



Operator dermal exposure and individual protection provided by personal protective equipment during application using a backpack sprayer in vineyards

Isabelle Thouvenin¹ · Françoise Bouneb² · Thierry Mercier²

Received: 2 June 2016 / Accepted: 17 August 2016 / Published online: 30 August 2016
© Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (BVL) 2016

Abstract According to Regulation (EC) No 1107/2009, the safety of the operator concerning plant protection products (PPP) must be evaluated. The levels of operator exposure with use of certified personal protective equipment can be estimated using a model or experimental exposure data. However, the existing models have shortcomings, especially the lack of operator exposure data during upward applications using a backpack sprayer. The aim of this study was to monitor the dermal exposure of operators using backpack motorised mist-blower power sprayers for application of fungicides in vineyards. The measured actual dermal exposure levels ranged from 49.3 mg/kg a.s. (active substance) applied (75th percentile) to 89.2 mg/kg a.s. applied (95th percentile), and were lower than those estimated with the European Food Safety Authority model (5–2 %, respectively). The transfer factors provided by the personal protective equipment (coverall and gloves) were low, 1.7 and 2.4 % (75th percentile) and 5.1 and 8.6 % (95th percentile) respectively.

Keywords Backpack sprayer · Pesticide · Personal protective equipment · Operator · Vineyard

1 Introduction

In accordance with the risk assessment required in the framework of Regulation (EC) No. 1107/2009, operator exposure must be estimated. Within the EU regulatory framework, plant protection products must be evaluated according to Regulation (EC) No. 1107/2009 prior to being authorised. No authorisation may be granted if the extent of operator exposure exceeds the acceptable operator exposure level (AOEL). The exposure to plant protection products is estimated by taking into account the material and the conditions of use, with or without personal protective equipment. When a vineyard site does not allow access to a vehicle (e.g., when the slope is steep), only hand-held application is possible. This means that for pesticide application, operators walk through vineyards with a backpack sprayer to apply the product to each vine stock. Even though operator exposure can be assessed for this scenario using the current EU harmonised predictive model (EFSA, 2014), all the data included in the calculation of operator exposure during hand-held application were generated for a lance connected to a large tank on other crops. Therefore, further exposure data were considered as necessary (Großkopf et al. 2013).

The study was performed in order to measure actual levels of operator exposure and to check the protection afforded under field conditions by personal protective equipment (PPE), regulated in Europe under Council Directive 89/686/EEC, and recommended in France during this type of foliar application.

In parallel to this experimental operator exposure study, the performance of the PPE according to ISO

✉ Thierry Mercier
thierry.mercier@anses.fr

¹ HumExpo SAS, 576 avenue de Grasse,
83300 Draguignan, France

² Regulated Products Assessment Department, French
agency for food, environmental and occupational
health safety, Maisons-Alfort, France

6529 was tested using currently recognised laboratory tests. Finally, the exposure levels measured during the experimental exposure study were compared to those calculated using the EFSA calculator.

2 Materials and methods

2.1 Operator exposure study

The study is based on the whole-body dosimetry method documented in the Organisation for Economic Cooperation and Development (OECD 1997). It was conducted in compliance with Regulation (EC) No 1107/2009, Guidance Documents on Residue Analysis SANCO/3029/99 rev.4 (2000), Good Laboratory Practices (GLP) Guidelines (OECD Series No. 1, 6 and 13), Directive 2004/10/EC, and Article D.523-8 and Appendix II of the French Environment Code (2007).

2.1.1 Personal protective equipment

One of the objectives in this study was to check the actual protection level of Category III Type 4-5-6 coveralls. The coverall used in this study was a Tyvek® Classic Plus, Model CHA5a, (DuPont®). Protective nitrile gloves (Ansell Sol-Vex®, 37-675; length 330 mm, Ansell Healthcare) complying with the EN 374-3 Standard were also supplied to the operators. The glove cuffs were pulled over the coverall cuffs. All operators wore a half-mask respirator (covering the mouth and nose) with cartridges against organic vapors. Some operators also wore protective goggles and/or earplugs or defenders.

2.1.2 Study sites

The study took place in France and included one team working for a vine growing farm (4 people) and one contractor company (2 teams of 3 people each), accounting for a total of 10 operators, close to the Rhône River in the south-eastern French départements of Ardèche and Drôme. In July, the vineyards had reached their maximum foliage development and the path between the rows was sometimes narrow.

