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Permeation of chlorothalonil through nitrile gloves: Collection solvent effects in the closed-loop permeation method

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ABSTRACT

The aim was to measure the permeation of the fungicide chlorothalonil from Bravo Ultrex through disposable (Safeskin) and chemically protective (Solvex) nitrile glove materials in a closed-loop ASTM type permeation cell system employing different collection side solvents. The permeated fungicide was measured in the collection medium by the internal standard method through capillary gas chromatography–mass spectrometry and selective ion monitoring using m/z 222 (internal standard 4,4′-dichlorobiphenyl), and 224 and 226 (chlorothalonil). The permeated glove materials did not show swelling or shrinkage and infrared reflectance changes. Different permeated masses for the same glove material for aqueous emulsion challenges of 2.2 mg/mL Bravo Ultrex for 8 h were observed for different solvents with isopropanol > hexane > water for Safeskin, and isopropanol = hexane > water for Solvex. Solvex gloves always permeated less than Safeskin gloves for the same challenge time. When challenges with solid Bravo Ultrex occurred, chlorothalonil was still found in the collection side in the same solvent order as for the aqueous emulsion challenges, with Solvex always less than Safeskin for the same collection solvent and same challenge time. Kinetic experiments showed isopropanol was not a suitable collection solvent for Safeskin for 4 and 8 h. Hexane was not a valid collection solvent for Solvex and Safeskin for 8 h, but was better than isopropanol.

1. Introduction

Chlorothalonil (tetrachloroisophthalonitrile; daconil; 2,4,5,6-tetrachloro-1,3-dinitrilo-benzene; 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile; CAS RN 1897-45-6) is a fungicide and nematicide [1–3]. It was commercially introduced in 1966 as an organochlorine general use pesticide in agriculture, silviculture, and urban settings, originally against *Alternaria solani*. It was classified by the United States (U.S.) Environmental Protection Agency (EPA) as "class II—moderately toxic", due to its potential for eye irritation. It was the major pesticide used on lawns and crops in both the U.S. and Canada to 1998 until it was found at high (270 μg/L) concentrations in the groundwater of four U.S. states [1–4]. Chlorothalonil was then found to affect the reproduction of freshwater fish and invertebrates [5]. It is moderately persistent in the environment due to biodegradation, hydrolysis, and slow photodegradation [5]. It undergoes rapid clearance from animal tissues [5]. Its use was reconsidered in the U.S. in 1999 [2] because of its potential to cause important environmental effects and risk to human health. This drastically decreased its U.S. use [1,2]. Since 2002, it has been also registered as highly toxic by the U.S. EPA pesticide product information system; it is included as a carcinogen "class B2—probable" on the list of chemicals evaluated for carcinogenic potential by the U.S. EPA Office of Pesticide Programs [3]. There are no U.S. occupational guidelines.

Various other countries have regulated its use. The International Maritime Organization (IMO Resolution A. 895 21, November 25, 1999) and then the European Union (Ordinance No. 782/2003, April 14, 2003) banned organotin-based antifouling coatings due to their negative impact on coastal ecosystems [6,7]. Only Sweden has banned it because it is carcinogenic [7]. When the Biocidal Product Directive (BPD, Directive 98/8/EC) went into effect in 2000 in the European Community, the toxic organotin compounds used in antifouling coatings, paints, and adhesives on ships, boats, and structures in contact with water were banned [6,7], and substitutes began replacing them, among them being chlorothalonil at concentrations ranging from 6% to 14%[7]. The European Union has reclassified pesticide registration in the revision of annex I of the Dangerous Substances Directive 67/548/EEC [7]. Beginning from June 2007, the New European Chemicals Regulation (REACH, Regulation (EC) No. 1907/2006) that combines and consolidates about 40 previous regulations, will oversee the continuing registration of European pesticides like chlorothalonil over the next 11 years of registration transition [7].

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Formulating and blending activities, greenhouse spraying, reentry after spraying, and sprayed crop/surface contact after spraying are currently the major situations of work exposure to humans from chlorothalonil [8]. Skin exposure is the major route of exposure to pesticides that are not fumigants like chlorothalonil and to solvents and liquid chemicals that are not volatile [8]. The major exposed parts of the body are usually the hands [8]. A review is available on pesticide permeation through gloves [9].

