperatures and concentrations

| Exposure temperature | Concentration of OPs | Average cumulative permeation (mg) | | | |
|----------------------|---|------------------------------------|----------------------------|-----------------------------|-----------------------------|
| | | Dichlorvos | | Diazinon | |
| | | <i>Excalibur</i> | <i>ProChoice</i> | <i>Excalibur</i> | <i>ProChoice</i> |
| 23°C | Application strength: • 6 mg/ml (dichlorvos) • 0.5 mg/ml (diazinon) | Not achieved | Not achieved | Not achieved | Not achieved |
| | Full strength: • 1,398 mg/ml (dichlorvos) • 804 mg/ml (diazinon) | 174 (± 9) BT 180 mins | 142 (± 12) BT 180 mins | Not achieved | Not achieved |
| 45°C | Application strength: • 6 mg/ml (dichlorvos) • 0.5 mg/ml (diazinon) | 12.3 (± 0.4) BT 180 mins | 6.2 (± 0.2) BT 240 mins | Not achieved | Not achieved |
| | Full strength: • 1,398 mg/ml (dichlorvos) • 804 mg/ml (diazinon) | 653 (± 48) BT 60 mins | 555 (± 3) BT 60 mins | 54.6 (± 4.0) BT 120 mins | 28.8 (± 3.8) BT 180 mins |

Mean values ± SD, n=4

BT denotes breakthrough time observed when flux reached 1 $\mu\text{g}/\text{cm}^2/\text{min}$, as per AS/NZS 2161 standard

'Not achieved' denotes breakthrough was not achieved over the 8-h test period

receptor fluid: maximum flux ($\mu\text{g}/\text{cm}^2/\text{min}$), breakthrough time (mins) and cumulative permeation (mg). Flux refers to the mass permeated across a defined glove area in a set time. Breakthrough time is based on the AS/NZS 2161 standard which defines that breakthrough only occurs when the flux reaches 1 $\mu\text{g}/\text{cm}^2/\text{min}$ ¹¹). Cumulative permeation (mg) is the amount of OPs recovered in the 16.4 ml of receptor fluid in the receptor chamber at the end of the 8-h tests.

Statistical analysis

One-way ANOVA with Tukey's Multi Comparisons tests and Kruskal-Wallis tests with Dunn's Multiple Comparisons tests were used to compare the sets of cumulative permeation outcomes between OPs.

Comparison of OP permeation through new unused gloves under variable conditions

Table 1 summarises the results of the glove performance (permeation resistance) tests under various temperature and test concentrations with the descriptors of glove permeation for dichlorvos and diazinon. In general, higher temperature resulted in shorter breakthrough time and greater average cumulative permeation. Application strength OPs did not achieve breakthrough at 23°C. However, at elevated temperature, application strength dichlorvos recorded breakthrough in 180 mins for *Excalibur* gloves (average cumulative permeation 12.3 (± 0.4) mg) and 240 mins for *ProChoice* gloves (average cumulative permeation 6.2 (± 0.2) mg).

Protection afforded by the gloves varied against undi-

luted OPs. Only undiluted diazinon tested at 23°C did not achieve breakthrough, while at elevated temperature the average cumulative permeation at the end of the 8-h experiments were 54.6 (± 4.0) mg (BT 120 mins) for *Excalibur* gloves and 28.8 (± 3.8) mg (BT 180 mins) for *ProChoice* gloves. Permeation of undiluted dichlorvos was comparably higher than diazinon, where at 23°C the breakthrough time was 180 mins for both glove brands, average cumulative permeation of 174 (± 9) mg for *Excalibur*, 142 (± 12) mg for *ProChoice*, and decreased to 60 mins at elevated temperature, with average cumulative permeations almost 4 times greater. Statistically, cumulative permeation outcomes of the tested OPs at 8 hrs for both glove brands were significantly different ($p < 0.0001$), when comparing both concentrations as well as under both temperature conditions.

Permeation of OPs through UV-exposed PVC gloves

Outcomes of the OPs (undiluted only) tested on UV-exposed PVC gloves at the end of the 8-h tests were compared with unused PVC gloves with the same variable conditions (Fig. 1).

Generally, cumulative permeation outcomes of the OPs through UV-exposed PVC gloves were higher (approximately 2-fold increase) than those tested on unused PVC gloves. Dichlorvos demonstrated significant difference ($p < 0.0001$) in cumulative permeation in the receptor fluid when compared to unused gloves; 1,046 (± 36) mg and 1,300 (± 62) mg for UV-exposed *Excalibur* and *ProChoice* gloves, respectively.

