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A preliminary comparison of three dermal exposure sampling methods: rinses, wipes and cotton gloves

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Melanie Gorman Ng,[ab] Stan de Poot,[ac] Kaspar Schmid,[a] Hilary Cowie,[a] Sean Semple[ab] and Martie van Tongeren*[ab]

Several methods exist to estimate dermal exposure and it is unclear how comparable they are. These methods fall into three main categories: (i) removal techniques (such as wiping or rinsing); (ii) interception techniques (such as gloves, patches, or coveralls); and (iii) fluorescent tracer techniques. Controlled experiments were conducted to compare two removal methods for exposure to particulate, and a removal method with an interception method for exposure to liquids. Volunteers' hands were exposed to three liquid solutions (glycerol–water solutions of different concentrations) and three particulates (Epsom salts, calcium acetate and zinc oxide) in simulated exposure scenarios. Both hands were exposed and a different sampling method was used on each to allow comparison of methods. Cotton glove samplers and a cotton wipe sampling method were compared for exposure to liquids. For exposure to powders a cotton wipe sampling method was compared to rinsing the hands in deionised water. Wipe and rinse methods generally yielded similar results for Epsom salts and zinc oxide (geometric mean [GM] ratios of wipe-to-rinse measurements of 0.6 and 1.4, respectively) but they did not for calcium acetate (GM wipe-to-rinse ratio of 4.6). For glycerol solutions measurements from the glove samplers were consistently higher than wipe samples. At lower levels of exposure the relative difference between the two methods was greater than at higher levels. At a hand loading level of 24 000 μg cm^{-2} (as measured by wiping) the glove-to-wipe ratio was 1.4 and at a hand loading of 0.09 μg cm^{-2} the ratio was 42.0. Wipe and rinse methods may be directly comparable but the relationship between glove and wipe sampling methods appears to be complex. Further research is necessary to enable conversion of exposure measurements from one metric to another, so as to facilitate more reliable risk assessment.

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Environmental impact

Dermal exposure sampling methods are used in occupational and environmental settings to estimate exposure to hazardous materials through contact with the skin. These methods are not standardised and a variety of techniques exist making it difficult to compare measurements across studies, or to pool measurements. This study compared a skin wipe measurement method with a skin rinsing method and a glove dosimeter method in exposure simulations. The wipe and rinse methods yielded similar results and it may be possible to directly compare measurements taken with these methods. However, the relationship between glove and wipe sampling was more complex. Although measurements from wipes were consistently exceeded by those from gloves, the factor by which they were exceeded ranged from 1.3 to 52 depending on the exposure pathway and magnitude. Measurements from wipes and gloves cannot be directly compared, and it is not possible to use a simple conversion factor to enable comparison.

Introduction

Contact between hazardous substances and the skin can be a significant route of exposure. It can result in local dermal toxicity and can also lead to systemic health effects if the substance is absorbed by the skin. Over the past 30 years a number of pragmatic exposure assessment methods have been developed to estimate dermal exposure.[1] These measurements are required to estimate the amount of hazardous material that comes into contact with the skin and could lead to dermal health effects, and/or be absorbed systemically through the skin. Additional estimates are generally required to predict the amount of exposure that may ultimately be absorbed.[2,3] Dermal exposure assessment methods are not standardised and a variety of techniques exist. These fall into three main categories: (i) removal techniques (such as wiping or rinsing); (ii) interception techniques (such as gloves, patches, or coveralls); and (iii) direct in-situ methods such as fluorescent tracers. Due to the

[a]*Institute of Occupational Medicine, Research Avenue North, Edinburgh, EH14 4AP, UK. E-mail: Martie.vanTongeren@iom-world.org; Fax: +44 (0)131 449 8084; Tel: +44 (0)131 449 8084*

[b]*Environmental & Occupational Medicine, Division of Applied Health Sciences, University of Aberdeen, Aberdeen, AB25 2Z9, UK*