2.1.3 Application equipment

The major types of motorised mist-blower power sprayers were represented in the study. Their capacity ranged from 12 to 15 L. The equipment of the first monitored team had been rinsed by the team of the

previous day (especially the outside) and the operators rinsed the inside of the tank after application. The equipment of the second team could not be rinsed before the monitoring day and was not rinsed at the end of the working day. The third team used the same sprayers as the second team, without preliminary rinsing.

2.1.4 Plant protection product and reference substance used as a tracer

The fungicide Selva® containing a nominal content of 30 g cymoxanil per litre was used as a representative product. The formulation was packed in 10 L containers which were obtained from local distributors.

2.1.5 Sampling method

To assess actual body exposure, an inner layer of clothing consisting of a full-length cotton undergarment (100 % white cotton long-sleeved T-shirt and long johns; Gebr.Oelkuch GbR) was worn below the protective coverall as described above. This full-length undergarment mimicking the skin was pre-washed once at 95 °C with soap. Operators were encouraged to wear the protective coverall-hood over their head, as 4 operators did. The others were offered a piece of cotton (same fabric as the undergarment) to wear like a bandana. Finally, data on head exposure could be collected for all operators either based on the coverall hood or on the bandana.

Several body parts were considered for analysis of each clothing layer: sectioning was performed to obtain 3 parts (from the coverall or undergarment; arms, legs and torso), plus the coverall hood when worn over the head. When the coverall hood was not worn over the head, it was not separated from the coverall torso at specimen preparation.

Dermal exposure of hands was also measured using the hand wash procedure (0.01 % dioctyl sulfosuccinate sodium solution). No measurements of inhalation exposure were conducted.

2.1.6 Storage and shipping of specimens

Each specimen was packed in aluminium foil or in a small HDPE bottle and then placed in a labelled plastic bag. The sectioned clothes, bandana (if applied), gloves and hand wash specimens were placed in temporary frozen storage as soon as possible for shipment to the analytical facility. Specimens were maintained in frozen storage until analysis.

2.1.7 Operators

Ten male farm employees or contractors were selected and monitored over a full working day. Details on operators and on the tasks they conducted are shown in Table 1.

2.1.8 Monitored tasks

The main task was application of the spray mixture contained in the 12–15 L tank of the backpack sprayer (Fig. 1). The time to apply this volume was short (usually no more than 15–20 min) and loading was performed frequently. Loading of the sprayer tank was done from a large tank or from an intermediate container, either by the operator himself, by another operator (already filling his own sprayer tank) or by another person (e.g., the mixer/loader in the third team) (Fig. 2). The spray mixture was prepared before the start of application in a large tank by an operator who spent most of his time during application moving the tank containing the mixture to follow the applicators as closely as possible. Exposure was not monitored during spray mixture preparation. Operators 4 (1st team) and 5 (2nd team) prepared the mixture and were also applicators. Operator 4 wore dedicated protective gloves and a Category III Type 4 coverall during mixture preparation carried out at the farm; this PPE was not collected. He was provided new PPE for field work (tank loading and application) which was collected. Operator 5 wore the same protective equipment (gloves and coverall) during mixing/loading and application because mixing/loading was done in the vineyard. In the 3rd team, the mixer/loader did not apply and his exposure was

not monitored at all during this working day. After one mix/load of 300–450 L was prepared in a high-capacity tank either at the farm (teams 1 and 3) or in the field (team 2), three to ten backpack tank loads were prepared for each operator. The application parameters (arithmetic mean, minimum and maximum) are presented in Table 2.

2.1.9 Weather conditions

The weather conditions were registered at approximately 1–2 h interval. The air temperature ranged from 21.1 to 27.8 °C and the relative humidity ranged from 23 to 50 % over all field sites. Even in the absence of wind, operators walked through the spray mist due to their own forward movement while the mist was still in the air.

2.1.10 Analytical methods and validation study

All specimens were analysed using the Eurofins Agroscience Services Chem SAS methods successfully validated during the operator exposure study. Depending on the type of matrix, extraction was done using ultra-pure water and acetone and/or acetonitrile/formic acid. Finally, cymoxanil residues present in the extracts were quantified by LC-MS/MS. The LOQs were 10 µg/1000 cm² coverall, 0.25 µg/1000 cm² undergarment, 0.5 µg/L hand wash, and 10 µg/pair of gloves.