A typical chemical protective glove that is recommended for chlorothalonil is polyvinyl alcohol [10]. Unfortunately, such a glove does not protect against aqueous emulsions or solutions, though that glove material will protect against the pure pesticide (a solid), and its non-aqueous and non-alcoholic solutions [11]. The usual warning about protection for this pesticide is "Use gloves, apron, rubber, or plastic boots" without designating the types of gloves to be used [12]. Cotton gloves are inadequate protection against chlorothalonil because the fungicide was detected on pads under the gloves, and biological monitoring showed urinary chlorothalonil in a skin exposure situation [13]. This complemented previous greenhouse worker skin and glove exposure data [14–16]. There is a lack of quantitative permeation data of chlorothalonil through other glove types like the much-used disposable and chemically protective nitrile rubber materials, these being copolymers of acrylonitrile and butadiene of various thicknesses (disposable gloves are thinner) and extents of polymerization and layering [17].

The method to assess how much chemical can pass through glove material without degrading it ("permeation") involves use of a permeation cell in which a circular piece of material is challenged by a liquid and the permeated compound is determined in the vapor phase (open loop system) or in liquid collection solvent (closed-loop system) [17–19]. In the United States, the major method using such a cell is the American Society for Testing and Materials (ASTM) method F739-99a [20].

We report the first measurement of chlorothalonil permeation through nitrile glove materials using the closed-loop ASTM F739-99a method and capillary gas chromatography–mass spectrometry (GC–MS), and the assessment of the influence of various collection solvents.

2. Experimental

2.1. Chemicals, solvents, and glove materials

Bravo Ultrex agricultural fungicide (82.5% water dispersible granules with 82.5% chlorothalonil and 17.5% inert ingredients) was from Zeneca Ag Products (Wilmington, DE). The recommended application concentration range was 0.9–5 lb/100 gallons (1.0–6.0 g/L), a pesticide equivalent of 0.89–4.93 g/L. Pure chlorothalonil (98% purity nominally) and internal standard 4,4′-dichlorobiphenyl (99%) were provided through ChemService (West Chester, PA). Optima grade hexanes and isopropanol were from Fisher Scientific (Pittsburgh, PA). All water was Millipore triple cartridge deionized.

Safeskin nitrile powder-free exam gloves (24.1 cm length; unspecified thickness; Kimberly Clark No. N330) were obtained from Fisher Scientific. Solvex unsupported and unlined nitrile chemical protective gloves (33 cm length; 11-mil thickness; No. 37-145) were from Ansell Occupational Healthcare (Coshocton, OH).

2.2. Equipment

A calibrated Marathon Electronic Digital Micrometer Model CO 030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific was used to measure the thickness of gloves before and after permeation testing. A calibrated Mettler analytical balance AE260 DeltaRange (Mettler, Hightstown, NJ) was used to weigh the gloves before and after permeation.

Infrared (IR) spectra were obtained with an Avatar 360 Fourier-transform (FT) spectrophotometer system (ThermoNicolet, Madison, WI), a single-beam FT-IR spectrophotometer using the reflectance mode and operated with OMNIC 6.0a software. The crystal was diamond in a single-reflection horizontal attenuated total reflectance mode. The spectral range was 4000–600 cm^{-1}, and the number of scans was 32.

Gas chromatography–mass spectrometry (GC–MS) was performed with an Agilent 6890N Network Gas Chromatograph (Agilent Technologies, Wilmington, DE) connected to an Agilent 5973 Network Mass Selective Detector (MSD) (Agilent Technologies). The MSD was a quadrupole with an electron multiplier detector. The GC column was an HP 5-MS 30 m × 0.25 mm i.d. (0.25 μm film) fused silica capillary column (Agilent Technologies). The carrier flow of helium (99.9999%, from Air Liquide, Long Beach, CA) was 3.00 ± 0.20 mL/min. The temperature of the injector was 200 °C and that of the transfer line was 280 °C. The 70 eV ion source and the quadrupole were held at 230 and 150 °C, respectively.

2.3. Water solubility of chlorothalonil

Chlorothalonil (15 mg) was mixed with 20 mL water in a centrifuge tube. The sample was sonicated at 40 °C for 60 min (screw cap on). After cooling to 25 °C, the solution was centrifuged at 900 g for 30 min, 1.0 mL of the supernatant transferred to a 3-mL vial, and the 1-mL volume evaporated just to dryness at 40 °C under a gentle nitrogen flow. One mL of isopropanol containing 5 mg/L of the internal standard (4,4′-dichlorobiphenyl) was then added. The amount of chlorothalonil was determined by GC–MS using the internal standard method (Section 2.6). The solubility was calculated from the mass in 1 mL divided by the 1 mL water volume. All experiments were done in triplicate.

