

Comparative study on exposure of workers and bystanders during pest control of the Oak Processionary Moth by spray application

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The responsibility for the contents of this publication lies with the authors.

This study was initiated and headed by the group “Exposure Scenarios” of the Federal Institute for Occupational Safety and Health (BAuA) in Dortmund. The Institute and Outpatient Clinic for Occupational, Social and Environmental Medicine (IPASUM) of the Erlangen-Nürnberg University dealt as project contractor with all aspects of dermal exposure, while all aspects of inhalation exposure were addressed by the BAuA group “Measurements of Hazardous Substances". The Federal Institute for Risk Assessment (BfR) dealt with the questions concerning the determination of bystander exposure and carried out the risk assessment outlined in this report on the basis of the data collected. The study was funded by the Federal Institute for Occupational Safety and Health (Project F 2343).

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Abstract

Biocidal products used for spray application against the oak processionary moth (OPM) require authorisation in accordance with Regulation (EU) No. 528/2012 of the European Parliament for that use. For authorisation, a risk assessment based on exposure estimation is performed for all intended uses of the respective product.

Detailed information on the application process and the resulting exposure of operators and of bystanders was lacking until now. It is expected that the main routes of exposure are dermal and inhalation. Spray applications carried out for control of OPM show significant differences to plant protection applications, thus assessing exposure from OPM control on the basis of plant protection models would bear a high level of uncertainty.

This study investigated the potential dermal and inhalation exposure of pest control operators during spray application against the OPM. Moreover, the potential exposure of bystanders was quantified. Task-specific exposure data for hand-held as well as vehicle mounted sprayers were collected during OPM control with a diflubenzuron-containing insecticide in 2014 and 2015.

The data collected within the field studies were grouped and evaluated with regard to the type of spray application and working task, covering also tasks such as weighing out and portioning of the biocidal product, on-site preparation and application of the spray liquid and cleaning of the equipment. The valid data obtained form a reliable database for the authorisation of biocidal products according to the EU-Regulation.

Key words:

Oak Processionary Moth, OPM, exposure scenario, spray application, diflubenzuron, Dimilin^{TM} 80 WG, workplace measurement, dermal exposure, inhalation exposure, exposure of bystanders, workers' exposure, insecticide

Vergleichende Untersuchung zur Exposition von Arbeitnehmern und Dritten bei der Bekämpfung des Eichenprozessionsspinners mittels Sprühanwendungen

Kurzreferat

Biozidprodukte, die zur chemischen oder biologischen Bekämpfung des Eichenprozessionsspinners (EPS) eingesetzt werden sollen, müssen entsprechend der Verordnung (EU) Nr. 528/2012 für diese Anwendung zugelassen werden. Im Rahmen der Produktzulassungen werden Expositionsszenarien für die Sprühanwendung dieser Mittel bewertet.

Bislang standen jedoch keine detaillierten Informationen über den Ablauf dieser Applikationen und die daraus resultierende Exposition der Arbeitnehmer sowie unbeteiligter Dritter für die Bewertung zur Verfügung. Neben einer inhalativen ist dabei auch von einer dermalen Belastung auszugehen. Die Sprühanwendungen, die bei der EPS-Bekämpfung mit Biozidprodukten erfolgen, unterscheiden sich erheblich von Anwendungsszenarien mit z. T. identischen Ausbringgeräten im Pflanzenschutzmittelbereich. Eine Bewertung auf Basis der im Pflanzenschutzmittelbereich etablierten Expositionsmodelle wäre daher mit großen Unsicherheiten behaftet.

Ziel des Projektes war die Erfassung der jeweils potenziellen dermalen und inhalativen Exposition von Beschäftigten bei der Bekämpfung des Eichenprozessionsspinners mittels Sprühanwendungen. Darüber hinaus wurde auch die mögliche Exposition unbeteiligter Dritter untersucht. Zu diesem Zweck wurden in den Jahren 2014 und 2015 schädlingsbekämpfende Firmen bei der Ausbringung von diflubenzuronhaltigen Insektiziden messtechnisch begleitet. Die Ausbringung des Insektizids erfolgte mit Aufsattelsprühgerät und mit handgeführtem Motorsprühgerät.

Die im Rahmen der Feldstudien ermittelten Messergebnisse wurden systematisch hinsichtlich Art der Sprühanwendung und Tätigkeit zusammengefasst und ausgewertet. Hierbei wurden neben den Sprühanwendungen selbst auch das Abwiegen und Portionieren des Granulats, das Anmischen der Sprühbrühe an den Einsatzorten sowie Reinigungsarbeiten erfasst. Die so erhaltenen validen Daten bilden eine verlässliche Basis für die Zulassung von Biozidprodukten unter der EU-Verordnung.

Schlagwörter:

Eichenprozessionsspinner, EPS, Expositionsszenario, Sprühanwendung, Diflubenzuron, Dimilin® 80 WG, Arbeitsplatzmessung, dermale Exposition, inhalative Exposition, Exposition unbeteiligter Dritter, *Bystander*-Exposition, Arbeitnehmerexposition, Insektizid

1 Introduction

The oak processionary moth (*Thaumetopoea processionea*; OPM), a species of moth native to Germany, has been spreading in Germany and other European countries since the 1990s. The living spaces of OPM are amongst others residential areas and public recreation areas (such as forest edges, parks and single standing trees in urban green). The OPM affects all types of oak trees with its caterpillars feeding in groups and moving about in nose-to-tail processions, a distinctive habit, from which they derive their name. From the third larval stage, the caterpillars form stinging hairs containing the nettle poison thaumetopoein. On contact, these hairs can cause skin, eye and respiratory irritation as well as pseudoallergic reactions to humans (JKI 2012). In addition, the caterpillars construct communal nests consisting of silk webbing, pupal shell fragments, threads and moulting remains, also containing considerable amounts of shed stinging hairs. As these hairs can remain active for a period of several years, the nests also represent a permanent hazard (LWF 2013).

Mainly pesticide spraying is applied to control the oak processionary moth. Ideal spray timing is when OPM larvae are in larvae stage 1 to 2 prior to the development of stinging hairs. When larvae reach larvae stage 3 spraying should be avoided as detached hairs can be blown in the air. In the late larvae stages nests may be removed manually, by vacuum equipment for example.

Where the OPM is to be controlled using insecticides for the protection of human beings, only those products may be used that are authorised as biocidal products in accordance with Regulation (EU) No. 528/2012 (EU 2012), or whose use is permitted in accordance with transitional regulations.

For authorisation of biocidal products, a risk assessment based on exposure estimation is performed. The toxicological reference values derived for the products and their active substances, respectively, are related to the expected exposure of the application applied for. If the expected exposure exceeds the derived reference values an attempt will be made to reduce the exposure to an acceptable limit by taking safety measures into account.
If compliance with limit values is not achieved, even when restrictive measures are taken into account, the application of the respective product cannot be authorised. Therefore, exact and reliable exposure assessment is very important in the evaluation process.

However, detailed information on the exposure situation and the resulting health hazards for the workers during pest control of the OPM is lacking until now.
Inhalation as well as dermal exposure is expected when spraying the caterpillars with insecticide, with dermal exposure possibly being the main route. Beside the commercial applicators casual bystanders may be exposed during pest control of the OPM in public space and on private ground, respectively. These bystanders are pedestrians and persons who are in public areas (e.g., in public parks, in gardens, on sports fields, in day care centres, etc.) and also residents.

In order to obtain detailed information on the procedure of spraying the caterpillars with insecticides and to get valid data on the exposure of workers and bystanders

during control of OPM with biocidal products, pest control companies were accompanied and exposure was measured during biocide application.

The exposure data were obtained in 2014 and 2015 from pest control operators using diflubenzuron. Diflubenzuron (N-[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide; $C_{14}H_9ClF_2N_2O_2$; CAS-No.: 35367-38-5) is an odourless, white-crystalline solid material having an insecticidal activity (EPA 1989; EPA 1997) and in accordance with (EU) Regulation No.528/2012 it is authorised as active substance (product type 18: insecticide). Diflubenzuron is a stomach poison, which inhibits the transport of UDP-N-acetyl glucosamine through the cell membranes, thus preventing chitin synthesis. The inhibition of the moulting process results either in the death of the caterpillars or larvae/pupae, or in non-viable adults. The insecticidal effect is thus not immediate but always delayed until the next stage of development (MITSUI et al., 1984).

The active substance diflubenzuron is available on the market as water dispersible granules (trade name Dimilin^{TM} 80 WG). During the field trials, this product was applied by the companies participating in this study using vehicle-mounted sprayer (VMS) and backpack hand-held sprayers (HHS). In accordance with biocide legislation, the application of Dimilin^{TM} 80 WG was allowed in 2014 and 2015 without approval based on the transitional regulations (BAuA 2013).

In the following, the data collected during the BAuA-Project F 2343 on potential dermal and inhalation exposure of workers as well as bystanders are presented. These exposure data can be taken as valid reference data for the evaluation of exposure scenarios within the authorisation of biocidal products in the EU.

2 Evaluation and authorisation of biocidal products

2.1 Authorisation of biocidal products

The (EU) Regulation No. 528/2012 (EU 2012) of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products has the following aims: improving the functioning of the internal market through the harmonisation of the rules on the making available on the market and the use of biocidal products while, at the same time, ensuring a high level of protection of both human and animal health and the environment. A core element of this Regulation is that biocidal products may only be made available on the market and used if they have been authorised in accordance with this Regulation. For this, a two-step procedure has been installed in which first of all the active substances contained in the biocidal products are approved and subsequently the corresponding biocidal products are authorised for use.

2.2 Exposure estimation and risk assessment

To have a biocidal product approved, it must, among others, be demonstrated that it has no unacceptable effects on human health. Other aspects, such as efficacy and protection of animals and the environment, are however not addressed by the present project and therefore not described here. To prove that a product has no unacceptable effects on human health, a risk assessment is carried out, whose procedure is detailed in the guideline “Biocides Human Health Exposure Methodology” (ECHA 2015a). The risk assessment is based on the one hand on toxicological reference values already derived during the active substance approval process, on the other hand on an estimate of the exposure for all intended uses applied for. Both the exposure of all prospective user groups (for example professional/non-professional users) and the potential exposure of bystanders (for example people out walking) are included in the estimation. For the risk assessment, the estimated exposure level is then put into relation with the derived toxicological reference values. If it is found that the reference values will be exceeded, a reduction in exposure level by specification of technical and organisational protective measures is first attempted. If the reduction in exposure level so obtained is not sufficient, this level is further reduced by applying personal protective equipment. Applications where the exposure level cannot be reduced below the toxicological reference values even when using restrictive protective measures, are then not authorised.

With the help of this short outline of the procedure it is quite obvious that the exposure estimation plays a major role in the risk assessment and therefore it is also important for the authorisation decision.

The exposure estimation is performed mostly on the basis of exposure models, which can be based on physicochemical considerations and calculations or on data from workplace measurements in the corresponding tasks. In addition, for exposure assessment, usually input parameters have to be established, for example the

duration and frequency of a particular task. Regulation (EU) No.528/2012 lays down that the assessment must be based on realistic worst-case conditions. The input parameters selected should therefore be correspondingly conservative. If data from workplace measurements are used, it should be borne in mind that such data always reflect a distribution of exposure levels, most of which follow a logarithmic normal distribution. Finally, as for the exposure assessment and therefore for the decision to approve, only one value can be taken as basis, specifications have been established as to which value from a given distribution is to be used. In accordance with the terms of the “Guidance on the Biocidal Products Regulation, Volume III, Human Health -Part B Risk Assessment” (ECHA 2015b), for the selection of the so-called “indicative value” to be used, the degree of uncertainty associated with the dataset is decisive. In this case first of all, especially the size and variation of the data are considered. For moderate uncertainty the 75th percentile, for considerable uncertainty the 95th percentile and for high uncertainty the maximum exposure value will be used. It can also happen, however, that no data are available for a use to be assessed but that, for exposure, analogies to other tasks can be drawn, for which data are available. In such cases the exposure estimate can be associated with a higher uncertainty, which makes the selection of a more conservative percentile necessary.

In practice, this tendentially results in higher exposure estimates in cases of applications for which only few or inaccurate data are available compared to cases with accurate data. This can result in the establishment of more restrictive protective measures, which in turn can mean a greater physical burden for the workers and lead to higher costs for employers and contractors. When the safety of use from the existing data base cannot be demonstrated, not even with restrictive protective measures, approval of this application for the biocidal product in question is impossible. The generation of high-quality exposure data is therefore to the advantage of all participants.

2.3 Exposure determinants in spray applications

2.3.1 Workers

As regards the patterns of use, the workers spraying the biocidal product in the field are, as handler, subject to direct (primary) exposure. In addition, workers are subject to indirect (secondary) exposure insofar as they are in the treated area during application of the biocidal product or come into contact with product residues after application, for example through contact with contaminated surfaces.

Worker`s exposure to the applied biocides may occur through inhalation and dermal.

The Guideline entitled “Biocides Human Health Exposure Methodology” differentiates between preparatory phase (mixing and loading), application phase and post application phase (ECHA 2015a). The preparatory phase deals with handling large quantities of the concentrated or ready-to-use product, the dilution of the concentrate and/or the filling of the product into the equipment. The application phase covers the application of the biocidal product and the post-application phase comprises exposure from cleaning and maintenance of the machines, equipment and tools.

The different tasks in connection with biocide application by spraying may be listed as follows:

Preparation phase

- Safety measures in area to be treated
- Weighing out and portioning of the biocide
- Preparation of the spray liquid by suspension of the biocide in water or transfer of already prepared spray liquid into the tank
- Checking/adjustment of the sprayers

Application phase

- Application of the spray liquid

Post application phase

- Clearing up and cleaning procedures in the treated area
- Cleaning the vehicles/spraying equipment
- Maintenance of the vehicles/spraying equipment

Differences in exposure level particularly result from the different tasks in the three phases described. Moreover, there may also be interindividual and intraindividual differences in exposure levels as tasks and procedures may differ from one user to another and as they may even vary when performed by the same worker depending on circumstances. Each type, duration and frequency of task before, during and after biocide application are here to be considered separately.
In practice, exposure is mostly evaluated on the basis of an 8-hour shift, so that it usually comprises all three phases of task.

2.3.2 Bystanders

The exposure of bystanders can take place both due to their being present close to the area of application and subsequently through contact with contaminated surfaces. The exposure data determined in this project serve to estimate exposure to the spray liquid during or directly after application; data for an exposure to contaminated surfaces in subsequent tasks were not recorded.

3 Description of field studies and methods

The exposure of workers and bystanders during pest control against the oak processionary moth by spraying was measured in 2014 and 2015 and samples were obtained from eight workers of three pest-control companies in different tasks. During the field studies Dimilin™ 80 WG was applied, containing 80 % diflubenzuron as active substance.

In workplace measurements, both biocide applications using a vehicle-mounted unit and the use of a backpack hand-held sprayer were investigated. These spray units operate by pumping the spray liquid into an airstream. This airstream is produced by a large fan and serves to carry the spray to the target. The biocide is generally sprayed from below into the treetops whereby it reaches the highest parts due to thermic processes. Depending on the height of the tree and the type of spray unit, between approximately 0.6 and 6 L spray liquid are applied per tree.

Apart from the actual biocide application, the weighing out and portioning of the Dimilin™ 80 WG granules, the preparation or transfer of the spray liquid and the cleaning of the vehicle/ vehicle-mounted sprayers at the end of the spraying season were also measured. The workplace measurements were carried out exclusively in relation to the activity. During sampling, the type and duration of the separate tasks were recorded and documented photographically.

3.1 Description of companies and of their general procedures

3.1.1 Company A

Company A has been active since 1998 as a service company in the field of pest control. It has been active in OPM control since 2003, performing OPM control activities throughout the entire Federal Republic for 5 years to the present. Company A has treated approximately 10000 to 20000 trees per year, here mainly using NeemAzal™ T/S, Dipel™ ES and Dimilin™ 80 WG. Four workers of company A participated in the measurements.

For the application of Dimilin™ 80 WG, as spray units, two vehicle-mounted sprayers were used and, as alternative for difficult terrain, a hand-held sprayer.
The vehicle-mounted sprayers were Dragone units of model series AZ with 800 L and 1000 L tank capacity, respectively; the sprayers were mounted at the rear of a small truck (Fig. 3.1 and Fig. 3.2). The pumps of model series AZ have a flow of 91 L/min at a capacity of 540 U/min. The total flow through the nozzles here depends on the number of active (open) nozzles, the nozzle size and the operating pressure, and is normally 20 to 30 L/min, with a maximum air flow of 36000 and 48500 m³/h, respectively.

Dimilin™ 80 WG application with the hand-held sprayer was always carried out with a Solo Port 423 spray unit (Fig. 3.3). The tank for the spray liquid held 12 L, with a nominal volume of 10 L. According to operating instructions, the applied quantity was between 0.32 and 1.46 L/min, with a maximum air flow of 1400 m³/h. Depending on

the type of trees to be sprayed, the application of a full tank lasted between 8 and 20 min, which corresponds to the theoretical application quantities given above.

Fig. 3.1 Light truck with vehicle-mounted sprayer (Dragone AZ with 800 L spray tank) of company A.

Fig. 3.2 Light truck with vehicle-mounted sprayer (Dragone AZ with 1000 L spray tank) of company A.

Fig. 3.3 Dimilin™ 80 WG application with hand-held sprayer (Solo Port 423; company A).

The Dimilin™ 80 WG granules were portioned at the beginning of the season and transported in an accompanying vehicle. The spray liquid for the vehicle-mounted sprayers was prepared in each case taking water from a hydrant. For the hand-held sprayer, water from the tank carried by the accompanying vehicle was used to prepare the spray liquid. Alternatively, the already prepared spray liquid from the tank of the vehicle-mounted sprayer was used and filled into the hand-held sprayer as required. At the end of the season, the vehicle-mounted sprayer and the vehicles were subjected to thorough cleaning.

3.1.2 Company B

Company B has been working several years as a service company in the field of pest control. Up to 2014, only mechanical removal of caterpillar nests had been carried out in OPM control. In 2014 pest control using biocides was carried out for the first time, preceding the mechanical removal. Two workers of company B took part in the measurements. Dimilin™ 80 WG was applied once by this company in 2014, after which Dipel™ ES was used for the remaining pest control season. Sampling was only performed during the application of Dimilin™ 80 WG.
The vehicle-mounted sprayer of company B was a Dragone AZ with a tank volume of 800 L (Fig. 3.4), which was mounted on the rear of a tractor. Unlike the spray units of company A, this vehicle-mounted sprayer had a separate pre-mix tank. The Dimilin™ 80 WG granules were weighed out on site from a small package. During application, the worker was seated in the closed cabin of the tractor, the cabin being ventilated via an air filter. In this case also, the flow rate was 91 L/min at a pump capacity of 540 U/min. The total flow through the nozzles depends on the number of active nozzles, the nozzle size and the operating pressure and is normally between 20 and 30 L/min, with a maximum air flow of 36000 or 48500 m^3/h. Company B had been commissioned to treat an alley lined with oak trees, applying the spray liquid continuously over a dense population of trees and a short driving distance. The very application of 800 L spray liquid lasted 40 min, which corresponded to an actual flow through the nozzles of 20 L/min.

Fig. 3.4 Vehicle-mounted sprayer (tractor) (Dragone AZ with 800 L spray tank) of company B.

3.1.3 Company C

Company C has been active as a service company in the pest control field for 65 years. For several years, company C has also been active in the field of OPM control, whereby biocides other than Dimilin^{TM} 80 WG are also applied. Two workers of the company participated in the measurements.
Company C used the vehicle-mounted sprayer Vicar Turbine 451 with a tank volume of 300 L (Fig. 3.5), which was mounted on the rear of a small truck. The most pronounced difference between the Dragone AZ models and the Vicar-spray unit lay in the fact that, the vehicle-mounted Dragone sprayers had hydraulically controlled canon heads to adjust the vertical and horizontal spray angle whereas, in the Vicar-spray unit, the spray liquid is mostly sprayed into the trees at a fixed angle. During application, the driver was in the cabin of the Unimog with the window open part of the time.
The pump capacity of the Vicar Turbine 451 is between 50 and 200 L/min. With this vehicle-mounted sprayer, the total flow through the nozzles also depends on the number of open nozzles, the nozzle size and the operating pressure. The maximum air flow is 16000 to 18000 m^3/h. Forty meters are cited by the manufacturer as maximum attainable spraying height.
At the beginning of the workplace measurements, the Dimilin^{TM} 80 WG granules were already portioned in paper sandwich bags stored in a bucket covered with a lid. The bucket was transported on the loading platform of the small truck. The spray liquid was either prepared at a hydrant or water from the water tank installed on the loading platform of the small truck was used.
At the end of the season, the vehicle-mounted sprayer and the vehicle were thoroughly cleaned.

Fig. 3.5 Light truck with vehicle-mounted sprayer (Vicar Turbine 451 with 300 L spray tank) of company C.

3.2 Description of tasks

Weighing out and portioning of the Dimilin™ 80 WG granulate

As task, the weighing out and portioning of Dimilin™ 80 WG was recorded separately only for company A. Company C already had the granules portioned into paper sandwich bags at the beginning of the spray season, which were transported in a sealable plastic bucket on the loading platform of the vehicle. In the case of company B, the worker had already weighed out the Dimilin™ 80 WG granules from a small package on site in order to prepare the spray liquid subsequently.

During the field studies of 2014 and 2015, the weighing out and portioning of the Dimilin™ 80 WG granules by the workers of company A took place in a storage hall of the public works department (Fig. 3.6 and Fig. 3.7), where 20 kg of the granules were weighed out and portioned in 2014, and 10 kg in 2015. During weighing out and portioning, the storage hall was open on one side in 2014, and closed in 2015. The respective worker portioned 240 g or 300 g of the granules into plastic bags using kitchen scales. The bags were subsequently sealed and deposited in an empty cardboard barrel for storage and later use. At the end of weighing out and portioning, the work table was cleaned by hand or with a hand brush. A detailed description of each sampling procedure is given in Annex 1.

Fig. 3.6 Weighing out and portioning of the Dimilin^{TM} 80 WG granulate in the 2014 field study.

Fig. 3.7 Weighing out and portioning of the Dimilin^{TM} 80 WG granulate in the 2015 field study.

Vehicle-mounted sprayer: Application of the Dimilin™ 80 WG suspension

Company A: The spray liquid was always prepared outdoor at a hydrant. The required Dimilin™ 80 WG - preportioned in plastic bags - was transported during the control measures in a cardboard barrel in the accompanying vehicle. For filling, the water hose was attached at the bottom of the tank on the vehicle-mounted sprayer (Fig. 3.8). The worker took a bag with preportioned granulate, removed the lid from the top of the tank and emptied the granules from the bag onto the strainer (Fig. 3.9). Just before reaching the required volume - with the lid closed - the agitator was started in order to flush the Dimilin™ 80 WG into the tank. The tank lid was removed a second time in order to check the mixing process.

Company B: The spray suspension was prepared outdoor at a hydrant. The required amount of Dimilin™ 80 WG was weighed out on site into a beaker using kitchen scales (Fig. 3.10). The biocide was put into the pre-mix tank, in which it was first of all preslurried in water (Fig. 3.11). This suspension was then flushed with running water into the large spray tank. A hose was attached to the hydrant to add water to the spray tank through the top tank filler opening after removing the lid. After closing the lid, the agitator was started to mix the spray liquid.

Company C: On the loading platform of its vehicle, company C had a 1000 L water tank installed, so that preparation of the spray liquid could also be done without approaching a hydrant. During the moth control measures, the Dimilin™ 80 WG was transported - preportioned in paper sandwich bags -in a bucket with closed lid on the loading platform of the vehicle. The water for preparing the spray liquid was withdrawn using a hose either from a hydrant or from the transported water tank and added through the tank filler opening at the top of the tank after removing the lid. With a half filled tank (150 L) the worker fetched the bag with the Dimilin™ 80 WG granules and emptied it onto the strainer (Fig. 3.12). The granules were flushed into the tank with more water (Fig. 3.13). The tank lid was closed and the spray liquid in the tank kept agitated during the entire application.

Fig. 3.9 to Fig. 3.13 show the preparation of the spray liquid for the vehicle-mounted sprayer during the field studies. A detailed description of the respective sampling is given in Annex 1.

Fig. 3.8 Vehicle-mounted sprayer: Preparation of the Dimilin™ 80 WG suspension - Adding of water to the tank (company A).

Fig. 3.9 Vehicle-mounted sprayer: Preparation of the Dimilin™ 80 WG suspension -Filling of the granules onto the strainer of the tank (company A).

Fig. 3.10 Vehicle-mounted sprayer: Preparation of the Dimilin™ 80 WG suspension - Weighing out of the granules directly prior to the preparation of the spray liquid (company B).

Fig. 3.11 Vehicle-mounted sprayer: Preparation of the Dimilin™ 80 WG suspension - Filling of the granules to the premix tank (company B).

Fig. 3.12 Vehicle-mounted sprayer: Preparation of the Dimilin^{TM} 80 WG suspension - Filling of the granules to the filler strainer (company C).

Fig. 3.13 Vehicle-mounted sprayer: Preparation of the Dimilin^{TM} 80 WG suspension - Adding of water to the tank (company C). The strainer can easily be seen.

Vehicle-mounted sprayer: Application of the Dimilin^{TM} 80 WG suspension

In all three companies, the spray liquid was further agitated by stirring in the tank during application to ensure a constant concentration of the spray liquid. During application, the workers stayed in the driver's cabins of their vehicles. The vehicle-mounted sprayers were controlled from the driver's cabin. Apart from switching the spraying process on and off, the vertical and horizontal angle of the canon head could be directed. With the vehicle-mounted Dragone sprayer used by companies A and B, the operator could aim the canon head in all directions to reach the targeted trees with the spray. With the Vicar Turbine 451 used by company C, the spray liquid was mostly sprayed into the trees at a fixed angle, as only the vertical spray angle could be controlled due to construction type.

During application of the Dimilin^{TM} 80 WG suspension, the vehicle-mounted unit was slowly driven past the oak trees. Where possible, groups or rows of contiguously standing trees were sprayed with a continuous spray beam. In the case of longer driving distances between individual trees or tree groups, the spray process was discontinued and not restarted until reaching the targeted oak trees. As a result, the application of a full tank often lasted as long as two to three hours depending on the number of trees and the distance driven, in spite of the high total flow.

During biocide application, an accompanying vehicle always drove behind the vehicle-mounted sprayer in order to caution the drivers of other vehicles that a pest control was underway and, if necessary, to mark the treated area with barrier tape. Fig. 3.1 to Fig. 3.5 show the application of the spray liquid using various vehicle-mounted sprayers during the field studies of 2014 and 2015. A detailed description of the respective sampling is given in Annex 1.

Hand-held sprayer

The Solo Port 423 backpack hand-held sprayer was used to apply the spray liquid where it was impossible to use the vehicle-mounted unit due to the location of the oak trees or difficult terrain. Only company A used the backpack version during the field trials, whereby biocide application with the hand-held sprayer was sampled both in 2014 and in 2015.

Hand-held sprayer: Preparation/transfer of the Dimilin^{TM} 80 WG suspension

Directly before the spraying of the Dimilin^{TM} 80 WG suspension, the spray liquid was prepared or transferred. When preparing the spray liquid, the screw lid at the top of the spray tank was removed and a measuring spoon of Dimilin^{TM} 80 WG granules (approximately 3-4 g) put onto the tank filler strainer (Fig. 3.14). Water was then taken from the water tank on the accompanying vehicle and filled into the tank of the hand-held sprayer (Fig. 3.15) with a watering can. The granules were suspended by adding water and flushed into the tank. Alternatively, the Dimilin^{TM} 80 WG suspension was taken from the spray tank of the vehicle-mounted spray unit (Fig. 3.16) and, using a bucket or canister, poured into the tank of the hand-held sprayer (Fig. 3.17).
After the preparation or transfer of the spray liquid, the lid was screwed back onto the tank, the motor was activated using the recoil starter, the hand-held sprayer shouldered, and the application process started.
Fig. 3.14 and Fig. 3.15 show the preparation of the spray liquid for the hand-held sprayer, Fig. 3.16 and Fig. 3.17 the transfer of Dimilin^{TM} 80 WG suspension from the tank of the vehicle-mounted sprayer into the tank of the hand-held sprayer. A detailed description of the respective sampling is given in Annex 1.

Fig. 3.14 Hand-held sprayer: Preparation of the Dimilin™ 80 WG suspension - the granules are put onto the tank filler strainer.

Fig. 3.15 Hand-held sprayer: Preparation of the Dimilin™ 80 WG suspension - Adding of water to the tank using a watering can.

Fig. 3.16 Hand-held sprayer: Transfer of the Dimilin™ 80 WG suspension - Taking the spray liquid from the tank of the vehicle-mounted sprayer.

Fig. 3.17 Hand-held sprayer: Transfer of the Dimilin™ 80 WG suspension - Pouring of the spray liquid into the tank of the hand-held sprayer.

Hand-held sprayer: Application of the Dimilin™ 80 WG suspension

The hand-held sprayer was used particularly to apply Dimilin™ 80 WG to isolated trees or groups of trees. The worker could start or terminate the spraying process moving the lever mounted on the spray tube, and regulate the amount of biocide sprayed using the dosage-sleeve.
According to the height of the trees, in OPM control using a hand-held sprayer, the direction of spraying was steep to vertically upward. The worker sprayed the trunks and the treetops of the oaks while, according to the location and size of the trees, he was walking round them partially or completely depending on the wind conditions. During application, the worker stood some of the time directly beneath the applied spray mist, thus being subjected to a rain of deposing droplets and falling drops of spray liquid.

The use of the hand-held sprayer to apply the Dimilin^{TM} 80 WG suspension was mostly continuous, so that application of the 12 L of spray liquid, as a rule, terminated after 8 to 10 min.

Cleaning procedures: Cleaning of the vehicles/ vehicle-mounted sprayers

At the end of the spray season, measurements were performed during the cleaning of the vehicle-mounted sprayer and the respective vehicles. In total, samples were taken three times in 2014 and 2015 during cleaning procedures, where high-pressure cleaners were used in all three cases.
In 2014, a worker of company A cleaned one vehicle and two vehicle-mounted sprayers. This work was carried out at a car-wash site with industrial high-pressure cleaner (Fig. 3.18). The worker additionally cleaned the surfaces with detergents and brush, also climbing onto the loading platform of the small truck for this purpose.
In 2015, with company A, samples were taken from the cleaning of one vehicle and one vehicle-mounted sprayer. The cleaning procedures took place on the company premises using a commercially available high-pressure cleaner (Fig. 3.19), with the worker, standing either on the loading platform or on a ladder, additionally wiping the surfaces with a cloth (Fig. 3.20).
In contrast to this, in 2015, the worker of company C only used a high-pressure cleaner to clean the vehicle and the vehicle-mounted unit. This process took place on the company grounds with a commercially available high-pressure cleaner. The worker cleaned the surfaces by walking round the vehicle (Fig. 3.21) without climbing up onto the loading platform of the small truck.
Fig. 3.18 to Fig. 3.21 show the cleaning of the vehicles and vehicle-mounted sprayer during the field studies of 2014 and 2015. A detailed description of the respective sampling is given in Annex 1.

Fig. 3.18 Cleaning of a vehicle and two vehicle-mounted sprayers by a worker of company A (worker #1; 2014 field study).

Fig. 3.19 Cleaning of a vehicle and a vehicle-mounted sprayer by a worker of company A (worker #8; 2015 field study). Standing on a ladder, the worker is cleaning the surfaces with a high-pressure cleaner.

Fig. 3.20 Cleaning of a vehicle and a vehicle-mounted sprayer by a worker of company A (worker #8; 2015 field study). Additional wiping of the surfaces with a cloth.

Fig. 3.21 Cleaning of a vehicle and a vehicle-mounted sprayer by a worker of company C (worker #7; 2015 field study).

3.3 Sampling

3.3.1 Workers

3.3.1.1 Dermal exposure

As dosimeters to determine the potential dermal exposure to diflubenzuron, coveralls with hood made of polyethylene (DuPont™ Tyvek™ Classic Xpert model CHF5; chemical protection suit, category III, type 5B and 6B) and cotton gloves were used. The use of these dosimeters had already proven useful in other investigations as a good sampling strategy for representative quantitation of potential dermal exposure (SCHÄFERHENRICH et al., 2012). The coveralls were worn by the workers over their normal work clothes. In addition, new disposable nitrile gloves (Marigold Industrial™ Green Nitrile G25G; chemical resistant protective gloves for category III activities in accordance with EN 374) were made available to them as required; these were worn underneath the cotton gloves.
The workers were helped in putting on their dermal sampler, first with the coveralls and then with the gloves. Special care was taken to avoid cross-contaminations. For example, before donning the coveralls, Tyvek™ shoe covers were pulled over the workers' work shoes to avoid a contamination of the inside of the coveralls (Fig. 3.22). After the measurement, the workers were helped in taking off their dosimeters. The gloves were first removed and packed, before the coveralls were taken off. Fig. 3.23 shows a completely dressed worker.

Fig. 3.22 Putting on the coverall. The worker is wearing Tyvek™ shoe covers over his work shoes to avoid contamination.

Fig. 3.23 Worker wearing a Tyvek™ coverall and cotton gloves.

Following the sampling, the dermal samplers were in each case cut into 21 segments (coveralls) or left whole (gloves) before being wrapped in aluminium foil to protect them from air and light and packed into sealable PE bags for storage in a portable cooler box at 4 °C. The samples were transported to the laboratory where they were stored in a freezer at -20 °C until processing.
Fig. 3.24 shows the cutting pattern of the dermal sampler.