2.1.11 Field fortifications

In order to assess the stability of the test substance under field, storage and transit conditions, field

Table 1 Operator details

Operator number	Date of trial	Age (years)	Height (cm)	Weight (kg)	Experience (years)	Tasks
1	09/07/2014	55	167	65	38	Sprayer tank loading; application; tank rinsing
2		37	180	87	1	Sprayer tank loading; application; tank rinsing
3		24	186	64	2	Sprayer tank loading; application; tank rinsing
4		31	185	94	6	Mixing in a big tank (with another pair of gloves and another protective coverall); sprayer tank loading; application
5	15/07/2014	29	184	82	6	Mixing in a big tank; sprayer tank loading; application
6		37	169	62	0.2	Sprayer tank loading; application
7		22	168	68	2	Sprayer tank loading; application
8	16/07/2014	38	183	120	20	Application
9		35	180	73	10	Application
10		27	170	77	5	Sprayer tank loading; application
Arithmetic mean		34	177	79	9	

Fig. 1 Application and rinsing

fortifications were performed close to the trial site (but out of the farm) where three or four operators were monitored on each day of the field study. Spiking levels carried out in triplicate corresponded to LOQ and $500 \times$ LOQ levels on each matrix. Blank specimens were also prepared.

2.1.12 Calculation methods of exposure and transfer factors

Quantitative determination of residues was carried out by external standardisation. A linear calibration curve was calculated using the method of least squares. The determination coefficient R^2 was ≥ 0.990 . Residues of cymoxanil were expressed in $\mu\text{g}/\text{specimen}$. No residue levels were measured below the LOQ.

The residue levels measured in/on operator's specimens were corrected by the mean recoveries obtained for the respective mean field spiked specimens if the mean recoveries were lower than 95 %. Transfer factors (TF) via clothing and protective

equipment were calculated according to the following formulae:

$$\text{TF coverall (\%)} = \frac{(\text{residues undergarment } (\mu\text{g}))}{(\text{residues undergarment } (\mu\text{g}) + \text{residues coverall } (\mu\text{g}))}$$

$$\text{TF gloves (\%)} = \frac{(\text{residues hand washes } (\mu\text{g}))}{(\text{residues gloves } (\mu\text{g}) + \text{residues hand washes } (\mu\text{g}))}$$

2.2 Laboratory permeation tests

2.2.1 Test methods for permeation

The cumulative mass of the test chemical that permeated the Tyvek® Classic Plus, Model CHA5a, coverall Category III Type 4-5-6 was measured using the ISO 6529:2001 (2001) test method. Samples were collected after 30 and 240 min. The tests on the materials were performed using undiluted (30 g/L) and diluted (0.24 g/L) Selva®. The mean and standard deviation of the cumulative permeation mass per

Fig. 2 Loading of the tank of the backpack sprayer



Table 2 Application parameters in the experimental study

	Arithmetic mean (minimum–maximum)
Estimated treated surface area per team	3 ha 1.5 ha (team 1), 2.8 ha (team 2) and 3.8 ha (team 3)
Rate of application of a.s. per team	66 g/ha (51.2–90)
Volume of spray applied per surface	96 L/ha (51.2–150)
Concentration of a.s. in the spray	0.756 g/L (0.6–1.0)
Volume of spray applied per operator	66 L (32–91)
Amount of a.s. applied per operator	49.2 g (19.2–74.5)
Duration of spraying	78 min (43–104)
Duration of working day ^a	165 min (114–206)

^a The total duration of a working day included the loading of the backpack sprayer tank when empty, short breaks and journeys

surface ($\mu\text{g}/\text{cm}^2$) of 3 replicates is presented. The tests were carried out to identify the resistance of protective clothing material to permeation.

2.2.2 Analytical method used for permeation test

The active substance was quantified by LC-MS/MS (Agilent[®]) using a Zorbax Eclipse Plus C18 RRHD column. The MS conditions were as follows: 340 °C gas temperature, 13 L/min gas flow, and a 25-psi nebuliser. The eluents consisted of a mixture of methanol, ammonium formate, and formic acid; a mixture of water, ammonium formate, and formic acid; and methanol or water of quality 1 (NF EN ISO 3696).

2.3 Estimated operator exposure with the EFSA model

Operator exposure was calculated with the EFSA calculator available on the EFSA website (<http://www.efsa.europa.eu/fr/efsajournal/pub/3874>) in October 2015. The parameters selected in the EFSA calculator

Table 3 Parameters used in the EFSA calculator

	Parameters used in EFSA calculator
Crop type	Grapes
Formulation type	SC
Maximum application rate of active substance	0.0492 kg a.s./ha ^a
Application	Outdoor
Application method	Upward spraying
Application equipment	Manual-knapsack
Season	Late (dense foliage)

^a The EFSA model is based on the total amount of active substance applied by operator per day as the driver for exposure. Therefore, the EFSA calculator was run with the amount of active substance applied in the study (mean: 49.2 g). As the area assumed in the calculator is 1 ha for this scenario, an application rate of 0.0492 kg/ha was used

to estimate exposure during application shows Table 3.