2.4. Chlorothalonil content of Bravo Ultrex

A 300 mg/L solution of Bravo Ultrex was prepared in isopropanol. A volume of 0.1 mL was diluted to 1 mL with isopropanol to contain 5 mg/L internal standard. GC–MS analysis by the internal standard method followed (Section 2.6). All experiments were done in triplicate.

2.5. Permeation procedure

The permeation procedure was based on a modified ASTM method F739-99a permeation method [20]. Out-of-the-box gloves were conditioned for 24 h in a desiccator, where the relative humidity was maintained at 55 ± 1% by saturated aqueous sodium dichromate as recommended by the ASTM method. Circular pieces of 42.5 mm diameter were cut from the palm area of six gloves of each type. Right before each permeation experiment, the thickness of each glove piece was measured using six random readings with the arithmetic mean and standard deviation calculated. The glove pieces were then weighed. The infrared reflectance of material near the cut piece was then measured at a specific clamp pressure.

Each circular piece was then held between the two Teflon gaskets and the Pyrex chambers of an I-PTC-600 ASTM type permeation cell (Pesce Lab, Kennett Square, PA) by a uniform torque, with the outer surface of the glove facing the challenge chamber. The test area of the glove between the two chambers had a diameter of 25.4 mm. A 10 mL volume of aqueous Bravo Ultrex emulsion at a

concentration of 2.2 mg/mL was pipeted into the challenge chamber, and 10 mL of solvent (hexane, isopropanol, and water) was pipeted into the collection chamber. Solid Bravo Ultrex powder (8500 g) was poured into the challenge side to fill it for the solid challenge experiments instead of the liquid.

The permeation cells were immersed six at a time in a Fisher Shaking Water Bath model 127 at 35.0 ± 0.5 °C. In kinetic experiments for isopropanol collection medium, the permeation cells were agitated for 0.5, 2, 4, or 8 h at an average horizontal shaking speed of 70 ± 5 cycles/min, with traveling distance of 10.24 cm/cycle. This velocity was necessary to ensure no concentration gradients in the collection and challenge sides. For the challenge side, no phase separation occurred after 8 h. For hexanes and water collection solvents, only 8-h permeations were done. After permeation testing, the collection solvent and the challenge solution were weighed. The permeation cells were disassembled, and the outer surfaces of glove pieces were blotted dry with Kimwipes. The glove pieces were re-conditioned in the desiccator for 24 h before final weighing, thickness, and infrared reflectance measurements.

Solvent blank tests with 10 mL solvent in the collection chamber, and only air in the challenge chamber, were also performed. The latter provides information on back permeation of the collection chamber solvent. The headspace of the challenge side was sampled with a 50 mL gas-tight syringe at the end of the permeation period and the solvent vapor quantified against known vapor concentrations generated in 10-L Tedlar gas bags using no solvent delay at the initial temperature of the GC–MS temperature program under total ion current conditions of *m*/*z* 30–550.

2.6. Quantitation of chlorothalonil after permeation

The collection and challenge aqueous solutions were evaporated under a gentle flow of nitrogen at 40 °C. A volume of 50 μL of 100 μg/mL 4,4′-dichlorobiphenyl internal standard in isopropanol was added, and isopropanol added to a final volume of 1.0 mL in a volumetric tube. A 2-μL aliquot was injected for analysis into the GC–MS.

The MS detected ions of mass to charge ratio (*m*/*z*) 222, 264, and 266 in the selected ion monitoring mode. The GC column was operated isothermally at 100 °C for 2 min, 20 °C/min to 170 °C, and maintaining the temperature at 170 °C for 25 min at 3.0 mL/min with a solvent delay of 3.5 min. Under these conditions chlorothalonil had a retention time of about 24.2 min and the internal standard had a retention time of 20.8 min. Each run was about 30 min in duration. It should be noted that chlorothalonil decomposes at 250 °C [12].

Ratios of chlorothalonil area for *m*/*z* 264 plus the area for *m*/*z* 266 over IS area for *m*/*z* 222 in the chromatograms were plotted versus corresponding chlorothalonil mass injected to provide the calibration curve. The linear portion (0.5–14 ng) was determined and that part subjected to linear regression to calculate the slope and intercept, their standard deviations, the correlation coefficient, and the *p*-value.