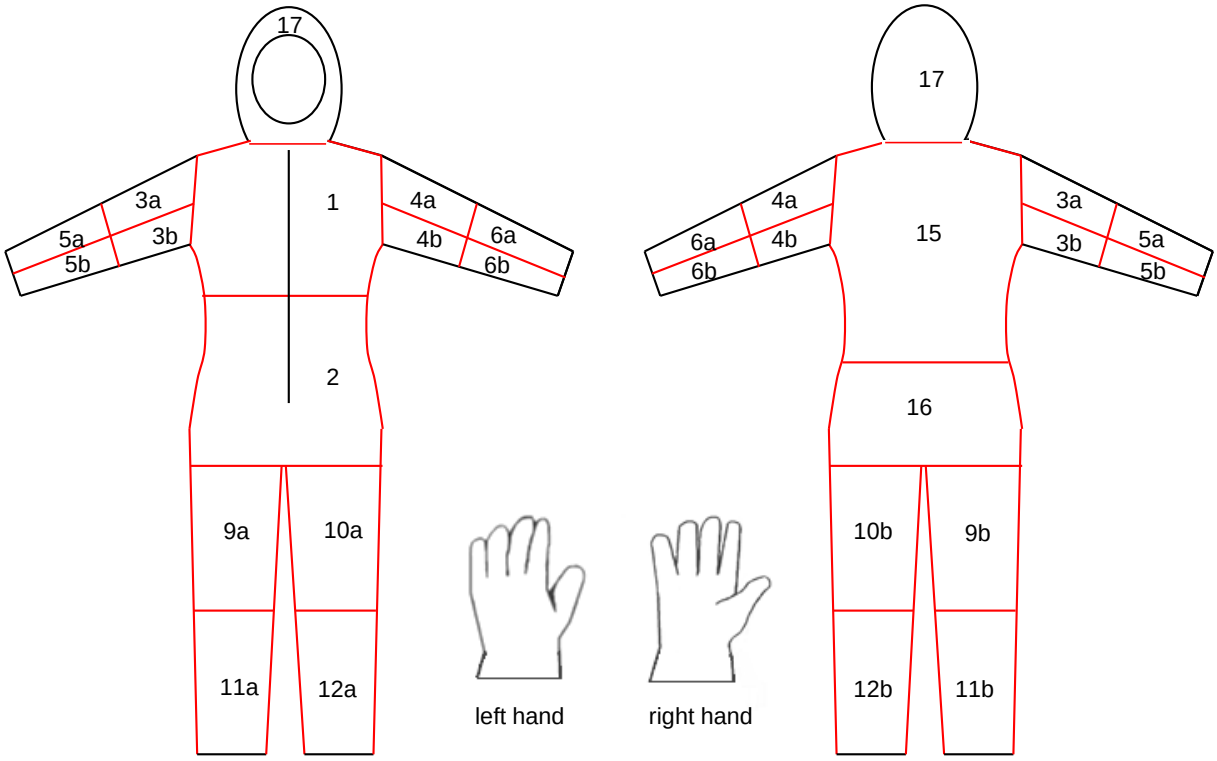

Fig. 3.24 Cutting pattern for the segmentation of the dermal samplers; the cutting pattern is marked in red and the numbering of the individual segments is provided.

The dermal exposure was measured separately for the following tasks: weighing out and portioning of the Dimilin™ 80 WG, preparation and/or application of the Dimilin™ 80 WG suspension with vehicle-mounted sprayer, preparation/transfer and application of the Dimilin™ 80 WG suspension with hand-held sprayer, and cleaning of the vehicles/ vehicle-mounted sprayers at the end of the spray season. A total of 51 coveralls and 85 pairs of gloves were obtained from eight participants. An overview of the measurements carried out is given in Tab. 3.1.

Tab. 3.1 Overview of the coveralls and gloves collected during the field studies to determine the workers' dermal exposure.

Sprayer	Task	Number of coveralls	Number of the pairs of gloves
---	Weighing out and portioning of Dimilin™ 80 WG	2	2
Vehicle-mounted sprayer	Preparation of the Dimilin™ 80 WG suspension	10	12
	Application of the Dimilin™ 80 WG suspension	12	15
	Preparation and application of the Dimilin™ 80 WG suspension	6	10
Hand-held sprayer	Preparation and application of the Dimilin™ 80 WG suspension	8	9
	Transfer and application of the Dimilin™ 80 WG suspension	10	34
---	Cleaning of the vehicle/ vehicle-mounted sprayer	3	3

It can be seen from Tab. 3.1 that, with some tasks, far more pairs of gloves than coveralls were collected and analysed. This is due to the fact that the gloves have been changed several times during some measurements. On the one hand, the gloves were changed when they had become wet and unpleasant to wear for the workers, on the other hand this was in order to determine the exposure of the hands in more detail for certain tasks.
Thus, for example, during the 2015 measurement period, four pairs of gloves were collected with each coverall during work with the hand-held sprayer. Here, the coveralls were worn during two application cycles, thus measuring in each case two times the transfer of the spray liquid and two times the application of a full tank. In contrast, the gloves were changed before each of these two tasks. Transfer and application procedures were thus recorded separately for the gloves. In the 2014 field study on the other hand, preparation and application or transfer and application were always measured together. The worker wore one coverall and one pair of gloves as dermal sampler for the entire work process.
In addition, in the 2015 measurement period, in working with the vehicle-mounted unit, dermal exposure was sampled separately for preparation and application, i.e., coverall and gloves were changed after preparation of the spray liquid. On the other hand, during the 2014 field study, dermal exposure was mostly recorded together for preparation and application of the spray liquid with the vehicle-mounted unit. The aim of the separate measurement of the individual tasks was to quantify the proportion of “preparation of the spray liquid” as well as of “application of the spray liquid” phases and to enable their assessment.

3.3.1.2 Inhalation exposure

Sampling to determine inhalation exposure was carried out both by personal air sampling and by stationary air sampling in the working environment of the employees. Ideally, inhalation exposure of the workers was to be recorded separately during the individual tasks (weighing out and portioning, preparation, application, cleaning). However such a separate determination of the inhalation exposure during preparation or application of the spray liquid with the vehicle-mounted unit was technically not possible, due to the short duration of the preparation step, taking less than five minutes. The reason for this lies in the quantification limit of the analytical method used for the active substance.
In the measurement period in 2014, preparation and application of the spray liquid from the vehicle-mounted unit were measured together (sampling point 1). In 2015, however, sampling point 1 was divided into two separate measurements in order to differentiate between the two tasks (preparation and application, respectively).
In one measurement, the inhalation exposure of the worker during preparation and application was recorded (cumulative measurement), in the other measurement only the exposure in the driver’s cabin during biocide application. Assuming that the separate measurements were carried out under identical external conditions, a subtraction of the second measurement from the first cumulative measurement should allow a statement to be made on exposure during preparation of the spray liquid.

The duration of the measurements was linked up with the quantity of spray liquid (tank contents) or with the duration of the respective task. Due to the given quantification limit, samples were taken for at least 15 min. With this minimum

sampling time, the conditions for an adequate analytical method according to EN 482 were fulfilled for the selected volume flow of the sampling pumps. In particular, the measuring range of the sampling method covers at least concentrations between the 0.1- and the 2-fold of the limit value with this measuring time.

For the different application sites, the following sampling points (SPs) were selected to determine the inhalation exposure of the workers:

- SP 1 personal sampling (p) sampling device attached to the worker (vehicle-mounted sprayer)
- SP 1a personal sampling (p) (preparation and application of the spray liquid)
- SP 1b stationary sampling (s) in the driver's cabin of the vehicle-mounted sprayer (application of the spray liquid)
- SP 2 personal sampling (p) sampling device attached to the worker (hand-held sprayer)
- SP 3 stationary sampling (s) directly on vehicle-mounted sprayer (*worst-case*)
- SP 6 personal sampling (p) during weighing out and portioning of the biocide
- SP 7 stationary sampling (s) during weighing out and portioning of the biocide
- SP 8 personal sampling (p) during cleaning procedures
- SP 9 stationary sampling (s) front right when cleaning the equipment
- SP 10 stationary sampling (s) rear right when cleaning the equipment
- SP 11 stationary sampling (s) centre left when cleaning the equipment

An overview of the number of measurements carried out is given in Tab. 3.2.

Tab. 3.2 Overview of the samples collected during the field studies to determine the workers' inhalation exposure.

Sprayer	Activity	Sampling point	Number of measurements
---	Weighing out and portioning of Dimilin™ 80 WG	SP 6	2
		SP 7	2
Vehicle-mounted sprayer	Preparation and application of the Dimilin™ 80 WG suspension	SP 1 SP 1a	6 10
	Application of the Dimilin™ 80 WG suspension	SP 1b	12
		SP 3	3
	Preparation of the Dimilin™ 80 WG suspension	theoretical assumption (SP 1a -SP 1b)	---
Hand-held sprayer	Preparation and application of the Dimilin™ 80 WG suspension	SP 2	8
	Transfer and application of the Dimilin™ 80 WG suspension	SP 2	10
---	Cleaning of the vehicle/ vehicle-mounted sprayer	SP 8	3
		SP 9	3
		SP 10	3
		SP 11	3

The particles were retained on glass-fibre filters as inhalable dust fraction (MN 85/70 ø 37 mm; organic binder). As air sampler pumps, either type SG 10/2 with 10 L/min or the VC 25 with 22.5 m³/h were used. After sampling, the charged sampling tubes were wrapped in aluminium foil to protect them from light.

On all measurement days, the weather conditions at the workplaces were also recorded. Temperature, air humidity and where necessary air flow were determined using a multifunction anemometer (Testotherm). Atmospheric pressure was measured using a DVR 2 (Vaccubrand) unit. The recorded weather data will not be individually mentioned in this report.

3.3.2 Bystanders

3.3.2.1 Dermal exposure

The dermal exposure of bystanders was determined by measurements taken during application of the Dimilin™ 80 WG suspension. Sampling was performed for both Dimilin™ 80 WG application with vehicle-mounted unit and application with a hand-held sprayer. For organisational reasons, sampling to investigate the exposure of bystanders only took place with companies A and B.

As sampler for the exposure of bystanders a cut square section of Tyvek™ fabric (1.75 m²; 1.90 x 0.92 m) representing the body surface of an adult was used. A rack frame to fix the Tyvek™ sheets was constructed using 2.3 cm rectangular aluminium hollow section. The rack frame could easily be taken apart for transport, due to plastic joints. Both the aluminium sections and the plastic joints could easily be cleaned on site, thus avoiding cross-contaminations. To secure the rack frames particularly where powerful sprayers were used for application, they were hold down with sand sacks and additionally fixed with guy ropes. The frame constructions were chosen with respect to their practicability for the field trial but can be considered only as a surrogate for “real” bystander exposure.

Fig. 3.25 gives a blue print of the rack frame, Fig. 3.26 shows the measurement set up during the 2015 field study. The Tyvek™ sheets attached to the rack frames, insofar as possible due to on-site conditions, were located downwind, at distances of 5 m and 10 m from the treated tree or group of trees. The minimum sampling time was 15 min so that possible spray drift after application was also recorded.

During the field studies measurements were carried out at 30 application sites, positioned at distances of 5 m and 10 m, which means that a total of 60 Tyvek™ sheets were collected (Tab. 3.3). After sampling, the Tyvek™ sheets were cut at a height of 1.00 m in order to assess the determined exposure of small children and adults separately. The potential exposure of a small child was calculated from the amount of diflubenzuron deposited on the lower segment of the Tyvek™ sheet, the potential exposure of an adult from the amount of diflubenzuron deposited on both Tyvek™ segments. In Fig. 3.27, the Tyvek™ sheet cut at a height of 1 m can easily be seen.

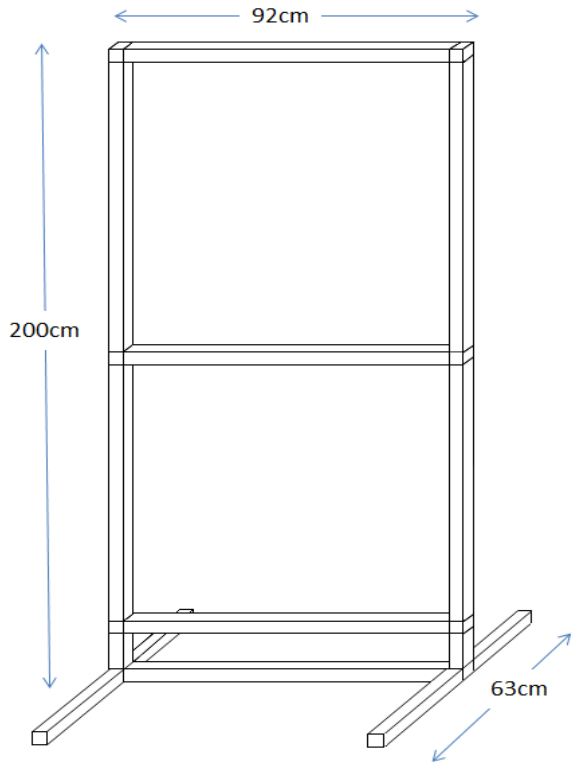

Fig. 3.25 Blue print of the rack frame used for the measurement of bystander exposure.

Fig. 3.26 Set-up to measure the dermal and inhalation exposure of bystanders during the 2015 field study.

Fig. 3.27 Removal of a cut Tyvek^{TM} sheet from the rack frame during the 2014 field study.

Tab. 3.3 Overview of the Tyvek^{TM} sheets collected during the field studies to determine the bystanders' dermal exposure.

Sprayer	Task	Number of Tyvek^{TM} sheets (5 m)	Number of Tyvek^{TM} sheets (10 m)
Vehicle-mounted sprayer-	Application of the Dimilin^{TM} 80 WG suspension	15	15
Hand-held sprayer	Application of the Dimilin^{TM} 80 WG suspension	15	15

The Tyvek^{TM} sheets were cut up after sampling (Fig. 3.27), folded up with the contaminated side inside, wrapped airtight and lightproof in aluminium foil and stored in a sealable PE bag inside a portable cooler box at 4 °C. Thus cooled, the samples were transported to the laboratory and stored in a freezer at -20 °C prior to work up. For processing, the folded Tyvek^{TM} sheets were cut up into approximately eight strips which were then put into one litre screwcap bottles using tweezers. The four segments of one measurement were processed simultaneously.
Fig. 3.28, Fig. 3.29 and Fig. 3.30 show the measurements carried out to determine bystanders` exposure during Dimilin^{TM} 80 WG application. The abbreviated designations of the individual measurements used in the captions are explained in Section 3.2 and the corresponding tasks are described in detail in Annex 2.

Fig. 3.28 Determination of bystanders` exposure during biocide application with vehicle-mounted sprayer. The picture shows the sampling VMS-application-dB-10 and VMS-application-iB-10 (company A).

Fig. 3.29 Determination of bystanders` exposure during biocide application with hand-held sprayer. The picture shows the sampling HHS-application-dB-8 and HHS-application-iB-8 (company A).

Fig. 3.30 Determination of bystander exposure during biocide application using a hand-held sprayer. The picture shows the sampling HHS-application-dB-11 and HHS-application-iB-11 (company A).

3.3.2.2 Inhalation exposure

The inhalation exposure of bystanders was recorded by stationary measurements only. The sampling devices were positioned downwind – where the terrain allows - at average adult breathing zone height (approximately 1.50 m). Sampling was carried out directly to the right or left of measurement set up for dermal exposure (see sampling tripod in Fig. 3.26).

Due to the quantification limit (see Section 3.3.1.2) the measurement had to last for at least 15 min. As a result of this minimum sampling time it was also possible to record any drift after spraying.

The following sampling points were selected at each application site:

- SP 4 stationary (s) at a distance of 5 m from the tree/tree row
- SP 5 stationary (s) at a distance of 10 m from the tree/tree row

The number and type of measurements of inhalation exposure is identical with the number of measurements of dermal exposure. The inhalation and dermal exposure of bystanders was always determined simultaneously (Tab. 3.3).

The particles were deposited in the form of an inhalable dust fraction on glass-fibre filters (ø 37 mm; organic binder). Air sampler pumps of the type SG 10/2 with 10 L/min were used. After sampling, the charged sampling tubes were wrapped in aluminium foil to protect them from light.

On all measurement days, the weather conditions at the measurement sites were also recorded. Temperature, air humidity and, where necessary, air velocity were determined with a multifunction anemometer (Testotherm). Atmospheric pressure was measured using a DVR 2 (Vaccubrand) unit. The recorded weather data will not be individually mentioned in this report.

3.4 Sample work up and analysis

3.4.1 Dermal exposure

3.4.1.1 Sample work up

Work up of the dermal samplers was carried out according to a standard operating procedure. Each segment of the Tyvek™ sheet was extracted with 500 mL acetone and the individual gloves with 100 mL acetone. In the case of the coverall segments, the solvent volume used for extraction was adapted to the material quantity. Up to 4 g Tyvek™ fabric was extracted with 50 mL acetone, 4-6 g Tyvek™ fabric with 100 mL, 6-12 g Tyvek™ fabric with 200 mL and more than 12 g Tyvek™ fabric with 250 mL. After extraction, 1 mL of the acetonic extract was transferred to a vial and 50 µg/L internal standard (see sections 3.4.1.2 and 3.4.1.3) was added. The sample was evaporated to dryness under a stream of nitrogen and the residue was resuspended in 1 mL toluene. The sample was subsequently filtered using a 1 µm syringe filter and the diflubenzuron concentration of the sample quantified using GC-PCI-MS. Insofar as a dilution of the extracts was necessary, 100 µL and 10 µL of the acetonic extract were used for this purpose resulting in a 1:10 and 1:100 dilution, respectively.

Simultaneously to each work up, unexposed Tyvek™ or cotton material was used to determine blank values and reagent blanks were also included. Solvents, chemicals, Tyvek™ and cotton material were free from the investigated diflubenzuron.

3.4.1.2 Equipment and chemicals

To determine diflubenzuron, a 7890A gas chromatograph with autosampler and 5975C mass spectrometer (Agilent Technologies) was used. The column was an Optima-35 MS-0.25 µm (60 m x 0.25 mm ID; Macherey Nagel). Helium 5.0 was used as carrier gas with a flow rate of 1.2 mL/min.

The temperature programme for the GC column oven was as follows: initial temperature 60 °C for 1.5 min, increase at 15 °C/min to 240 °C, increase at 35 °C/min to 300 °C, 5 min at 300 °C. The injector temperature was 280 °C and the detector temperature 300 °C. A 1 µL sample each was injected for analysis.
Diflubenzuron (Dr. Ehrenstorfer; Germany) was used as standard. A fourfold deuterated diflubenzuron (CDN Isotopes, Canada) was used as internal standard. The Dimilin™ 80 WG was provided by Spiess-Urania Chemicals GmbH. The stock solutions of the standards were prepared in toluene, working solutions and calibration standards diluted in toluene.

The solvents used were of p.a. quality (Merck, Germany).

3.4.1.3 Analytical method

For analysis, the method of WIMMER and SMITH (1991) was further developed. The diflubenzuron was quantified by GC-PCI-MS using a deuterated internal standard. Thereby, diflubenzuron formed three degradation products after thermodegradation: 4-chlorophenyl isocyanate, 4-chloroaniline and 2,6-difluorobenzamide. Due to the

deuterisation pattern of the internal standard two deuterated and one non-deuterated degradation product were obtained by thermic degradation, so that both the 4-chlorophenyl isocyanate and the 4-chloroaniline peak, but not the 2,6-difluorobenzamide peak, were used for quantification of the diflubenzuron content. The evaluation of the 4-chlorophenyl isocyanate peak in accordance with DIN 32645 (2008) enabled the quantification of diflubenzuron with a quantification limit of 1.79 µg/L.

3.4.2 Inhalation exposure

3.4.2.1 Sample work up

The samples packed lightproof in aluminium foil were processed following each measurement period in the laboratory of the BAuA.

For sample work up, the filters were overlaid with 5 mL acetonitrile as extraction agent. The sample container was sealed and shaken on a shaking platform for 30 min. Using a disposable syringe, an aliquot of the solvent was filtered (CHROMAFIL 0-45/15MS disposable filter) and transferred into an autosampler vial.

Simultaneously to each test series, blank filters were included. Solvents, chemicals and filters were free of diflubenzuron.

3.4.2.2 Equipment and chemicals

Determination of the diflubenzuron was carried out using a high-performance liquid chromatograph with autosampler and UV detector manufactured by Knauer or Shimdazu. A ChromCart Nucleosil 100-5 C18 column (250 x 3 mm; 5 µm) of Macherey Nagel was used. As solvent, a mixture of acetonitrile in ultrapure water was used.

Dimilin^{TM} 80 WG in the form of an aqueous suspension in acetonitrile was used as external calibration standard. The Dimilin^{TM} 80 WG was provided by Spiess-Urania Chemicals GmbH. The stock solution of the standard compound was prepared with ultrapure water, working solutions and calibration standards were diluted in acetonitrile.

The used solvents had ROTISOLV^{TM} HPLC Ultra Gradient Grade quality (Carl Roth GmbH & Co. KG, Germany). The ultrapure water had Milli-Q^{TM} quality.

3.4.2.3 Analytical method

The diflubenzuron content in the samples was determined via isocratic separation. Separation was carried out using isocratic elution with acetonitrile in ultrapure water (65/35 volume %) at a flow of 0.35 mL/min at 25 °C (detection wavelength: 260 nm; analysis time: 20 min). A 10 µL sample each was injected for analysis.
The analytical quantification limits were 34 µg/L (Knauer unit) and 52 µg/L (Shimadzu unit), respectively. Quantitative evaluation of the chromatograms was computer-assisted using a calibration function.

3.5 Overview of the collected samples

Both in the text and in the tables, the dermal samples and the air samples were uniformly designated by abbreviations. The sample identifiers are made up from the abbreviated name of the task and a combination of letters assigned to them, making it possible to identify the type of sampling (dermal or inhalation) as well as the sampling media involved (coverall/ gloves/ bystander and personal sampling/ stationary sampling/ bystander). The samples collected during the separate tasks were consecutively numbered. Tab. 3.4 and Tab. 3.5 provide an overview of this method to designate the samples.
Thus, for example, the second measurement of dermal exposure carried out when weighing out and portioning Dimilin™ 80 WG granules using gloves as dermal sampler is designated “weighing-dH-2”; the fourth personal sampling of inhalation exposure when preparing and applying the Dimilin™ 80 WG suspension with a hand-held sprayer is designated “HHS-preparation-application-ip-4”; the sixth measurement of dermal exposure of bystanders during application of Dimilin™ 80 WG suspension with a vehicle-mounted sprayer is designated “VMS-application dB-6”.

Tab. 3.4 Overview of the sample identifier (task).

Task	**Concise designation of the task**
Weighing out and portioning of the Dimilin™ 80 WG	Weighing
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation-application
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation-application
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer-application
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning

Tab. 3.5 Overview of the sample identifier (sampling and samplers).

Type of sampling	**Type of sampling Abbreviation**	**Sampler**	**Sampler Abbreviation**	**Sample identifier**
dermal	d	Coverall	O-	dO-
		Gloves	G-	dG-
		Bystander	B-	dB-
inhalation	i	personal measurement	p-	ip-
		stationary measurement	s-	is-
		Bystander	B-	iB-

3.5.1 Workers

3.5.1.1 Dermal exposure

Tab. 3.6 presents in tabular form the coveralls and gloves collected to determine dermal exposure including the task, sample identifier, worker, spray unit, sampling time and the amount of active substance used. The tasks performed by the workers and variations during sampling possibly important for exposure assessment are detailed in text form in Section 3.2 or listed in Annex 1. In this presentation, the sequence listed in Tab. 3.6 was adhered to. An overview of the different measurement series can be found in Tab. 1 in Annex 1. Here, each collected coverall is unambiguously assigned to the corresponding gloves and air samples.

3.5.1.2 Inhalation exposure

A detailed description of the samples collected to determine inhalation exposure is shown in Tab. 3.7 including the task, sample identifier (sampling point, type of measurement, pump used and sampling time), worker, spray unit as well as the applied/handled amount of active substance. In Section 3.2 or in Annex 1, the tasks of the workers and, where necessary, details important for the assessment of exposure during sampling are provided in a tabular overview (Annex 1, Tab. 1) as well as in text form. Both in the description of activities during sampling and in the tabular overview, the samples of the air sampling have been assigned to the collected coveralls and gloves. Where no assignment was possible, the samples are listed separately in Annex 1.

3.5.2 Bystanders

3.5.2.1 Dermal and inhalation exposure

A detailed overview of the measurements of dermal and inhalation exposure of bystanders, quoting sample identifier, sampling time, the year, the company, the worker as well as the spray unit used, is given in Tab. 3.8 and Tab. 3.9, respectively.

Tab. 3.6 Detailed overview of the coveralls and gloves collected during the field studies to determine workers' dermal exposure.

Task	Sample identifier					Worker	Sprayer	Applied Dimilin™ 80 WG-suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Coverall	Sampling time [min]	Gloves -	Sampling time [min]					
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dO-1	65	dG-1	65	5	--	--	--	16000
		dO-2	37	dG-2	37	1	--	--	--	8000
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS - preparation	dO-1	3	dG-1	3	1	Dragone AZ 800 L	800	0.3	192
		dO-2	3	dG-2	3	2	Dragone AZ 1000 L	1000	0.3	240
		dO-3	3	dG-3	3	2	Dragone AZ 1000 L	1000	0.3	240
		dO-4	4	dG-4	4	2	Dragone AZ 1000 L	1000	0.3	240
		dO-5	7	dG-5	7	2	Dragone AZ 1000 L	1000	0.3	240
		dO-6	5	dG-6	5	2	Dragone AZ 1000 L	1000	0.3	240
		dO-7	5	dG-7	5	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-8	5	dG-8	5	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-9	7	dG-9	7	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-10	5	dG-10	5	6	Vicar Turbine 451 300 L	300	0.42	100
		--	--	dG-11	5	1	Dragone AZ 800 L	--	--	192
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application-	dO-1	261	dG-1.1 dG-1.2	64 197	1	Dragone AZ 800 L	800	0.3	192
		dO-2	90	dG-2.1 dG-2.2	59 31	4	Dragone AZ 800 L	800	0.3125	200
		dO-3	63	dG-3	63	1	Dragone AZ 800 L	800	0.3	192

Tab. 3.6 (continued)

Task	Sample identifier					Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Coverall	Sampling time [min]	Gloves	Sampling time [min]					
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG-suspension	VMS-application	dO-4	129	dG-4	129	2	Dragone AZ 1000 L	1000	0.3	240
		dO-5	156	dG-5	156	2	Dragone AZ 1000 L	1000	0.3	240
		dO-6	127	dG-6.1 dG-6.2	52 75	2	Dragone AZ 1000 L	1000	0.3	240
		dO-7	118	dG-7	118	2	Dragone AZ 1000 L	1000	0.3	240
		dO-8	146	dG-8	146	2	Dragone AZ 1000 L	1000	0.3	240
		dO-9	106	dG-9	106	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-10	74	dG-10	74	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-11	95	dG-11	95	6	Vicar Turbine 451 300 L	300	0.42	100
		dO-12	62	dG-12	62	6	Vicar Turbine 451 300 L	300	0.42	100
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG-suspension	VMS-preparation application	dO-1	163	dG-1.1 dG-1.2 dG-1.3	6 17 137	1	Dragone AZ 800 L	800	0.3	192
		dO-2	174	dG-2.1 dG-2.2	9 160	1	Dragone AZ 800 L	800	0.3	192
		dO-3	117	dG-3	117	1	Dragone AZ 800 L	800	0.3	192
		dO-4	146	dG-4	146	1	Dragone AZ 800 L	800	0.3	192
		dO-5	124	dG-5[a]	14	2	Dragone AZ 1000 L	400	0.3	96
		dO-6	95	dG-6.1 dG-6.2 dG-6.3	18 46 30	3	Dragone AZ 800 L	800	0.3125	200

Tab. 3.6 (continued)

Task	Sample identifier					Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Coverall	Sampling time [min]	Gloves	Sampling time [min]					
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	37	dG-1.1 dG-1.2	6 31	2	Solo Port 423	7	0.3	1.68
		dO-2	24	dG-2	24	2	Solo Port 423	24	0.3	5.76
		dO-3	23	dG-3	23	2	Solo Port 423	24	0.3	5.76
		dO-4	26	dG-4	26	2	Solo Port 423	24	0.3	5.76
		dO-5	28	dG-5	28	2	Solo Port 423	24	0.3	5.76
		dO-6	52	dG-6	52	5	Solo Port 423	18	0.3	4.32
		dO-7	39	dG-7	39	5	Solo Port 423	21	0.3	5.04
		dO-8	26	dG-8	26	5	Solo Port 423	24	0.3	5.76
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	dO-1	32	dG-1	32	5	Solo Port 423	24	0.3	5.76
		dO-2	28	dG-2	28	5	Solo Port 423	24	0.3	5.76
		dO-3	45	dG-3.1 dG-3.2 dG-3.3 dG-3.4	9 15 3 15	5	Solo Port 423	24	0.3	5.76
		dO-4	27	dG-4.1 dG-4.2 dG-4.3 dG-4.4	3 12 2 8	5	Solo Port 423	24	0.3	5.76
		dO-5	23	dG-5.1 dG-5.2 dG-5.3 dG-5.4	3 10 2 10	5	Solo Port 423	24	0.3	5.76

Tab. 3.6 (continued)

Task	Sample identifier					Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Coverall	Sampling time [min]	Gloves	Sampling time [min]					
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG-suspension	HHS-transfer application	dO-6	23	dG-6.1 dG-6.2 dG-6.3 dG-6.4	2 8 2 10	5	Solo Port 423	22	0.3	5.28
		dO-7	23	dG-7.1 dG-7.2 dG-7.3 dG-7.4	2 8 2 9	5	Solo Port 423	24	0.3	5.76
		dO-8	36	dG-8.1 dG-8.2 dG-8.3 dG-8.4	1 10 2 17	5	Solo Port 423	24	0.3	5.76
		dO-9	33	dG-9.1 dG-9.2 dG-9.3 dG-9.4	2 19 2 10	5	Solo Port 423	24	0.3	5.76
		dO-10	32	dG-10.1 dG-10.2 dG-10.3 dG-10.4	4 13 3 9	5	Solo Port 423	24	0.3	5.76
Cleaning procedures Vehicle/ Vehicle-mounted sprayer	Cleaning	dO-1	55	dG-1	55	1	Dragone AZ 800 L/1000 L	1 vehicle/ 2 vehicle-mounted sprayers		
		dO-2	7	dG-2	7	7	Vicar Turbine 451 300 L	1 vehicle/ 1 vehicle-mounted sprayer		
		dO-3	40	dG-3	40	8	Dragone AZ 1000 L	1 vehicle/ 1 vehicle-mounted sprayer		

[a]: The gloves VMS-preparation-application-dG-5 were only worn when preparing the Dimilin™ 80 WG suspension.

Tab. 3.7 Detailed overview of the samples collected during the field studies to determine workers' inhalation exposure.

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Measurement point		Type of measure-ment	Volume flow [L/min]	Sampling time [min]					
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	ip-1	6	p	10	63	5	--	--	--	16000
		is-1	7	s	22.5 m³/h	63	--	--	--	--	16000
		ip-2	6	p	10	39	1	--	--	--	8000
		is-2	7	s	22.5 m³/h	39	--	--	--	--	8000
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	ip-1	1	p	10	154	1	Dragone AZ 800 L	800	0.3	192
		ip-2	1	p	10	175	1	Dragone AZ 800 L	800	0.3	192
		ip-3	1	p	10	116	1	Dragone AZ 800 L	800	0.3	192
		ip-4	1	p	10	147	1	Dragone AZ 800 L	800	0.3	192
		ip-5	1	p	10	119	2	Dragone AZ 1000 L	400	0.3	96
		ip-6	1	p	10	87	3	Dragone AZ 800 L	800	0.3125	200
		ip-7	1a	p	10	69 (4)*	1	Dragone AZ 800 L	800	0.3	192
		ip-8	1a	p	10	127 (3)*	2	Dragone AZ 1000 L	1000	0.3	240
		ip-9	1a	p	10	160 (8)*	2	Dragone AZ 1000 L	1000	0.3	240
		ip-10	1a	p	10	131 (4)*	2	Dragone AZ 1000 L	1000	0.3	240
		ip-11	1a	p	10	109 (2)*	2	Dragone AZ 1000 L	1000	0.3	240
		ip-12	1a	p	10	69 (2)*	2	Dragone AZ 1000 L	1000	0.3	240

Tab. 3.7 (continued)

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Measurement point		Type of measurement	Volume flow [L/min]	Sampling time [min]					
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	ip-13	1a	p	10	74 (4)*	6	Vicar Turbine 451 300 L	300	0.42	100
		ip-14	1a	p	10	84 (5)*	6	Vicar Turbine 451 300 L	300	0.42	100
		ip-15	1a	p	10	104 (6)*	6	Vicar Turbine 451 300 L	300	0.42	100
		ip-16	1a	p	10	68 (6)*	6	Vicar Turbine 451 300 L	300	0.42	100
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	is-1	3	s	10	25	--	Dragone AZ 800 L	800	0.3	192
		is-2	3	s	10	109	--	Dragone AZ 800 L	800	0.3	192
		is-3	3	s	10	140	--	Dragone AZ 800 L	800	0.3	192
		ip-1	1	p	10	257	1	Dragone AZ 800 L	800	0.3	192
		ip-2	1	p	10	87	4	Dragone AZ 800 L	800	0.3125	200
		is-4	1b	s	10	65	1	Dragone AZ 800 L	800	0.3	192
		is-5	1b	s	10	124	2	Dragone AZ 1000 L	1000	0.3	240
		is-6	1b	s	10	152	2	Dragone AZ 1000 L	1000	0.3	240
		is-7	1b	s	10	127	2	Dragone AZ 1000 L	1000	0.3	240
		is-8	1b	s	10	107	2	Dragone AZ 1000 L	1000	0.3	240
		is-9	1b	s	10	147	2	Dragone AZ 1000 L	1000	0.3	240
		is-10	1b	s	10	70	6	Vicar Turbine 451 300 L	300	0.42	100

Tab. 3.7 (continued)

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Measurement point		Type of measurement	Volume flow [L/min]	Sampling time [min]					
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	is-11	1b	s	10	79	6	Vicar Turbine 451 300 L	300	0.42	100
		is-12	1b	s	10	98	6	Vicar Turbine 451 300 L	300	0.42	100
		is-13	1b	s	10	62	6	Vicar Turbine 451 300 L	300	0.42	100
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS preparation application	ip-1	2	p	10	39	2	Solo Port 423	7	0.3	1.68
		ip-2	2	p	10	23	2	Solo Port 423	24	0.3	5.76
		ip-3	2	p	10	22	2	Solo Port 423	24	0.3	5.76
		ip-4	2	p	10	26	2	Solo Port 423	24	0.3	5.76
		ip-5	2	p	10	27	2	Solo Port 423	24	0.3	5.76
		ip-6	2	p	10	50	5	Solo Port 423	18	0.3	4.32
		ip-7	2	p	10	26	5	Solo Port 423	21	0.3	5.04
		ip-8	2	p	10	24	5	Solo Port 423	24	0.3	5.76
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	ip-1	2	p	10	31	5	Solo Port 423	24	0.3	5.76
		ip-2	2	p	10	26	5	Solo Port 423	24	0.3	5.76
		ip-3	2	p	10	27	5	Solo Port 423	24	0.3	5.76
		ip-4	2	p	10	22	5	Solo Port 423	24	0.3	5.76
		ip-5	2	p	10	20	5	Solo Port 423	24	0.3	5.76
		ip-6	2	p	10	21	5	Solo Port 423	22	0.3	5.28

Tab. 3.7 (continued)

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Measurement point		Type of measurement	Volume flow [L/min]	Sampling time [min]					
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	ip-7	2	p	10	21	5	Solo Port 423	24	0.3	5.76
		ip-8	2	p	10	28	5	Solo Port 423	24	0.3	5.76
		ip-9	2	p	10	28	5	Solo Port 423	24	0.3	5.76
		ip-10	2	p	10	32	5	Solo Port 423	24	0.3	5.76
Cleaning procedures Vehicle/ vehicle-mounted sprayer Cleaning procedures Vehicle/vehicle-mounted sprayer	Cleaning	ip-1	8	p	10	54	1	Dragone AZ 800 L/1000 L	1 vehicle/ 2 vehicle-mounted sprayers		
		is-1	9	s	10	53	--	Dragone AZ 800 L/1000 L			
		is-2	10	s	10	53	--	Dragone AZ 800 L/1000 L			
		is-3	11	s	10	53	--	Dragone AZ 800 L/1000 L			
Cleaning procedures Vehicle / vehicle-mounted sprayer Cleaning procedures Vehicle / vehicle-mounted sprayer	Cleaning	ip-2	8	p	10	7	7	Vicar Turbine 451 300 L	1 vehicle/ 1 vehicle-mounted sprayer		
		is-4	9	s	10	7	--	Vicar Turbine 451 300 L			
		is-5	10	s	10	7	--	Vicar Turbine 451 300 L			
		is-6	11	s	10	7	--	Vicar Turbine 451 300 L			
		ip-3	8	p	10	43	8	Dragone AZ 1000 L	1 vehicle/ 1 vehicle-mounted sprayer		
		is-7	9	s	10	40	--	Dragone AZ 1000 L			
		is-8	10	s	10	40	--	Dragone AZ 1000 L			
		is-9	11	s	10	40	--	Dragone AZ 1000 L			

* The sampling time given in brackets corresponds to the time required for the task “Preparation of the Dimilin™ 80 WG suspension”.