[c]*Radbout University Nijmegen Medical Centre, Nijmegen, 6525GA, Netherlands*

differences in the sample collection mechanisms, measurements taken with different methods are not directly comparable.[4,5] Removal methods capture only what is removable from the skin and do not collect material that has been absorbed through the stratum corneum or has been removed (for example, by evaporation or hand washing). Interception techniques aim to sample all material that comes into contact with the skin, including the portion that is absorbed. However, the absorptive capacity of materials used to intercept exposure can differ from that of skin so these may not necessarily reflect realistic dermal exposure levels. Fluorescent tracer techniques involve placing a fluorescent marker into source material, fluorescent imaging techniques are then used to determine the mass (and area) of the material on the skin. These methods rely on the retention of fluorescent tracers to the skin which may differ from retention of the substance of interest to the skin.[6] The variety of measurement methods that have been used make it difficult to pool together available measurement data for analysis. This could be an obstacle in the development of robust predictive exposure models that help exposure assessors to screen exposure scenarios and identify those which may require further investigation. Measurement data is needed for the development and validation of these models and the inability to use measurements taken with different methods would limit the amount of available data. Furthermore, due to the practicalities of sampling many studies use different methods for the hands and face than for the rest of the body[7–10] making direct comparison between body parts difficult and potentially leading to erroneous conclusions about the relative contribution of different body parts to overall exposure. The aim of this study was to conduct preliminary side-by-side comparisons of different dermal exposure assessment methods, typical of those used in occupational hygiene practice, to contribute to the development of conversion methods to enable comparison or pooling of measurements from different methods for risk assessment or exposure modelling.

Methods

To compare dermal sampling methods both the right and left hand were subjected to the same exposure procedure but exposure on each hand was measured using a different sampling method. It was possible to compare two sampling methods at a time. For exposure to liquids a removal method (wiping) was compared to an interception skin method (cotton gloves) and for exposure to powders two removal methods (wiping and rinsing) were compared. These methods were chosen because they have not previously been compared in a controlled laboratory setting. Comparisons were done alongside a study that investigated the effect of substance characteristics (specifically, viscosity and dustiness) on dermal transfer by each of three pathways: (1) deposition of airborne material onto the skin; (2) transfer by contact between the skin and contaminated surfaces; and (3) transfer to skin immersed in a material.[11] Dermal exposure to liquids of differing viscosity and powders of differing dustiness was simulated by each of these three pathways of exposure to assess the effect of dustiness and viscosity on dermal exposure. For ethical reasons, substances with the appropriate properties that are non-toxic by the dermal route of exposure were used rather than chemicals of occupational health concern. In each simulation, exposure was measured on both hands. The hand (dominant *vs.* non dominant) chosen for each sampling method was varied randomly for different volunteers and exposure scenarios. Four volunteers participated in the experiments. Each experiment was carried out by each volunteer once. Volunteers provided informed consent and ethical approval for the study was obtained from the University of Aberdeen College of Life Sciences and Medicine Ethics Review Board (Certificate number: CERB/2010/7/528). A risk assessment was carried out before the experiments began to ensure the safety of the volunteers.

Exposure simulation methodology

The exposure simulation methodology was described in detail by Gorman Ng *et al.* and is summarised here.[11]

The substances used in the experiments were chosen to meet the needs of the portion of the study that examined the effect of substance characteristics on dermal exposure. The particulates used in experiments were calcium acetate (hydrate 99%, Acros Organics, Belgium), zinc oxide (Zoco 112 USP grade, Combined Chemical Services Ltd, UK) and magnesium sulphate heptahydrate, commonly known as Epsom salts (Food & Bath Grade, The Essential Oil Company Ltd, UK). The liquids were glycerol solutions (molecular biology reagent grade, Sigma-Aldrich Company Ltd, UK) diluted with deionised water to create solutions of differing viscosity. Solutions of 20%, 50% and 87% glycerol were used.

To simulate exposure by immersion 25 mL beakers were filled with 20 mL of the test substance and the volunteers placed their index finger into the substance until the tip of the finger reached the bottom of the beaker. The finger remained in the beaker for 10 s and was then removed and exposure on the skin was measured. The procedure was conducted with both hands and a different sampling method used for each hand.

To simulate exposure by contact with contaminated surfaces, liquid and particulate were loaded onto steel, timber and fabric (polyester/cotton) surface samples measuring at least 14.5 × 26 cm. This was accomplished using particulate and liquid loading chambers described by Gorman Ng *et al.*[11] These were designed to achieve relatively uniform loading across each experimental trial. Surface loading was measured using gauze swabs (Topper 8 brand 5 × 5 cm) and Whatman glass microfiber filters (GE Healthcare UK Limited, Buckinghamshire, UK) as deposition coupons for liquids and particulate respectively. The loaded surfaces were placed onto a Salter Bathroom scale (HoMedics Group Ltd, Tonbridge, UK). Subjects pressed the palm and fingers of one hand to the surface with a force of about 50 N for 5 s. The hand was then removed and dermal exposure measured. Each trial was immediately repeated with the volunteer's other hand using a test surface of the same type freshly loaded with the same substance and dermal exposure was measured using a different measurement method.