Fourier transform reflectance infrared scan analysis of the dried glove materials was performed from 4000 to 600 cm^{-1}. The major reflectance maxima at 740 and 1485 cm^{-1} were scrutinized.

3. Results and discussion

3.1. Chlorothalonil solubility in water

The solubility triplicate results were 6.2, 5.6, and 5.9 in mg/L to provide an arithmetic mean and standard deviation of 5.9 ± 0.3 mg/L. Literature solubility values for 25 °C are 0.6 mg/L [12] and 1.8 mg/L [21]. There is order of magnitude agreement though our value is higher probably because 40 °C was the initial temperature. The solubility at a specific temperature sets the upper concentration that a water collection vehicle can attain in the absence of adjuvants.

3.2. Bravo Ultrex chlorothalonil content and analytical standard purity

The chlorothalonil contents for three replicates were in % (w/w): 77.7, 78.8, and 80.8 with arithmetic mean and standard deviation of 79.1 ± 1.6%. This is significantly lower at $p \leq 0.05$ than the label value of 82.5%.

The major impurities (<1%) in the analytical standard were pentachlorobenzonitrile and hexachlorobenzene. The analytical

Table 1
Permeation data for chlorothalonil through Safeskin nitrile from 2.2 mg/mL aqueous Bravo Ultrex emulsion challenges in a ASTM type permeation cell at 35 °C.

Collection solvent	Time (h)	Replicate	Total mass (ng)	Mass/area (ng/cm^2)	Linear flux (ng/cm^2/min)
Water	8	1	<10	<2	<0.004
		2	197	39	0.082
		3	<10	<2	<0.004
		Average	69 ± 110[a]	14 ± 22	0.029 ± 0.046
Hexanes	8	1	3,370	674	1.40
		2	6,060	1,210	2.53
		3	5,320	1,060	2.21
		Average	4,920 ± 1,390	983 ± 278	2.05 ± 0.58
Isopropanol	8	1	26,500	5,300	11.0
		2	30,700	6,140	2.8
		3	32,700	6,540	13.6
		Average	30,000 ± 3,200	5,990 ± 630	12.5 ± 1.3
	4	1	30,600	6,040	25.2
		2	23,900	4,720	19.7
		3	30,200	5,950	24.8
		Average	28,200 ± 3,800	5,570 ± 740	23.2 ± 2.5
	2	1	1,950	385	3.21
		2	615	121	1.01
		3	941	185	1.55
		Average	1,170 ± 700	231 ± 138	1.92 ± 0.94

Notes: The ±quantities after the average (arithmetic mean) are standard deviations.
[a] Half the lower quantifiable limit for <quantities was used in calculating the arithmetic mean [29].

Table 2
Permeation data for chlorothalonil through Solvex nitrile from 2.2 mg/mL aqueous Bravo Ultrex emulsion challenges in a ASTM type permeation cell at 35 °C.

Collection solvent	Time (h)	Replicate	Total mass (ng)	Mass/area (ng/cm^2)	Linear flux (ng/cm^2/min)
Water	8	1	12.5	2.50	0.005
		2	45.8	9.2	0.019
		3	<10	<2	<0.004
		Average	21 ± 22[a]	4.2 ± 4.4[a]	0.0087 ± 0.0091[a]
Hexanes	8	1	2,813	563	1.17
		2	4,688	938	1.95
		3	3,750	750	1.56
		Average	3,750 ± 940	980 ± 280	1.56 ± 0.39
Isopropanol	8	1	2,490	497	1.04
		2	2,170	434	0.904
		3	5,965	1,193	2.49
		Average	3,500 ± 2,100	710 ± 420	1.48 ± 0.88
	4	1	80.2	16.0	0.0667
		2	25.1	5.00	0.0208
		3	58.6	11.7	0.0488
		Average	55 ± 28	10.9 ± 5.5	0.045 ± 0.023
	2	1	<10	<2	<0.004
		2	<10	<2	<0.004
		3	<10	<2	<0.004
		Average	<10	<2	<0.004

Notes: The ±quantities after the average (arithmetic mean) are standard deviations.
[a] Half the lower quantifiable limit for <quantities was used in calculating the arithmetic mean [29].

standard purity was determined to be 97.3 ± 2.3%. The recovery was 98.1 ± 2.2%.