Tab. 3.8 Detailed overview of the Tyvek™ sheets collected during the field studies to determine bystanders' dermal exposure.

Task	Sample identifier		Sampling time [min]	Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Bystander						
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dB-1	17	1	Dragone AZ 800 L	24*	0.3	5.76
		dB-2	15	1	Dragone AZ 800 L	24*	0.3	5.76
		dB-3	15	1	Dragone AZ 800 L	48*	0.3	11.5
		dB-4	15	1	Dragone AZ 800 L	48*	0.3	11.5
		dB-5	15	1	Dragone AZ 800 L	24*	0.3	5.76
		dB-6	55	3	Dragone AZ 800 L	48*	0.3	11.5
		dB-7	29	1	Dragone AZ 800 L	24*	0.3	5.76
		dB-8	15	1	Dragone AZ 800 L	24*	0.3	5.76
		dB-9	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		dB-10	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		dB-11	15	2	Dragone AZ 1000 L	48*	0.3	11.5
		dB-12	16	2	Dragone AZ 1000 L	48*	0.3	11.5
		dB-13	16	2	Dragone AZ 1000 L	48*	0.3	11.5
		dB-14	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		dB-15	15	1	Dragone AZ 800 L	72*	0.3	17.3

Tab. 3.8 (continued)

Task	Sample identifier		Sampling time [min]	Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier	Bystander						
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	HHS-application	dB-1	30	2	Solo Port 423	7	0.3	1.68
		dB-2	52	2	Solo Port 423	48	0.3	11.52
		dB-3	16	2	Solo Port 423	24	0.3	5.76
		dB-4	15	5	Solo Port 423	12	0.3	2.88
		dB-5	15	5	Solo Port 423	12	0.3	2.88
		dB-6	53	5	Solo Port 423	45	0.3	10.8
		dB-7	30	5	Solo Port 423	24	0.3	5.76
		dB-8	15	5	Solo Port 423	12	0.3	2.88
		dB-9	27	5	Solo Port 423	24	0.3	5.76
		dB-10	24	5	Solo Port 423	24	0.3	5.76
		dB-11	17	5	Solo Port 423	12	0.3	2.88
		dB-12	21	5	Solo Port 423	24	0.3	5.76
		dB-13	15	5	Solo Port 423	12	0.3	2.88
		dB-14	29	5	Solo Port 423	24	0.3	5.76
		dB-15	30	5	Solo Port 423	24	0.3	5.76

* For the vehicle-mounted sprayer it is assumed that 24 L of the spray liquid were applied in the immediate vicinity of the set-up of the measuring equipment each time the vehicle-mounted unit drove past (for more detailed information, see **Section 4.2.1**). For the hand-held sprayer, the entire volume of the spray liquid applied during the individual measurement was considered to be relevant.

Tab. 3.9 Detailed overview of the samples collected during the field studies to determine bystanders' inhalation exposure.

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier		Measure-ment point	Type of measure-ment	Volume flow [L/min]	Sampling time [min]					
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	iB-1	4+5	s	10	17	1	Dragone AZ 800 L	24*	0.3	5.76
		iB-2	4+5	s	10	15	1	Dragone AZ 800 L	24*	0.3	5.76
		iB-3	4+5	s	10	15	1	Dragone AZ 800 L	48*	0.3	11.5*
		iB-4	4+5	s	10	15	1	Dragone AZ 800 L	48*	0.3	11.5
		iB-5	4+5	s	10	15	1	Dragone AZ 800 L	24*	0.3	5.76
		iB-6	4+5	s	10	55	3	Dragone AZ 800 L	48*	0.3	11.5
		iB-7	4+5	s	10	29	1	Dragone AZ 800 L	24*	0.3	5.76
		iB-8	4+5	s	10	15	1	Dragone AZ 800 L	24*	0.3	5.76
		iB-9	4+5	s	10	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		iB-10	4+5	s	10	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		iB-11	4+5	s	10	15	2	Dragone AZ 1000 L	48*	0.3	11.5
		iB-12	4+5	s	10	16	2	Dragone AZ 1000 L	48*	0.3	11.5
		iB-13	4+5	s	10	16	2	Dragone AZ 1000 L	48*	0.3	11.5
		iB-14	4+5	s	10	15	2	Dragone AZ 1000 L	24*	0.3	5.76
		iB-15	4+5	s	10	22	1	Dragone AZ 800 L	72*	0.3	17.3

Tab. 3.9 (continued)

Task	Sample identifier						Worker	Sprayer	Applied Dimilin™ 80 WG suspension [L]	Concentration of the Dimilin™ 80 WG suspension [g/L]	Applied amount of active substance [g]
	Task identifier		Measurement point	Type of measurement	Volume flow [L/min]	Sampling time [min]					
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	HHS-application	iB-1	4+5	s	10	30	2	Solo Port 423	7	0.3	1.68
		iB-2	4+5	s	10	54	2	Solo Port 423	48	0.3	11.52
		iB-3	4+5	s	10	16	2	Solo Port 423	24	0.3	5.76
		iB-4	4+5	s	10	15	5	Solo Port 423	12	0.3	2.88
		iB-5	4+5	s	10	15	5	Solo Port 423	12	0.3	2.88
		iB-6	4+5	s	10	53	5	Solo Port 423	45	0.3	10.8
		iB-7	4+5	s	10	30	5	Solo Port 423	24	0.3	5.76
		iB-8	4+5	s	10	15	5	Solo Port 423	12	0.3	2.88
		iB-9	4+5	s	10	27	5	Solo Port 423	24	0.3	5.76
		iB-10	4+5	s	10	24	5	Solo Port 423	24	0.3	5.76
		iB-11	4+5	s	10	17	5	Solo Port 423	12	0.3	2.88
		iB-12	4+5	s	10	21	5	Solo Port 423	24	0.3	5.76
		iB-13	4+5	s	10	15	5	Solo Port 423	12	0.3	2.88
		iB-14	4+5	s	10	29	5	Solo Port 423	24	0.3	5.76
		iB-15	4+5	s	10	30	5	Solo Port 423	24	0.3	5.76

* Assumptions for the calculation see **Section 4.2.1**.

4 Results

This section presents the results from investigations of dermal and inhalation exposure to diflubenzuron in workers and bystanders during the pest control activities against the oak processionary moth by spraying.

A detailed description of the samples collected to determine dermal and inhalation exposure giving the sample identifier, year, company, worker, spray unit, sampling time as well as the amount of active substance applied has already been made in Tab. 3.6 to Tab. 3.9 in Section 3.5.2. The general procedure applied by the workers is described in Section 3.2, and particular details regarding sampling are given in the description of the different measurements in Annex 1. More detailed information on sampling obtained for bystanders is given in Annex 2.

4.1 Workers

4.1.1 Dermal exposure

4.1.1.1 Body exposure: Coveralls

Tab. 4.1 shows the absolute amount of diflubenzuron detected on the coveralls - broken down by the different coverall segments -whereby the coveralls are grouped according to Tab. 3.6. In Tab. 4.2, the diflubenzuron exposure of the coveralls is related to the applied amount of active substance according to Tab. 3.6, and the results are given in mg/kg. A relation to the applied amount of active substance, however, was not possible for cleaning procedures. For this reason, the diflubenzuron exposure on the three coveralls belonging to this field of tasks are given in relation to the duration of the cleaning process, here in mg/min.

Tab. 4.1 Workers' dermal exposure (coveralls): absolute amount of diflubenzuron [µg].

Task	Sample identifier (coverall)		Coverall segments																				
			1	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**9a**	**9b**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**15**	**16**	**17**	**Σ**
Weighing out/ portioning of Dimilin™ 80 WG	Weighing	dO-1	1130	3980	934	361	203	95.6	3010	5090	387	274	136	92.5	236	79.6	67.9	79.3	51.7	48.5	769	383	422	**17800**
		dO-2	479	880	300	199	126	45.7	855	1430	140	276	39.9	29.1	23.7	42.3	26.4	24.3	26.0	25.7	350	122	336	**5770**
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	42.1	120	4.71	7.58	5.69	6.72	12.2	82.2	27.8	496	30.5	6.43	36.2	5.86	3.51	3.32	15.0	6.30	16.2	18.8	15.5	**962**
		dO-2	45.7	110	3.95	5.68	3.74	6.70	5.26	95.9	9.20	85.0	9.30	4.42	27.1	6.32	3.38	3.36	2.72	2.84	13.9	24.8	53.7	**523**
		dO-3	275	1070	84.4	162	10.6	69.6	50.2	885	32.9	356	208	9.85	54.5	21.5	8.18	7.16	10.0	4.59	98.5	78.8	14.8	**3510**
		dO-4	659	1080	102	445	6.88	42.5	74.7	1180	27.9	452	233	21.4	27.4	21.1	7.92	4.93	5.55	7.31	214	147	23.5	**4780**
		dO-5	170	370	43.1	64.8	28.4	31.7	32.9	91.4	36.8	285	125	35.7	31.8	11.9	10.4	6.88	6.25	6.54	80.8	64.9	16.7	**1550**
		dO-6	114	377	20.0	133	18.4	22.6	39.3	195	49.9	110	32.8	12.7	41.1	11.0	4.51	3.28	3.77	3.05	60.7	44.9	113	**1410**
		dO-7	1.66	1.84	0.292	0.225	0.317	0.214	1.65	1.95	0.978	1.20	0.150	0.224	0.187	0.067	0.322	0.307	0.222	0.221	0.521	0.295	0.505	**13.3**
		dO-8	36.6	154	4.58	49.1	25.1	4.59	16.7	61.7	14.1	90.7	61.4	59.1	48.2	8.29	57.5	132	34.2	15.7	34.1	42.7	6.69	**957**
		dO-9	20.3	165	12.9	46.0	2.21	3.10	17.3	85.7	51.1	51.2	39.6	46.8	50.7	12.1	5.60	37.6	62.6	46.9	15.1	148	9.06	**929**
		dO-10	10.7	89.4	1.13	3.73	1.68	1.92	3.47	9.43	4.90	59.2	9.69	30.3	19.8	4.71	11.6	20.2	17.1	8.85	14.3	66.5	4.28	**393**
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	38.6	358	6.14	1.69	10.0	30.2	6.50	7.34	14.0	53.4	29.8	26.0	242	39.7	35.7	74.6	247	93.6	28.8	55.6	14.3	**1410**
		dO-2	4.17	8.73	1.07	4.48	0.363	0.354	0.893	14.0	1.09	0.710	15.7	0.723	2.79	0.419	1.00	0.961	3.46	3.18	10.3	0.767	8.23	**83.4**
		dO-3	4.89	23.6	8.60	2.05	1.95	2.56	2.85	2.65	1.39	2.94	15.3	3.64	11.4	6.74	6.04	2.08	13.7	2.61	10.4	24.1	2.41	**152**
		dO-4	369	113	12.8	11.2	8.47	20.9	56.8	60.4	23.6	98.2	99.8	30.4	100	20.6	3.46	6.56	6.52	9.57	32.0	79.3	11.3	**1170**
		dO-5	161	622	35.5	137	50.9	25.1	41.5	378	21.3	110	126	30.2	78.9	29.2	7.72	9.31	5.55	6.79	285	177	26.3	**2360**

Tab. 4.1 (continued)

Task	Sample identifier (coverall)		Coverall segments																				
			1	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**9a**	**9b**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**15**	**16**	**17**	**Σ**
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-6	47.5	169	43.5	52.0	15.0	16.5	31.5	44.2	16.1	8.38	82.5	31.2	20.3	30.0	41.1	23.2	39.1	54.3	300	497	92.2	**1650**
		dO-7	240	247	55.3	93.4	37.9	36.5	64.8	207	39.7	119	78.2	29.3	38.0	23.9	5.42	8.06	10.3	6.61	113	149	10.7	**1610**
		dO-8	282	774	48.4	70.4	24.9	71.0	59.6	132	117	145	241	54.9	211	51.7	14.9	10.7	18.4	9.16	69.1	167	79.9	**2650**
		dO-9	4.58	18.3	1.10	0.688	3.28	5.07	1.32	3.50	0.944	6.11	6.90	64.2	14.3	16.4	97.2	595	103	26.9	8.78	3.61	1.06	**981**
		dO-10	14.4	32.4	0.197	0.667	4.12	176	1.64	3.50	5.08	47.7	2.87	15.8	5.52	6.84	65.1	124	34.0	14.3	19.0	5.76	1.75	**581**
		dO-11	3.23	17.8	1.01	4.09	0.935	3.94	1.82	9.36	2.22	3.87	6.93	26.9	4.69	6.93	55.3	182	23.7	7.98	4.82	6.05	2.37	**376**
		dO-12	2.76	18.8	0.405	0.687	0.378	0.485	0.256	1.21	0.557	0.301	7.85	25.2	15.1	8.32	19.1	63.0	20.3	7.77	30.9	233	1.38	**458**
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	dO-1	55.5	322	181	18.7	40.1	14.1	19.8	293	51.0	60.2	100	6.41	22.6	5.19	12.0	6.99	6.30	6.30	32.7	13.6	13.2	**1280**
		dO-2	50.7	566	8.82	7.61	4.37	36.7	16.9	202	22.8	82.5	35.7	8.10	38.6	12.2	21.0	16.6	14.6	11.0	33.0	30.1	12.2	**1230**
		dO-3	66.0	464	13.5	33.3	25.9	31.5	67.3	340	104	197	199	43.7	160	31.6	27.1	13.2	26.4	20.0	99.7	75.4	27.9	**2070**
		dO-4	62.4	395	7.41	18.4	61.8	72.0	17.5	87.1	19.9	136	131	28.3	81.7	27.7	9.76	17.2	29.9	26.1	80.3	82.0	28.5	**1420**
		dO-5	818	2490	194	245	70.8	237	130	686	144	706	254	142	418	56.8	28.7	32.9	43.2	34.2	168	157	128	**7190**
		dO-6	55.7	69.4	12.1	32.8	11.0	6.00	31.3	35.5	16.6	17.2	6.77	7.50	3.96	3.95	2.83	3.73	5.14	12.4	9.07	7.31	23.1	**373**
Hand-held sprayer Preparation/ application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	3550	1270	942	392	456	210	193	127	225	120	417	265	321	201	330	184	301	193	2390	1770	763	**14620**
		dO-2	1660	1160	526	73.1	704	72.5	355	155	538	144	461	155	567	166	226	171	192	153	1290	311	1430	**10500**
		dO-3	2310	2290	499	272	762	108	379	497	510	179	1420	395	943	311	389	288	355	336	2430	645	1940	**17270**
		dO-4	3140	2360	1150	202	861	178	754	188	806	397	992	759	1160	680	496	366	404	346	2274	1360	2240	**21110**

Tab. 4.1 (continued)

Task	Sample identifier (coverall)		Coverall segments																				
			1	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**9a**	**9b**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**15**	**16**	**17**	**Σ**
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-5	1640	4400	511	211	737	881	355	143	681	255	4530	3850	4140	6960	1870	2360	3690	5030	16700	7130	1760	**67850**
		dO-6	1040	1440	463	262	367	104	285	389	229	291	465	350	336	449	284	173	224	490	2240	1430	914	**12220**
		dO-7	603	560	211	211	69.4	38.0	217	168	58.8	40.7	137	33.6	93.1	25.0	41.2	35.3	46.0	35.4	559	266	345	**3790**
		dO-8	811	378	81.1	78.9	61.9	41.0	81.7	116	66.2	39.7	67.0	107	166	406	62.5	442	221	207	1590	731	273	**6030**
Hand-held sprayer Transfer/ application of the Dimilin™ 80 WG suspension	HHS-transfer application	dO-1	316	317	109	82.8	86.5	31.3	67.2	80.4	78.3	29.1	99.0	43.1	89.6	57.9	70.7	50.1	88.8	55.3	441	187	268	**2650**
		dO-2	507	876	249	130	261	31.1	191	122	246	62.3	320	67.6	267	123	111	62.1	129	104	994	597	632	**6080**
		dO-3	164	222	93.6	24.2	87.4	17.7	75.8	40.3	83.0	17.1	184	44.2	75.1	61.2	97.0	56.7	65.9	89.9	229	346	202	**2280**
		dO-4	99.3	152	44.0	42.9	46.2	17.3	65.3	25.0	33.2	42.1	63.4	21.8	35.1	41.4	30.4	26.0	33.0	60.3	217	184	112	**1390**
		dO-5	849	1010	218	124	67.5	92.1	298	1630	79.1	939	600	106	226	64.7	15.1	15.4	14.4	16.9	297	215	745	**7620**
		dO-6	110	151	46.1	13.3	54.8	16.7	37.4	15.9	42.1	16.5	55.8	25.0	65.8	15.7	33.2	17.2	29.8	17.5	264	192	160	**1380**
		dO-7	92.0	153	27.5	19.0	18.1	12.3	18.4	23.3	18.1	9.09	36.0	12.8	42.8	11.4	10.9	10.4	10.6	7.54	200	136	89.1	**958**
		dO-8	855	530	186	92.4	452	128	54.7	273	210	141	162	47.3	86.9	35.4	39.3	28.3	30.6	24.3	307	164	112	**3960**
		dO-9	409	449	103	116	105	33.1	38.1	58.9	40.7	43.0	140	93.1	95.6	380	57.1	95.1	77.0	283	1190	689	570	**5060**
		dO-10	259	325	92.5	53.5	124	41.7	36.7	38.3	42.7	27.7	92.7	85.3	46.3	16.8	24.9	26.9	30.3	20.8	236	173	76.8	**1870**
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning	dO-1	1040	8070	1660	649	877	1150	1550	942	1140	2930	1260	1170	3960	1280	683	713	2180	776	1590	1250	1240	**36120**
		dO-2	29.7	175	6.37	4.77	30.8	8.50	6.05	7.74	35.9	20.3	40.5	31.0	96.7	28.7	15.4	22.8	77.6	22.7	35.3	29.2	34.8	**760**
		dO-3	440	2150	43.1	41.0	474	294	514	336	1220	868	401	82.1	1100	187	623	328	981	579	834	162	119	**11770**

Tab. 4.2 Workers' dermal exposure (coveralls): exposure to diflubenzuron in relation to the applied amount of active substance or - in the case of cleaning procedures - the duration of the respective task [mg/kg or mg/min].

Task	Sample identifier (coverall)		Coverall segments																				
			1	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**9a**	**9b**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**15**	**16**	**17**	**Σ**
Weighing out/ portioning of Dimilin™ 80 WG	Weighing	dO-1	0.071	0.249	0.058	0.023	0.013	0.006	0.188	0.318	0.024	0.017	0.009	0.006	0.015	0.005	0.004	0.005	0.003	0.003	0.048	0.024	0.026	1.11
		dO-2	0.060	0.110	0.037	0.025	0.016	0.006	0.107	0.178	0.018	0.035	0.005	0.004	0.003	0.005	0.003	0.003	0.003	0.003	0.044	0.015	0.042	0.722
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	0.219	0.623	0.025	0.039	0.030	0.035	0.063	0.428	0.145	2.58	0.159	0.033	0.188	0.031	0.018	0.017	0.078	0.033	0.084	0.098	0.081	5.01
		dO-2	0.191	0.460	0.016	0.024	0.016	0.028	0.022	0.400	0.038	0.354	0.039	0.018	0.113	0.026	0.014	0.014	0.011	0.012	0.058	0.103	0.224	2.18
		dO-3	1.15	4.47	0.352	0.675	0.044	0.290	0.209	3.69	0.137	1.48	0.866	0.041	0.227	0.090	0.034	0.030	0.042	0.019	0.411	0.328	0.061	14.6
		dO-4	2.75	4.51	0.425	1.85	0.029	0.177	0.311	4.90	0.116	1.88	0.970	0.089	0.114	0.088	0.033	0.021	0.023	0.030	0.893	0.613	0.098	19.9
		dO-5	0.710	1.54	0.179	0.270	0.118	0.132	0.137	0.381	0.153	1.19	0.520	0.149	0.133	0.050	0.043	0.029	0.026	0.027	0.336	0.271	0.069	6.46
		dO-6	0.474	1.57	0.083	0.553	0.077	0.094	0.164	0.812	0.208	0.460	0.137	0.053	0.171	0.046	0.019	0.014	0.016	0.013	0.253	0.187	0.470	5.87
		dO-7	0.017	0.018	0.003	0.002	0.003	0.002	0.017	0.019	0.010	0.012	0.002	0.002	0.002	0.001	0.003	0.003	0.002	0.002	0.005	0.003	0.005	0.133
		dO-8	0.366	1.54	0.046	0.491	0.251	0.046	0.167	0.617	0.141	0.907	0.614	0.591	0.482	0.083	0.575	1.32	0.342	0.157	0.341	0.427	0.067	9.57
		dO-9	0.203	1.65	0.129	0.460	0.022	0.031	0.173	0.857	0.511	0.512	0.396	0.468	0.507	0.121	0.056	0.376	0.626	0.469	0.151	1.48	0.091	9.29
		dO-10	0.107	0.894	0.011	0.037	0.017	0.019	0.035	0.094	0.049	0.592	0.097	0.303	0.198	0.047	0.116	0.202	0.171	0.089	0.143	0.665	0.043	3.93
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	0.201	1.87	0.032	0.009	0.052	0.157	0.034	0.038	0.073	0.278	0.155	0.135	1.26	0.207	0.186	0.388	1.29	0.487	0.150	0.290	0.075	7.36
		dO-2	0.021	0.044	0.005	0.022	0.002	0.002	0.004	0.070	0.005	0.004	0.078	0.004	0.014	0.002	0.005	0.005	0.017	0.016	0.052	0.004	0.041	0.417
		dO-3	0.025	0.123	0.045	0.011	0.010	0.013	0.015	0.014	0.007	0.015	0.080	0.019	0.060	0.035	0.031	0.011	0.071	0.014	0.054	0.125	0.013	0.791
		dO-4	1.54	0.469	0.053	0.047	0.035	0.087	0.237	0.252	0.098	0.409	0.416	0.127	0.417	0.086	0.014	0.027	0.027	0.040	0.133	0.330	0.047	4.89
		dO-5	0.672	2.59	0.148	0.570	0.212	0.105	0.173	1.58	0.089	0.456	0.525	0.126	0.329	0.122	0.032	0.039	0.023	0.028	1.19	0.739	0.110	9.85

Tab. 4.2 (continued)

Task	Sample identifier (coverall)		Coverall segments																				
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Σ
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-6	0.198	0.705	0.181	0.217	0.063	0.069	0.131	0.184	0.067	0.035	0.344	0.130	0.084	0.125	0.171	0.097	0.163	0.226	1.25	2.07	0.384	6.89
		dO-7	1.00	1.03	0.230	0.389	0.158	0.152	0.270	0.862	0.165	0.497	0.326	0.122	0.158	0.100	0.023	0.034	0.043	0.028	0.472	0.620	0.045	6.72
		dO-8	1.17	3.23	0.201	0.293	0.104	0.296	0.248	0.549	0.486	0.603	1.00	0.229	0.877	0.216	0.062	0.045	0.076	0.038	0.288	0.697	0.333	11.0
		dO-9	0.046	0.183	0.011	0.007	0.033	0.051	0.013	0.035	0.009	0.061	0.069	0.642	0.143	0.164	0.972	5.95	1.03	0.269	0.088	0.036	0.011	9.81
		dO-10	0.144	0.324	0.002	0.007	0.041	1.76	0.016	0.035	0.051	0.477	0.029	0.158	0.055	0.068	0.651	1.24	0.340	0.143	0.190	0.058	0.018	5.81
		dO-11	0.032	0.178	0.010	0.041	0.009	0.039	0.018	0.094	0.022	0.039	0.069	0.269	0.047	0.069	0.553	1.82	0.237	0.080	0.048	0.061	0.024	3.76
		dO-12	0.028	0.188	0.004	0.007	0.004	0.005	0.003	0.012	0.006	0.003	0.079	0.252	0.151	0.083	0.191	0.630	0.203	0.078	0.309	2.33	0.014	4.58
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	dO-1	0.289	1.67	0.941	0.097	0.209	0.073	0.103	1.53	0.265	0.314	0.521	0.033	0.118	0.027	0.063	0.036	0.033	0.033	0.170	0.071	0.069	6.67
		dO-2	0.264	2.95	0.046	0.040	0.023	0.191	0.088	1.05	0.119	0.430	0.186	0.042	0.201	0.064	0.109	0.086	0.076	0.057	0.172	0.157	0.064	6.42
		dO-3	0.344	2.42	0.070	0.174	0.135	0.164	0.351	1.77	0.543	1.03	1.04	0.227	0.835	0.164	0.141	0.069	0.137	0.104	0.519	0.393	0.145	10.8
		dO-4	0.325	2.06	0.039	0.096	0.322	0.375	0.091	0.454	0.104	0.709	0.683	0.147	0.425	0.144	0.051	0.090	0.155	0.136	0.418	0.427	0.148	7.40
		dO-5	8.52	26.0	2.02	2.56	0.737	2.47	1.36	7.14	1.50	7.36	2.65	1.48	4.35	0.592	0.299	0.342	0.450	0.356	1.75	1.64	1.33	74.9
		dO-6	0.278	0.347	0.060	0.164	0.055	0.030	0.156	0.177	0.083	0.086	0.034	0.038	0.020	0.020	0.014	0.019	0.026	0.062	0.045	0.037	0.116	1.87
Hand-held sprayer Preparation/ application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	2110	756	561	234	271	125	115	75.8	134	71.7	248	158	191	120	196	109	179	115	1420	1050	454	8700
		dO-2	288	201	91.3	12.7	122	12.6	61.7	26.9	93.5	25.0	80.0	26.9	98.5	28.8	39.2	29.7	33.3	26.5	224	53.9	248	1820
		dO-3	402	398	86.6	47.3	132	18.8	65.8	86.3	88.6	31.1	247	68.5	164	54.0	67.6	50.0	61.6	58.3	422	112	337	3000
		dO-4	545	410	199	35.1	149	30.9	131	32.7	140	68.9	172	132	201	118	86.1	63.6	70.1	60.1	395	236	389	3660

Tab. 4.2 (continued)

Task	Sample identifier (coverall)		Coverall segments																				
			1	**2**	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**	**6a**	**6b**	**9a**	**9b**	**10a**	**10b**	**11a**	**11b**	**12a**	**12b**	**15**	**16**	**17**	**Σ**
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-5	285	764	88.7	36.7	128	153	61.7	24.8	118	44.3	787	669	718	1210	325	410	640	874	2900	1240	305	11800
		dO-6	240	334	107	60.7	84.9	24.0	65.9	90.0	53.0	67.3	108	81.1	77.8	104	65.7	40.0	52.0	114	518	332	212	2830
		dO-7	120	111	41.9	41.9	13.8	7.54	43.1	33.3	11.7	8.07	27.1	6.67	18.5	4.96	8.17	7.00	9.12	7.02	111	52.9	68.5	753
		dO-8	141	65.7	14.1	13.7	10.8	7.11	14.2	20.2	11.5	6.89	11.6	18.6	28.9	70.5	10.9	76.7	38.4	35.9	277	127	47.4	1050
Hand-held sprayer Transfer/ application of the Dimilin™ 80 WG suspension	HHS-transfer application	dO-1	54.8	55.0	18.9	14.4	15.0	5.43	11.7	14.0	13.6	5.05	17.2	7.49	15.6	10.1	12.3	8.69	15.4	9.60	76.5	32.5	46.5	460
		dO-2	88.1	152	43.3	22.6	45.3	5.39	33.2	21.1	42.7	10.8	55.5	11.7	46.3	21.3	19.3	10.8	22.3	18.1	173	104	110	1060
		dO-3	28.4	38.6	16.2	4.20	15.2	3.07	13.2	7.00	14.4	2.97	31.9	7.68	13.0	10.6	16.8	9.84	11.4	15.6	39.8	60.0	35.1	395
		dO-4	17.2	26.4	7.64	7.45	8.02	3.00	11.3	4.34	5.76	7.30	11.0	3.79	6.09	7.20	5.28	4.51	5.73	10.5	37.7	32.0	19.4	242
		dO-5	147	175	37.8	21.5	11.7	16.0	51.7	283	13.7	163	104	18.4	39.2	11.2	2.61	2.67	2.50	2.94	51.5	37.3	129	1320
		dO-6	20.8	28.5	8.73	2.52	10.4	3.15	7.09	3.02	7.98	3.13	10.6	4.73	12.5	2.97	6.29	3.25	5.65	3.31	50.0	36.5	30.2	261
		dO-7	16.0	26.5	4.78	3.30	3.14	2.13	3.20	4.04	3.14	1.58	6.24	2.23	7.43	1.98	1.89	1.81	1.85	1.31	34.7	23.6	15.5	166
		dO-8	148	91.9	32.3	16.0	78.4	22.2	9.50	47.3	36.4	24.4	28.1	8.21	15.1	6.15	6.83	4.91	5.31	4.22	53.4	28.4	19.5	687
		dO-9	71.0	78.0	17.9	20.1	18.2	5.74	6.62	10.2	7.06	7.46	24.3	16.2	16.6	66.0	9.91	16.5	13.4	49.1	206	120	99.0	879
		dO-10	44.9	56.5	16.1	9.29	21.5	7.24	6.36	6.66	7.41	4.81	16.1	14.8	8.03	2.91	4.33	4.67	5.25	3.60	41.0	30.1	13.3	325
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning*	dO-1*	0.019	0.147	0.030	0.012	0.016	0.021	0.028	0.017	0.021	0.053	0.023	0.021	0.072	0.023	0.012	0.013	0.040	0.014	0.029	0.023	0.023	0.657*
		dO-2*	0.004	0.025	0.001	0.001	0.004	0.001	0.001	0.001	0.005	0.003	0.006	0.004	0.014	0.004	0.002	0.003	0.011	0.003	0.005	0.004	0.005	0.109*
		dO-3*	0.011	0.054	0.001	0.001	0.012	0.007	0.013	0.008	0.030	0.022	0.010	0.002	0.028	0.005	0.016	0.008	0.025	0.014	0.021	0.004	0.003	0.294*

* the values are related to the duration of the respective task [mg/min].

The exposure levels shown in Tab. 4.2, which are related to the amount of active substance handled and which are shown in Tab. 4.3 in form of an overview, reveal considerable differences between the different tasks. The median value for weighing out and portioning is below 1 mg/kg, for work with the vehicle-mounted unit the median values are in a single-digit mg/kg range, and for work with the hand-held sprayer they are in a three- to four-digit mg/kg range. For the assessment of the exposure levels, however, it should be taken into account that, in these tasks, very different amounts of active substance are handled (see Tab. 3.6) and that they are carried out with varying frequencies. With regard to assessment of the exposure levels, it should be mentioned that the differences between the exposure levels shown in Tab. 4.3 have to be put into perspective, as soon as these are related to the amount of handled active substance. For example, the exposure level related to the handled amount of active substance appears to be low regarding the task “weighing out and portioning”. However, large amounts of active substance are handled within a short time, so that absolute exposures are very high. On the other hand, this task is only performed once in the season and not several times per day, like other tasks.

Tab. 4.3 Workers’ dermal exposure (coveralls): data compilation of the exposure to diflubenzuron in relation to the applied amount of active substance or - in the case of cleaning procedures - the duration of the respective measurement [mg/kg or mg/min].