Exposure by deposition was simulated using two 0.039 m^3 acrylic glass deposition chambers (one for dusts and one for mists). There were two holes fitted with nitrile cuffs on the front faces of both chambers through which the volunteer placed both

of his or her hands. Aerosol was generated in the chamber by dropping five grams of particulate through a tube from the top to the bottom of the chamber, creating a dust cloud when the particulate hit the bottom of the chamber. Liquids were introduced to the chamber by spraying 42 mg of glycerol solution into a small hole at the top back face of the chamber (opposite and above the hands). Airborne concentrations within the chambers were monitored using XAD-7 OVS tubes (Product 226-57, SKC Ltd. Dorset, UK) for glycerol and an IOM sampler with a pre-weighed Whatman 25 mm glass fibre filter for airborne particles.[12] Volunteers held both hands inside the chamber for 30 min and either dust or mist was introduced to the chamber at the beginning of the test and again every 5 min for a total of six introduction events. At the end of the 30 min exposure period the hands were removed from the chamber with the nitrile cuffs still attached to the wrist to avoid contact between the hands and the side of the chamber. Dermal exposure was measured using a different measurement method for each hand.

Dermal sampling methods

The wiping methodology was based on skin wipe methods described by Fenske *et al.*[13] The palm, fingers and back of the hand were wiped systematically with separate gauze wipes. In surface transfer and deposition trials the whole hand was wiped and in immersion experiments only the finger immersed into the test substance was wiped. When the whole hand was wiped, wipes for the palm, fingers and back of the hand were analysed as a single sample. Topper 8 brand 5 × 5 cm gauze (Systagenix Wound Management Ltd, Gargrave, UK) moistened with 0.5 mL of isopropyl alcohol was used to assess exposure to glycerol solutions and Premier 12 ply 7.5 × 7.5 cm gauze (Shermond Surgical Supply Ltd, Peacehaven, UK) moistened with 1.0 mL of deionised water was used for particulates. Samples were stored in either Sterilin® tubes (Sterilin Ltd, Newport, UK) (particulate) or amber glass jars (glycerol).

Hand rinse methods were based on methods described in a review of hand wash and skin wipe methodology by Brouwer *et al.*[14] Subjects placed their entire hand in a 19 × 19 cm sealable plastic bag (Empire Tapes PLC, Rotherham, UK) filled with 500 mL of deionised water and shook the hand for 30 s to dislodge material. The hand was then removed from the water and held above the opening of the bag to allow excess water on the hand to drip into the bag. The bag was then sealed and stored within a second sealable bag before analysis.

Cotton fourchette gloves (www.justgloves.co.uk product number VP0873) were used as an interception device. These were placed on the hands prior to exposure simulation and then removed at the end of each trial. They were pulled off from the cuff by a researcher wearing clean nitrile gloves and placed in glass jars where they were stored prior to chemical analysis.

Hand surface areas were estimated from hand traces and finger width measurements taken with a Toolzone Electronic Digital Caliper (KDP Tools Ltd., Devon, UK) using methods described by Gorman Ng *et al.*[11]

Pre-exposure hand wipes or hand rinses and blank glove samples were taken to capture background levels of exposure. Subjects thoroughly washed their hands and rinsed with deionised water before each background sample was taken. Hands were allowed to air dry to prevent contamination from towels and soap was not used in trials where glycerol was used.

Analytical methods

Calcium acetate, Epsom salts and zinc oxide were determined on wipes and in rinses as calcium, magnesium and zinc respectively using OSHA ID 121.[15] Wipes were digested in concentrated nitric acid for calcium acetate and Epsom salts samples, and in concentrated hydrochloric acid for zinc oxide samples. An aliquot of each sample was analysed by Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES).

Glycerol solutions were determined as glycerol on gloves and wipes and deposition coupons using the analytical measurement techniques described by NIOSH method 5523.[16] Samples were desorbed in methanol and an aliquot of each sample was analysed by gas chromatography with a flame ionisation detector (GC/FID).