3 Results

3.1 Operator exposure study

3.1.1 Analytical results: field recoveries

The stability of cymoxanil residues in the various matrices under the field, storage and transit conditions of the study was confirmed. The mean recovery of field fortification specimens was in the range of 93–104 % and the relative standard deviation was below 20 % at each fortification level for all matrices.

3.1.2 Analytical results: operator specimens

Individual residue levels are presented as $\mu\text{g}/\text{day}$ in Table 4. Detailed contributions of potential and actual dermal exposure (arithmetic mean) in $\mu\text{g}/\text{day}$ of each body part are presented in Figs. 3 and 4. Individual transfer factors through the coverall and the gloves are presented in Table 5. The statistical endpoints for potential dermal exposure and actual dermal exposure in mg/kg a.s. applied are illustrated in Table 6.

3.1.3 Body exposure

Operator 10 was the most exposed person via the coverall and the undergarment, particularly on the legs but also on the torso and to a lesser extent on the arms. On his undergarment, the torso was more

exposed than the legs and exposure on the arms was two orders of magnitude lower than on the other body parts. The residue level measured on operator 9's coverall torso was very low and was excluded as an outlier value considering the residue level itself on the basis of the observations (including photos) recorded on the coverall torso and on the undergarment torso of operator 9. Inversion of the coverall torso specimen with the hood specimen was likely for this operator. As a result, the residue levels on the coverall torso and hood of operator 9 were not considered in further calculations. The least exposed Tyvek® Classic Plus coverall under the conditions of this study received almost 33 mg of cymoxanil when the amount applied was approximately 50 g per operator, which represented a high contamination ratio. Below the protective coverall, the second clothing layer was sometimes highly exposed. Transfer through the coverall was mainly through the torso. Transfer was calculated via the Tyvek® Classic Plus coverall. Transfer through the coverall was 1.7 % (75th percentile) and 5.1 % (95th percentile), with the torso being less protected (14 % transfer) than the legs (0.29 % transfer) or arms (0.46 % transfer) considering the 75th percentiles.

3.1.4 Head exposure

The highest exposure levels on the head were measured for operators who were wearing the coverall hood. A bandana does not cover the neck and the circumference of the face whereas a coverall hood does. Head exposure represented 5.6 % of potential dermal exposure (based on $\mu\text{g}/\text{day}$, arithmetic means). Face exposure was not measured because the exposed surface was small due to the half mask respirator all operators were wearing.

3.1.5 Hand exposure

The residue levels measured on gloves ranged from 1053 to 7733 $\mu\text{g}/\text{day}$. During breaks, the gloves were put on the pickup platform where the sprayers are stored during the journeys. Overall, the gloves worn during the various phases collected 8.4 % of potential dermal exposure (based on $\mu\text{g}/\text{day}$, arithmetic means).

The highest residue level on hands was measured for operator 10 who did not fully comply with instructions: he was observed to start rinsing his hands using a bottle before the field monitor could collect the hand wash specimen. The operator had nevertheless been informed at the start of

Table 4 Individual residue results for operators (µg/day)

Operator No.	Active substance (µg/day) corrected for field recoveries when required [§]									
	1	2	3	4	5	6	7	8	9	10
Amount active substance applied (kg)	0.0486	0.0282	0.0390	0.0192	0.0440	0.0580	0.0603	0.0745	0.0460	0.0740
Coverall										
Arms	3741	7669	6900	6228	7710	7997	6945	6020	3080	9240
Legs	24,208	34,345	29,185	29,073	29,775	39,813	25,268	27,420	26,401	43,425
Torso	4304	9172	5827	8300	3875	2340	1811	7471	335 [#]	26,265
Hood [§]	–	–	–	–	9799	4339	9035	–	13,268 [#]	–
Bandana	667	743	635	773	–	–	–	599	–	596
Total coverall + bandana	32,920	51,929	42,547	44,374	51,159	54,488	43,058	41,511	29,481 [#]	79,525
Undergarment										
Arms	10.4	94.8	19.3	1.67	40.6	5.37	16.2	15.7	20.3	11.0
Legs	6.69	101	77.9	12.5	29.4	79.1	35.3	40.0	86.6	1153
Torso	103	1482	40.6	65.1	330	204	336	664	4410	4217
Potential dermal exposure excluding hands ^a	33,040	53,608	42,685	44,453	51,559	54,777	43,446	42,230	– [#]	84,906
Gloves	4973	3444	4579	6794	5506	7733	6372	2679	1053	2326
Hand washes (actual hand exposure)	4.70	60.9	5.10	6.40	130	183	147	67.8	54.1	308
Potential hand exposure ^b	4978	3505	4584	6800	5636	7916	6519	2747	1107	2634
Potential dermal exposure ^c	38,018	57,112	47,269	51,253	57,195	62,692	49,965	44,977	– [#]	87,540
Actual dermal exposure excluding hands ^d	120	1679	138	79.3	400	288	387	719	4517	5381
Actual dermal exposure ^e	125	1740	143	85.7	530	471	534	787	4571	5689