Task	Minimum	Median	75th percentile	95th percentile	Maximum
Weighing out/ portioning of the Dimilin^{TM} 80 WG (n=2)	0.722	-	-	-	1.11
Vehicle-mounted sprayer Preparation of the Dimilin^{TM} 80 WG suspension (n=10)	0.133	6.17	9.50	17.5	19.9
Vehicle-mounted sprayer Application of the Dimilin^{TM} 80 WG suspension (n=12)	0.417	6.27	7.97	10.4	11.0
Vehicle-mounted sprayer Preparation and application of the Dimilin^{TM} 80 WG suspension (n=16)	1.87	10.4	15.8	38.8	74.9
Hand-held sprayer Preparation and application of the Dimilin^{TM} 80 WG suspension (n=8)	753	2910	4920	10700	11800
Hand-held sprayer Transfer and application of the Dimilin^{TM} 80 WG suspension (n=10)	166	427	831	1200	1320
Hand-held sprayer Preparation/ transfer and application of the Dimilin^{TM} 80 WG suspension (n=18)	166	963	2580	9160	11800
Cleaning procedures Vehicle/ vehicle-mounted sprayer (n=3)	0.109*	0.294*	-	-	0.657*

* the marked values are related to the duration of the respective measurement [mg/min].

The exposure grouped according to type of application and task is shown as box plots for the vehicle-mounted unit in Fig. 4.1 and for the hand-held sprayer in Fig. 4.2. In Fig. 4.1, in the dataset “preparation and application“, some of the included data have not already been included in the individual tasks, as both tasks were measured together a couple of times.

With the vehicle-mounted unit, it is clearly seen from the median values that, in this type of application, preparation and application of the Dimilin^{TM} 80 WG suspension produces a similarly high exposure of the coveralls. The fact that in individual cases a considerably higher dermal exposure can be obtained with vehicle-mounted units as well can be seen in the case of the coverall VMS-preparation-application-dO-5 which, with an exposure of 74.9 mg/kg, is ten times higher than the exposure on the other coveralls from this field of task. The high measured value can be explained with the observation that the worker dismounted from the vehicle during Dimilin^{TM} 80 WG application to talk with a female cyclist who had ridden through the cloud of spray mist. During this time, the worker was standing in the spray mist he had just applied.

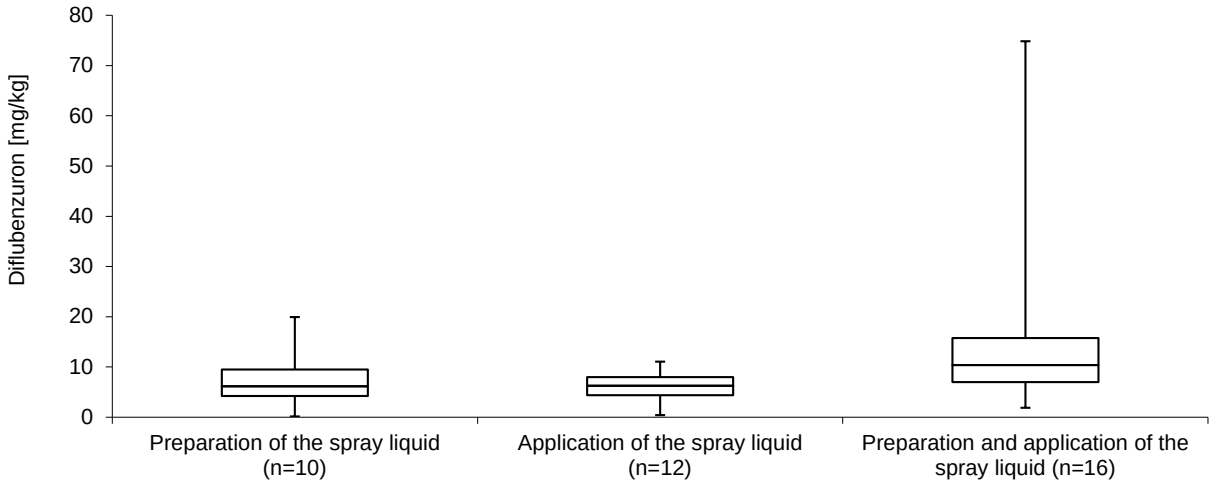

Fig. 4.1 Workers’ exposure (coveralls) related to the applied amount of active substance resulting from working with the vehicle-mounted sprayer.

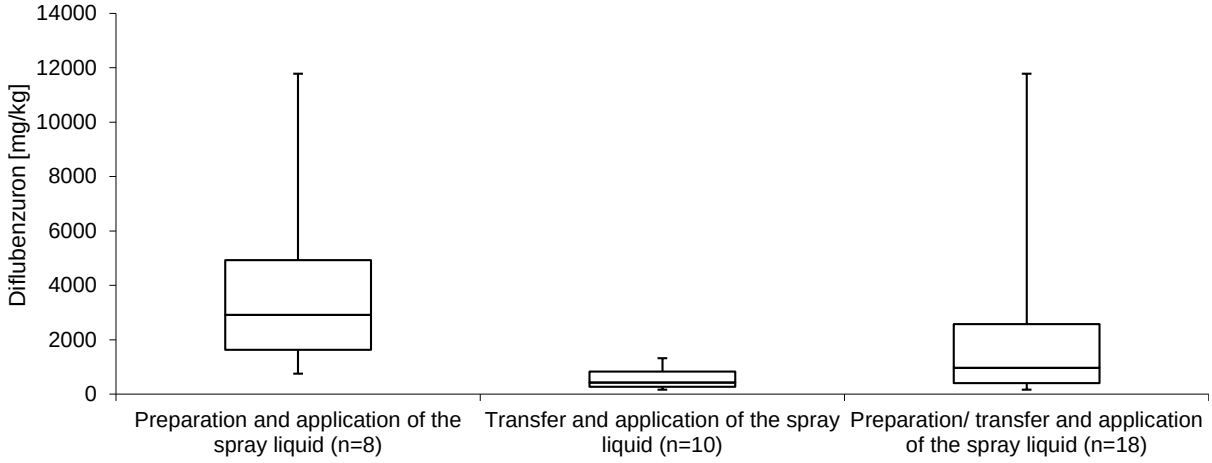

Fig. 4.2 Workers’ exposure (coveralls) related to the applied amount of active substance resulting from working with the hand-held sprayer.

The highest level of exposure could be detected with the coveralls worn during preparation and application and during transfer and application of the Dimilin^{TM} 80 WG suspension with the hand-held sprayer, respectively. The box plots in Fig. 4.2 indicate that the preparation of the Dimilin^{TM} 80 WG suspension with subsequent application results in a clearly higher exposure of the coveralls than transfer of the Dimilin^{TM} 80 WG suspension with subsequent application. On closer analysis, however, it becomes clear that the difference in the exposure can partly also be due to individual differences between the workers (Fig. 4.3).
Fig. 4.3 makes it clear that preparation and application of the Dimilin^{TM} 80 WG suspension as task was particularly carried out by worker #2, whereas transfer and application of the Dimilin^{TM} 80 WG suspension was exclusively the task of worker #5.
An activity-related component in exposure can still be identified if only the data for worker #5 are taken into account, but it is less pronounced than in the complete dataset. The fact, that the exposure tends to be higher during preparation than during transfer is explicitly shown by the data obtained for the gloves. This result would be expected, considering that the hands are more exposed than other parts of the body during preparation (towards the granules) and during transfer (towards the application liquid).

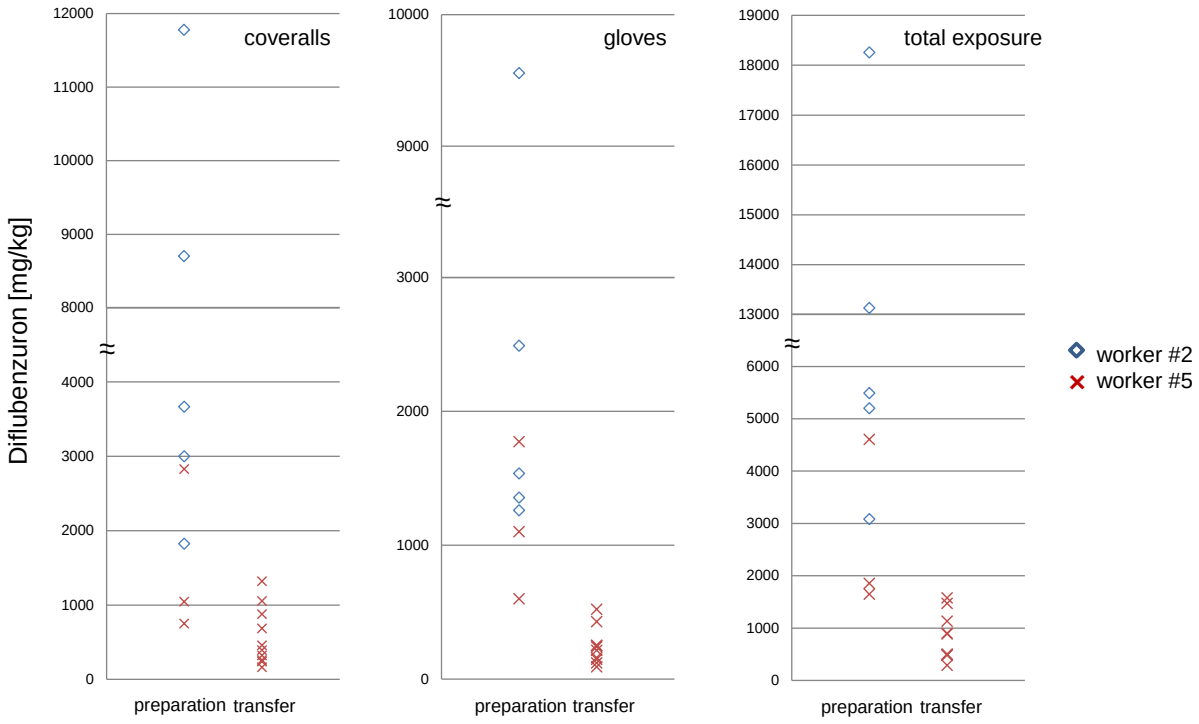

Fig. 4.3 Individual differences between workers after working with the hand-held sprayer. The figures show the exposure from “preparation and application of the Dimilin^{TM} 80 WG suspension” as well as from “transfer and application of the Dimilin^{TM} 80 WG suspension”.

Then again, the exposure patterns discussed later in this section (Fig. 4.9) show that the workers’ bodies are particularly exposed “from above”, which can only be explained by the spraying process and, above all, by the spraying direction. The comparison of the two workers shows that this characteristic exposure pattern is more distinct for worker #2 than for worker #5. The differences in the exposure

patterns can also be attributable to personal behaviour; worker #2 probably sprays more vertically upwards than worker #5.

Exposure from cleaning of the vehicles and vehicle-mounted sprayers yields a median of 0.294 mg/min (range 0.109-0.657 mg/min; n=3) and cannot be directly compared with the other results as they relate to the task duration.

In order to recognise exposure patterns on the coveralls, the diflubenzuron amounts from different coverall segments were related to the total exposure of the corresponding coverall. The percentage distribution calculated in this way for the different coverall segments is shown in Tab. 4.4. In order to emphasise the pattern more clearly, the cells were coloured by values using a 3-colour scale. For the different activity fields (weighing out and portioning, work with the vehicle-mounted sprayer, work with the hand-held sprayer or cleaning procedures), the lowest values are marked in green, the medium values in yellow and the highest values in red. This representation makes it easy to identify the differences between the individual processes and any singular events which may occur, as well as possible differences between the activities, the employees and the companies.

When looking at these data, it should be noted that the segments have different sizes so that larger segments such as the belly, the chest and the back are more pronounced when the exposure is evenly distributed over the body. Therefore, in order to obtain scaled and comparable values in the units ng/(g × cm²) and ng/(min×cm²), in Tab. 4.5 the diflubenzuron amounts found on the individual segments were divided by the area of the corresponding segment and, in addition, by the amount of active substance used or – for the cleaning procedures - by the duration, respectively. The values shown in Tab. 4.5 were colour-coded analogously to the data in Tab. 4.4. With this scaling, the individual activities (transfer of spray liquid, working with the semi-mounted sprayer, working with the engine spraying machine or cleaning activities) can be summarised and displayed graphically.

For this purpose, at first the percentage ratio of each individual segment to the respective maximum value was calculated from the values listed in Tab. 4.5, individually for each suit. For each segment, an average value was then calculated from the ratios of all coveralls assigned to a respective activity. From these average values, colour gradations of the individual segments were generated analogously to Tables 4 and 5, and then used for the graphic representation of the corresponding body parts (Fig. 4.4 to Fig. 4.6, Fig. 4.9, Fig. 4.11 and Fig. 4.12). In this way, the exposure patterns of the individual body parts can be compared well and highly exposed areas can be emphasized. When comparing different activities, however, it should be noted that the colours represent different exposure heights due to the conversions, so that a comparison of absolute exposure heights between activities is no longer possible based on these figures.

Tab. 4.4 Workers' dermal exposure (coveralls): percentage of diflubenzuron on the individual segments [%]. For the individual tasks, the lowest exposures were marked in green, medium exposures in light yellow, and the highest exposures in red (five colour gradations, each indicating a 20 % step in values).

Task	Sample identifier		Exposure level on the coverall segments																				
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Σ
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dO-1	6.36	22.3	5.24	2.03	1.14	0.536	16.9	28.5	2.17	1.54	0.765	0.519	1.32	0.446	0.381	0.445	0.290	0.272	4.31	2.15	2.37	100
		dO-2	8.30	15.2	5.19	3.45	2.18	0.792	14.8	24.7	2.43	4.79	0.690	0.504	0.410	0.732	0.458	0.421	0.450	0.445	6.07	2.11	5.83	100
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	4.37	12.4	0.490	0.788	0.591	0.699	1.26	8.54	2.89	51.6	3.17	0.668	3.76	0.609	0.365	0.345	1.56	0.655	1.68	1.95	1.61	100
		dO-2	8.74	21.1	0.755	1.09	0.715	1.28	1.01	18.3	1.76	16.2	1.78	0.844	5.19	1.21	0.647	0.643	0.519	0.543	2.65	4.74	10.2	100
		dO-3	7.83	30.5	2.40	4.61	0.301	1.98	1.43	25.2	0.937	10.1	5.91	0.280	1.55	0.613	0.233	0.204	0.284	0.131	2.80	2.24	0.420	100
		dO-4	13.8	22.6	2.13	9.31	0.144	0.889	1.56	24.6	0.583	9.45	4.87	0.448	0.573	0.441	0.166	0.103	0.116	0.153	4.48	3.08	0.492	100
		dO-5	11.0	23.9	2.78	4.18	1.83	2.04	2.12	5.89	2.37	18.4	8.05	2.30	2.05	0.769	0.670	0.443	0.403	0.422	5.21	4.19	1.08	100
		dO-6	8.08	26.7	1.42	9.42	1.30	1.61	2.79	13.8	3.54	7.83	2.33	0.902	2.92	0.779	0.320	0.233	0.267	0.216	4.31	3.19	8.01	100
		dO-7	12.4	13.8	2.19	1.69	2.38	1.61	12.4	14.6	7.33	8.99	1.12	1.68	1.40	0.504	2.41	2.30	1.66	1.66	3.90	2.21	3.79	100
		dO-8	3.82	16.1	0.479	5.13	2.62	0.479	1.74	6.45	1.47	9.48	6.42	6.18	5.04	0.867	6.01	13.8	3.57	1.64	3.56	4.46	0.699	100
		dO-9	2.18	17.8	1.38	4.95	0.238	0.333	1.87	9.22	5.51	5.51	4.26	5.04	5.45	1.30	0.602	4.05	6.74	5.05	1.62	15.9	0.976	100
		dO-10	2.71	22.8	0.288	0.950	0.428	0.488	0.885	2.40	1.25	15.1	2.47	7.72	5.04	1.20	2.96	5.13	4.35	2.25	3.65	16.9	1.09	100
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	2.73	25.4	0.435	0.120	0.708	2.14	0.460	0.519	0.993	3.78	2.11	1.84	17.1	2.81	2.53	5.28	17.5	6.62	2.04	3.94	1.01	100
		dO-2	5.00	10.5	1.29	5.37	0.435	0.424	1.07	16.8	1.30	0.851	18.8	0.866	3.35	0.502	1.19	1.15	4.15	3.81	12.4	0.919	9.86	100
		dO-3	3.22	15.5	5.66	1.35	1.28	1.69	1.88	1.75	0.917	1.93	10.1	2.39	7.53	4.44	3.97	1.37	9.03	1.72	6.86	15.8	1.59	100
		dO-4	31.4	9.59	1.09	0.953	0.722	1.78	4.84	5.15	2.01	8.37	8.51	2.59	8.53	1.76	0.295	0.559	0.556	0.816	2.73	6.76	0.967	100
		dO-5	6.83	26.3	1.50	5.79	2.15	1.06	1.75	16.0	0.901	4.63	5.33	1.28	3.34	1.24	0.327	0.394	0.235	0.287	12.1	7.51	1.11	100

Tab. 4.4 (continued)

Task	Sample identifier		Exposure level on the coverall segments																				
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Σ
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-6	2.87	10.2	2.63	3.15	0.908	0.995	1.90	2.67	0.974	0.506	4.99	1.89	1.22	1.81	2.48	1.40	2.36	3.28	18.1	30.0	5.57	100
		dO-7	14.9	15.3	3.43	5.79	2.35	2.26	4.02	12.8	2.46	7.40	4.85	1.81	2.35	1.48	0.336	0.500	0.641	0.410	7.02	9.23	0.664	100
		dO-8	10.6	29.2	1.82	2.66	0.939	2.68	2.25	4.97	4.40	5.46	9.10	2.07	7.94	1.95	0.561	0.404	0.692	0.345	2.61	6.31	3.01	100
		dO-9	0.466	1.86	0.112	0.070	0.335	0.517	0.134	0.356	0.096	0.623	0.703	6.54	1.45	1.67	9.91	60.6	10.5	2.75	0.894	0.368	0.108	100
		dO-10	2.48	5.58	0.034	0.115	0.709	30.3	0.283	0.602	0.874	8.21	0.494	2.73	0.949	1.18	11.2	21.4	5.85	2.47	3.27	0.990	0.301	100
		dO-11	0.857	4.73	0.267	1.09	0.248	1.05	0.483	2.49	0.590	1.03	1.84	7.14	1.25	1.84	14.7	48.5	6.29	2.12	1.28	1.61	0.630	100
		dO-12	0.603	4.11	0.089	0.150	0.083	0.106	0.056	0.264	0.122	0.066	1.72	5.50	3.29	1.82	4.18	13.7	4.44	1.70	6.75	50.9	0.300	100
Vehicle-mounted sprayer Preparation/ application of the Dimilin™ 80 WG suspension	VMS-preparation application	dO-1	4.34	25.1	14.1	1.46	3.13	1.10	1.54	22.9	3.98	4.70	7.82	0.501	1.77	0.405	0.938	0.546	0.492	0.492	2.55	1.06	1.03	100
		dO-2	4.12	46.0	0.716	0.618	0.355	2.98	1.37	16.4	1.85	6.70	2.90	0.658	3.14	0.991	1.70	1.34	1.18	0.894	2.68	2.44	0.990	100
		dO-3	3.19	22.4	0.654	1.61	1.25	1.52	3.26	16.4	5.04	9.54	9.65	2.11	7.75	1.53	1.31	0.640	1.27	0.967	4.82	3.65	1.35	100
		dO-4	4.39	27.8	0.522	1.30	4.35	5.07	1.23	6.13	1.40	9.59	9.24	1.99	5.75	1.95	0.687	1.21	2.10	1.84	5.65	5.78	2.00	100
		dO-5	11.3	34.7	2.70	3.41	0.985	3.30	1.81	9.54	2.00	9.83	3.54	1.98	5.82	0.791	0.400	0.457	0.601	0.476	2.34	2.18	1.78	100
		dO-6	14.9	18.6	3.23	8.79	2.94	1.61	8.38	9.50	4.45	4.60	1.82	2.01	1.06	1.06	0.759	1.00	1.38	3.32	2.43	1.96	6.20	100
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	24.3	8.69	6.45	2.68	3.12	1.44	1.32	0.871	1.54	0.824	2.85	1.81	2.19	1.38	2.26	1.26	2.06	1.32	16.4	12.1	5.22	100
		dO-2	15.8	11.0	5.01	0.696	6.70	0.691	3.38	1.48	5.13	1.37	4.39	1.48	5.40	1.58	2.15	1.63	1.82	1.45	12.3	2.96	13.6	100
		dO-3	13.4	13.3	2.89	1.58	4.41	0.628	2.20	2.88	2.95	1.04	8.22	2.29	5.46	1.80	2.26	1.67	2.05	1.94	14.1	3.73	11.3	100
		dO-4	14.9	11.2	5.44	0.959	4.08	0.843	3.57	0.892	3.82	1.88	4.70	3.60	5.48	3.22	2.35	1.73	1.91	1.64	10.8	6.43	10.6	100

Tab. 4.4 (continued)

Task	Sample identifier		Exposure level on the coverall segments																				
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Σ
Hand-held sprayer Preparation/ application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-5	2.42	6.48	0.753	0.311	1.09	1.30	0.524	0.21	1.00	0.376	6.68	5.68	6.10	10.3	2.76	3.48	5.44	7.42	24.6	10.5	2.59	100
		dO-6	8.49	11.8	3.79	2.14	3.00	0.849	2.33	3.18	1.87	2.38	3.80	2.87	2.75	3.67	2.32	1.41	1.84	4.01	18.3	11.7	7.47	100
		dO-7	15.9	14.8	5.57	5.56	1.83	1.00	5.72	4.43	1.55	1.07	3.60	0.886	2.46	0.658	1.08	0.929	1.21	0.932	14.7	7.02	9.10	100
		dO-8	13.4	6.27	1.34	1.31	1.03	0.679	1.35	1.93	1.10	0.658	1.11	1.78	2.76	6.74	1.04	7.32	3.67	3.43	26.4	12.1	4.53	100
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	dO-1	11.9	12.0	4.12	3.13	3.27	1.18	2.54	3.04	2.96	1.10	3.74	1.63	3.39	2.19	2.67	1.89	3.36	2.09	16.6	7.07	10.1	100
		dO-2	8.34	14.4	4.10	2.14	4.29	0.511	3.15	2.00	4.04	1.02	5.26	1.11	4.39	2.02	1.83	1.02	2.12	1.72	16.3	9.81	10.4	100
		dO-3	7.19	9.76	4.11	1.06	3.84	0.776	3.33	1.77	3.65	0.753	8.08	1.94	3.30	2.69	4.26	2.49	2.90	3.95	10.1	15.2	8.88	100
		dO-4	7.14	10.9	3.16	3.08	3.32	1.24	4.69	1.80	2.39	3.02	4.56	1.57	2.52	2.98	2.19	1.87	2.37	4.33	15.6	13.2	8.01	100
		dO-5	11.1	13.2	2.86	1.63	0.886	1.21	3.91	21.4	1.04	12.3	7.87	1.39	2.96	0.85	0.198	0.202	0.189	0.222	3.89	2.82	9.77	100
		dO-6	7.95	10.9	3.34	0.963	3.98	1.21	2.71	1.15	3.05	1.20	4.05	1.81	4.77	1.14	2.41	1.24	2.16	1.27	19.1	14.0	11.6	100
		dO-7	9.60	16.0	2.87	1.98	1.89	1.28	1.92	2.43	1.89	0.949	3.75	1.34	4.47	1.19	1.14	1.09	1.11	0.787	20.8	14.2	9.30	100
		dO-8	21.6	13.4	4.71	2.33	11.4	3.23	1.38	6.89	5.30	3.55	4.09	1.19	2.20	0.895	0.994	0.715	0.773	0.614	7.77	4.14	2.84	100
		dO-9	8.08	8.87	2.03	2.28	2.07	0.653	0.753	1.16	0.803	0.848	2.77	1.84	1.89	7.50	1.13	1.88	1.52	5.58	23.5	13.6	11.3	100
		dO-10	13.8	17.4	4.94	2.86	6.62	2.23	1.96	2.05	2.28	1.48	4.96	4.56	2.47	0.897	1.33	1.44	1.62	1.11	12.6	9.25	4.11	100
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning	dO-1	2.87	22.3	4.59	1.80	2.43	3.19	4.28	2.61	3.16	8.11	3.49	3.25	11.0	3.53	1.89	1.97	6.05	2.15	4.41	3.46	3.44	100
		dO-2	3.91	23.1	0.838	0.627	4.05	1.12	0.796	1.02	4.72	2.67	5.33	4.09	12.7	3.78	2.03	3.00	10.2	2.98	4.64	3.84	4.57	100
		dO-3	3.74	18.2	0.366	0.348	4.02	2.50	4.37	2.85	10.3	7.38	3.41	0.698	9.35	1.59	5.30	2.78	8.34	4.92	7.08	1.37	1.01	100

Tab. 4.5 Workers' dermal exposure (coveralls): amount of diflubenzuron related to the surface area of each segment and to the applied amount of active substance or duration of the respective task [ng/(g × cm²) or ng/(min × cm²)]. For the individual tasks, the lowest exposures were marked in green, medium exposures in light yellow, and the highest exposures in red (five colour gradations, each indicating a 20 % step in values).

Task	Sample identifier		Exposure level on the coverall segments																					
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Ø
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dO-1	0.027	0.059	0.077	0.027	0.017	0.007	0.327	0.528	0.042	0.028	0.007	0.005	0.012	0.004	0.004	0.005	0.003	0.003	0.012	0.009	0.013	0.037
		dO-2	0.023	0.026	0.049	0.029	0.021	0.007	0.186	0.296	0.030	0.058	0.004	0.003	0.002	0.004	0.003	0.003	0.003	0.003	0.011	0.006	0.021	0.024
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	0.085	0.148	0.032	0.046	0.039	0.041	0.110	0.711	0.252	4.29	0.127	0.027	0.150	0.024	0.017	0.016	0.074	0.031	0.021	0.036	0.039	0.165
		dO-2	0.074	0.109	0.022	0.028	0.021	0.033	0.038	0.665	0.067	0.588	0.031	0.015	0.090	0.021	0.013	0.013	0.011	0.011	0.015	0.038	0.109	0.072
		dO-3	0.444	1.06	0.463	0.793	0.058	0.340	0.363	6.13	0.238	2.46	0.691	0.033	0.181	0.071	0.032	0.028	0.040	0.018	0.105	0.122	0.030	0.482
		dO-4	1.06	1.07	0.559	2.17	0.038	0.208	0.541	8.14	0.202	3.12	0.774	0.071	0.091	0.070	0.031	0.020	0.022	0.029	0.228	0.228	0.048	0.657
		dO-5	0.274	0.365	0.235	0.317	0.155	0.155	0.238	0.633	0.266	1.98	0.415	0.118	0.106	0.039	0.041	0.027	0.025	0.026	0.086	0.101	0.034	0.213
		dO-6	0.183	0.373	0.110	0.649	0.101	0.111	0.285	1.35	0.362	0.764	0.109	0.042	0.137	0.036	0.018	0.013	0.015	0.012	0.065	0.070	0.229	0.194
		dO-7	0.006	0.004	0.004	0.003	0.004	0.003	0.029	0.032	0.017	0.020	0.001	0.002	0.001	0.001	0.003	0.003	0.002	0.002	0.001	0.001	0.002	0.004
		dO-8	0.141	0.365	0.060	0.576	0.330	0.054	0.290	1.03	0.245	1.51	0.490	0.468	0.385	0.066	0.547	1.25	0.325	0.149	0.087	0.159	0.033	0.316
		dO-9	0.078	0.392	0.170	0.540	0.029	0.036	0.301	1.42	0.888	0.851	0.316	0.371	0.405	0.096	0.053	0.356	0.595	0.444	0.039	0.551	0.044	0.307
		dO-10	0.041	0.212	0.015	0.044	0.022	0.023	0.060	0.157	0.085	0.984	0.077	0.240	0.158	0.037	0.110	0.191	0.163	0.084	0.036	0.248	0.021	0.130
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	0.078	0.444	0.042	0.010	0.069	0.184	0.059	0.064	0.127	0.462	0.124	0.107	1.01	0.164	0.177	0.368	1.23	0.462	0.038	0.108	0.036	0.243
		dO-2	0.008	0.010	0.007	0.026	0.002	0.002	0.008	0.116	0.009	0.006	0.063	0.003	0.011	0.002	0.005	0.005	0.017	0.015	0.013	0.001	0.020	0.014
		dO-3	0.010	0.029	0.059	0.013	0.013	0.016	0.026	0.023	0.013	0.025	0.064	0.015	0.048	0.028	0.030	0.010	0.068	0.013	0.014	0.047	0.006	0.026
		dO-4	0.595	0.111	0.070	0.055	0.046	0.102	0.412	0.419	0.171	0.680	0.332	0.101	0.333	0.068	0.014	0.026	0.026	0.038	0.034	0.123	0.023	0.161
		dO-5	0.260	0.615	0.195	0.669	0.279	0.123	0.301	2.63	0.154	0.758	0.419	0.100	0.263	0.097	0.031	0.037	0.022	0.027	0.303	0.275	0.054	0.325

Tab. 4.5 (continued)

Task	Sample identifier		Exposure level on the coverall segments																				
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Ø
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-6	0.077	0.167	0.238	0.255	0.082	0.081	0.228	0.306	0.117	0.058	0.275	0.103	0.067	0.099	0.163	0.092	0.155	0.214	0.318	0.771	0.187	0.227
		dO-7	0.386	0.244	0.302	0.457	0.208	0.178	0.469	1.43	0.287	0.826	0.260	0.097	0.126	0.079	0.022	0.032	0.041	0.026	0.120	0.231	0.022	0.222
		dO-8	0.452	0.767	0.264	0.344	0.137	0.348	0.431	0.912	0.845	1.00	0.798	0.181	0.700	0.171	0.059	0.042	0.073	0.036	0.073	0.259	0.162	0.363
		dO-9	0.018	0.043	0.015	0.008	0.043	0.060	0.023	0.058	0.016	0.102	0.055	0.508	0.114	0.130	0.924	5.64	0.980	0.255	0.022	0.013	0.005	0.324
		dO-10	0.056	0.077	0.003	0.008	0.054	2.07	0.029	0.058	0.088	0.793	0.023	0.125	0.044	0.054	0.619	1.18	0.323	0.136	0.048	0.021	0.009	0.192
		dO-11	0.013	0.042	0.013	0.048	0.012	0.046	0.032	0.156	0.039	0.064	0.055	0.213	0.037	0.055	0.526	1.72	0.225	0.076	0.012	0.023	0.012	0.124
		dO-12	0.011	0.045	0.005	0.008	0.005	0.006	0.004	0.020	0.010	0.005	0.064	0.200	0.121	0.066	0.182	0.597	0.193	0.074	0.079	0.867	0.007	0.151
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	dO-1	0.112	0.396	1.24	0.114	0.275	0.086	0.179	2.54	0.461	0.522	0.416	0.026	0.094	0.021	0.059	0.035	0.031	0.031	0.043	0.026	0.034	0.220
		dO-2	0.102	0.700	0.060	0.047	0.030	0.224	0.153	1.74	0.207	0.714	0.148	0.033	0.160	0.050	0.104	0.082	0.072	0.054	0.044	0.059	0.031	0.212
		dO-3	0.133	0.574	0.093	0.204	0.178	0.193	0.610	2.94	0.944	1.71	0.830	0.180	0.667	0.130	0.134	0.065	0.130	0.099	0.132	0.146	0.071	0.357
		dO-4	0.126	0.489	0.051	0.113	0.423	0.440	0.159	0.754	0.181	1.18	0.545	0.116	0.339	0.114	0.048	0.085	0.147	0.129	0.106	0.159	0.072	0.244
		dO-5	3.29	6.17	2.66	3.01	0.969	2.90	2.36	11.9	2.61	12.2	2.12	1.17	3.47	0.469	0.284	0.324	0.428	0.337	0.446	0.611	0.649	2.47
		dO-6	0.107	0.082	0.079	0.193	0.072	0.035	0.271	0.294	0.144	0.143	0.027	0.030	0.016	0.016	0.014	0.018	0.024	0.059	0.012	0.014	0.057	0.062
Hand-held sprayer Preparation/ application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	815	179	738	275	356	147	200	126	233	119	198	125	152	95.0	186	103	170	109	362	391	221	287
		dO-2	111	47.7	120	14.9	160	14.8	107	44.7	163	41.5	63.9	21.3	78.6	22.8	37.3	28.1	31.7	25.1	57.1	20.1	121	60.1
		dO-3	155	94.5	114	55.5	174	22.1	114	143	154	51.7	197	54.2	131	42.8	64.3	47.4	58.6	55.2	108	41.7	164	99.1
		dO-4	211	97.3	262	41.2	196	36.3	228	54.3	243	114	137	105	160	93.4	81.9	60.3	66.7	57.0	101	87.9	190	121

Tab. 4.5 (continued)

Task	Sample identifier		Exposure level on the coverall segments																			
			1	2	3a	3b	4a	4b	5a	5b	6a	6b	9a	9b	10a	10b	11a	11b	12a	12b	15	16	17	Ø
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-5	110	181	117	43.1	168	180	107	41.2	205	73.6	628	530	573	958	309	389	609	828	739	462	149	390
		dO-6	92.7	79.3	141	71.3	112	28.2	115	150	92.1	112	86.2	64.2	62.1	82.3	62.5	37.9	49.5	108	132	124	103	93.4
		dO-7	46.4	26.3	55.1	49.2	18.1	8.85	74.9	55.3	20.3	13.4	21.6	5.28	14.8	3.93	7.77	6.63	8.67	6.65	28.3	19.7	33.4	24.9
		dO-8	54.5	15.6	18.5	16.1	14.2	8.35	24.7	33.6	20.0	11.4	9.26	14.7	23.1	55.8	10.4	72.7	36.5	34.0	70.6	47.3	23.1	34.7
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	dO-1	21.2	13.1	24.9	16.9	19.7	6.38	20.3	23.3	23.6	8.39	13.7	5.93	12.5	8.00	11.7	8.24	14.6	9.10	19.5	12.1	22.7	15.2
		dO-2	34.0	36.1	56.9	26.5	59.6	6.33	57.7	35.1	74.2	17.9	44.3	9.26	37.0	16.9	18.4	10.2	21.2	17.2	44.1	38.7	53.7	35.0
		dO-3	11.0	9.16	21.3	4.93	20.0	3.60	22.9	11.6	25.0	4.93	25.5	6.08	10.4	8.39	16.0	9.33	10.8	14.8	10.1	22.3	17.1	13.0
		dO-4	6.65	6.27	10.0	8.75	10.5	3.52	19.6	7.21	10.0	12.1	8.78	3.00	4.86	5.70	5.02	4.27	5.45	9.95	9.60	11.9	9.46	7.99
		dO-5	56.8	41.5	49.7	25.2	15.4	18.8	89.9	470	23.8	271	83.0	14.6	31.3	8.87	2.48	2.53	2.38	2.79	13.1	13.9	62.9	43.6
		dO-6	8.04	6.76	11.5	2.96	13.7	3.70	12.3	5.02	13.9	5.20	8.46	3.75	9.98	2.35	5.98	3.08	5.37	3.14	12.7	13.6	14.7	8.62
		dO-7	6.18	6.29	6.29	3.87	4.13	2.50	5.56	6.71	5.46	2.63	4.98	1.77	5.93	1.57	1.80	1.72	1.76	1.24	8.84	8.79	7.56	5.48
		dO-8	57.2	21.8	42.5	18.8	103	26.1	16.5	78.6	63.3	40.5	22.4	6.50	12.1	4.87	6.50	4.65	5.05	4.00	13.6	10.6	9.51	22.7
		dO-9	27.4	18.5	23.5	23.6	23.9	6.74	11.5	16.9	12.3	12.4	19.4	12.8	13.3	52.3	9.42	15.6	12.7	46.5	52.5	44.7	48.3	29.0
		dO-10	17.3	13.4	21.2	10.9	28.3	8.50	11.1	11.1	12.9	7.99	12.9	11.7	6.41	2.30	4.12	4.43	4.99	3.41	10.4	11.2	6.49	10.7
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning	dO-1	7.30*	34.9*	39.7*	13.9*	20.9*	24.7*	48.8*	28.4*	36.2*	88.6*	18.3*	16.9*	57.4*	18.4*	11.8*	12.3*	37.8*	13.4*	7.36*	8.45*	11.0*	21.7*
		dO-2	1.64*	5.93*	1.20*	0.800*	5.77*	1.42*	1.50*	1.84*	8.90*	4.82*	4.62*	3.51*	11.0*	3.25*	2.09*	3.09*	10.6*	3.07*	1.28*	1.55*	2.42*	3.60*
		dO-3	4.25*	12.7*	1.42*	1.21*	15.5*	8.64*	22.4*	14.0*	52.8*	36.1*	7.98*	1.62*	22.0*	3.70*	14.8*	7.76*	23.3*	13.7*	5.30*	1.50*	1.45*	9.71*

* the marked values are related to the duration of the respective task [mg/min]

For the weighing out and portioning activity, the absolute exposure levels found on individual coverall segments show the highest exposure at the belly (segment 2) and the right forearm (segments 5a and 5b), which fits well with the observation that the employees reached with the right hand into the Dimilin™ 80 WG container. Weighing out and portioning was performed on a table. The difference between the body areas above and below the table edge is clearly visible in the absolute exposure heights (segments 9-12 in Tab. 4.4) as well as in the surface area-related values (Tab. 4.5 and Fig. 4.4).