The efficiency of the sampling methods for determining the substances was estimated and expressed as a percentage of recovered material. This was done for all test substances from all test matrices (hand wipe, hand rinse, glove) and was described by Gorman Ng *et al.*[11] The analytical methods for dermal sampling, limits of detection (LOD), and sampling efficiency are summarised in Table 1. All samples were analysed once.

Particulate collected on filters in the airborne particulate samples from the deposition trials and deposition coupons from the surface transfer trials was determined by gravimetric analysis on a Sartorius model KC BA100 balance. The XAD tubes used to measure airborne glycerol in deposition trials were capped following the experiment and stored in a refrigerator at 5 °C prior to chemical analysis by GC/FID.

Data processing and statistical analysis

All analytical results were corrected for the identified sampling efficiencies by multiplying each result by 100/SE where SE = the sampling efficiency. After correction for SE, the mass of glycerol determined was multiplied by 1.15, 2 or 5 to calculate the mass of 87%, 50% or 20% glycerol solution respectively. In all exposure scenarios the mass determined on the pre-exposure rinse or wipe or the blank glove sample was subtracted from the post-exposure rinse, wipe or glove. Observations in which the background measurement was equal to or greater than the post-exposure measurement resulting in an exposure estimate less than or equal to zero were coded as 0.01 μg cm^{-2} to enable log transformation if required. Mass per unit area exposure was estimated by dividing the mass of material determined on the hand or the finger by the surface area sampled.

Data from the different exposure pathway simulations were pooled and analysed using ANOVA with mass per unit area exposure as an outcome variable and sampling method, substance, and exposure pathway as explanatory variables. All models were blocked by subject to examine the effect of intra- and inter-subject variation. Interactions between explanatory variables were also examined.

Table 1 Analytical methods

	Substance	Epsom salts	Zinc oxide	Calcium acetate	Glycerol
Sampling method	Analysed as analytical method	Magnesium OSHA ID 121 ICP/AES[a]	Zinc OSHA ID 121 ICP/AES[a]	Calcium OSHA ID 121 ICP/AES[a]	Glycerol NIOSH 5523 GC/FID[b]
Glove	Limit of detection (mg)	—	—	—	0.60
	Sampling efficiency (%)	—	—	—	53[c], 63[d]
Wipe	Limit of detection (mg)	0.10	0.16	0.030	0.02
	Sampling efficiency (%)	53	85	70	68[c], 44[d]
Rinse	Limit of detection (mg)	0.010	0.010	0.010	—
	Sampling efficiency (%)	85	97	110	—

[a] Inductively coupled plasma/atomic emission spectrometry. [b] Gas chromatography/flame ionisation detection. [c] Samples > 50 mg. [d] Samples < 50 mg.

Separate analyses were carried out for liquids and particulates. For liquids the difference between glove and wipe sampling methods was examined; for powders the difference between wipe and rinse sampling methods was examined.

The distribution of the mass per unit area data for both liquids and particulate was examined with histograms and *Q*–*Q* plots. Data that appeared to be log-normally distributed were analysed on a natural log scale.

Results

All experimental trials were carried out indoors at room temperature (20–22 °C). The four volunteers ranged in age from 19–30 years; two were male and two were female.

Air concentrations and surface loadings

Average air concentrations within the deposition chambers in deposition simulations varied by substance type and are reported in Table 2. Among the powders the air concentration was highest for the dustiest powder, calcium acetate. Air concentration decreased with increasing glycerol concentration (and hence increasing viscosity) among the liquids. These findings were discussed by Gorman Ng *et al.*[11] Average surface loadings in surface transfer simulation varied less with substance type and are also reported in Table 2.

Table 2 Average air concentrations in the deposition chambers during deposition experiments and average surface loadings for surface transfer experiments

	Air concentration (mg m^{-3})			Surface loading (μg cm^{-2})		
	N	AM[a]	SD[a]	*N*[b]	AM[a]	SD[a]
Powders						
Calcium acetate	4	44	14	12	90	52
Epsom salts	4	0.90	0.90	12	140	97
Zinc oxide	4	0.60	0.40	12	110	35
Liquids						
20% glycerol	4	67	8.4	3	86	18
50% glycerol	4	34	14	3	130	20
87% glycerol	4	18	18	3	130	20

[a] AM = arithmetic mean, SD = standard deviation. Arithmetic means and standard deviations are reported because the data for liquids approximated a normal distribution, and the data for solids more closely approximated a normal distribution than a lognormal distribution. [b] Note that in experiments of surface loading of powders surface loading was measured using deposition coupons placed alongside each surface. This was not possible for surface loading of liquids so test surfaces were used to estimate the surface loading. This is the reason for the difference in number of observations.