The figures were rounded to three significant digits but the calculation of the following types of exposure was done using the figures from the analytical phase report which may explain some differences in the sums

[§] Corrected for field recoveries when required

[§] Hood collected with the coverall torso when not worn over the head; – not worn

[#] The residue level measured on the coverall torso of operator 9 is unlikely (based on field observations and on the residue level measured on the undergarment torso). As an inversion was suspected with the coverall hood but could not be confirmed, both residue levels were excluded from further calculations

^a Potential dermal exposure excluding hands = total coverall (including hood) + bandana, if any + undergarment

^b Potential hand exposure = gloves + hand washes

^c Potential dermal exposure = potential dermal exposure excluding hands + potential hand exposure

^d Actual dermal exposure excluding hands = undergarment

^e Actual dermal exposure = undergarment + hand washes (actual hand exposure)

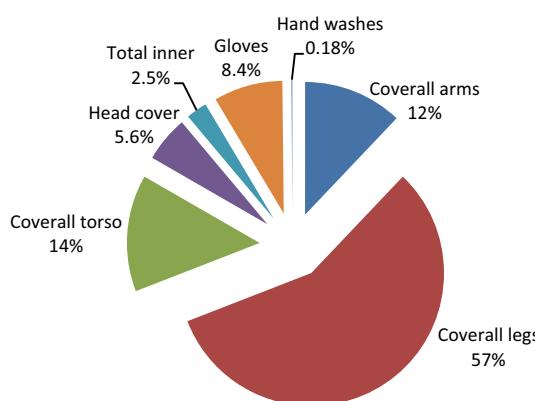


Fig. 3 Mean contribution of each body part to the potential dermal contamination of backpack sprayer operators

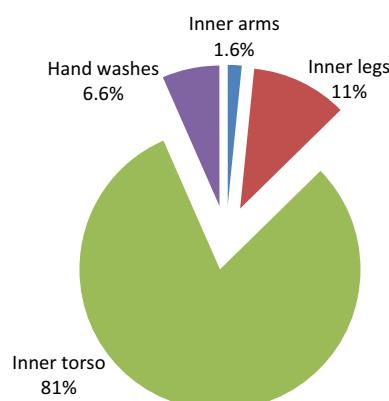


Fig. 4 Mean contribution of each body part to the actual dermal contamination of backpack sprayer operators

Table 5 Transfer factors via coverall and gloves

Operator No.	Transfer factors (%)									
	1	2	3	4	5	6	7	8	9	10
Coverall										
Arms ^a	0.28	1.2	0.28	0.027	0.52	0.067	0.23	0.26	0.66	0.12
Legs ^a	0.028	0.29	0.27	0.043	0.099	0.20	0.14	0.15	0.33	2.6
Torso ^a	2.3	14	0.69	0.78	7.8	8.0	16	8.2	#	14
Total ^b	0.37	3.2	0.33	0.18	0.96	0.57	1.1	1.7	#	6.4
Gloves ^c	0.094	1.7	0.11	0.094	2.3	2.3	2.3	2.5	4.9	12

The residue level measured on the coverall torso of operator 9 is unlikely (based on field observations and on the residue level measured on the undergarment torso). As an inversion was suspected with the coverall hood but could not be confirmed, both residue levels were excluded from further calculations. No transfer factor was calculated through the torso or through the total coverall for operator 9

^a Residue undergarment (arms or legs or torso)/[residue undergarment (arms or legs or torso) + residue coverall (arms or legs or torso)]

^b Residue undergarment/[residue undergarment + residue coverall]

^c Hand washes/[residue gloves + residue hand washes]

Table 6 Summary of operator exposure statistics (mg/kg a.s. applied)

	Potential dermal	Actual dermal
Arithmetic mean	1298	28.8
Geometric mean	1175	13.4
Minimum	604	2.56
50th percentile	1183	9.71
75th percentile	1300	49.3
95th percentile	2412	89.2
Maximum	2669	99.4

monitoring that hand washes would be collected. Overall hand exposure represented 6.6 % of actual dermal exposure (based on $\mu\text{g}/\text{day}$, arithmetic means).