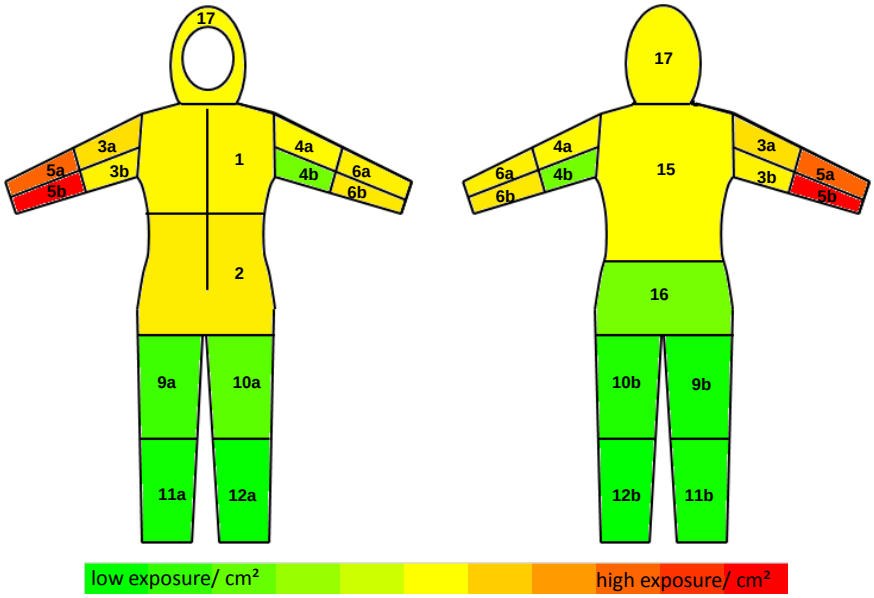

Fig. 4.4 Weighing out and portioning of the Dimilin™ 80 WG granules: schematic representation of the average diflubenzuron exposure of the coverall segments.

As regards the tasks in connection with the vehicle-mounted unit, especially in data relating to “preparation of the Dimilin™ 80 WG suspension” and to “preparation and application of the Dimilin™ 80 WG suspension”, the belly area is generally subject to high exposure (segment 2), in some of the dermal samplers also the chest area (segment 1, Tab. 4.4). Both observations can also be made in the surface area-related data (Tab. 4.5, Fig. 4.5 and Fig. 4.6). In addition, underneath the forearms (segment 5b and 6b), high levels of exposure to diflubenzuron were found. These highly exposed areas agree well with the observation that the workers, during preparation of the spray liquid, leaned towards the vehicle-mounted sprayer with the front side of their body and their forearms (Fig. 4.7 and Fig. 4.8).

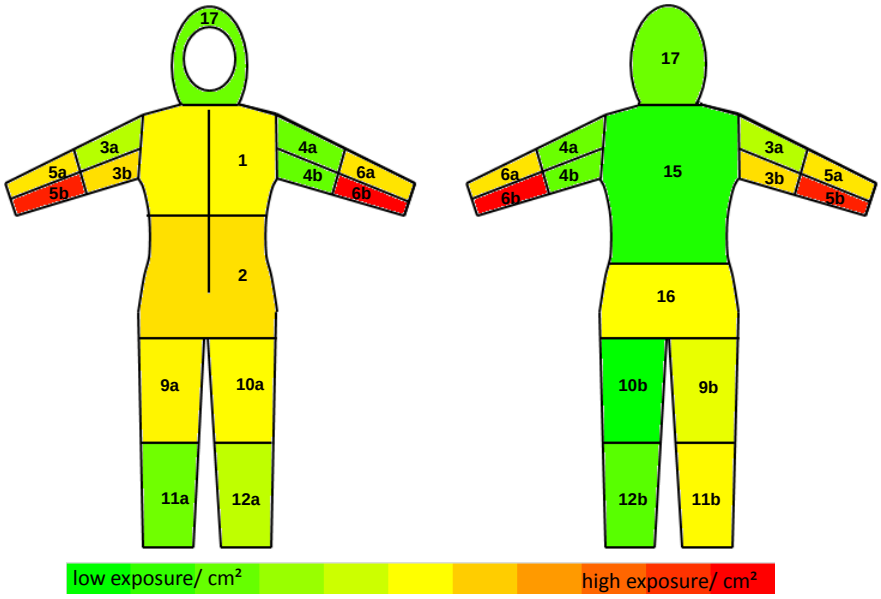

Fig. 4.5 Vehicle-mounted sprayer: schematic representation of the average diflubenzuron exposure of the coverall segments after preparation of the spray liquid.

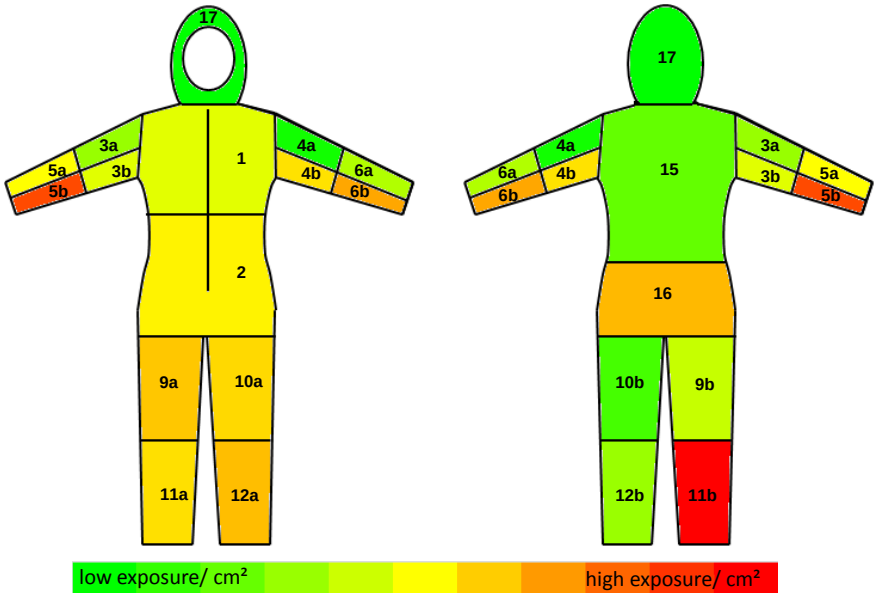

Fig. 4.6 Vehicle-mounted sprayer: schematic representation of the average diflubenzuron exposure of the coverall segments after application of the spray liquid.

Fig. 4.7 Vehicle-mounted sprayer: Preparation of the Dimilin^{TM} 80 WG suspension - the worker is resting his chest, belly and forearms against the sprayer.

Fig. 4.8 Vehicle-mounted sprayer: Preparation of the Dimilin^{TM} 80 WG suspension (company C).

In preparation and application of the diflubenzuron suspension with the vehicle-mounted unit (Tab. 4.5) it is striking that the coveralls that were worn when the vehicle or vehicle-mounted spray unit surfaces had not yet been contaminated with diflubenzuron (beginning of the spray season), show very low exposure or not the typical exposures on chest and belly. This applies for the coveralls VMS-preparation-dO-1 (company A), VMS-preparation-dO-2 (company A) and VMS-preparation-dO-7 (company C), for the coverall VMS-preparation-application-dO-6 (company B) and basically also for the corresponding coveralls in application of Dimilin^{TM} 80 WG suspension VMS-application-dO-2 (referring to VMS-preparation-application-dO-6), VMS-application-dO-3 (referring to VMS-preparation-dO-1), VMS application-dO-4 (referring to VMS-preparation-dO-2) and VMS-application-dO-9 (referring to VMS-preparation-dO-7) (Tab. 4.5). An exception is found in segment 11b (back side of the right lower leg) of coverall VMS-application-dO-9 which in contrast to the rest of the

coveralls, was subjected to an extremely high exposure. From the also high exposures of segment 11b on the following coveralls of company C, it can be assumed that the contamination of the lower thigh of the coverall VMS-application-dO-9 is carried over and subsequently found - with a continuous decrease - on the lower thighs of the subsequent dermal sampler.

When applying Dimilin^{TM} 80 WG suspension with vehicle-mounted sprayer it becomes noticeable that the coveralls of company A apart from chest, belly and forearms, show with back and buttocks a further highly exposed body part (segments 15 and 16). This agrees with the observation that worker #2 of company A frequently leaned against the Unimog or the accompanying vehicle while telephoning (VMS-application-dO-4 to VMS-application-dO-8). On the other hand, the coveralls of company C particularly revealed a diflubenzuron exposure on the lower thighs (segments 11a/b and 12a/b); the cause of this is not clear. The high exposure of the lower thighs occurred with the first sampling of company C and subsequently -with a continuous decrease- on the following coveralls, indicating a carryover (VMS-application-dO9 to VMS-application-dO12). In the case of Dimilin^{TM} 80 WG application with vehicle-mounted unit (Tab. 4.5), the coverall VMS-preparation-application-dO-5 is an exception from the remaining measured values, as it clearly differs from the five remaining coveralls from this activity field with an average exposure of 2.47 ng/g × cm². Again is it the coverall of worker #2, who had to dismount from his Unimog during Dimilin^{TM} 80 WG application to talk to a female cyclist who had ridden directly through the cloud of spray mist.

Following Dimilin^{TM} 80 WG application with hand-held sprayer, the coveralls used as dermal sampler were found to have a very uniform exposure pattern (Tab. 4.4 and Tab. 4.5), independently of whether the Dimilin^{TM} 80 WG suspension was prepared from granules or transferred as already prepared spray liquid. Fig. 4.9 shows that high-level exposure areas are chest and belly (segments 1 and 2), as well as back, buttocks and head (segments 15, 16 and 17). Elevated exposures were also seen on the outsides of the arms (segments 3a, 4a, 5a and 6a) as well as on the front sides of the upper thighs (particularly segment 9a). The workers who applied Dimilin^{TM} 80 WG with hand-held sprayer were rather exposed to an even spray mist from above. It is therefore not surprising that the largest coverall segments - head, chest, belly, back and buttocks - were also found to have the highest percentages of exposure. It is also understandable that the parts of the body exposed to the spray mist (outer sides of the arms, fronts of the legs) show a higher percentage of exposure than the inner side of the arms or the back side of the legs.

As we have discussed above, the exposure levels on the coveralls worn by worker #2 (HHS-preparation-application-dO-1 to HHS-preparation-application-dO-5) were on average markedly higher than those worn by worker #5 (HHS-preparation-application-dO-6 to HHS-preparation-application-dO-8 as well as HHS-transfer-application-dO-1 to HHS-transfer-application-dO-10). These differences are presumably due to individually different approaches during application of Dimilin^{TM} 80 WG suspension with the hand-held sprayer, such as for example the way of holding the spray tubes and whether by preference the trunks or the tops of the trees were sprayed. This assumption is not only supported by the absolute exposure heights, but also by the fact that in the case of worker #2 the pattern of highly exposed outsides of the arms, front sides of the legs as well as head and chest is more

striking (Fig. 4.9). However, the high exposure level on legs, buttocks and back measured on the coveralls HHS-preparation-application-dO-1 and HHS-preparation-application-dO-5 is due to the fact that worker #2 tested the functioning of the hand-held sprayer by spraying towards the ground several times.

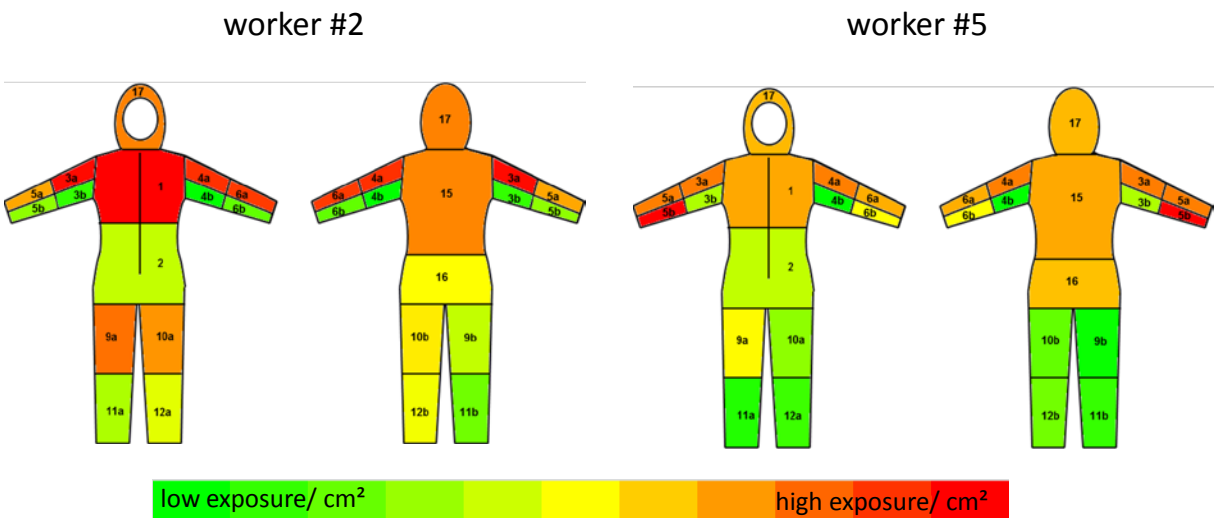

Fig. 4.9 Individual differences in the average diflubenzuron exposure of the coverall segments after preparation and application or preparation/ transfer and application of the spray liquid using a hand-held sprayer.

The differences in the coveralls of workers #2 and #5 can easily be seen from the box plot in Fig. 4.10.

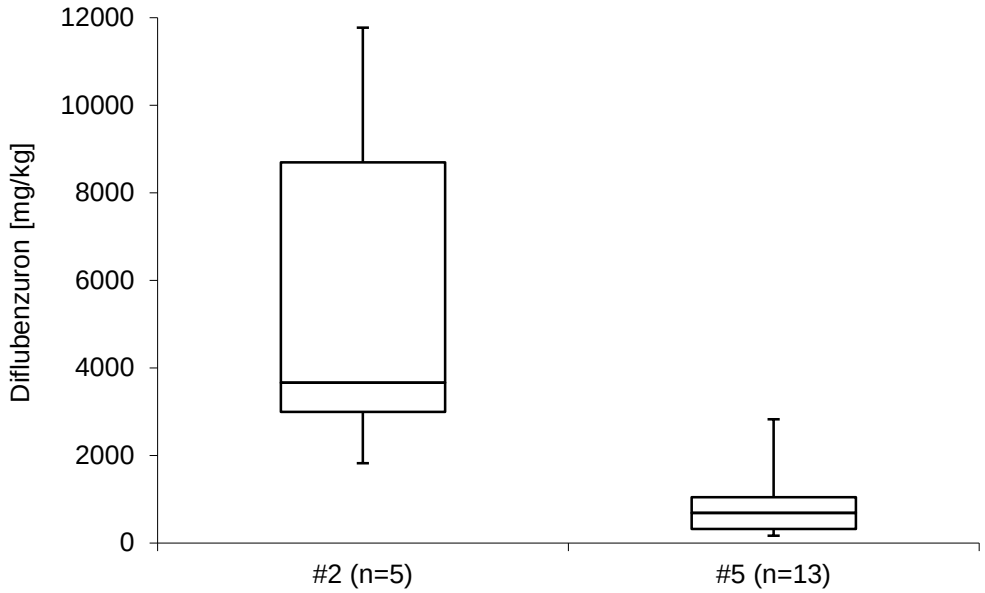

Fig. 4.10 Exposure on the coveralls from working with the hand-held sprayer. The exposure is related to the applied amount of active substance and broke down by workers.

The cleaning of the vehicles/ vehicle-mounted sprayers led to high-level exposure on the belly (segment 2), on the left forearm (segments 6a and 6b) as well as on the front side of the left leg (segments 10a and 12a) (Tab. 4.4, Tab. 4.5 and Fig. 4.11 and Fig. 4.12). On account of the work posture mostly adopted (see Fig. 3.21), these parts of the body were most exposed to the rebounded water of the high-pressure cleaner. While in company C the vehicle was only cleaned with the pressure cleaner, in company A an additional manual cleaning of the contaminated vehicles/ vehicle-mounted sprayers (cleaning-dO-1: brush; cleaning-dO-3: cloth) was carried out. A comparison of data from these two companies indicates that manual cleaning results in increased exposure of the right forearm (segments 5a and 5b); this did not occur during cleaning with high-pressure cleaner only (cleaning-dO-2).

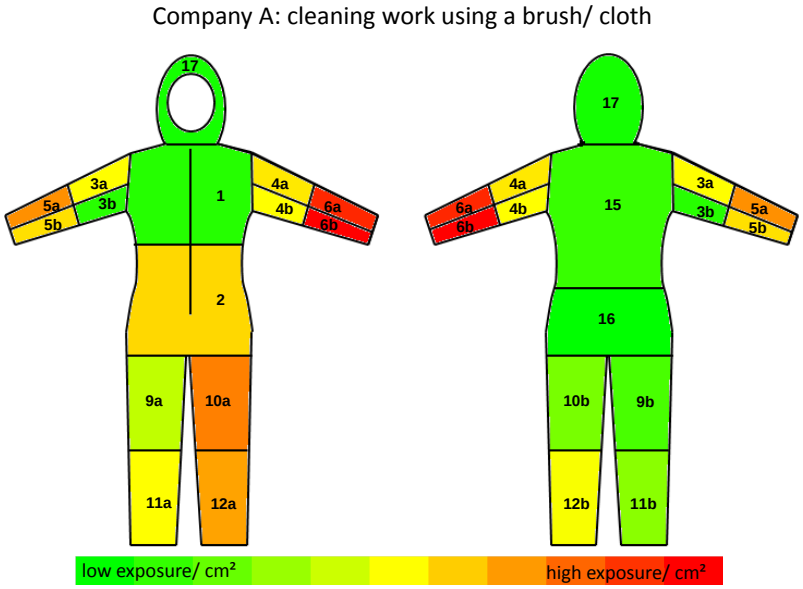

Fig. 4.11 Cleaning procedures carried out by company A: schematic representation of the average diflubenzuron exposure of the coverall segments.

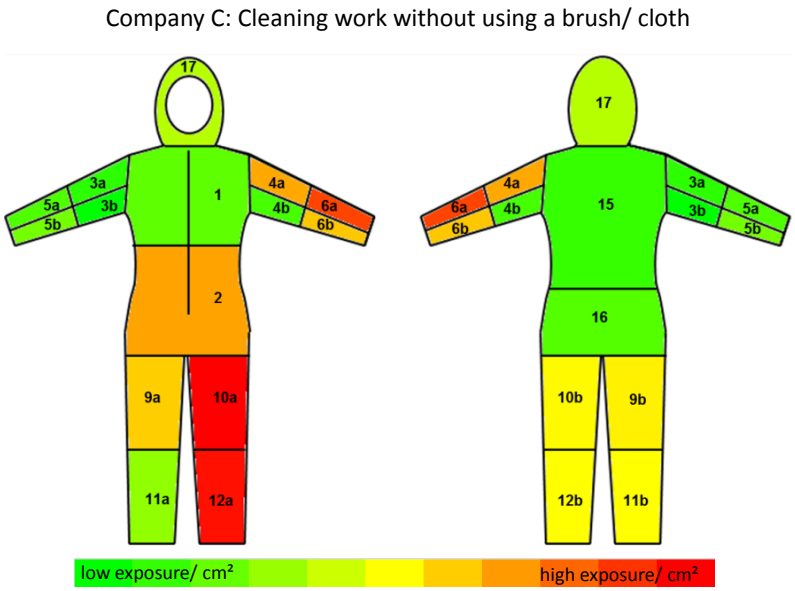

Fig. 4.12 Cleaning procedures carried out by company C: schematic representation of the average diflubenzuron exposure of the coverall segments.

4.1.1.2 Hand exposure: Gloves

Tab. 4.6 shows the absolute amounts of diflubenzuron determined from the cotton gloves used as dermal sampler as well as the amounts related to the applied amount of active substance or – in case of the cleaning procedure – to the duration of this activity. The respective amounts and durations have been taken from Tab. 3.6.
It must here be noted that, when using the hand-held sprayer in the 2015 field study as compared with the 2014 field study, the exposure levels on the gloves were recorded separately for the preparation and for the application of the spray liquid (see chapter 3.3.1.1 for details). As in most cases two full tanks were applied wearing the same coverall, four pairs of gloves were collected along with each coverall in 2015. In Tab. 4.6, the gloves belonging to the respective coveralls are given both as sum and as individual values, hence this data appears in duplicate in this table. For pairs of gloves that were changed on the request of the workers, the exposure is always given as sum in Tab. 4.6. The exposure levels of the gloves related to the applied/handled amount of active substance and for the cleaning procedure related to the duration of the task are also shown in Tab. 4.6.

Tab. 4.6 Workers' dermal exposure (gloves): absolute amount of diflubenzuron [µg] as well as amount of diflubenzuron related to the applied amount of active substance or to the duration of the respective task [mg/kg] or [mg/min].

Task	**Sample identifier**		**Exposure level [µg]**			**Exposure level [mg/kg] or [mg/min]**		
			right hand	**left hand**	**total**	**right hand**	**left hand**	**total**
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dG-1	53000	63300	116300	3.31	3.96	7.27
		dG-2	16400	7470	23870	2.06	0.933	2.99
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dG-1	1520	1270	2790	7.93	6.64	14.6
		dG-2	992	541	1530	4.13	2.25	6.39
		dG-3	7660	3490	11150	31.9	14.6	46.5
		dG-4	6440	2210	8650	26.8	9.22	36.0
		dG-5	1040	707	1750	4.34	2.94	7.28
		dG-6	2010	1790	3800	8.37	7.45	15.8
		dG-7	29.1	14.8	43.9	0.291	0.148	0.439
		dG-8	5430	4070	9500	54.3	40.7	95.0
		dG-9	5480	5460	10940	54.8	54.6	109
		dG-10	1890	3050	4940	18.9	30.5	49.4
		dG-11	1920	533	2450	9.99	2.78	12.8
		VMS-preparation-application-dG-5 [a]	12500	14100	26600	130	147	276
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	Σ dG-1.1-dG-1.2	589	574	1160	3.07	2.99	6.05
		Σ dG-2.1 dG-2.2	308	114	422	1.54	0.570	2.11
		dG-3	136	229	365	0.710	1.19	1.90
		dG-4	1710	1590	3300	7.12	6.63	13.8
		dG-5	2880	2710	5590	12.0	11.3	23.3

Tab. 4.6 (continued)

Task	Sample identifier		Exposure level [µg]			Exposure level [mg/kg] or [mg/min]		
			right hand	left hand	total	right hand	left hand	total
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	Σ dG-6.1-dG-6.2	8680	7490	16170	36.2	31.2	67.4
		dG-7	740	1000	1740	3.08	4.17	7.26
		dG-8	5290	3940	9230	22.0	16.4	38.5
		dG-9	134	245	379	1.34	2.45	3.79
		dG-10	207	359	566	2.07	3.59	5.66
		dG-11	203	73.8	277	2.03	0.738	2.77
		dG-12	60.6	22.3	82.9	0.606	0.223	0.829
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	Σ dG-1.1-dG-1.3	5090	3490	8580	26.5	18.2	44.7
		Σ dG-2.1-dG-2.2	2760	2940	5700	14.4	15.3	29.6
		dG-3	4370	3220	7590	22.8	16.8	39.5
		dG-4	3210	3060	6270	16.7	15.9	32.6
		Σ dG-6.1-dG-6.3	377	253	630	1.89	1.27	3.15
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	Σ dG-1.1-dG-1.2	8360	7690	16050	4980	4580	9560
		dG-2	4050	3200	7250	704	555	1260
		dG-3	7240	7090	14330	1260	1230	2490
		dG-4	4890	3950	8840	849	685	1530
		dG-5	5130	2680	7810	890	465	1350

Tab. 4.6 (continued)

Task	Sample identifier		Exposure level [µg]			Exposure level [mg/kg] or [mg/min]		
			right hand	left hand	total	right hand	left hand	total
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dG-6	4390	3270	7660	1017	756	1770
		dG-7	2520	3030	5550	500	600	1100
		dG-8	1030	2420	3450	179	420	599
Hand-held sprayer Transfer of the Dimilin™ 80 WG suspension	HHS-transfer	dG-3.1	35.2	44.9	80.1	12.2	15.6	27.8
		dG-3.3	83	100	184	29.0	34.8	63.8
		dG-4.1	257	412	669	89.3	143	232
		dG-4.3	359	120	478	124	41.6	166
		dG-5.1	137	278	416	47.7	96.7	144
		dG-5.3	65.3	93.2	159	22.7	32.4	55.1
		dG-6.1	47.2	59.3	107	16.4	20.6	37.0
		dG-6.3	347	601	948	144	250	395
		dG-7.1	153	65.7	219	53.2	22.8	76.0
		dG-7.3	110	65.2	175	38.2	22.6	60.8
		dG-8.1	144	225	369	50.0	78.2	128
		dG-8.3	104	102	206	36.0	35.4	71.4
		dG-9.1	136	187	323	47.2	65.1	112
		dG-9.3	238	290	528	82.7	101	183
		dG-10.1	168	124	291	58.3	42.9	101
		dG-10.3	62.8	232	294	21.8	80.4	102

Tab. 4.6 (continued)

Task	Sample identifier		Exposure level [µg]			Exposure level [mg/kg] or [mg/min]		
			right hand	left hand	total	right hand	left hand	total
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	HHS-application	dG-3.2	47.1	57.4	105	16.4	19.9	36.3
		dG-3.4	66.2	86.0	152	23.0	29.9	52.9
		dG-4.2	78.3	114	192	27.2	39.5	66.7
		dG-4.4	46.6	60.4	107	16.2	21.0	37.2
		dG-5.2	97.6	125	222	33.9	43.2	77.1
		dG-5.4	23.4	26.7	50.1	8.14	9.27	17.4
		dG-6.2	37.5	41.6	79.1	13.0	14.4	27.5
		dG-6.4	53.6	80.3	134	22.4	33.5	55.8
		dG-7.2	55.0	123	178	19.1	42.6	61.7
		dG-7.4	37.6	82.8	120	13.1	28.8	41.8
		dG-8.2	170	198	368	59.0	68.7	128
		dG-8.4	182	103	285	63.3	35.9	99.1
		dG-9.2	210	143	353	72.9	49.5	122
		dG-9.4	105	134	239	36.5	46.4	82.9
		dG-10.2	76.8	82.8	160	26.7	28.7	55.4
		dG-10.4	77.6	97.7	175	27.0	33.9	60.9
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	dG-1	993	1476	2470	172	256	429
		dG-2	1310	1690	3000	227	293	521
		dG-3.1- dG-3.2	82.3	102	185	28.6	35.5	64.1

Tab. 4.6 (continued)

Task	Sample identifier		Exposure level [µg]			Exposure level [mg/kg] or [mg/min]		
			right hand	left hand	total	right hand	left hand	total
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application	dG-3.3 - dG-3.4	150	186	336	52.0	64.7	117
		dG-4.1 - dG-4.2	336	526	861	117	182	299
		dG-4.3 - dG-4.4	405	180	585	141	63	203
		dG-5.1 - dG-5.2	235	403	638	81.6	140	221
		dG-5.3 - dG-5.4	88.7	120	209	30.8	41.6	72.5
		dG-6.1 - dG-6.2	84.8	101	186	29.4	35.0	64.5
		dG-6.3 - dG-6.4	400	681	1080	139	237	376
		dG-7.1 - dG-7.2	208	188	397	72.3	65.4	138
		dG-7.3 - dG-7.4	148	148	296	51.2	51.4	103
		dG-8.1 - dG-8.2	314	423	737	109	147	256
		dG-8.3 - dG-8.4	286	205	491	99.3	71.3	171
		dG-9.1 - dG-9.2	346	330	676	120	115	235
		dG-9.3 - dG-9.4	343	424	767	119	147	266
		dG-10.1 - dG-10.2	245	206	451	84.9	71.6	157
		dG-10.3 - dG-10.4	140	329	470	48.8	114	163
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning	dG-1	24300	36600	60900	0.442*	0.665*	1.11*
		dG-2	14.2	141	155	0.002*	0.020*	0.022*
		dG-3	25700	69400	95100	0.642*	1.74*	2.38*

[a] the pair of gloves worn for the task “Coverall VMS-preparation-application-dO-5” was only worn while preparing the Dimilin™ 80 WG suspension.
* the marked values are related to the duration of the respective task [mg/min].

Over all applications, the absolute amounts of diflubenzuron on the gloves were between 43.9 and 116300 µg and therefore at similar orders of magnitude to those on the coveralls.

The gloves worn during the weighing out and portioning of Dimilin™ 80 WG showed high absolute exposure values of 23870 or 116300 µg. Related to the handled amount of diflubenzuron, an exposure of the hands of 2.99 or 7.27 mg/kg is obtained. This high exposure level for the hands during the weighing out and portioning agrees with the observation that the workers while weighing out the granules repeatedly came into contact with the granules or with the dust generated, for example when they reached into the Dimilin™ 80 WG cardboard barrels to take out granules with the measuring spoon. The extremely high exposure of the gloves of worker #5 is also due to the fact that, after weighing out and portioning, he cleaned the tabletop with paper tissues and then wiped the Dimilin™ 80 WG into his hand before disposing it in the cardboard barrel containing the Dimilin™ 80 WG bags.

The amounts of diflubenzuron collected on the gloves during the cleaning procedures were in company A in the five-digit µg range at 60900 or 95100 µg. On the gloves worn by worker #8 of company C during the cleaning of the vehicle and the vehicle-mounted sprayer (cleaning-dG-2), 155 µg diflubenzuron was quantified, being two magnitudes below the corresponding dermal sampler of company A. These very different exposures of the hands show - as already mentioned with the coveralls - that the workers of company A had with their hands direct contact with the contaminated surfaces of the vehicle/ vehicle-mounted spray unit, as they cleaned these with a brush or cloth in addition to the high-pressure cleaning. In addition, worker #8 of the company C -unlike the workers of company A - did not climb onto the loading platform of the vehicle during the cleaning procedures, which also can have contributed to the differences in exposure.

The statistical distribution of the exposure levels on the gloves related to the applied/handled amounts of active substance or to the task durations are given in Tab. 4.7 for the separate tasks. For the transfer and application of Dimilin™ 80 WG suspension with hand-held sprayer, partly summarised data are listed so that they are shown twice in the table.

Tab. 4.7 Workers' dermal exposure (gloves): data compilation of the amount of diflubenzuron related to the applied amount of active substance or to the duration of the respective task [mg/kg] or [mg/min].

Task	Exposure level [mg/kg] or [mg/min]				
	Minimum	**Median**	**75th percentile**	**95th percentile**	**Maximum**
Weighing out/ portioning of the Dimilin™ 80 WG (n=2)	2.99	-	-	-	7.27
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension (n=12)	0.439	25.9	60.8	185	276
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension (n=12)	0.829	5.86	16.1	51.5	67.4
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension (n=16)	3.15	36.1	58.2	105	112
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension (n=8)	599	1440	1950	7080	9560
Hand-held sprayer Transfer of the Dimilin™ 80 WG suspension (n=16)	27.8	102	150	273	395
Hand-held sprayer Application of the Dimilin™ 80 WG suspension (n=16)	17.4	58.3	78.6	124	128
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension (n=18)	64.1	187	264	442	521
Hand-held sprayer Preparation/ transfer and application of the Dimilin™ 80 WG suspension (n=18)	90.4	475	1330	3550	9560
Cleaning procedures Vehicle/ vehicle-mounted sprayer (n=3)	0.022*	1.11*	-	-	2.38*

* the marked values are related to the duration of the respective task [mg/min].