Comparison of sampling methods

The differences between sampling methods were assessed in analysis of data pooled from the different exposure pathways. Forty-three of the seventy-two samples (60%) collected during the surface transfer experiments using the glycerol solutions were below the analytical LODs (78% of glove samples, and 42% of wipe samples). Due to the larger bulk of the glove samples relative to wipes a larger volume of solvent was required to extract glycerol from these samples and LODs were about 30 times higher than for wipes. Sixty-seven percent of the dermal exposure measurements taken following deposition of powders were below the analytical LODs. For zinc oxide and Epsom salts only one out of eight samples was detectable. Due to the large percentage of non-detect samples from the surface transfer of liquids and deposition of powders simulations, data from these experiments were excluded from analyses. All values for immersion of both particulates and liquids, and for surface contact with particulates were above LODs and greater than zero following background correction. All values for deposition of liquids were above LODs; to enable log transformation substitution with 0.01 μg cm^{-2} was required for five samples (21%) that were less than zero after background correction.

Comparison of rinse and wipe methods

Rinse and wipe methods for measuring exposure to powders were compared using ANOVA (Table 3). There was a statistically significant difference between measurements from rinse and wipe sampling methods but there was also a significant interaction between the effect of the substance and the sampling method on measured exposure. This suggests that the difference between the two sampling methods varied by substance. For both zinc oxide and calcium acetate measured exposures were higher in wipes than rinses (on average 4.6 times higher

Table 3 Comparison of wipe and rinse sampling methods ($N = 94$). Mass per unit area (μg cm^{-2}) by exposure pathway, sampling method and powder[a]

Exposure pathway		Surface contact			Immersion		
Particulate		CA	ES	ZO	CA	ES	ZO
Wipe	*N*	12	12	12	4	4	4
	GM	30	23	16	400	100	300
	GSD	2.9	3.5	2.7	1.4	3.1	3.3
Rinse	*N*	12	12	12	3	3	4
	GM	6.5	36	12	110	110	210
	GSD	5.9	4.4	2.3	6.8	10.5	2.6
Wipe to rinse ratio		4.6	0.6	1.4	3.6	0.9	1.4
P-values (ANOVA)	Sampling method						0.022
	Substance						0.302
	Exposure pathway						<0.001
	Interaction exposure pathway and substance						0.053
	Interaction substance and sampling method						0.005

[a] CA = calcium acetate; ES = Epsom salts; ZO = zinc oxide GM = geometric mean; GSD = geometric standard deviation.

Table 4 Comparison of glove and wipe sampling methods ($N = 48$). Mass per unit area (μg cm^{-2}) by exposure pathway, sampling method and glycerol solution[a]

Exposure pathway		Immersion			Deposition		
Glycerol Solution		20%	50%	87%	20%	50%	87%
Glove	*N*	4	4	4	4	4	4
	GM	28 000	39 000	32 000	15	6.3	3.8
	GSD	2.5	2.5	1.7	1.5	1.2	1.6
Wipe	*N*	4	4	4	4	4	4
	GM	2700	7400	24 000	0.34	0.12	0.09
	GSD	1.9	1.2	1.5	11	5.7	4.7
Glove to wipe ratio		10	5.3	1.3	44	53	42
P-values (ANOVA)	Sampling method						<0.001
	Substance						0.919
	Exposure pathway						<0.001
	Interaction exposure pathway and substance						0.007
	Interaction exposure pathway and sampling method						<0.001

[a] GM = geometric mean; GSD = geometric standard deviation.

for calcium acetate and 1.4 times higher for zinc oxide). For Epsom salts rinse samples were 1.6 times higher than wipe samples. There was a significant difference between exposure by the different pathways, this finding was discussed by Gorman Ng *et al.*[11]

Surface transfer was simulated using three different surface types. Differences in exposure related to surface type in this dataset were discussed by Gorman Ng *et al.*[11] To investigate whether surface type has any effect on measurements by different sampling methods an additional ANOVA was carried out, restricted to data from the simulations of surface transfer of powders. In this analysis surface type and sampling method were both significantly related to the measured mass per unit area exposure but there was no significant interaction between the two, indicating that the effect of sampling method on measurement value does not vary with surface type. Measurements from different surface types are therefore combined in Table 3.