3.3. Permeation

Tables 1 and 2 show the results for permeation experiments with aqueous Bravo Ultra for disposable Safeskin and chemically protective Solvex nitrile gloves, respectively. Table 3 shows the results of solid powder challenges for various collection side solvents and the two types of nitrile gloves. The mass permeated, the mass/area permeated factor, and the linear flux are tabulated. The latter assumes linear permeation kinetics, and is not necessarily related to the steady state permeation rate. The mass permeated at a specific time is the primary reference because the permeated mass is related directly to bioaccessible hazard. Interrun precision decreased as the permeated mass approached analytical detection limits. Shrinking or swelling of all glove materials did not occur at $p \leq 0.05$ (the thickness of the Safeskin gloves was 0.104 ± 0.004 mm; that for the Solvex gloves was 0.349 ± 0.010 mm). Fourier transform infrared reflectance measurements did not detect chlorothalonil on the dried inside surface of glove materials or any inner surface damage. The fungicide was detected on the dried challenge side after permeation experiments.

As expected, Solvex gloves were far more protective than Safeskin gloves for the same 8-h exposure time for the aqueous solution challenge (Tables 1 and 2). Assuming the average chlorothalonil mass permeated as the index of hazard, Solvex is 1.2 times more protective than Safeskin for hexanes collection. For isopropanol, it is 8.6 times more protective, and for water 3.3 times. This suggests that isopropanol is not a suitable collection solvent for Safeskin.

Table 3
Permeation of chlorothalonil from Bravo Ultrex powder (8.5 g) in the challenge compartment of an ASTM type permeation cell relative to collection solvent and nitrile glove type at 35 °C.

Glove type	Collection solvent	Time (h)	Replicate	Total mass (ng)	Mass/area (ng/cm^2)	Linear flux (ng/cm^2/min)
Safeskin	Water	8	1	169	33.9	0.0705
			2	185	36.9	0.0769
			3	654	131	0.272
			Average	340 ± 280	67 ± 55	0.40 ± 0.115
	Hexanes	8	1	890	178	0.371
			2	5011	1,002	2.09
			3	27,300	5,460	11.4
			Average	11,000 ± 14,000	2,210 ± 2,840	4.6 ± 5.9
	Isopropanol	8	1	55,300	11,100	23.1
			2	4,280	856	1.78
			3	79,900	16,000	33.3
			Average	46,500 ± 39,000	9,320 ± 7,730	23 ± 18
Solvex	Water	8	1	34.8	6.97	0.0145
			2	33.2	6.64	0.0138
			3	43.5	8.69	0.0181
			Average	37.2 ± 5.5	7.43 ± 1.10	0.0155 ± 0.0023
	Hexanes	8	1	2,030	406	0.845
			2	2,355	471	0.981
			3	3,620	724	1.51
			Average	2,670 ± 840	534 ± 170	1.11 ± 0.35
	Isopropanol	8	1	294	58.8	0.122
			2	6,010	1,200	2.50
			3	29,200	5,830	12.2
			Average	11,800 ± 15,300	2,360 ± 3,060	4.9 ± 6.4

Notes: The ±quantities after the average (arithmetic mean) are standard deviations.

The most striking result was the much lower permeated mass for water collection than for isopropanol and hexanes collections at the same conditions. Isopropanol allowed 6 times more permeation for Safeskin than did hexanes. For Solvex, the ratio was 0.93, not significantly different from 1 at $p \leq 0.05$, indicative of its more protective nature. Water collection collected 180 times less analyte than hexanes for the 8-h Solvex experiments, and 71 times less for Safeskin.

The isopropanol kinetic data in Table 1 for Safeskin indicate that that permeation was mostly complete by 4 h with most of the permeation occurring between 2 and 4 h of exposure. In contrast, Solvex gloves show mass/area ratios of <250 ng/cm^2 [20] for up to 4 h but not for 8 h for isopropanol collection (Table 2). The water collection data infer that both nitrile gloves would be acceptable to define a normalized breakthrough time over 8 h but not with hexane collection for 8 h.