Transfer through gloves was 2.4 % (75th percentile) and 8.6 % (95th percentile). This transfer was higher than 10 % for operator 10 only. Indirect contamination could have happened when this operator was standing bare handed during breaks or during journeys, or at the end of the monitoring period.

3.2 Laboratory permeation tests

Cumulative permeation through the material for the Tyvek® Classic Plus, Model CHA5a, coverall Category III Type 4-5-6 according to Directive 89/686/EEC by undiluted and diluted Selva® shows Table 7. Significant cumulative permeation was observed after 240 min for the undiluted product. No significant permeation was measured under other conditions.

3.3 Comparison of exposure between our experimental vineyard exposure study and estimated exposure using the EFSA model

Table 8 shows a comparison of potential and actual dermal exposures (75th percentile and 95th percentile based on data in mg/kg active substance handled) between the experimental vineyard exposure results and estimated exposure using the EFSA model. In the EFSA model, the data used for exposure calculation during hand-held upward application on crops were generated using a lance connected to a large tank. In the experimental study, the tank was in contact with the back of the operators and often had to be filled with spray solution. The exposure that could occur during a mixing/loading phase of a product into a small tank and during the loading of a spray mix from a large tank to a small tank may not be completely similar. Nevertheless, the inclusion of mixing/loading exposure in the EFSA assessment could lead to a more relevant comparison. This is why two comparisons of exposure were performed with the experimental results compared to the EFSA data during application only, and with the experimental results compared to the EFSA data during mixing/loading and application. The inclusion of exposure during mixing/loading in the EFSA assessment in fact had a low impact on the comparison, except on potential and actual hand exposures.

At the 75th percentile, the exposure levels measured during the experimental exposure study were lower for potential dermal exposure excluding

Table 7 Mean and standard deviation of cumulative permeation mass per surface ($\mu\text{g}/\text{cm}^2$) (according to ISO 6529:2001) of plant protection product SELVA® through Dupont®, Tyvek® Classic Plus, Model CHA5a, coverall Category III type 4-5-6

	Sampling times (min)	Selva® Cymoxanil concentrations (g/L)	
		30 (undiluted)	0.24 (diluted)
Dupont®, Tyvek® Classic Plus, Model CHA5a, coverall Cat. III type 4-5-6 ^a	30	27.5 \pm 24.3	0
	240	585.7 \pm 237.5	30.7 \pm 25

^a According to directive 89/686/EEC

hands, actual dermal exposure excluding hands, and actual dermal exposures, representing 8, 5 and 5 %, respectively, of the exposure levels during application only in the EFSA model. On the contrary, the exposure levels measured during the experimental exposure study were higher for the head and hands protected or hands not protected, i.e., 515, 1542 or 426 %, respectively, when compared to the exposure levels during application only in the EFSA model.

The transfer factor (TF) (Table 9) calculated during application considering either the 75th or the 95th percentile was lower for the coverall in the experimental exposure study. For the gloves, the TFs calculated using the 75th and 95th percentiles were respectively 4 and 11 times higher in the experimental operator exposure study than in the EFSA model.

4 Discussion

In vineyards where access using a vehicle is not possible, backpack sprayers are used and the resulting work constraints for the operator (walking on steep ground with a backpack sprayer) and the materials used can increase exposure. We compared the results of our experimental study conducted under realistic field conditions with results of the EFSA model based on surrogate data and with previous experimental operator exposure studies in vineyards.

Based on the 75th or 95th percentiles, actual dermal exposure measured during the experimental represented 5 or 2 % of the exposure levels estimated with the EFSA model (Table 8). However, the EFSA model underestimates exposures to not protected heads and protected hands. The differences could be associated with the material used in the

experimental study (i.e., backpack motorised mist-blower sprayer).