Comparison of glove and wipe methods

Results of the comparison of glove and wipe methods are presented in Table 4. In both the deposition and immersion experiments the mass per unit area of glycerol solution measured on glove samples was significantly higher than the mass per unit area measured on wipe samples. The difference between measurements from wipe and glove sampling methods was greatest for the deposition pathway, and this is indicated by a significant interaction between exposure pathway and sampling method. The exposures measured on the hand were also much lower for deposition suggesting that the difference between glove and wipe sampling may decrease with increasing mass per unit area exposure. The interaction between substance and sampling method was not significant and was excluded from the final model. The relationship between substance, exposure pathway and measured exposure was discussed by Gorman Ng *et al.*[11]

Discussion

Use of controlled laboratory exposure simulations allowed direct comparison of dermal sampling methods, but it is important to note that these preliminary results may not be directly applicable to measurements taken in the field where conditions are less controlled. The experimental measurements were taken very shortly after exposure but in the field the duration between exposure and measurement could be much longer and this may affect the retention of materials on glove dosimeters and the dislodgeability of materials in removal sampling methods.

The experiments involved side-by-side comparisons of different sampling methods used on the right and left hands and assumed that exposures on these two hands would be equivalent. While there are may be differences in size, muscularity and skin thickness between the dominant and non-dominant hand these were largely accounted for by varying the use of the dominant and non-dominant hand randomly across volunteers and scenarios and by adjusting exposure measurements by hand surface area measurements taken for each hand. There may be differences in dermal absorptive rate and capacity across the two hands but this is unlikely to have affected the conclusions of the study. The exposure durations were too short to allow significant absorption and the powders used in the study are not readily absorbed by the skin. Glycerol can be

absorbed by the skin but in this case a removal method was compared to an interception method (which does not involve contact between the substances and the skin) so differing rates of absorption across the two hands would not affect the results.

The large number of results below the LODs reduced the amount of data available for analysis. Additional experimental work at higher levels of exposure could provide information about the differences between sampling methods for surface transfer of liquids and deposition of powders. This may be important as the differences in the glove-to-wipe ratio between the immersion and deposition pathways provided evidence that the effect of sampling methods on exposure can vary by the exposure pathway. Despite this limitation the laboratory experiments provided useful, preliminary information about the effect of dermal sampling methods on exposure estimates.

In all experiments, much higher masses of glycerol solution were determined on glove samples than on wipes. The absorption of glycerol by the gloves probably contributed to the differences between the two sampling methods. Glycerol can be absorbed into the stratum corneum and wipe samples will fail to determine glycerol that has been absorbed and will underestimate exposure, however the exposure durations ($\leq$30 min) were probably too short for this have contributed significantly to the differences between gloves and wipes.[17] Additionally, cotton gloves rapidly absorb liquids and may overestimate exposure. Experiments conducted by Brouwer suggest that cotton gloves may also overestimate exposure to powders.[18] The difference between glove and wipe measurements were lower for the deposition pathway than for the immersion pathway and this may have been related to the lower exposure in deposition scenarios. Again this may have been due to absorption of liquid by the gloves. As the gloves and skin were saturated with glycerol in immersion experiments there may have been less scope for overestimation by the gloves. Additionally, the exposure duration in the deposition simulations (the lowest exposure scenario) was 30 min which was much longer than the 10 s exposure duration in the immersion simulation. This longer exposure duration may have provided a greater opportunity for absorption of glycerol into the stratum corneum and could have contributed to the large difference between wipe and glove samples during the deposition experiments. However, the 30 min exposure duration is too short to allow sufficient dermal absorption to fully explain the difference. Differences between the absorption rates and carrying capacity of sampling media and the skin probably contribute significantly to the differences between interception and removal methods for all substances. These results suggest that it may not be possible to use a simple multiplier to make glove and wipe measurements directly comparable as their differences may depend on the amount and duration of exposure.