Related to the handled amount of active substance, the average exposure levels for the weighing out and portioning of Dimilin™ 80 WG granules as well as for the application of the spray liquid with vehicle-mounted unit are in the single-digit mg/kg range. Tasks including preparation of the Dimilin™ 80 WG suspension for the vehicle-mounted unit result in median exposures in the two-digit mg/kg range. In the case of diflubenzuron application with the hand-held sprayer, the adding of Dimilin™ 80 WG granules and water to the tank results in median values in the four-digit mg/kg range, while direct filling of the hand-held sprayer with Dimilin™ 80 WG suspension results in lower values in the three-digit mg/kg range.

These results suggest that, where diflubenzuron is applied using a vehicle-mounted unit, it is the preparation of the Dimilin™ 80 WG suspension that constitutes the main

factor in the exposure of the hands. Correspondingly, the exposure levels obtained by measuring the application where the worker is sitting in the driver's cabin of the truck, is considerably lower.

For the vehicle-mounted unit and the hand-held sprayer, the exposure levels grouped according to the type of application or task are shown in the form of box plots in Fig. 4.13 and Fig. 4.14, respectively. In both figures, the plot shown right includes data from the two plots shown left and in the middle.

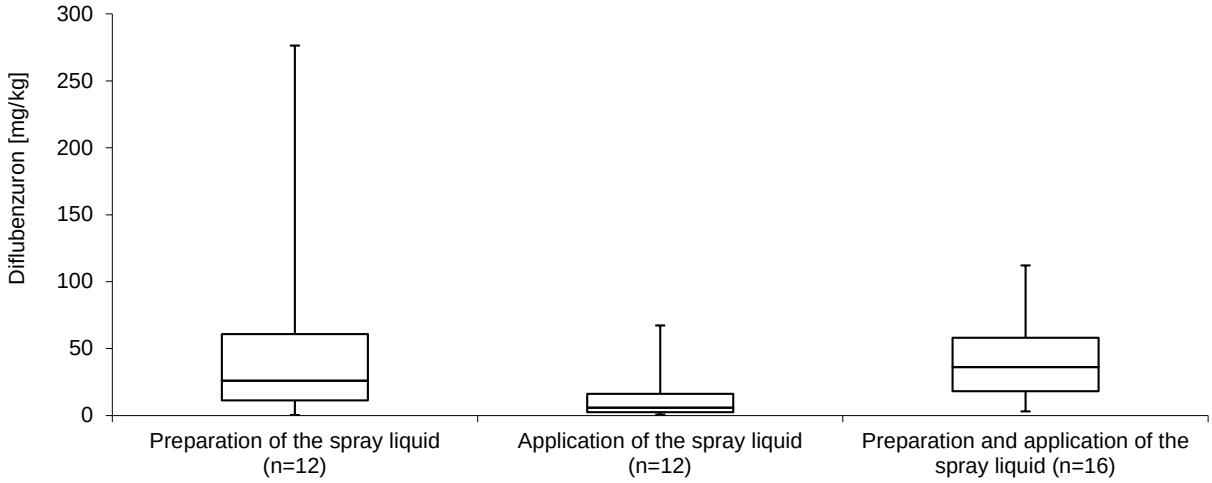

Fig. 4.13 Vehicle-mounted sprayer: exposure of the workers' hands during preparation, during application, as well as during preparation and application. Additional measurements were carried out during preparation and application, where no distinction was made between the two working steps.

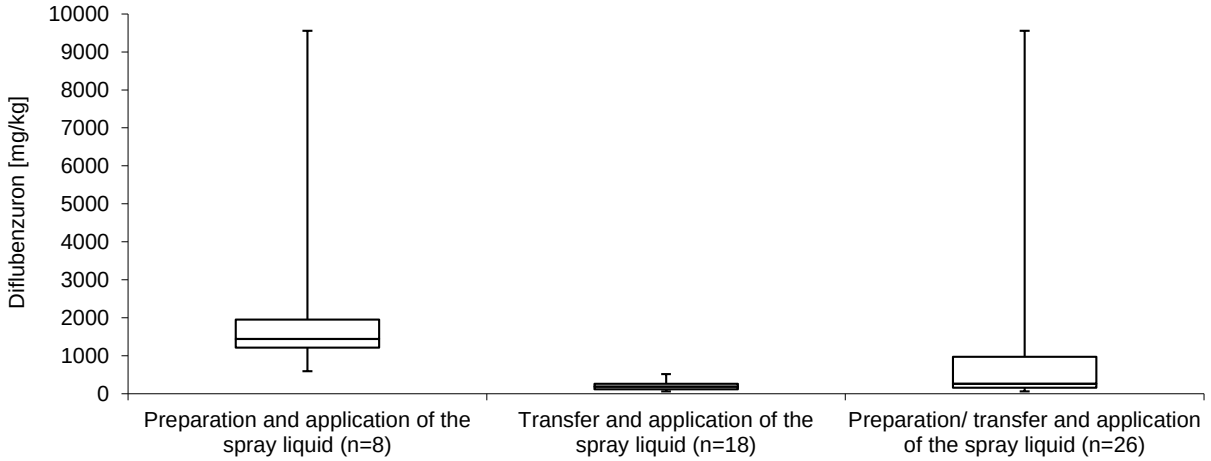

Fig. 4.14 Hand-held sprayer: exposure of the workers' hands during preparation and application, during transfer and application as well as during preparation/ transfer and application.

The separate determination of the hand exposure resulting from transferring the spray liquid into the hand-held sprayer or from application of the spray liquid allows a statement about the contribution of the two different working steps to the total hand exposure. Evaluation of the data shows that the transfer of the Dimilin^{TM} 80 WG suspension produces a tendentially higher hand exposure than the application. In Fig. 4.15, these data are shown in the form of box plots.

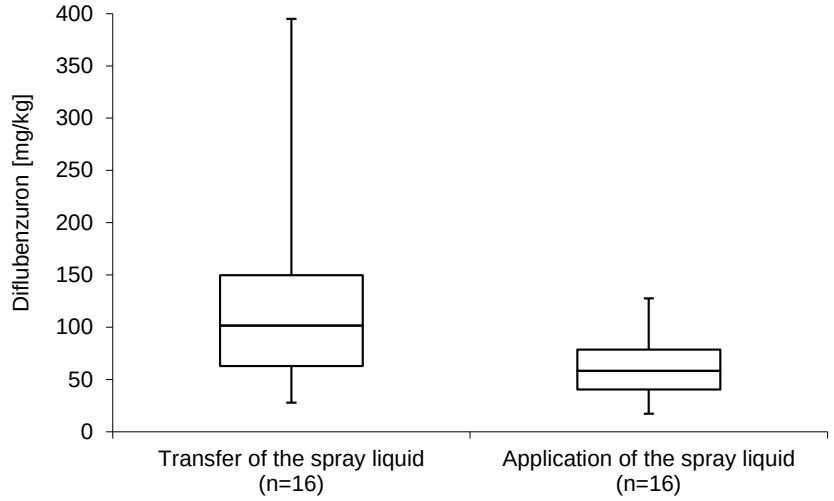

Fig. 4.15 Hand-held sprayer: exposure of the workers' hands during transfer and application of the spray liquid, respectively.

4.1.1.3 Total dermal exposure

In Tab. 4.8, the dermal exposure of coveralls and gloves sampled together is given individually and as total amount. In the last column of the table, the percentage of the hands` exposure in relation to the total dermal exposure is given. From these percentage values it can be seen whether a task resulted in a particular exposure of the hands or of the rest of the body.

Tab. 4.8 Workers' dermal exposure (coveralls and gloves): amount of diflubenzuron related to the amount of active substance or to the duration of the respective task [mg/kg or mg/min].

Task	**Sample identifier (coverall/ gloves)**			**Exposure level [mg/kg] or [mg/min]**			**Percentage of diflubenzuron on the gloves [%]**
				coverall	**gloves**	**total**	
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dO-1	dG-1	1.11	7.27	8.39	86.7
		dO-2	dG-2	0.722	2.99	3.71	80.6
Vehicle-mounted sprayer Preparation of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	dG-1	5.01	14.6	19.6	74.4
		dO-2	dG-2	2.18	6.39	8.57	74.5
		dO-3	dG-3	14.6	46.5	61.1	76.0
		dO-4	dG-4	19.9	36.0	56.0	64.4
		dO-5	dG-5	6.46	7.28	13.7	53.0
		dO-6	dG-6	5.87	15.8	21.7	72.9
		dO-7	dG-7	0.133	0.439	0.572	76.7
		dO-8	dG-8	9.57	95.0	105	90.9
		dO-9	dG-9	9.29	109	119	92.2
		dO-10	dG-10	3.93	49.4	53.3	92.6
		--	dG-11	--	12.8	--	--
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	dG-1.1-dG-1.2	7.36	6.05	13.4	45.1
		dO-2	dG-2.1-dG-2.2	0.417	2.11	2.53	83.5
		dO-3	dG-3	0.791	1.90	2.69	70.6
		dO-4	dG-4	4.89	13.8	18.6	73.8
		dO-5	dG-5	9.85	23.3	33.2	70.3
		dO-6	dG-6.1-dG-6.2	6.89	67.4	74.3	90.7
		dO-7	dG-7	6.72	7.26	14.0	51.9
		dO-8	dG-8	11.0	38.5	49.5	77.7
		dO-9	dG-9	9.81	3.79	13.6	27.8
		dO-10	dG-10	5.81	5.66	11.5	49.3
		dO-11	dG-11	3.76	2.77	6.53	42.4
		dO-12	dG-12	4.58	0.829	5.41	15.3

Tab. 4.8 (continued)

Task	Sample identifier (coverall/ gloves)			Exposure level [mg/kg] or [mg/min]			Percentage of diflubenzuron on the gloves [%]
				coverall	gloves	total	
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation application	dO-1	dG-1.1-dG-1.3	6.67	44.7	51.3	87.0
		dO-2	dG-2.1-dG-2.2	6.42	29.6	36.1	82.2
		dO-3	dG-3	10.8	39.5	50.3	78.6
		dO-4	dG-4	7.40	32.6	40.0	81.5
		dO-5	dG-5 [a]	74.9	276	351	78.7
		dO-6	dG-6.1-dG-6.3	1.87	3.15	5.02	62.8
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation application	dO-1	dG-1.1-dG-1.2	8700	9560	18260	52.3
		dO-2	dG-2	1820	1260	3080	40.8
		dO-3	dG-3	3000	2490	5490	45.4
		dO-4	dG-4	3660	1530	5190	29.5
		dO-5	dG-5	11800	1350	13150	10.3
		dO-6	dG-6	2830	1770	4600	38.5
		dO-7	dG-7	753	1100	1850	59.4
		dO-8	dG-8	1050	599	1650	36.4
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer application MSG-	dO-1	dG-1	460	429	888	48.3
		dO-2	dG-2	1060	521	1580	33.0
		dO-3	dG-3.1-dG-3.4	395	90.4	485	18.6
		dO-4	dG-4.1-dG-4.4	242	251	493	51.0
		dO-5	dG-5.1-dG-5.4	1320	147	1470	10.0
		dO-6	dG-6.1-dG-6.4	261	240	501	47.9
		dO-7	dG-7.1-dG-7.4	166	120	286	4.9
		dO-8	dG-8.1-dG-8.4	687	213	900	23.7
		dO-9	dG-9.1-dG-9.4	879	251	1130	22.2
		dO-10	dG-10.1-dG-10.4	325	160	485	33.0
Cleaning procedures Vehicle/ vehicle-mounted sprayer	Cleaning	dO-1	dG-1	0.657*	1.11*	1.76*	62.8
		dO-2	dG-2	0.109*	0.022*	0.131*	17.0
		dO-3	dG-3	0.294*	2.38*	2.67*	89.0

[a] the pair of gloves worn for the task "Coverall VMS-preparation-application-dO-5" was only worn while preparing the Dimilin™ 80 WG suspension.
* the marked values are related to the duration of the respective task [mg/min].

From the compilation in Tab. 4.8, it can be seen that work in connection with Dimilin^{TM} 80 WG application using a vehicle-mounted unit especially results in an exposure of the hands. With the vehicle-mounted unit, the percentage of Dimilin^{TM} 80 WG exposure on the gloves in relation to the total exposure is 53.0 to 92.6 % (median: 75.3 %) for the preparation of the spray liquid, 15.3 % to 90.7 % (median: 61.1 %) for the application of the spray liquid and 62.8 % to 87.0 % (median: 80.1 %) for the preparation and application of the spray liquid.

In the case of Dimilin^{TM} 80 WG application with hand-held sprayer, the coveralls contribute to the total exposure with more than 60 % (median: 62.6 %), whereby the difference between the tasks HHS-preparation-application (median: 60.3 %) and HHS-transfer-application (median: 67.0 %) is small.

These results reflect the fact that, during application of the spray liquid using a vehicle-mounted unit, the greater part of the dermal exposure of the workers is due to direct contact of the hands and body with contaminated surfaces whereas, during application using the hand-held sprayer, exposure to the spray mist is predominant. These results are additionally supported by the exposure patterns on the coveralls (see Fig. 4.5, Fig. 4.6 and Fig. 4.9).

As regards the cleaning procedures carried out by company A, 62.8 % or 89.0 % of the total exposure occurs on the hands; in the case of company C, this value is only 17.0 %. These differences in the exposure of the hands can be explained by the additionally performed manual cleaning of the vehicles/ vehicle-mounted sprayers by the workers of company A (using a brush or a cloth) (see also Fig. 3.20, as well as Fig. 4.11 and Fig. 4.12).

4.1.2 Inhalation exposure

In Tab. 4.9, broken down according to the different tasks, the inhalation exposure is given in µg/m³, and the samples are grouped corresponding to Tab. 3.7.
On the basis of the measured air concentrations [µg/m³], the exposure levels were calculated assuming an inhalation rate of the worker of 1.25 m³/h (ECHA 2015a) and related to the applied/handled amount of active substance. The data are given in mg/kg in column 5 of Tab. 4.9 (exposure level). When comparing the results with each other, it must always be kept in mind that, in this case, no statement is made as regards the task frequency per shift.

Tab. 4.9 Workers' inhalation exposure: the amount of diflubenzuron is specified as air concentration [µg/m³] as well as exposure level in [mg/kg].

Task	Sample identifier		Air concentration [µg/m³]	Exposure level (amount of diflubenzuron inhaled) [mg/kg]
Weighing out/ portioning of the Dimilin™ 80 WG	**Weighing**	ip-1	274 (34.2*)	0.022
		is-1	29.8 (3.72*)	0.002
		ip-2	694 (56.4*)	0.070
		is-2	135 (11.2*)	0.014
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	**VMS-preparation application**	ip-1	0.35	0.006
		ip-2	0.22	0.004
		ip-3	1.92	0.024
		ip-4	2.92	0.047
		ip-5	0.61	0.016
		ip-6	0.26	0.002
		ip-7	0.46	0.003
		ip-8	2.41	0.027
		ip-9	1.92	0.027
		ip-10	0.59	0.007
		ip-11	0.31	0.003
		ip-12	11.4	0.068
		ip-13	< 0.35	< 0.005
		ip-14	2.45	0.043
		ip-15	0.29	0.006
		ip-16	< 0.38	0.005
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	**VMS-application**	is-1	< 0.68	--
		is-2	8.69	--
		is-3	5.37	--
		ip-1	0.08	0.002
		ip-2	1.58	0.014
		is-4	< 0.40	< 0.003
		is-5	0.30	0.003

* values corrected with regard to time on the assumption that no other tasks involving Dimilin™ 80 WG are carried out.

Tab. 4.9 (continued)

Task	Sample identifier		Air concentration [µg/m³]	Exposure level (amount of diflubenzuron inhaled) [mg/kg]
Vehicle-mounted sprayer - Application of the Dimilin™ 80 WG suspension	**VMS-application**	is-6	0.35	0.005
		is-7	0.50	0.006
		is-8	0.71	0.007
		is-9	0.25	0.003
		is-10	< 0.37	< 0.005
		is-11	< 0.33	< 0.005
		is-12	< 0.27	< 0.006
		is-13	< 0.42	< 0.005
Hand-held sprayer - Preparation and application of the Dimilin™ 80 WG suspension	**HHS-preparation-application**	ip-1	7.57	3.66
		ip-2	17.4	1.45
		ip-3	5.47	0.44
		ip-4	13.5	1.27
		ip-5	8.4	0.82
		ip-6	16.2	3.91
		ip-7	4.68	0.50
		ip-8	4.03	0.35
Hand-held sprayer - Transfer and application of the Dimilin™ 80 WG suspension	**HHS-transfer-application**	ip-1	1.52	0.17
		ip-2	2.41	0.23
		ip-3	2.37	0.23
		ip-4	3.14	0.25
		ip-5	< 1.30	< 0.09
		ip-6	2.08	0.17
		ip-7	< 1.24	< 0.09
		ip-8	< 0.93	< 0.09
		ip-9	< 0.93	< 0.09
		ip-10	< 0.81	< 0.09

For the cleaning of the vehicle-mounted sprayer, the data cannot be related to the amount of active substance. During the field studies, it was observed that the spray unit and the vehicle were regularly exposed to the spray mist during application. A part of the spray liquid ran off, thus washing away existing contaminations, on the other hand there remained a certain amount of wetting, which with time dried up.
As this happens regularly during the pest control season, a for the most part constant level of contamination occurs after a short time, which is removed by cleaning. In order to obtain generally valid data for “cleaning” as a task, the air concentration of diflubenzuron additionally related to the non-volatile portion of the biocide, because

all volatile components have evaporated at the time of cleaning. Since the product contains approximately 80 % of the active substance diflubenzuron, the amount of all non-volatile constituents (including the active substance) corresponds to about 1.25 times the amount of the active substance. In addition, assuming an inhalation rate of the worker of 1.25 m³/h (ECHA 2015a), this value is related to the duration of the task in order to obtain the data in µg/min given in the last column of Tab. 4.10.

Tab. 4.10 Workers' inhalation exposure: the air concentration is given in [µg/m³]. The right-hand column indicates the exposure to the non-volatile portion of the insecticide assuming an inhalation rate of the worker of 1.25 m³/h based on the duration of the respective task [µg/min].

Task	**Sample identifier**		**Diflubenzuron**	**Non-volatile matter**
			Air concentration [µg/m³]	**Exposure/ duration of the respective task [µg/min]**
Cleaning procedures - Vehicle/ vehicle-mounted sprayer	**Cleaning**	ip-1	1.68	0.04
		is-1	0.15	0.004
		is-2	0.82	0.02
		is-3	2.44	0.06
		ip-2	< 3.71	< 0.10
		is-4	< 3.71	< 0.10
		is-5	< 3.71	< 0.10
		is-6	< 3.71	< 0.10
		ip-3	1.69	0.04
		is-7	8.91	0.23
		is-8	< 0.65	< 0.02
		is-9	5.18	0.13

From Tab. 4.9 and Tab. 4.10, clearly graded exposure levels are obtained, which are shown in Tab. 4.11 in the form of an overview. The median value for weighing out and portioning Dimilin^{TM} 80 WG is 0.046 mg/kg, for work with the vehicle-mounted sprayer the median values are 0.006 mg/kg at maximum, and for work with the hand-held sprayer they are 1.05 mg/kg at maximum.

The median inhalation exposure when cleaning the vehicles and vehicle-mounted sprayers is 0.08 µg/min. If only the results of the personal air sampling are considered, a median of 0.04 µg/min (range: 0.04- <0.10 µg/min; n=3) is obtained. The results of the cleaning procedures can, due to the relationship to task duration, not be compared directly with the other results.

As all values are task-related without any relationship to the shift, they are not to be used in relationship to the highest exposure of the workers.

Tab. 4.11 Workers' inhalation exposure: data compilation in [mg/kg]. In derogation from that, for cleaning procedures the amount of collected non-volatile matter assuming an inhalation rate of the worker of 1.25 m^3/h based on the duration of the task [µg/min] is given.

Task	Exposure level [mg/kg] or [µg/min]				
	Minimum	**Median**	**75th percentile**	**95th percentile**	**Maximum**
Weighing out/ portioning of the Dimilin™ 80 WG (n=2)	0.022	0.046	0.058	0.068	0.070
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension (n=16)	0.002	0.006	0.026	0.052	0.068
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension (n=12)	0.002	0.005	0.006	0.010	0.014
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension (n=8)	0.35	1.05	2.00	3.82	3.91
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension (n=10)	0.094	0.13	0.21	0.24	0.25
Cleaning procedures Vehicle/ vehicle-mounted sprayer (n= 12 or n=3 (personal))	0.004* 0.04*	0.08* 0.04*	0.10* 0.07*	0.18* 0.07*	0.23* 0.10*

* the marked values indicate the amount of non-volatile matter in relation to the duration of the task [µg/min].

The inhalation exposure to diflubenzuron grouped according to application type and task is given in the form of box plots for the vehicle-mounted unit in Fig. 4.16 and for the hand-held sprayer in Fig. 4.17.

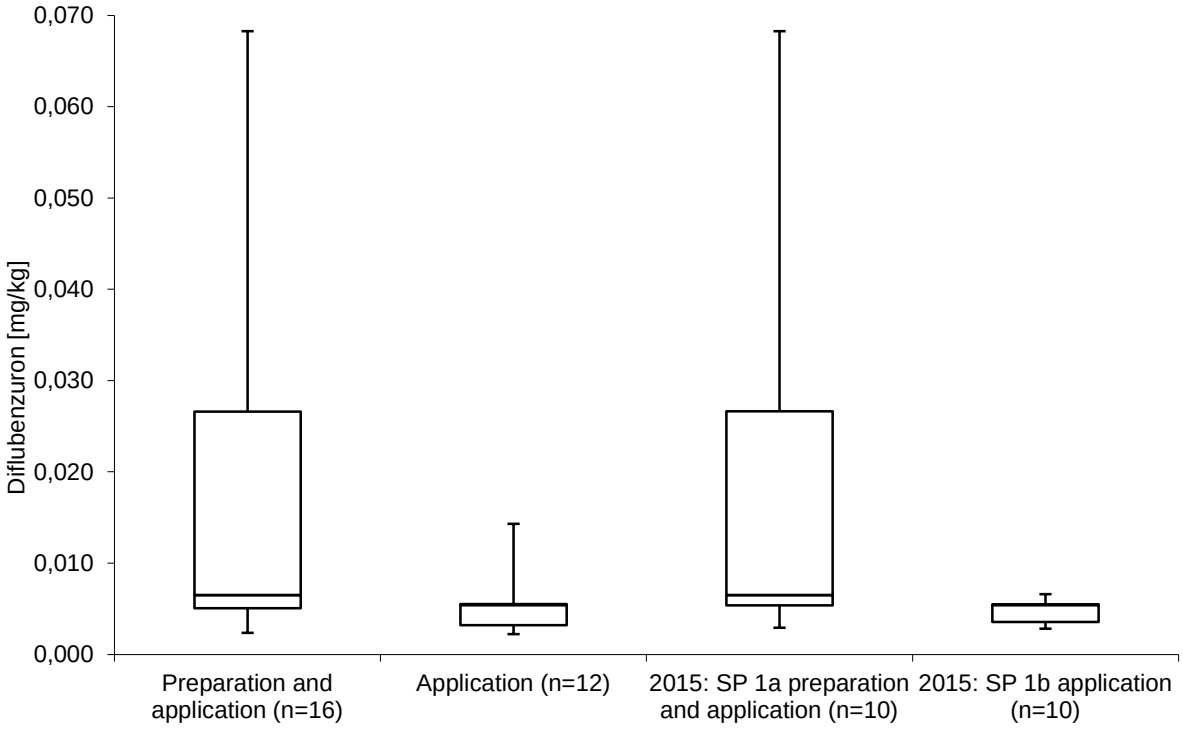

Fig. 4.16 Vehicle-mounted sprayer (workers' inhalation exposure during preparation and application as well as during application of the spray liquid (data taken from Tab. 4.11). Representation of sampling point 1 split into two separate measurements 1a and 1b in 2015.

Inhalation exposure is clearly different between the two types of spray application (vehicle-mounted sprayer or hand-held sprayer) (Fig. 4.16 and Fig. 4.17). When using the hand-held sprayer, the worker is exposed to a higher level of diflubenzuron than when using the vehicle-mounted sprayer.

The originally envisaged subtraction of the measured values 1b from the corresponding values 1a to determine exposure during the preparation of Dimilin^{TM} 80 WG suspension was not found to be useful. This is due to the low number of measured values and the external conditions while sampling at the workplace. However, it can be seen from the median values in Fig. 4.16 that with the vehicle-mounted unit the preparation of the spray liquid results in a higher inhalation exposure of the worker than the application of the spray liquid. This becomes clear when comparing the sampling points 1a (personal sampling during preparation and application) and 1b (stationary sampling in the driver's cabin; representing inhalation exposure during application).

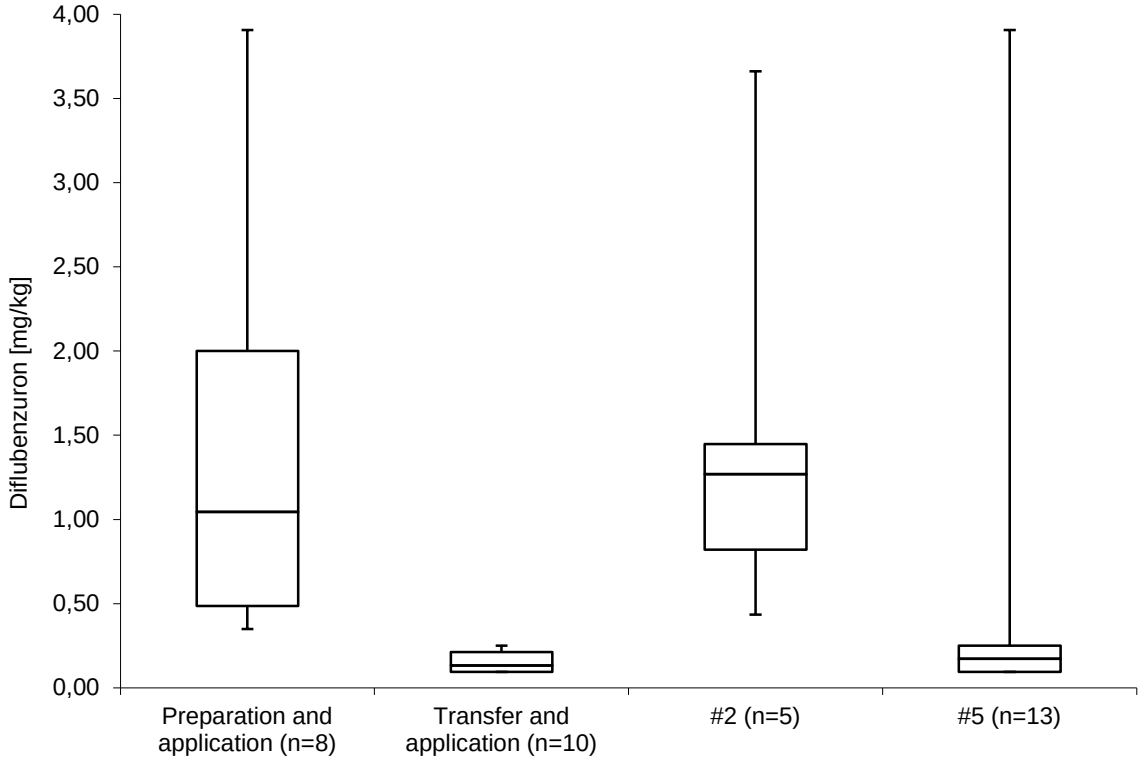

Fig. 4.17 Hand-held sprayer (workers' inhalation exposure during both preparation and application and both transfer and application of the spray liquid (data taken from Tab. 4.11). Besides, the exposure levels of worker #2 and worker #5 are compared.

The highest exposure was demonstrated when using the hand-held sprayer. The box plots in Fig. 4.17 show that the preparation of the Dimilin^{TM} 80 WG suspension with subsequent application results in a clearly higher level of exposure than the transfer of an already prepared spray liquid with subsequent application. On closer analysis, however, it becomes clear that differences in the work habits of the individual workers can affect exposure levels as well (comparison of workers). This is shown in Fig. 4.17. The task "preparation and application of Dimilin^{TM} 80 WG suspension" was mainly carried out by worker #2, whereas the task "transfer and application of Dimilin^{TM} 80 WG suspension" only by worker #5. Whether the different exposure levels result from task-related or interindividual differences, cannot be clarified on the basis of the available data.

Furthermore, from Tab. 4.11 it is possible to read off that the very high air concentrations when weighing out and portioning Dimilin^{TM} 80 WG (274 or 694 µg/m³ diflubenzuron, Tab. 4.9) becomes relative, as soon as the value is related to the amount of active substance handled. Thus, when related to the amount of active substance handled, the task "weighing out and portioning Dimilin^{TM} 80 WG" only shows an average level among the samples grouped according to task. For a final assessment of the individual tasks, however, the handling of large amounts of active substance within a short period of time should not be neglected.

4.2 Bystanders

4.2.1 Dermal exposure

The exposure levels for bystanders measured from the Tyvek™ sheets are given in Tab. 4.12. In the table, both the absolute values and the values related to the applied amount of active substance are given. Diflubenzuron was found on all Tyvek™ sheets; the lowest values were in a single-digit µg-range and the highest values in a five-digit µg range.

Where Dimilin™ 80 WG was applied with a vehicle-mounted unit, a median value of 441 µg diflubenzuron was determined for a distance of 5 m (range: 19.8-12118 µg), and of 237 µg for a distance of 10 m (range: 3.86-3966 µg). Where application was carried out using a hand-held sprayer, median values of 390 µg diflubenzuron were found on the 5 m Tyvek™ sheets (range: 4.24-4694 µg) and of 194 µg on the 10 m Tyvek™ sheets (range: 1.96-4590 µg). These absolute values show that the exposure on the Tyvek™ sheets placed at a distance of 10 m from the treated tree/treated group of trees was on average clearly lower than that on the Tyvek™ sheets placed at a distance of 5 m.

In order to compare the two types of application with each other, the measured values were related to the applied amount of active substance (Tab. 4.12). Contrary to the exposure measurements for the workers, however, it is not the total amount of active substance stored in the spray tank that is relevant here, but only the amount applied immediately surrounding the measuring set up. In the case of Dimilin™ 80 WG application with vehicle-mounted unit the sprayed amount was estimated as follows: at a driving speed of 5 km/h, a total flow of 20 L/min and a wind drift of approximately 50 m, 5.76 g diflubenzuron are applied in the area around the sampling set up (location ± 50 m) at a single pass-by. A correspondingly higher amount of active substance is applied when driving past two or more times (Tab. 3.8).
This calculation is a rough estimate, which can be very inaccurate in individual cases. This approach has been adopted despite potential inaccuracies as only the reference to the applied amount of active substance allows for a comparison of the two types of application.

Where the biocide was applied with a hand-held sprayer, the volume of spray liquid applied in the proximity of the sampling set up was taken as basis to calculate the amount of active substance, whereby between 7 L and 48 L spray liquid were applied (Tab. 3.8).

If the measured exposure levels are additionally related to the surface area of the Tyvek™ sheets used as dermal sampler, the values listed in Tab. 4.13 are obtained.

Tab. 4.12 Bystanders' dermal exposure (Tyvek™ sheets): absolute exposure levels and exposure levels in relation to the amount of active substance applied near the measurement setup [µg] or [mg/kg]. The applied amounts of active substance are specified in Tab. 3.8.

Task	Sample identifier (bystanders)		Exposure level [µg]						Exposure level [mg/kg]					
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total	5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	**VMS-application**	dB-1	335	431	766	135	270	406	58.1	74.8	133	23.5	47.0	70.4
		dB-2	126	281	407	11.5	9.17	20.7	21.8	48.8	70.6	2.00	1.59	3.59
		dB-3	33.2	49.6	82.8	7.47	8.21	15.7	2.89	4.30	7.19	0.649	0.713	1.36
		dB-4	96.4	150	246	5.31	4.13	9.44	8.37	13.0	21.4	0.461	0.358	0.819
		dB-5	58.4	79.6	138	20.8	10.3	31.1	10.1	13.8	23.9	3.61	1.79	5.39
		dB-6	351	346	696	230	163	393	30.4	30.0	60.5	20.0	14.2	34.1
		dB-7	1240	1710	2950	2180	1790	3970	216	297	513	378	311	689
		dB-8[a]	5230	6890	12100	881	1160	2040	908	1200	2100	153	201	354
		dB-9	336	419	755	324	400	723	58.3	72.8	131	56.2	69.4	126
		dB-10	118	144	262	98.4	105	204	20.5	25.0	45.5	17.1	18.3	35.4
		dB-11	12.6	7.22	19.8	1.29	2.56	3.86	1.09	0.627	1.72	0.112	0.222	0.335
		dB-12	298	316	614	194	200	394	25.9	27.4	53.3	16.8	17.4	34.2
		dB-13	119	192	311	45.5	67.6	113	10.4	16.6	27.0	3.95	5.87	9.82
		dB-14	211	230	441	104	133	237	36.6	40.0	76.6	18.1	23.1	41.2
		dB-15	1250	1480	2730	1000	889	1890	72.3	85.5	158	58.1	51.4	110

Tab. 4.12 (continued)

Task	Sample identifier (bystanders)		Exposure level [µg]						Exposure level [mg/kg]					
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total	5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	HHS-application	dB-1	7.27	7.79	15.1	7.07	5.73	12.8	4.33	4.64	8.97	4.21	3.41	7.62
		dB-2	1550	1090	2640	300	500	800	134	94.6	229	26.0	43.0	69.0
		dB-3	81.1	113	195	85.6	89.1	175	14.1	19.7	33.8	14.9	15.5	30.3
		dB-4	641	907	1550	187	115	302	222	315	538	64.9	39.9	105
		dB-5[b]	645	623	1270	51.9	45.3	97.2	224	216	440	18.0	15.7	33.7
		dB-6	1000	1210	2210	2290	2300	4590	92.7	112	205	212	213	425
		dB-7	72.2	85.7	158	119	112	231	12.5	14.9	27.4	20.6	19.5	40.1
		dB-8	176	213	390	5.81	2.48	8.29	61.2	74.0	135	2.02	0.863	2.88
		dB-9	48.2	84.9	133	14.5	26.7	41.2	8.37	14.7	23.1	2.51	4.64	7.15
		dB-10	1.17	3.08	4.24	0.979	0.983	1.96	0.202	0.534	0.737	0.170	0.171	0.341
		dB-11	936	957	1890	264	251	515	325	332	657	91.8	87.2	179
		dB-12	2770	1920	4690	1410	903	2310	481	334	815	244	157	401
		dB-13	159	229	387	74.7	119	194	55.2	79.4	135	25.9	41.5	67.4
		dB-14	855	339	1190	340	238	577	148	58.9	207	58.9	41.3	100
		dB-15	144	187	331	41.7	70.3	112	25.0	32.4	57.5	7.24	12.2	19.5

[a]: The rack frame located at 5 m was blown over by the force of the spray jet, however, it was set up again after about 1 min.
[b]: The 5 m measuring equipment was set up at a distance of just 4.3 metres to the tree.