Baldi et al. (2006) performed operator exposure measurements in vineyards (with backpack sprayers) using the method of patch dosimeters and washing techniques for the hands. It was reported that no coveralls were worn by one operator among four monitored in the study. Differences were observed in the distribution (%) of total ADE between Baldi et al. (2006) and the present study (Fig. 4), i.e., hands (43.9 vs. 6.6 %), arms + forearms (25.5 vs. 1.6 %), legs (15.6 vs. 11 %) and torso (4.3 vs. 81 %). The dosimetry methodologies may have had an influence on the results. The median of actual dermal contamination of 133 mg/kg a.s. applied (min. – max. 9.3 – 739 mg/kg a.s. applied) calculated from Baldi et al. (2006) was much higher than the median ADE (9.71 mg/kg a.s. applied) from our experimental exposure study. However, the median ADE from Baldi et al. (2006) was lower than the median PDE (1183 mg/kg a.s. applied), which highlights the importance of the type of PPE and of training to manage individual protection to reduce operator exposure.

With regard to another previous study (Machera et al. 2001), designed to measure operator exposure during vineyard application with backpack sprayers using the whole-body dosimetry method, comparison was not possible as exposure levels were expressed in mL spray liquid per hour. However, Tsakirakis et al. (2014) reported that the levels of potential body exposure as well as the potential hand exposure levels in the study performed by Machera et al. 2001 were in the same order of magnitude between operators spraying in vineyards with a lance connected to a large tank (Tsakirakis et al. 2014) and operators applying with backpack sprayers. The comparative distribution of PDE (in %) between the results of Tsakirakis et al. 2014 (hand-held application with a lance) and the present study was similar for the upper body (torso) and arms (approximately 26 %) and the hands (approximately 9 %), slightly different for the lower body (legs) (62 vs. 57 %), and higher for the head (2 vs. 5.6 %). On the contrary, based on the 75th percentile, the level of potential dermal exposure expressed in mg/kg a.s. applied (Table 6) was 4.5 times higher with a backpack motorised mist-blower which could be due to the conditions of use under high constraints in the study summarised in this paper and to the different types of sprayers. Transfer factors through the coverall were in the same range in the present experimental study (0.18–6.4 %) compared to Tsakirakis et al. (2014) (0.40–15.4 %). However, the maximum TF was lower in our

Table 8 Comparison of operator exposure between the experimental operator study and the EFSA model

Operator exposure study	Active substance (mg/kg a.s.)—75th percentile			Active substance (mg/kg a.s.)—95th percentile		
	EFSA model—Mixing/loading (M/L)—backpack	Operator exposure study/EFSA model—Hand-held application (%)	Operator exposure study/EFSA model—M/L + application (%)	EFSA model—Mixing/loading (M/L)—backpack	Operator exposure study/EFSA model—Hand-held application (%)	Operator exposure study/EFSA model—M/L + application (%)
Unprotected body ^a	1139	16.3	15,320	7	7	2115
Protected body ^b	47.1	0.508	913	5	5	86.7
Unprotected head ^c	74.8	0.102	14.5	515	511	194
Potential dermal exposure excluding hands ^d	1172	16.4	15,335	8	8	2150
Actual dermal exposure excluding hands ^e	47.1	0.508	913	5	5	86.7
Potential hand exposure ^f	127.1	193	29.8	426	57	256
Protected hands (actual hand exposure) ^g	2.82	0.366	0.183	1542	514	3.71
Actual dermal exposure ^{h,i}	49.3	0.874	913	5	5	89.2
						5.43
						3822
						2
						2

^a Unprotected body = arms + legs + torso from coverall and undergarment^b Protected body: undergarments^c Unprotected head: bandana or hood^d Potential dermal exposure excluding hands = total coverage (including bandana or hood) + undergarment in study or unprotected body + unprotected head in model^e Actual dermal exposure excluding hands = undergarment^f Potential hand exposure = gloves + hand washes^g Actual hand exposure = hand washes^h Actual dermal exposure = undergarment + hand washes in study or protected body + protected hands in modelⁱ Actual exposure on head was not measured and not included

Table 9 Comparison of transfer factors via coverall and gloves between the field operator study and the EFSA model

Transfer factor (%)—75th percentile			Transfer factor (%)—95th percentile		
Operator exposure study	EFSA model—application	Operator exposure study/EFSA model (%)	Operator exposure study	EFSA model—application	Operator exposure study/EFSA model (%)
Coverall ^a	1.7	6.0	28	5.1	8.8
Gloves ^b	2.4	0.61	393	8.6	0.77

^a Residue undergarment/(residue undergarment + residue coverall)

^b residue hand washes/(residue gloves + residue hand washes)

experimental study, which may be due to the application of the certified coverall (Table 7). Thus, the transfer factors that were determined from the experimental study indicated that Category III Type 4/5/6 coveralls (according to Directive 89/686/EEC) offer a protection to operators and were in the same range as those determined by Driver et al. (2007), Großkopf et al. (2013), EFSA (2014) and Spaan et al. (2014).