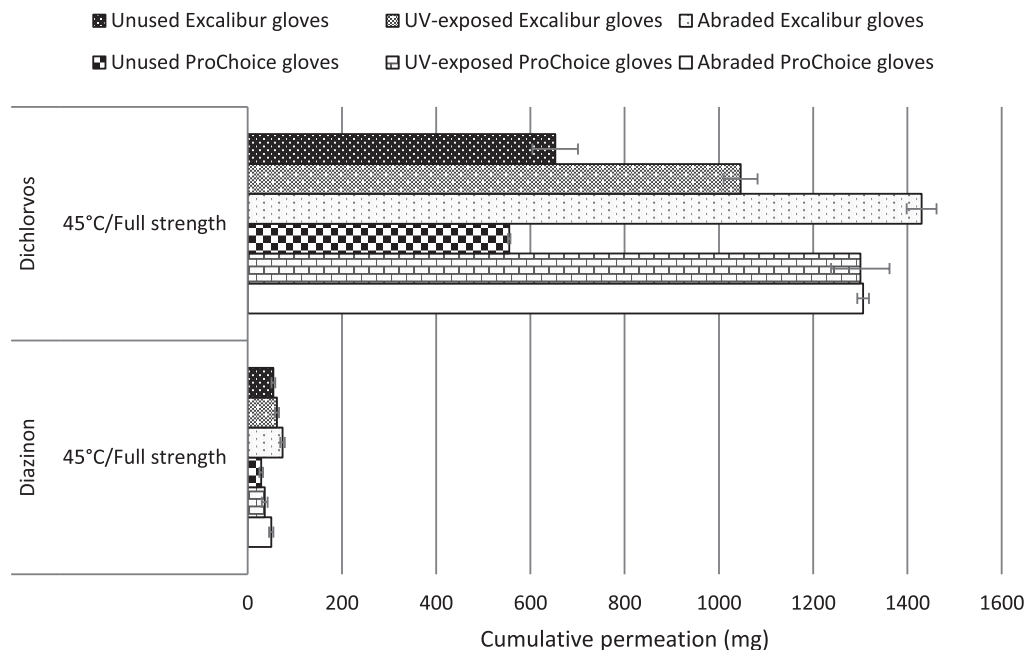


Fig. 1. Comparison of permeation of dichlorvos and diazinon under worst case conditions (high concentration and high temperature) through unused gloves, UV-exposed gloves and abraded gloves. Mean value, \pm SD, $n=4$.

In contrast, the mass of diazinon permeated at 8 hrs through UV-exposed *Excalibur* and *ProChoice* gloves were not significantly different ($p=0.07$) when compared to unused gloves. The permeated amounts were $62.2 (\pm 4.3)$ mg and $36.2 (\pm 6.1)$ mg, for *Excalibur* gloves and *ProChoice* gloves, respectively.

Permeation of OPs through abraded PVC gloves

Outcomes of the OPs (undiluted only) tested on abraded PVC gloves were compared with unused PVC gloves with the same variable conditions (Fig. 1).

Abraded PVC gloves (both *Excalibur* and *ProChoice*) showed consistently greater cumulative permeation of OPs compared to unabraded gloves. The mass of dichlorvos permeating through abraded gloves was more than 2-fold greater than new unused gloves; $1,430 (\pm 32)$ mg (*Excalibur* gloves) and $1,306 (\pm 12)$ mg for *ProChoice* gloves by 8 h of exposure. As for diazinon, abrasion of gloves resulted in $74.0 (\pm 4.8)$ mg of diazinon permeating through abraded *Excalibur* gloves, compared to only $54.6 (\pm 4.0)$ mg for unused *Excalibur* gloves, while abraded *ProChoice* gloves showed a two-fold increase to $50.0 (\pm 4.6)$ mg. As a whole, the two glove brands did not show significant difference in terms of cumulative permeation outcomes ($p=0.10$) between one another.

OP permeation through two glove brands was greater with increased exposure concentration and temperature. The greater cumulative permeation of dichlorvos through

gloves may be due to its relative higher concentrations in diluted and undiluted forms, compared with diazinon. It may also be attributed to dichlorvos having a smaller molecular volume (155.5) and polar surface area (44.8), compared to diazinon (273.1 and 53.5, respectively).

The findings in this study on concentration and temperature effects are consistent with previous work for other OPs, where shorter breakthrough times were reported for technical grade malathion at test concentrations 58% compared to 1%, under 22°C and 37°C , and no breakthrough of malathion when recorded for up to 1,440 mins¹²). Outcomes in our study showed breakthrough as early as 60 mins (for worst case scenario; undiluted at 45°C) which should be highlighted in occupational settings where protective clothing are typically worn. This may consequently influence permeation of OPs through gloves and the skin¹³). Increased temperature may also degrade or alter the glove material, hence shortening the lifespan of gloves significantly when used in hot conditions.

It appears that new *ProChoice* gloves afford marginally better protection than new *Excalibur* gloves in all test conditions. Possibility of considerable variation has been noted within a particular brand and model of gloves, even if they are produced by the same manufacturer¹⁴).

Heat and sunlight have been reported to cause degradation of PVC glove materials, i.e. surface topographic and elemental changes, loss of strength, elastic properties and puncture resistance^{6, 15}). Although the properties were not

tested in the present study, the findings are in agreement with a previous study where exposure of natural rubber gloves to UV-A radiation enhanced permeability of 2,4-D, although no effect was observed on the permeation of DDT⁵). It is also worth noting that in real life conditions, gloves may be exposed for a longer or shorter period of time, but with additional degradation factors such as repeated heating/cooling and other weathering effects that are not simulated in the present study. Re-use or improper use of gloves may add to health risk, via ongoing permeation and/or internal contamination.

The findings for abraded PVC gloves suggest that increased permeation is likely attributed to barrier thickness reduction⁷). However, it is possible that the pores/cavities of the glove material may have also been 'filled in' during the abrasion process, somewhat modifying permeation behaviour in the opposite direction. It should also be noted that thickness reduction in the present study is uniform, while the reality in farming situations may be otherwise.

At moderate temperatures, PVC gloves seem to provide adequate protection while handling application strength dichlorvos and diazinon. However, prolonged use under elevated temperature conditions may reduce protection when handling application strength dichlorvos. Protection offered by PVC gloves is reduced when handling high concentrations of OPs, especially under elevated temperature (45°C) conditions. Although unlikely to be in direct contact for 8 h, gloves contaminated with undiluted OPs should not be worn for extended periods. Exploring additional modifying factors e.g. occlusion and flexing in real life exposure conditions may provide more accurate information and establish a better understanding of the permeation behaviour. The reuse of gloves may still be appropriate, however gloves must be carefully examined before use, and substituted more regularly in conditions of hot weather and potential abrasion.

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