Tab. 4.13 Bystanders' dermal exposure (Tyvek™ sheets): the absolute amount of diflubenzuron the exposure levels in relation to the amount of active substance applied near the measurement setup was additionally related to the surface area of the Tyvek™ sheets used as dermal sampler [ng/cm²] or [ng/(g × cm²)]. The applied amounts of active substance are specified in Tab. 3.8.

Task	Sample identifier (bystanders)		Exposure level [ng/cm²]						Exposure level [ng/g × cm²]					
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total	5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	**VMS-application**	dB-1	40.4	46.8	43.8	16.3	29.4	23.2	7.01	8.12	7.60	2.83	5.10	4.03
		dB-2	15.2	30.5	23.2	1.39	1.00	1.18	2.63	5.29	4.03	0.241	0.173	0.205
		dB-3	4.01	5.38	4.73	0.902	0.892	0.897	0.348	0.467	0.411	0.078	0.077	0.078
		dB-4	11.6	16.3	14.1	0.641	0.448	0.539	1.01	1.41	1.22	0.056	0.039	0.047
		dB-5	7.04	8.64	7.88	2.51	1.12	1.78	1.22	1.50	1.37	0.435	0.194	0.308
		dB-6	42.3	37.6	39.8	27.7	17.7	22.5	3.67	3.26	3.45	2.41	1.54	1.95
		dB-7	150	186	169	263	194	227	26.0	32.2	29.3	45.6	33.7	39.3
		dB-8[a]	631	748	692	106	126	117	109	130	120	18.5	21.9	20.3
		dB-9	40.5	45.5	43.2	39.0	43.4	41.3	7.03	7.90	7.49	6.78	7.54	7.18
		dB-10	14.3	15.6	15.0	11.9	11.4	11.6	2.48	2.71	2.60	2.06	1.98	2.02
		dB-11	1.51	0.784	1.13	0.156	0.278	0.220	0.131	0.068	0.098	0.014	0.024	0.019
		dB-12	36.0	34.3	35.1	23.4	21.7	22.5	3.12	2.97	3.04	2.03	1.89	1.95
		dB-13	14.4	20.8	17.8	5.49	7.34	6.46	1.25	1.81	1.54	0.476	0.637	0.561
		dB-14	25.5	25.0	25.2	12.6	14.4	13.6	4.42	4.34	4.38	2.19	2.51	2.36
		dB-15	151	160	156	121	96.5	108	8.72	9.28	9.02	7.01	5.58	6.26

Tab. 4.13 (continued)

Task	Sample identifier (bystanders)		Exposure level [ng/cm²]						Exposure level [ng/g × cm²]					
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total	5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	**HHS-application**	dB-1	0.877	0.846	0.861	0.853	0.622	0.731	0.522	0.504	0.512	0.508	0.370	0.435
		dB-2	186	118	151	36.2	53.8	45.4	16.2	10.3	13.1	3.14	4.67	3.94
		dB-3	9.79	12.3	11.1	10.3	9.68	10.0	1.70	2.14	1.93	1.79	1.68	1.73
		dB-4	77.3	98.5	88.5	22.6	12.5	17.2	26.8	34.2	30.7	7.83	4.33	5.99
		dB-5[b]	77.8	67.6	72.4	6.26	4.92	5.55	27.0	23.5	25.1	2.17	1.71	1.93
		dB-6	121	131	126	276	250	262	11.2	12.2	11.7	25.6	23.1	24.3
		dB-7	8.71	9.30	9.02	14.3	12.2	13.2	1.51	1.62	1.57	2.48	2.11	2.29
		dB-8	21.3	23.1	22.3	0.701	0.270	0.474	7.39	8.03	7.73	0.243	0.094	0.165
		dB-9	5.82	9.22	7.61	1.75	2.90	2.35	1.01	1.60	1.32	0.303	0.504	0.409
		dB-10	0.141	0.334	0.243	0.118	0.107	0.112	0.024	0.058	0.042	0.021	0.019	0.019
		dB-11	113	104	108	31.9	27.3	29.5	39.2	36.1	37.5	11.1	9.46	10.2
		dB-12	334	209	268	170	98.1	132	58.0	36.3	46.6	29.5	17.0	22.9
		dB-13	19.2	24.8	22.1	9.01	13.0	11.1	6.66	8.61	7.69	3.13	4.50	3.85
		dB-14	103	36.8	68.2	41.0	25.8	33.0	17.9	6.39	11.8	7.11	4.48	5.73
		dB-15	17.4	20.3	18.9	5.03	7.64	6.40	3.02	3.52	3.28	0.873	1.33	1.11

[a]: The rack frame located at 5 m was blown over by the force of the spray jet, however, it was set up again after about 1 min.
[b]: The 5 m measuring equipment was set up at a distance of just 4.3 metres to the tree.

The high fluctuation of measured values as regards the exposure of bystanders indicates a high variability in exposure situations. Possible influencing factors, which here play a role are, apart from the weather (adverse wind, change in wind direction), the number and position of the treated trees (individual trees, groups of trees or tree rows), the number of passages of the spray vehicle at different distances from the Tyvek^{TM} sheets (vehicle-mounted sprayer) or the movement pattern of the pest control operators around the treated tree/trees (hand-held sprayer). As, with the hand-held sprayer, the worker moved around the tree during application in most cases, an exposure of the Tyvek^{TM} sheets on both sides during these measurements could not be excluded.

In the case of Dimilin^{TM} 80 WG application with vehicle-mounted sprayer, the up-and-down movement of the spray cannon head additionally meant that some individual Tyvek^{TM} sheets were exposed directly to the spray jet, others only to spray mist diffusely blown towards the sheets. This results, as can clearly be seen in the box plots in Fig. 4.18, in extreme exposure levels in individual cases. For example, the 5 m Tyvek^{TM} sheet in measurement VMS-application-dB-8, exposed to 2104 mg/kg, was directly hit by spray jet and was even blown over by the force of the fan.

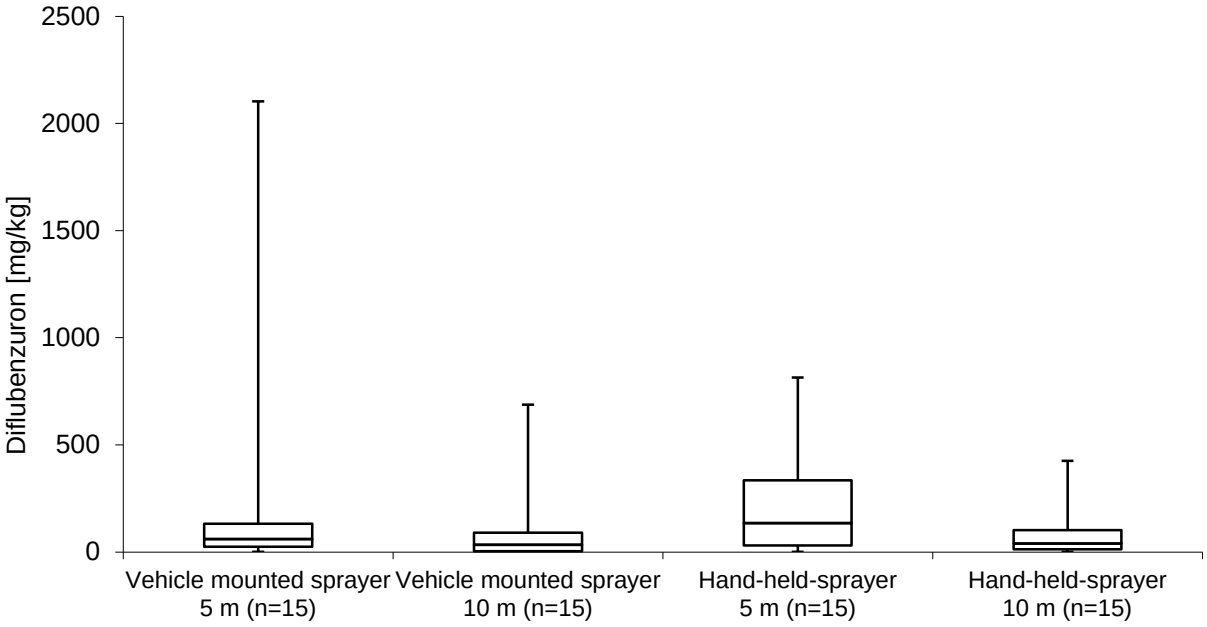

Fig. 4.18 Bystanders' dermal exposure after spray application using a vehicle-mounted sprayer and a hand-held sprayer, respectively.

The statistical distribution of the individual values found in Tab. 4.13 is given in Tab. 4.14 for both types of application.

Tab. 4.14 Bystanders' dermal exposure: data compilation of the exposure levels in relation to the amount of active substance applied in the immediate surrounding of the measurement setup [mg/kg]. The applied amounts of active substance are specified in Tab. 3.8.

Type of application		**Exposure level [mg/kg]**				
		Minimum	**Median**	**75th percentile**	**95th percentile**	**Maximum**
Vehicle-mounted sprayer (n=15)	**5 m upper segment**	1.09	25.9	58.2	423	908
	5 m lower segment	0.627	30.0	73.8	567	1196
	5 m total	1.72	60.5	132	990	2104
	10 m upper segment	0.112	17.1	39.8	220	378
	10 m lower segment	0.222	17.4	49.2	234	311
	10 m total	0.335	34.2	90.0	455	689
Hand-held sprayer (n=15)	**5 m upper segment**	0.202	61.2	185	372	481
	5 m lower segment	0.534	74.0	164	333	334
	5 m total	0.737	135	334	704	815
	10 m upper segment	0.170	20.6	61.9	222	244
	10 m lower segment	0.171	19.5	42.2	174	213
	10 m total	0.341	40.1	103	408	425

The data demonstrate that the exposure levels in the respective upper and lower Tyvek^{TM} sheet segments are comparable. Tendentially, the exposure of bystanders decreases with increasing distance from the treated tree/group of trees.

4.2.2 Inhalation exposure

The inhalation exposure levels recorded - next to the Tyvek^{TM} sheets used to measure the dermal exposure of the bystanders - are given as absolute values in Tab. 4.15.
To compare the two types of application, i.e. with vehicle-mounted sprayer or with a hand-held sprayer, the values obtained were related to the applied amount of active substance. For calculation, the parameters from Section 4.2.1 as well as the amount of applied Dimilin^{TM} 80 WG suspension from Tab. 3.9 were used.

Tab. 4.15 Bystanders' inhalation exposure: the measured amount of diflubenzuron is given as air concentration [µg/m³] as well as exposure level in [mg/kg], assuming an inhalation rate of an adult of 1.25 m^3/h.

Task	**Sample identifier (bystander)**		**Air concentration [µg/m³]**		**Exposure level (assuming an inhalation rate of 1.25 m³/h) [mg/kg]**	
			5 m	**10 m**	**5 m**	**10 m**
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	iB-1	< 1.00	1.08	< 0.06	0.07
		iB-2	< 1.13	< 1.13	< 0.06	< 0.06
		iB-3	2.53	1.67	0.07	0.05
		iB-4	< 1.13	< 1.13	< 0.03	< 0.03
		iB-5	1.12	< 1.13	0.06	< 0.06
		iB-6	< 0.31	< 0.31	< 0.03	< 0.03
		iB-7	0.71	< 0.59	0.07	< 0.06
		iB-8	4.48	3.57	0.24	0.19
		iB-9	< 1.73	< 1.73	< 0.09	< 0.09
		iB-10	1.87	1.78	0.10	0.10
		iB-11	< 1.73	< 1.73	< 0.05	< 0.05
		iB-12	3.56	< 1.63	0.10	< 0.05
		iB-13	2.48	3.17	0.07	0.09
		iB-14	< 1.73	< 1.73	< 0.09	< 0.09
		iB-15	< 1.18	< 1.18	< 0.03	< 0.03
Hand-held sprayer Application of the Dimilin™ 80 WG suspension	HHS-application	iB-1	< 0.57	< 0.57	< 0.21	< 0.21
		iB-2	0.72	1.07	0.07	0.10
		iB-3	1.19	< 1.06	0.06	0.06
		iB-4	27.3	23.8	2.96	2.58
		iB-5	29.5	10.1	3.20	1.09
		iB-6	2.11	1.97	0.22	0.20
		iB-7	0.80	1.17	0.09	0.13
		iB-8	< 1.73	< 1.73	< 0.19	< 0.19
		iB-9	3.08	1.65	0.30	0.16
		iB-10	< 1.08	< 1.08	< 0.09	< 0.09
		iB-11	4.79	3.41	0.59	0.42
		iB-12	1.60	4.33	0.12	0.33
		iB-13	< 1.73	< 1.73	< 0.18	< 0.19
		iB-14	< 0.90	< 0.90	< 0.09	< 0.09
		iB-15	< 0.89	< 0.89	< 0.10	< 0.10

From the measurement results it becomes clear that a large part of the data are below the quantification limit of the analytical method. When using the vehicle-mounted sprayer, a median value of 0.07 µg diflubenzuron (range: 0.03-0.24 µg; n=15) was obtained at a distance of 5 m and a median value of 0.06 µg (range: 0.03-0.19 µg; n=15) at a distance of 10 m. When using the hand-held sprayer for applications, a median value of 0.19 µg diflubenzuron (range: 0.06-3.20; n=15) was determined at a distance of 5 m and a median value of 0.19 µg diflubenzuron (range: 0.06-2.58 µg; n=15) on the 10 m Tyvek^{TM} sheets.
The data on the statistical distribution of the measured values related to the amount of active substance are shown in Tab. 4.16 and given as box plots in Fig. 4.19.

The results in Tab. 4.16 make it clear that bystanders located at a distance of 5 m or 10 m from the treated trees are exposed to approximately the same extent by inhalation. This applies for both types of application. In addition, Fig. 4.19 clearly indicates that spray application with hand-held sprayers cause a higher inhalation exposure of the bystanders than spray application with vehicle-mounted sprayers.

The high fluctuation of measured values determined for bystanders indicates a high variability in exposure situations. Possible influencing factors that here play a role are, apart from the weather (adverse wind, changing wind direction), the number and arrangement of the treated trees (individual trees, groups of trees or tree rows), the number of passages of the spraying vehicle at different distances from the set-up of the measurement set up (vehicle-mounted sprayer) or the movement pattern of the pest control operators around the treated tree/tree groups (hand-held sprayer).

Tab. 4.16 Bystanders' inhalation exposure: data compilation of the amount of diflubenzuron related to the amount of active substance applied in the immediate surrounding of the measurement setup [mg/kg]. The applied amounts of active substance are specified in Tab. 3.9. For the determination of the exposure level, an inhalation rate of 1.25 m^3/h was assumed.

Type of application		**Exposure level (assuming an inhalation rate of 1.25 m³/h) [mg/kg]**				
		Minimum	**Median**	**75th percentile**	**95th percentile**	**Maximum**
Vehicle-mounted sprayer (n=15)	5 m	0.03	0.07	0.09	0.15	0.24
	10 m	0.03	0.06	0.09	0.13	0.19
Hand-held sprayer (n=15)	5 m	0.06	0.19	0.26	3.03	3.20
	10 m	0.06	0.19	0.27	1.54	2.58

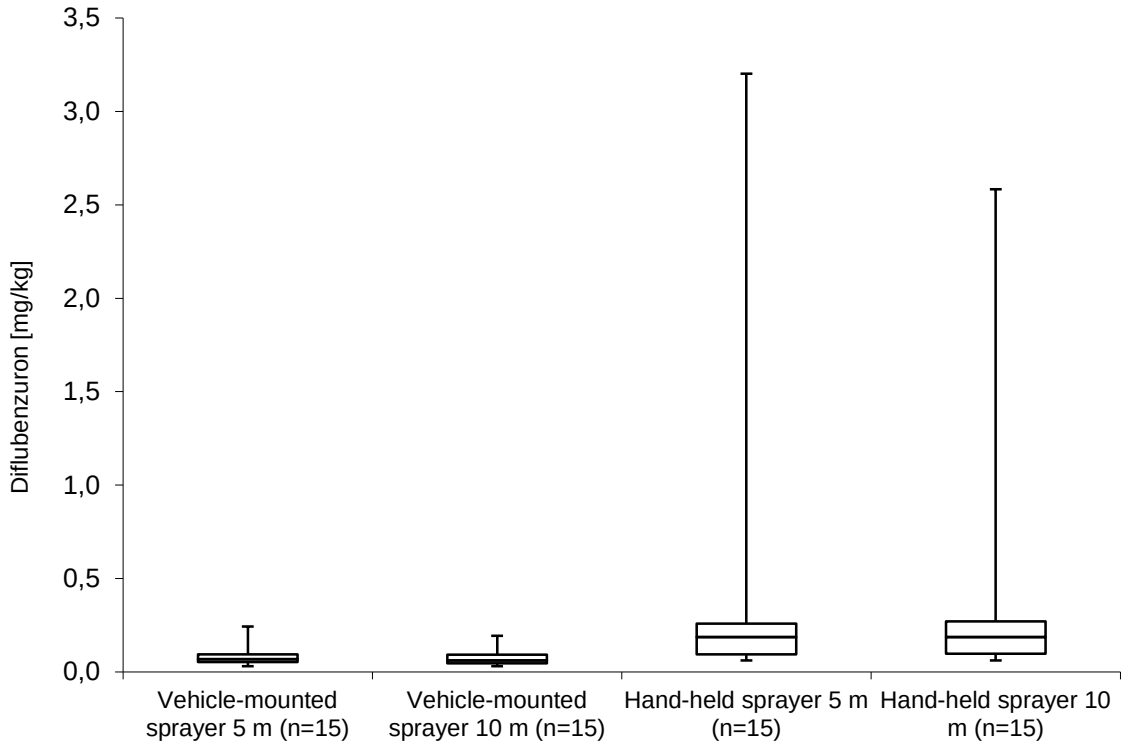

Fig. 4.19 Bystanders' inhalation exposure after spray application using a vehicle-mounted sprayer and a hand-held sprayer, respectively (assuming an inhalation rate of 1.25 m^3/h, values taken from Tab. 4.15).

4.3 Data compilation and correlation analysis

4.3.1 Workers

4.3.1.1 Total exposure

In Tab. 4.17 and Tab. 4.18, the exposure levels of the workers, belonging to the individual measurement series, are listed. The dermal as well as air samples taken simultaneously in a measurement series are clearly assigned; the specified order given in Annex 1, Tab. 1 is adhered to. The given data are related to the applied amount of active substance [mg/kg] (Tab. 4.17) or those taken during the cleaning procedures to the duration of the respective task [mg/min] (Tab. 4.18).

Tab. 4.17 Total exposure of workers: exposure levels related to the applied amount of active substance [mg/kg]. Overview of the dermal and air samples taken simultaneously according to Annex 1, Tab. 1.

Task	**Sample identifier**	**Dermal exposure [mg/kg]**				**Inhalation exposure [mg/kg]**			
		Coveralls		**Gloves**		**Personal sampling**		**Stationary sampling**	
Weighing out/ portioning of the Dimilin™ 80 WG	Weighing	dO-1	1.11	dG-1	7.27	ip-1	0.022	is-1	0.002
		dO-2	0.722	dG-2	2.99	ip-2	0.070	is-2	0.014
Vehicle-mounted sprayer Preparation and/ or application of the Dimilin™ 80 WG suspension	VMS-preparation	dO-1	5.01	dG-1	14.6	ip-7	0.003		
	VMS-application	dO-3	0.791	dG-3	1.90			is-4	< 0.003
	VMS-preparation	dO-2	2.18	dG-2	6.39	ip-8	0.027		
	VMS-application	dO-4	4.89	dG-4	13.8			is-5	0.003
	VMS-application	dO-3	14.6	dG-3	46.5	ip-9	0.027		
	VMS-application	dO-5	9.85	dG-5	23.3			is-6	0.005
	VMS-application	dO-4	19.9	dG-4	36.0	ip-10	0.007		
	VMS-application	dO-6	6.89	dG-6.1- dG-6.2	67.4			is-7	0.006
	VMS-preparation	dO-5	6.46	dG-5	7.28	ip-11	0.003		
	VMS-application	dO-7	6.72	dG-7	7.26			is-8	0.007
	VMS-application	dO-6	5.87	dG-6	15.8	ip-12	0.068		
	VMS-application	dO-8	11.0	dG-8	38.5			is-9	0.003
	VMS-preparation	dO-7	0.133	dG-7	0.439	ip-13	< 0.005		
	VMS-application	dO-9	9.81	dG-9	3.79			is-10	< 0.005

Tab. 4.17 (continued)

Task	Sample identifier	Dermal exposure [mg/kg]				Inhalation exposure [mg/kg]			
		Coveralls		Gloves		Personal sampling		Stationary sampling	
Vehicle-mounted sprayer Preparation and/ or application of the Dimilin™ 80 WG suspension	VMS-preparation	dO-8	9.57	dG-8	95.0	ip-14	0.043		
	VMS-application	dO-10	5.81	dG-10	5.66			is-11	< 0.005
	VMS-preparation	dO-9	9.29	dG-9	109	ip-15	0.006		
	VMS-application	dO-11	3.76	dG-11	2.77			is-12	< 0.006
	VMS-preparation	dO-10	3.93	dG-10	49.4	ip-16	0.005		
	VMS-application	dO-12	4.58	dG-12	0.829			is-13	< 0.005
	VMS-preparation	--	--	dG-11	12.8				
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dO-1	7.36	dG-1.1- dG-1.2	6.05	ip-1	0.002		
		dO-2	0.417	dG-2.1- dG-2.2	2.11	ip-2	0.014		
Vehicle-mounted sprayer Preparation and application of the Dimilin™ 80 WG suspension	VMS-preparation-application	dO-1	6.67	dG-1.1- dG-1.3	44.7	ip-1	0.006		
		dO-2	6.42	dG-2.1- dG-2.2	29.6	ip-2	0.004		
		dO-3	10.8	dG-3	39.5	ip-3	0.024		
		dO-4	7.40	dG-4	32.6	ip-4	0.047		
		dO-5	74.9	dG-5 [a]	276	ip-5	0.016		
		dO-6	1.87	dG-6.1- dG-6.3	3.15	ip-6	0.002		

a: The gloves VMS-preparation-application-dG-5 were only worn while preparing the Dimilin™ 80 WG suspension.

Tab. 4.17 (continued)

Task	Sample identifier	Dermal exposure [mg/kg]				Inhalation exposure [mg/kg]			
		Coveralls		Gloves		Personal measurement		Stationary measurement	
Hand-held sprayer Preparation and application of the Dimilin™ 80 WG suspension	HHS-preparation-application	dO-1	8700	dG-1.1- dG-1.2	9560	ip-1	3.66		
		dO-2	1820	dG-2	1260	ip-2	1.45		
		dO-3	3000	dG-3	2490	ip-3	0.44		
		dO-4	3660	dG-4	1530	ip-4	1.27		
		dO-5	11800	dG-5	1350	ip-5	0.82		
		dO-6	2830	dG-6	1770	ip-6	3.91		
		dO-7	753	dG-7	1100	ip-7	0.50		
		dO-8	1050	dG-8	599	ip-8	0.35		
Hand-held sprayer Transfer and application of the Dimilin™ 80 WG suspension	HHS-transfer-application	dO-1	460	dG-1	429	ip-1	0.17		
		dO-2	1060	dG-2	521	ip-2	0.23		
		dO-3	395	dG-3.1-dG-3.4	90.4	ip-3	0.23		
		dO-4	242	dG-4.1-dG-4.4	251	ip-4	0.25		
		dO-5	1320	dG-5.1-dG-5.4	147	ip-5	< 0.09		
		dO-6	261	dG-6.1-dG-6.4	240	ip-6	0.17		
		dO-7	166	dG-7.1-dG-7.4	120	ip-7	< 0.09		
		dO-8	687	dG-8.1-dG-8.4	213	ip-8	< 0.09		
		dO-9	879	dG-9.1-dG-9.4	251	ip-9	< 0.09		
		dO-10	325	dG-10.1- dG-10.4	160	ip-10	< 0.09		

Tab. 4.18 Total exposure of workers: exposure levels related to the duration of the respective task [µg/min]. Overview of the dermal and air samples taken simultaneously according to Annex 1, Tab. 1.

Task	**Sample identifier**	**Dermal exposure [µg/min]**				**Inhalation exposure [µg/min]**			
		Coveralls		**Gloves**		**Personal measurement**		**Stationary measurement**	
Cleaning procedures Vehicle /vehicle-mounted sprayer	**Cleaning**	dO-1	657	dG-1	1110	ip-1	0.04	is 1	0.004
								is 2	0.02
								is 3	0.06
		dO-2	109	dG-2	22.2	ip-2	< 0.10	is 4	< 0.10
								is 5	< 0.10
								is 6	< 0.10
		dO-3	294	dG-3	2380	ip-3	0.04	is 7	0.23
								is 8	< 0.02
								is 9	0.13

4.3.1.2 Correlation analysis

In the case of the workers' dermal exposure from spray applications the question arises as to whether the exposures measured occur predominantly due to contact with contaminated surfaces or on an airborne basis from exposure to spray mist and/or spray drift. To address this question, the measured dermal exposure and inhalation exposure assuming an inhalation rate of 1.25 m³/h were subjected to a correlation analysis. For this purpose, individually sampled tasks were combined where necessary and the measured values were added.

To obtain a first impression of a possible association between dermal and inhalation exposure, the respective data were displayed as absolute values in µg in scatter diagrams (Fig. 4.20 to Fig. 4.23). For the spray applications under consideration, the absolute diflubenzuron exposure measured on the coveralls is plotted against the inhalation exposure in Fig. 4.20 and Fig. 4.22, and the absolute diflubenzuron exposure of the gloves is plotted against the inhalation exposure in Fig. 4.21 and Fig. 4.23.

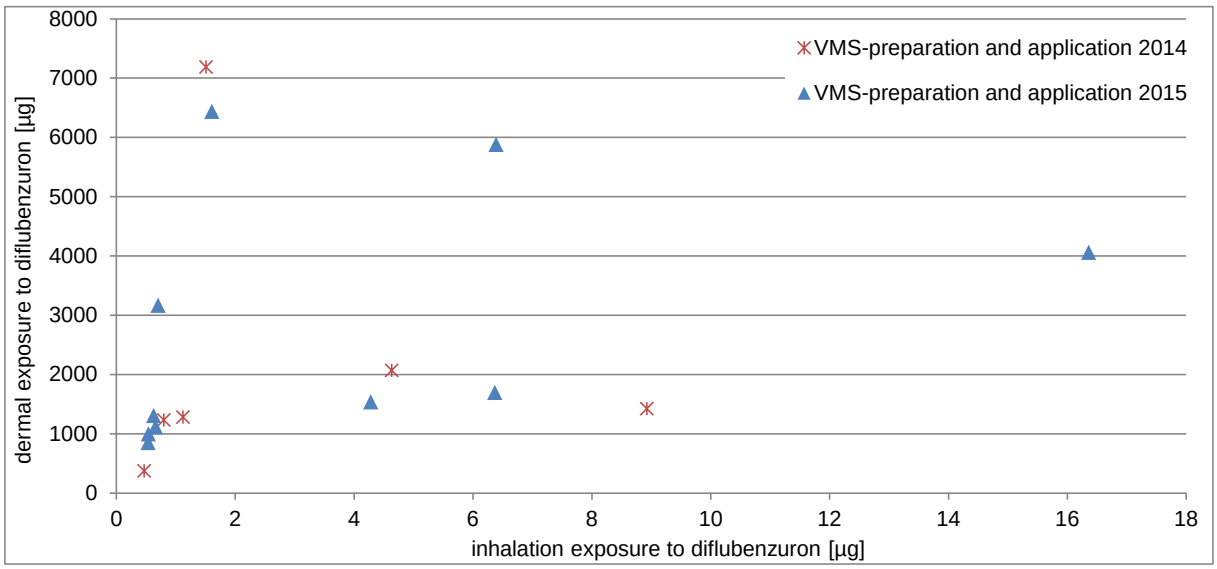

Fig. 4.20 Vehicle-mounted sprayer: dermal exposure (coveralls only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as absolute values [µg].

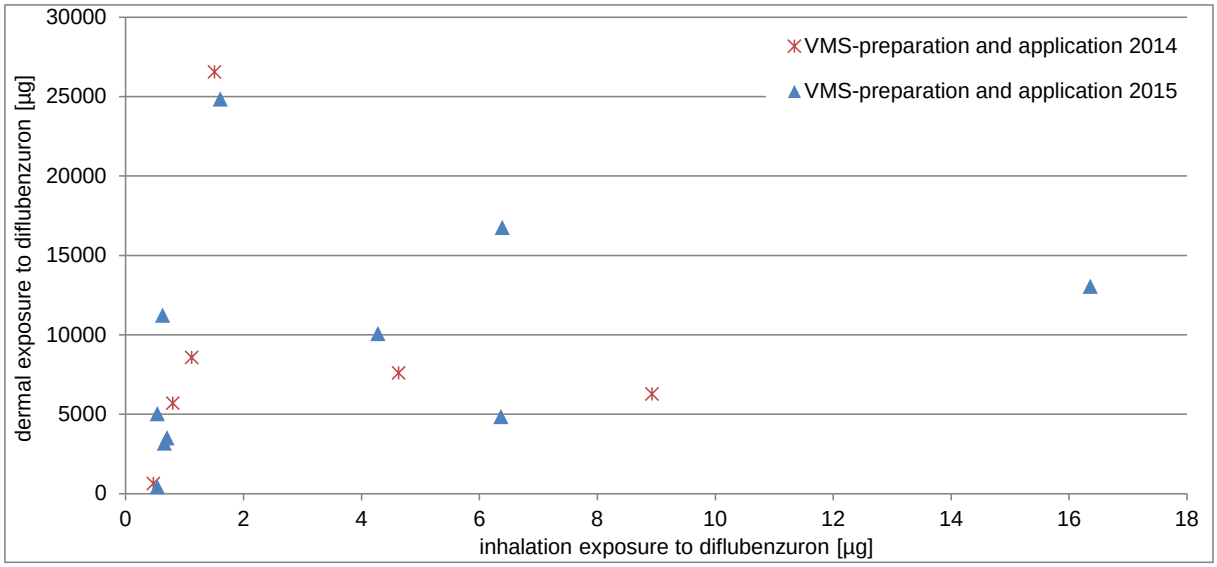

Fig. 4.21 Vehicle-mounted sprayer: dermal exposure (gloves only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as absolute values [µg].

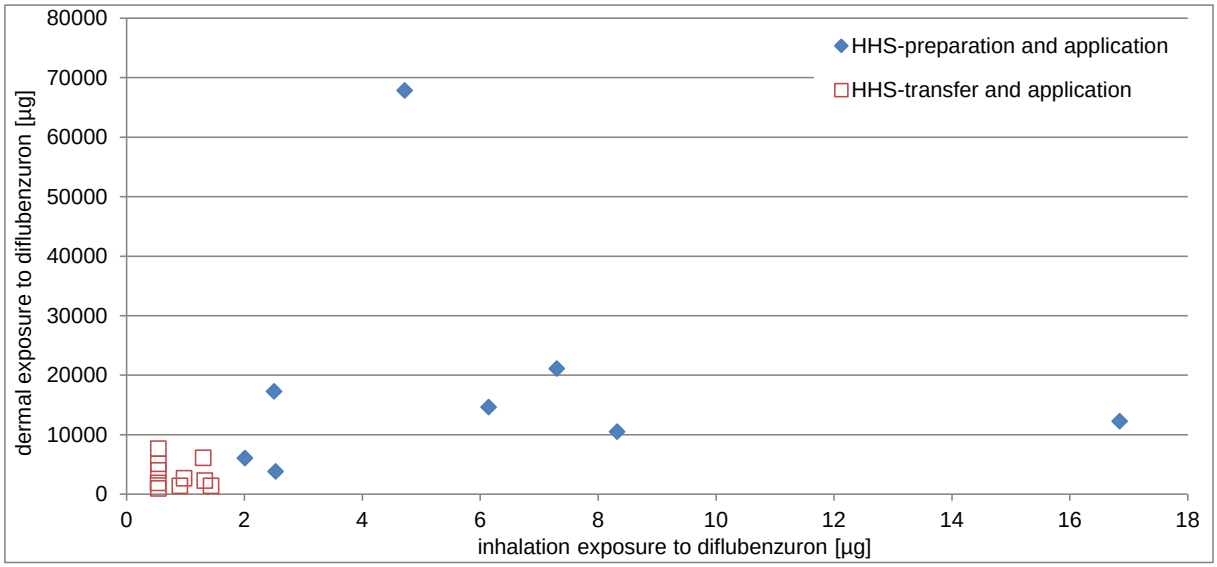

Fig. 4.22 Hand-held sprayer: dermal exposure (coveralls only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as absolute values [µg].