The effect of exposure level and duration on the relative performance of different sampling methods is supported by other studies. Davis *et al.* compared a cotton glove sampling method with ethanol hand rinses in field measurements of dermal exposure to azinphosmethyl during apple thinning at 1, 2, 6 and 9 days after pesticide application.[19] In general the measurements were higher for gloves than for rinses. Between day 2 and day 9 the estimated exposures decreased by nearly half due to pesticide decay. The ratio of glove measurement to rinse measurement was 4.7 on day 2 and was 5.5 on day 9; the authors did not determine whether or not this difference in ratios was statistically significant.

Fenske *et al.* also compared cotton glove and alcohol rinse sampling among orchard workers. They measured dermal exposure to captan among 4 fruit pickers in a side-by-side comparison in which one hand was sampled with a cotton glove sampler and the other with a rinse.[20] They also assessed the effect of sampling time on measured exposure and measured exposure at intervals of 0.5, 1.0, 1.5 and 3.0 h of picking. Again the measurements from gloves were consistently higher than rinse measurements. They also found that exposure duration had an effect on the measured exposure rate from glove samples. The rate of exposure measured by gloves at 0.5 h (43.6 mg h^{-1}) was double the rate measured at 3.0 h (21.0 mg h^{-1}). The authors attributed this difference to a reduction in absorptive capacity after initial absorption due to collection of moisture, soil and/or sweat, and captan residues on the gloves. In further analysis of the data they also found that amongst workers with a high picking rate (and therefore high exposure) the effect of sampling time on measured exposure was especially pronounced. The difference between measurements from gloves and rinses was significant at 0.5 h (glove to rinse ratio of 2.4) and decreased with increasing exposure duration and consequent higher cumulative exposure (ratio of 1.4 at 3.0 h).

In the current study, results from rinse and wipe samples were also compared in side-by-side experiments of exposure to three powders. For both zinc oxide and calcium acetate measurements were higher on wipe samples than rinse samples (about 4 times higher for calcium acetate and about 1.3 times higher for zinc oxide). Epsom salts rinse samples were 1.6 times higher than wipe samples. It is not surprising that wipes yielded slightly higher measurements than rinses for zinc oxide as it is insoluble in water. However, calcium acetate is very soluble in water so it is unexpected that wipe samples were higher in this case. Analysis of background samples indicated that background levels of calcium were higher than those of magnesium or zinc. However, this was adjusted for so it cannot fully explain the finding. Both wipe and rinse samples were stored in plastic containers prior to analysis. Wipes were stored in Sterilin® tubes and rinse samples were stored in sealable plastic bags. Although the tubes were rinsed with solvent prior to sample analysis and bags were agitated to evenly distribute solute, losses due to adsorption onto the walls of the storage vessels may have differed between the tubes and bags. This was not investigated in the current study but may provide further information on differences between sampling methods if studied in future work.

Epsom salts were granular particles while zinc oxide and calcium acetate were fine powders. The researchers who carried out the experiments observed that it was difficult to pick up large particles on the skin with wipes. This may explain the lower values measured by wipes relative to rinses for Epsom salts. In real-life scenarios such large particles are unlikely to

remain on the skin so the relatively poor performance of wipe sampling for measuring these materials is probably not a concern for exposure assessors. In general, these results suggest that for exposure to powders wipe sampling measurements produce data broadly comparable to those generated by rinse sampling techniques. No previously published studies have compared wipe and rinse sampling methods for exposure to particulate. Fenske *et al.*[13] compared a wipe and rinse method in field measurements of exposure to the pesticide azinphos-methyl amongst orchard workers and found that rinse measurements were about 6 times higher than wipe measurements.[13] The difference between the findings of the current study and the Fenske *et al.* study may be due to the substance characteristics, differences in the sampling methods used, or differences between field and laboratory experiments.

Conclusions

This preliminary study was carried out to investigate the possibility of developing conversion methods for dermal exposure methods so that measurements taken with different methods can be converted to a common scale for risk assessment and exposure modelling. The results showed that while the measurements of dermal exposure to powders from two removal methods were generally similar to one another, the relationship between a removal (wipe) and interception (glove) method for measurement of dermal exposure to liquids was complex and varied with the level of exposure. More work is required before exposure measurements gathered using removal and interception methods can be directly compared, or before data from different methods can be pooled together for the development of dermal exposure models.

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