Our experimental water solubility of chlorothalonil of 5.9 mg/L at 40 °C is equivalent to a 10 mL collection solution containing an analyte mass of 59 μg, No water collection solution (at 35 °C) contained this amount of chlorothalonil at the end of the permeation period even though the volume of water had the capacity. Even if the temperature was 25 °C during the sample processing phase, there were still no water collections that contained a mass close to the theoretical capacity of 6 μg/10 mL assuming a chlorothalonil solubility of 0.6 mg/L. Since the water in the collection side did not contain a surfactant unlike the challenge side, it is possible that chlorothalonil covered the collection side surface, although subsequent infrared examination of that dried surface revealed no detectable chlorothalonil. Blockage of the membrane could have happened deeper within the rubber membrane bulk. The mechanism bears further investigation. The solubility of chlorothalonil at the same temperature is far higher in organic solvents like isopropanol and hexane than in water.

Manufacturer data show that normalized breakthrough times for Safeskin are about 21 min for both isopropanol and hexane [24]. Solvex does not allow chlorothalonil breakthrough within 480 min for both isopropanol and hexane [11]. The validity of the liquid collection method depends on the solvent being inert to the glove and yet being able to solubilize the analyte without concentration gradients since just permeation through the material is of interest.

Another interesting result is that challenge of nitrile with dry Bravo Ultrex powder produces the same generalized results as aqueous emulsion challenges, but with higher amounts of permeated chlorothalonil (Table 3). Thus at 8 h for Safeskin, the ratios for average mass permeated for solid/aqueous emulsion data for water, hexane, and isopropanol were 4.9, 2.2, and 1.6, respectively. The corresponding data for Solvex were 1.8, 0.71, and 3.4, respectively. The hexanes result for Solvex is anomalous, probably because the two situations are nearly equivalent.

Water collection data infer both Safeskin and Solvex are acceptably resistant for 8 h. The phenomenon of organic solids producing permeation across glove material was first observed by Fricker and Hardy [22,23] who used a modification of the ASTM permeation cell. Other such data have been published by Bunge and co-workers for methyl paraben and 4-cyanophenol [25–28].

The mechanism for the solid challenges probably involves the collection medium wetting the glove material enough to back-permeate to the challenge surface where some solid is dissolved that then diffuses back to the collection medium compartment. Because there is a large concentration gradient, even a minimal wetting of the solid on the challenge side would cause the reverse diffusate to be very concentrated. Another possibility is the presence of microholes in the glove material so constituting a penetration component, but such microholes were not observed by microscopic observation in any of the materials examined. Back permeation experiments with an empty challenge side showed that Safeskin allowed both hexane and isopropanol vapor to be detected in the challenge chamber with isopropanol being more back permeative. Solvex organic vapor challenge side concentrations were much lower than for the Safeskin material because of its greater thickness and multiple non-polar layers. Back permeation of water was not assessed via headspace analysis, but water is not likely to back-permeate Solvex appreciably.

If chlorothalonil is not regarded as a carcinogen, the normalized breakthrough time is probably an adequate index of potential permeation hazard, that is, any exposure below the threshold of 250 ng/cm^2 is not harmful. Thus for the aqueous emulsion challenges and considering the mass/area parameters in Tables 1 and 2, Safeskin is potentially safe to wear only for water collection for 8 h and isopropanol collection for 2 h. Solvex is safe to wear only for water collection for 8 h and isopropanol collection for 2 and 4 h, demonstrating its inherent greater protectiveness relative to Safeskin. For the solid challenge (Table 3) both Solvex and Safeskin are safe to wear only for water collection for 8 h. Hexanes and isopropanol were always unacceptable for both challenge types for 8 h. A similar criterion for a carcinogen depends on what risk, for example, 1 in a million, is acceptable, a discussion beyond the scope of this article. No risk would mean all the glove materials would be unsuitable for wearing for 8 h because a mean permeated mass was always observed for all three collection solvents above the lower quantifiable limit of the analytical chemistry technique.

4. Conclusions

The permeation of the fungicide chlorothalonil from both concentrated aqueous emulsion and dry solid Bravo Ultrex has been reported through disposable and chemically protective nitrile gloves for the first time. The permeation results differ with collection solvent, the mass permeated for water collection medium being the lowest at 8 h, increasing for hexane, and then highest for isopropanol. The chemically protective glove was permeated the least for each solvent, as expected. Isopropanol was not an adequate collection solvent for the disposable nitrile glove except for the aqueous emulsion challenge for 2 h, and the aqueous emulsion challenge for the Solvex glove for 2 and 4 h. The solid challenges surprisingly generally resulted in more permeated mass for the same permeation time for a given glove material and collection solvent than for the aqueous emulsion challenges. The mechanism to explain the observations was discussed.

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