When high exposure is likely to occur under field conditions, a high level of performance for protective clothing is required, i.e., level 3 in ISO 27065:2011 (2011). Transfer factors cannot be determined by this ISO method. However, comparing the performance of the coverall materials showed that the transfer factors should not differ significantly under the same conditions of use if the performance levels according to ISO 6529:2001 (2001) are comparable. Thus, the ISO 6529:2001 (2001) laboratory methods can be used to verify and rank the performance of different materials.

The results of this experimental field exposure study could be used to increase the robustness of operator exposure estimates in the context of pesticide upward applications using a backpack-motorised mist-blower.

Acknowledgments The authors would like to thank STAPHY acting as the test facility for the study, C.H. Roussel for his key support as field principal investigator and Eurofins Agro-science Services Chem SAS which took care of all the specimen analyses and Institut Français du Textile et de l'Habillement, Ecuy, France for performing the permeation tests.

Compliance with ethical standards

Funding Anses-French agency for food, environmental and occupational health & safety.

Conflict of interest The authors declare that they have no conflict of interest.

Disclaimer The findings and conclusions in this report are those of the authors and do not necessarily represent the views of Anses.

References

Baldi I, Lebailly P, Jean S, Rougetet L, Dulaurent S, Marquet P (2006) Pesticide contamination of workers in vineyards in France. *J Expo Sci Environ Epidemiol* 16(2):115–124

Commission Regulation (EC) (2009) No 1107/2009 of the European parliament and of the council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. OJ. L309/1

Commission Regulation (EU) (2011) No 546/2011 of 10 June 2011 implementing Regulation (EC) No 1107/2009 of the European Parliament and of the Council as regards uniform principles for evaluation and authorisation of plant protection products. OJ. L155/127

Council Directive of 21 December 1989 (1989) on the approximation of the laws of the Member States relating to personal protective equipment (89/686/EEC). OJ. L399/18

Driver J, Ross J, Mihlan G, Luchick C, Landenberger B (2007) Derivation of single layer clothing penetration factors from the pesticide handlers exposure database. *Regul Toxicol Pharmacol* 49:125–137

EFSA (2014) Guidance on the assessment of exposure of operators, workers, residents and bystanders in risk assessment for plant protection products. EFSA J 12(10):3874, 55

Großkopf C, Mielke H, Westphal D, Erdtmann-Vourliotis M, Hamey P, Bouneb F, Rautmann D, Stauber F, Wicke H, Maasfeld W, Salazar JD, Chester G, Martin S (2013) A new model for the prediction of agricultural operator exposure during professional application of plant protection products in outdoor crops. *J Verbr Lebensm* 8:143–153

International Organisation for standardization (ISO) (2001) Protective clothing—protection against liquid chemicals—determination of resistance of protective clothing materials to permeation by liquids and gases. (Standard N° ISO 6529:2001) Geneva, Switzerland: ISO

International Organisation for standardization (ISO) (2011) Protective clothing—performance requirements for protective clothing worn by operators applying pesticides. (Standard N° ISO 27065:2011) Geneva, Switzerland: ISO

Machera M, Goumenou M, Kapetanakis E, Kalamarakis A, Glass R (2001) Determination of the potential dermal and inhalation exposure of operators, following spray applications of the fungicide penconazole in vineyards and greenhouses. *Fresenius Environ Bull* 10:464–469

OECD/GD (97)148 (1997) Guidance document for the conduct of studies of occupational exposure to pesticides during agricultural application. OECD Environmental Health and Safety Publications, Paris

Spaan S, Marrufo Valenzuela N, Glass R, Gerritsen R (2014) Bystanders, residents, operators and workers exposure

models for plant protection products—efficacy of work wear and PPE. BROWSE seventh framework programme. <http://www.browseproject.eu>

Tsakirakis A, Kasiotis K, Charistou A, Arapaki N, Tsatsakis A, Tsakalof A, Machera K (2014) Dermal and inhalation

exposure of operators during fungicide application in vineyards. Evaluation of coverall performance. *Sci Total Environ* 470–471:282–289