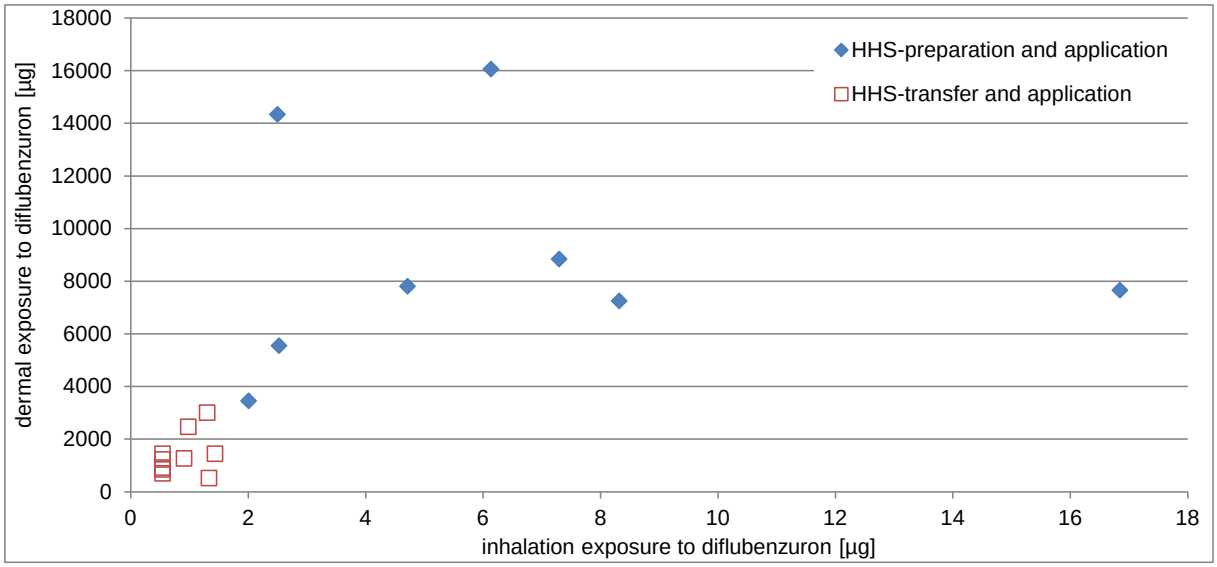

Fig. 4.23 Hand-held sprayer: dermal exposure (gloves only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as absolute values [µg].

Thereafter, the normal distribution of the data was checked for correlation analysis using the Shapiro-Wilk test. The measured values were log 10 transformed due to the lack of normal distribution of the measured values (positive inclination). The data transformed in this way were -with the exception of the inhalation exposure (p=0.046) measured for the vehicle-mounted unit- normally distributed.
From an outlier test carried out on the data, two outliers were obtained in the log 10 transformed dataset for the dermal exposure of the hands after preparation and application of Dimilin™ 80 WG suspension with a vehicle-mounted unit; these data were left in the dataset. The Pearson correlation was calculated using a two-tailed test (IBM SPSS Statistics 22). For the work with vehicle-mounted unit or hand-held sprayer, the correlation coefficients and significance levels given in Tab. 4.19 were obtained.

Tab. 4.19 Dermal vs. inhalation exposure: Pearson correlation coefficients and significance levels for the spray application with vehicle-mounted sprayer and hand-held sprayer, respectively.

Task	Type of exposure	inhalation	dermal (gloves)
VMS-preparation and application	dermal (coveralls)	0.480	0.758*
	dermal (gloves)	0.487	-
HHS-preparation/ transfer and application	dermal (coveralls)	0.675*	0.639*
	dermal (gloves)	0.827*	-

* Correlation is significant at the 0.01 level (two-tailed).

From Tab. 4.19, it can be seen that there is no significant correlation between dermal and inhalation exposure for the task “preparation and application of Dimilin^{TM} 80 WG suspension with the vehicle-mounted sprayer”. This agrees with the observation that, in biocide application with the vehicle-mounted unit, the workers were not exposed to the airborne spray mist as a main factor, but dermal exposure was mainly by contact with contaminated surfaces.
After Dimilin^{TM} 80 WG application with the hand-held sprayer, a strong positive, significant correlation between the measured inhalation exposure and both, the coveralls and the gloves, is obtained (Fig. 4.26 and Fig. 4.27). This reflects the fact that exposure to the spray mist is the main factor when spraying biocides using a hand-held sprayer.
In addition, a strong positive, statistically significant correlation is obtained between the amount of diflubenzuron on the coveralls and on the gloves as well. This applies both for biocide application with the vehicle-mounted sprayer and for biocide application with the hand-held sprayer.
The relationship between dermal and inhalation exposure shown in Tab. 4.19 are given graphically in Fig. 4.24 to Fig. 4.27, whereby the measured values were log 10 transformed before creating the diagram.

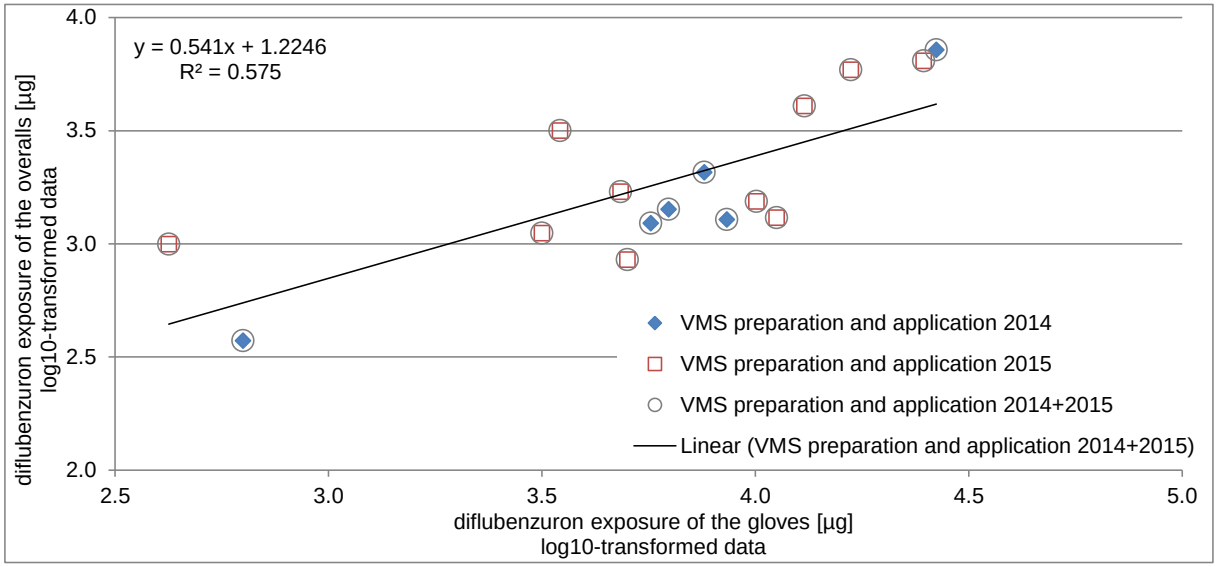

Fig. 4.24 Vehicle-mounted sprayer: dermal exposure of workers (coveralls vs. gloves), the data are given as log 10-transformed absolute values.

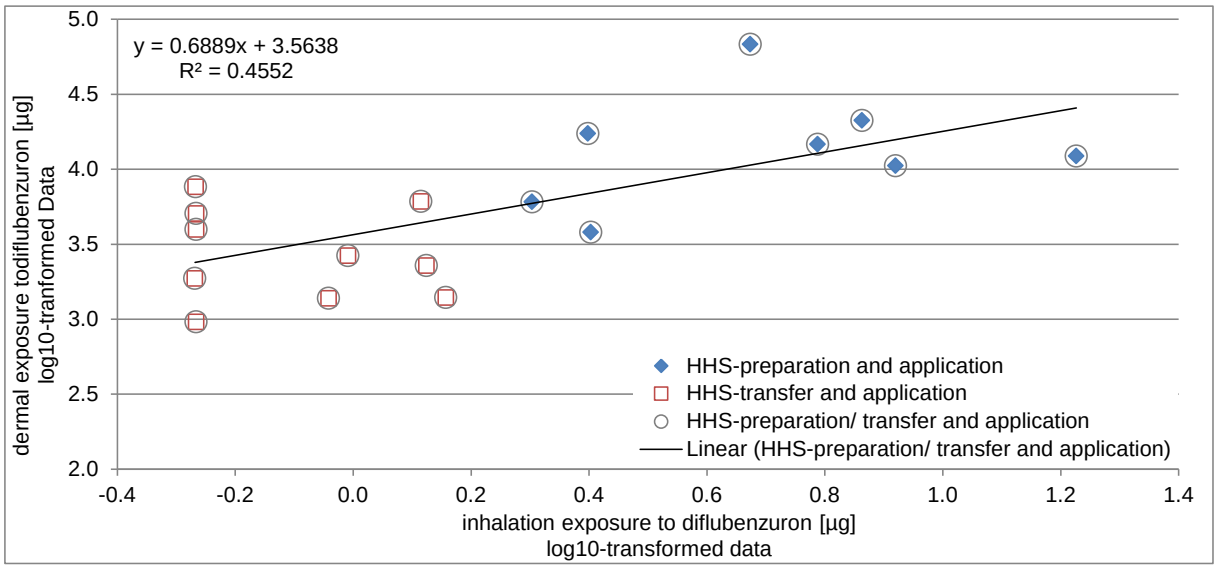

Fig. 4.25 Hand-held sprayer: dermal exposure (coveralls only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as log 10-transformed absolute values [µg].

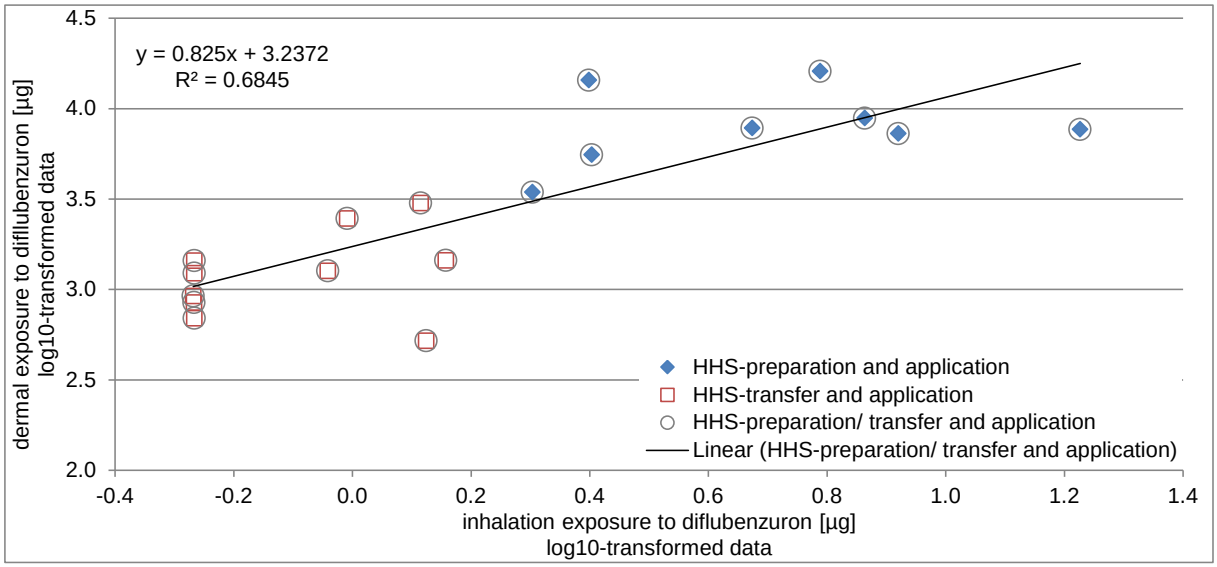

Fig. 4.26 Hand-held sprayer: dermal exposure (gloves only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are given as log 10-transformed absolute values [µg].

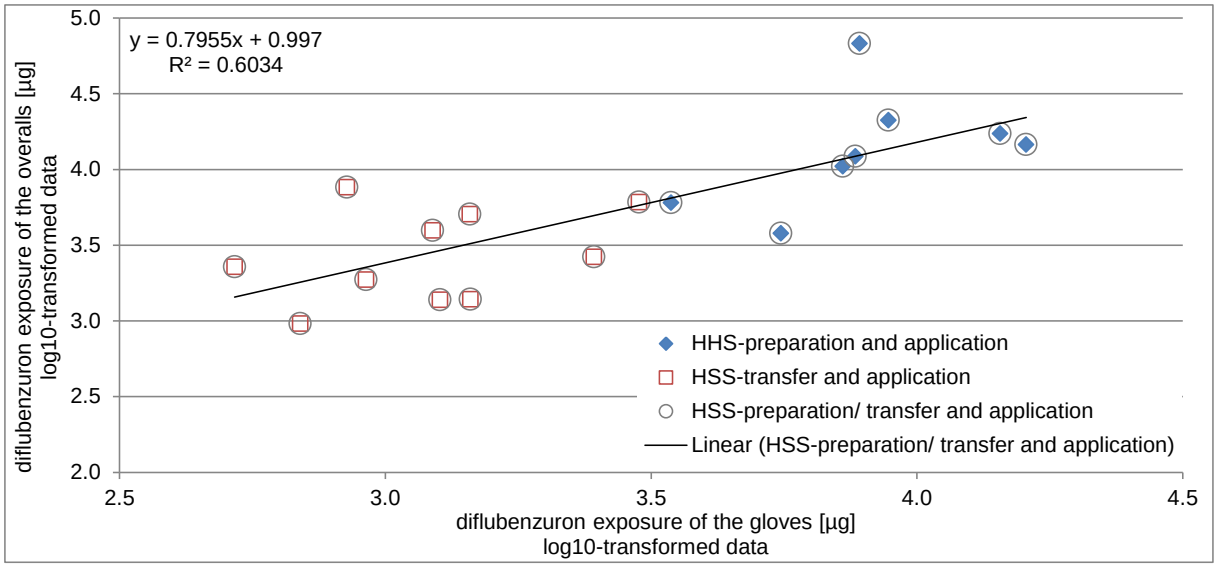

Fig. 4.27 Hand-held sprayer: dermal exposure of workers (coveralls vs. gloves), the data are given as log 10-transformed absolute values [µg].

The dermal and inhalation exposure, related to the amount of active substance, show, both for the coveralls and for the gloves, a clear cluster formation in the scatter diagrams (Fig. 4.28 and Fig. 4.29). In these figures, it can clearly be recognised that both types of application cause substantially different dermal and inhalation exposures to diflubenzuron. In the case of the hand-held sprayer, the transfer of the spray liquid can be distinguished from the preparation of the spray liquid by the levels of inhalation exposure.
It is not possible to present the data for cleaning procedures in this scatter diagram, as this task cannot be related to the applied amount of active substance.

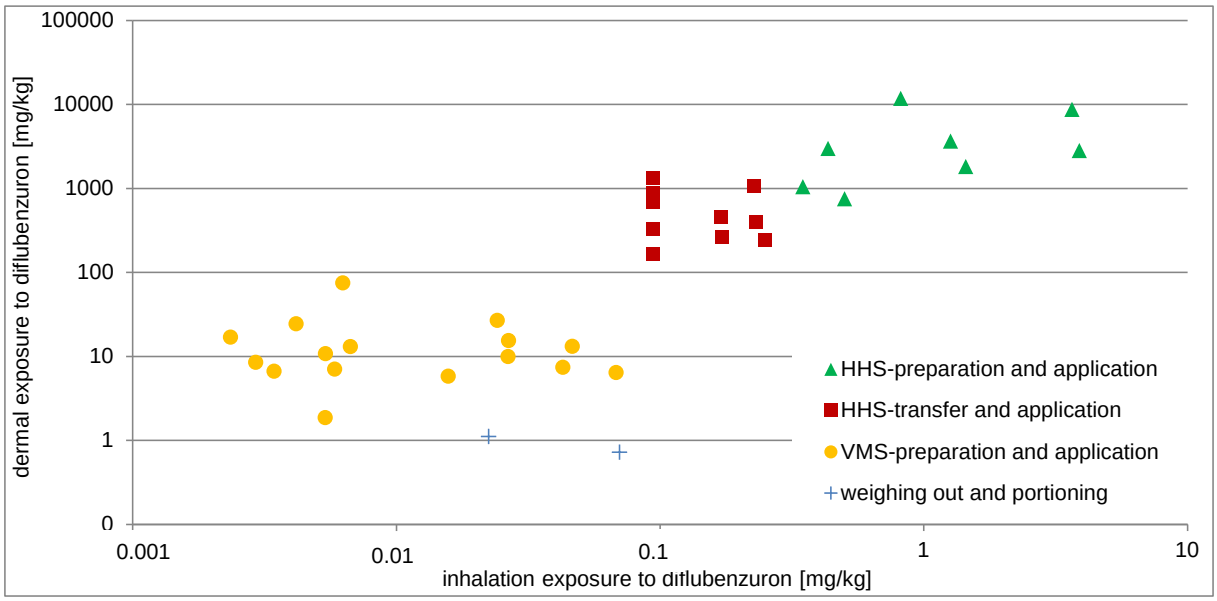

Fig. 4.28 Dermal exposure (coveralls only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h. The data are related to the amount of active substance applied. It has to be taken into account that different quantities of active substance were handled during the tasks presented in the diagram.

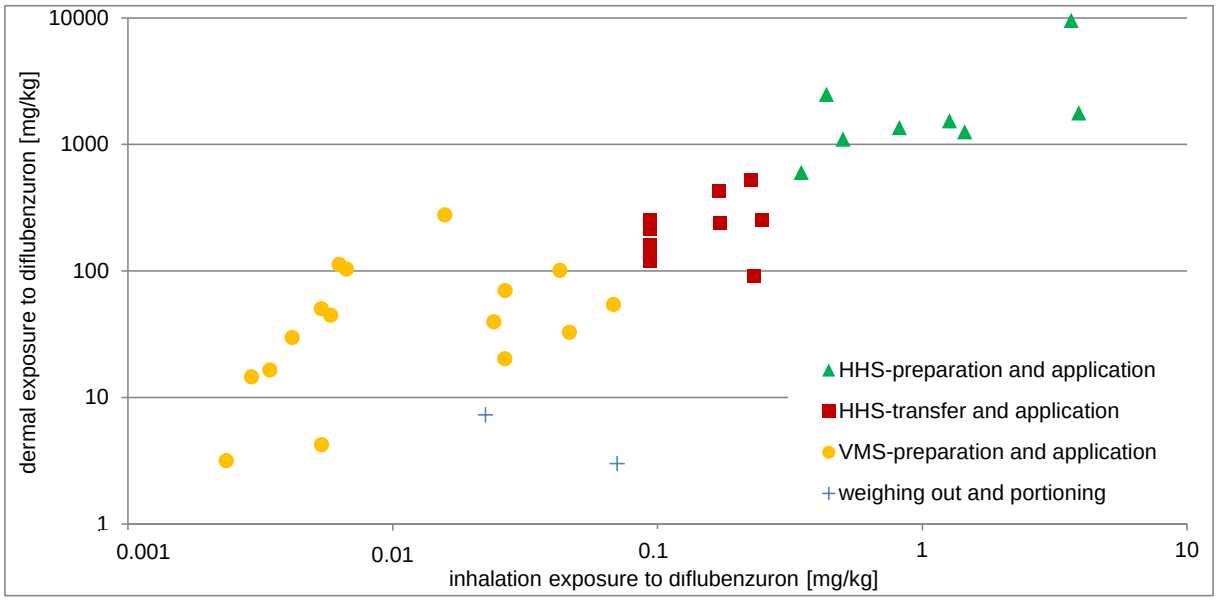

Fig. 4.29 Dermal exposure (gloves only) vs. inhalation exposure at an inhalation rate of 1.25 m³/h. The data are related to the amount of active substance applied. It has to be taken into account that different quantities of active substance were handled during the tasks presented in the diagram.

4.3.1.3 Comparison of tasks in relation to one work shift

To be able to compare the different tasks carried out in OPM control by spraying on a daily basis, the workers` exposure resulting from the individual tasks has been related to a work shift of eight hours. As initial data, the absolute diflubenzuron amounts on the sampler (filters, coveralls, gloves) were used. For the weighing out and portioning of Dimilin™ 80 WG granules, maximum task duration of 60 min per work shift is assumed, as also for the cleaning procedures. Based on the experience gathered during the field trials, it is assumed that during an 8 hour work shift a total quantity of 2000 L spray liquid can be prepared and applied. For the preparation/transfer and application of the spray liquid with the hand-held sprayer a quantity of 200 L is taken as calculation basis; these volumes were considered to be the maximum amounts that can be applied during a work shift.
With these parameters, the dermal and inhalation exposure of workers can be calculated for a work shift. The different tasks are given in Tab. 4.20 with the corresponding parameters.

The dermal and inhalation exposure data of the workers related to a work shift are presented in Fig. 4.30 in the form of a scatter diagram. The diagram shows a clear difference between the task “HHS-preparation-application” and “VMS-preparation-application” as regards both, dermal and inhalation exposure. The exposure during the task HHS-transfer-application is -when considering a work shift- in the middle of the point cloud for the task VMS-preparation-application.

The dermal exposure to diflubenzuron during Dimilin™ 80 WG weighing out and portioning lies within the other tasks; by contrast, the inhalation exposure differs clearly from the other tasks. From this presentation, it becomes clear that the working step Dimilin™ 80 WG weighing out and portioning is associated with the highest inhalation exposure for the workers.

Tab. 4.20 Workers’ dermal and inhalation exposure: parameters for the work shift.

Task	**Parameters for the work shift**
Weighing out and portioning	Task duration of 60 min [a]
VMS-preparation-application	Preparation and application of 2000 L spray liquid
HHS-preparation-application	Preparation and application of 200 L spray liquid
HHS-transfer-application	Transfer and application of 200 L spray liquid
Cleaning	Task duration of 60 min [a]

[a]: These tasks are mostly carried out once per spraying season.

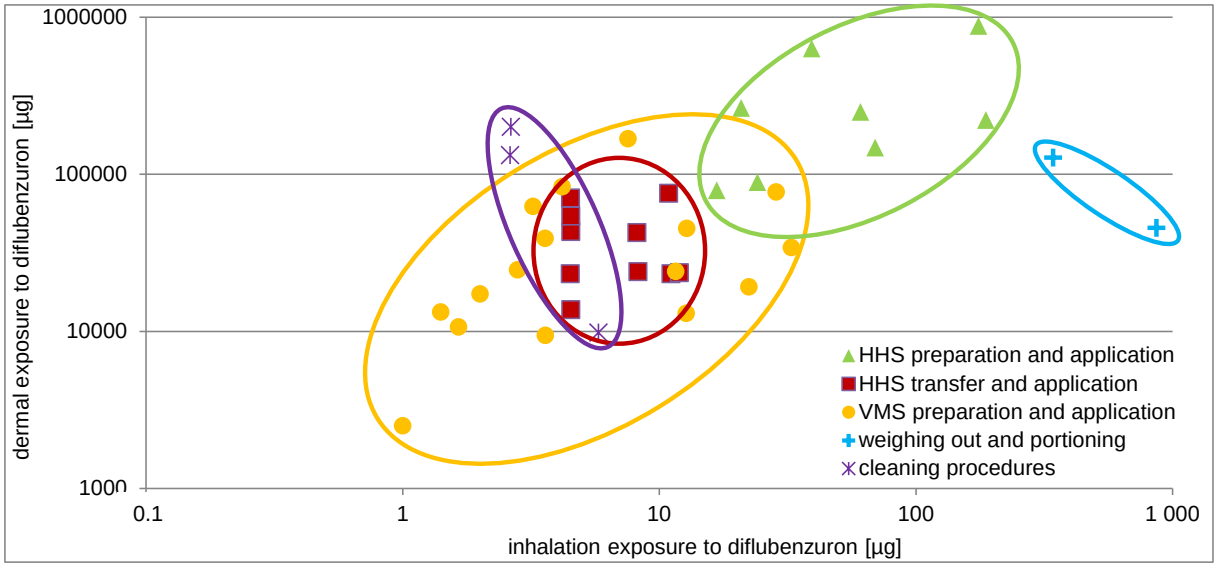

Fig. 4.30 Dermal exposure (coveralls and gloves) vs. inhalation exposure at an inhalation rate of 1.25 m³/h, the data are related to one work shift according to Tab. 4.20.

4.3.1.4 Comparison of the workers' exposure in OPM control and in plant protection

Whereas no detailed exposure data for the use of biocides in OPM control were available until carrying out this project, a rather good database and several established models exist for the exposure assessment of spray applications with plant protection products (PPP).

As, in the OPM control, equipment is used which was usually conceived for PPP applications, and since the products used are often also approved PPPs, it seems to be an obvious option to use the corresponding PPP models in the assessment of OPM control with biocides as well. For example, when approving the active substance "Margosa-Extract" for product type 18 ("insecticides, acaricides and products against other arthropods") exposure estimates were carried out on the basis of the PPP models "German Model" and "UK POEM" (EC 2011).

However, the spray applications with which OPM control is carried out are different from those in PPP in a number of important aspects, so that an assessment of OPM control using PPP models involves many uncertainties. In the following, therefore, a comparison of exposure levels in PPP applications with the exposure levels occurring in OPM control is made.

As representative for PPP applications in this comparison, the "*Agricultural Operator Exposure Model*" (AOEM), which was developed by the BfR (*Bundesinstitut für Risikobewertung*, Federal Institute for Risk Assessment), is used (BfR, 2013). Although this model is a successor of the "German Model" and the "UK POEM", it has been developed entirely based on new data.
The AOEM makes a difference between vehicle-mounted sprayer and hand-held sprayer. In addition, a difference is made between high crop and low crop applications. Data for low crop comprise for the most part applications to different species of cereal or, for example, to potatoes. For a comparison with OPM

applications, only those data collected in the treatment of high crops are considered. These were mostly determined with vineyards and orchards as well as with olive plantations. These plants are, however, considerably lower in height then the oak trees treated in OPM control.

For OPM control it is necessary to spray the biocide into the treetops as high as possible. The user must therefore spray much more directed upwards than this is normally necessary in PPP applications. In addition, this means that there is also an additional special requirement for such spray units, since they must be able to spray targeted into the treetops from a greater distance. Although the units used in OPM control for this project were all developed and approved for the PPP application, they are not the same as the units mainly used to determine the exposure data in the AOEM model, as other requirements had to be met with those sprayers.

Furthermore, differences also exist with regard to the general conditions. In plant protection, mostly large, continuous plantations are treated, whereas OPM control using biocidal products is carried out mostly with trees or smaller groups of trees as targets, located in areas frequented particularly often by humans. As a result, the amounts of time taken to drive back and forth from the individual application sites represent a considerable part of the total work shift. The amount of spray liquid applied is, in total, less and the area treated smaller than it is usually the case in PPP applications. In addition, not all of the trees are freely accessible from all sides so that sometimes compromises have to be accepted regarding the best possible position for spraying.

The differences described are, as expected, reflected by the exposure data determined. Tab. 4.21 shows a comparison between the exposure levels determined in OPM control and data from the AOEM documentation (BfR, 2013); the data are broken down according to the empirical percentiles. For the hand-held sprayer, data on preparation or transfer are combined with the data on application; in the case of the vehicle-mounted unit, preparation and application are given individually. All exposure levels are here considered in relationship to the applied amount of active substance.

Tab. 4.21 Comparison of workers' dermal and inhalation exposure during OPM control and PPP-applications. The data on PPP-applications are taken from the AOEM documentation (BfR 2013). The exposure data are given in [µg/kg].

Vehicle-mounted sprayer: preparation[1]											
Route of exposure	**Source**	**Minimum**	**Factor**	**Median**	**Factor**	**75th percentile**	**Factor**	**95th percentile**	**Factor**	**Maximum**	**Factor**
dermal: body	OPM EPS	133	**3.6**	6170	**14.0**	9500	**9.9**	17500	**5.3**	19900	**4.8**
	AOEM	37		441		962		3275		4135	
dermal: hands	EPS	439	**41**	25900	**114**	60800	**68**	184000	**61.5**	276000	**39**
	AOEM	11		228		894		3008		7162	
inhalation	EPS	not determined separately									
	AOEM	0.00		4.6		9.4		14		39	
Vehicle-mounted sprayer: application[2]											
Route of exposure	**Source**	**Minimum**	**Factor**	**Median**	**Factor**	**75th percentile**	**Factor**	**95th percentile**	**Factor**	**Maximum**	**Factor**
dermal: body	EPS	417	**18**	6270	**8.1**	7970	**2.8**	10400	**1.2**	11000	**1.0**
	AOEM	23		771		2877		8516		11542	
dermal: hands	EPS	829		5860	**42.6**	16200	**14**	51500	**25.1**	67400	**2.8**
	AOEM	0		137		1126		2052		24211	
inhalation	EPS	2.1	**20**	6.3	**2.5**	6.3	**1.1**	10	**0.5**	15	**0.3**
	AOEM	0.10		2.0		5.3		21		45	
Hand-held sprayer: preparation/ transfer and application[3]											
Route of exposure	**Source**	**Minimum**	**Factor**	**Median**	**Factor**	**75th percentile**	**Factor**	**95th percentile**	**Factor**	**Maximum**	**Factor**
dermal: body	EPS	166000	**344**	965000	**11.5**	2578000	**11**	9165000	**15.9**	11800000	**13**
	AOEM	482		83785		233403		576730		903621	
dermal: hands	EPS	90400	**406**	475000	**18.4**	1328000	**26**	3550000	**29.4**	9560000	**35**
	AOEM	223		25793		52052		120892		272164	
Inhalation	EPS	90	**450**	240	**2.4**	740	**3.5**	3030	**9.1**	3660	**4.9**
	AOEM	0.20		100		211		334		747	

[1] For AOEM: "ML Tank, WG˚, Chapter 18.1 of the AOEM documentation
[2] For AOEM: "Application HCTM, cabin", Chapter 18.4 of the AOEM documentation
[3] For AOEM: "ML Knapsack", added to "Application HCHH, all", Chapters 18.2 and 18.6 of the AOEM documentation

As a result, exposure related to the applied amount of active substance is, in nearly all of the data listed, higher for OPM control than for PPP applications. When considering the values obtained for the 75th percentiles, which are frequently used in exposure assessments for biocides, they show that in OPM control especially dermal exposure is considerably higher; the differences regarding the exposure of hands are again greater than those for the rest of the body. These differences can be attributed especially to the above described differences in the growth height of the treated plants. Such heights require from the workers a more horizontal or at most partial upward spraying in the field of PPP, when using the hand-held sprayer. On the other hand, in OPM control, the spray direction must be steeply upward or even vertical. As a result, the workers in OPM control stand mostly beneath the applied spray mist and can therefore be exposed to falling droplets and dripping of the spray liquid down from the trees (Fig. 4.31).

These assumptions are confirmed by the exposure pattern found on the coveralls (see Fig. 4.9 in chapter 4.1.1.1). It can clearly be seen in this figure that, in accordance with the spraying scenario described above, the exposure of the body areas (head, upper part of the body, upper side of the arms) to the spray mist coming from above is particularly high. However, the question as to whether the clearly higher exposure of the hands is caused mainly from contact with contaminated surfaces or from direct exposure to the spray mist, cannot be conclusively answered. The level of inhalation exposure during application with the hand-held sprayer is, in OPM control, also higher, though it remains within the same range as in PPP applications.

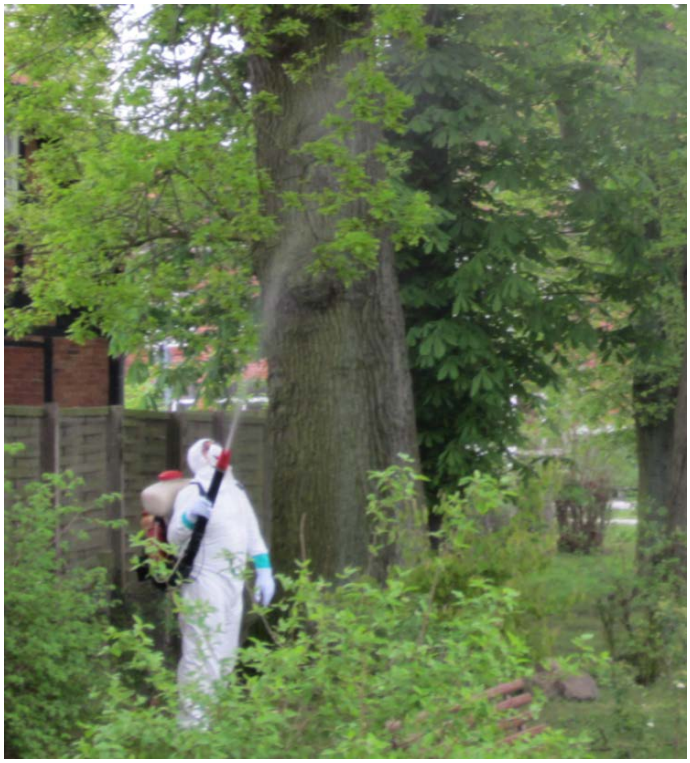

Fig. 4.31 Hand-held sprayer: Application of the Dimilin^{TM} 80 WG suspension.

The higher exposure level when using the vehicle-mounted sprayer can also be associated with the height of the trees and the therefore resultant upwards directed spraying. During the field studies, it was observed that after spraying the outer surface of the sprayer and of the spray tank was subject to a constant wetting with spray liquid, and it can be assumed that the steeply upwards applied spray mist wets the surfaces of the vehicles and spraying units to a greater extent than a cloud of spray directed for the most part sideways. As a result, the exposure of the workers also increases considerably by coming into contact with the surfaces of the sprayer. With the majority of the sprayers used during the project, the biocidal product has to be filled through the tank filler opening at the top of the VMS-tank. In order to reach the tank filler opening of the man-high tank, the operator had to lean against the spray tank and open the hinged lid, whereby his hands, the underside of his forearms, chest, belly and front sides of his upper thighs (Fig. 4.7 in chapter 4.1.1.1 and Fig. 4.32) came into contact with the contaminated surfaces, thus producing a corresponding exposure pattern.

Fig. 4.32 Vehicle-mounted sprayer: Preparation of the spray liquid.

The inhalation exposure of the workers during application with vehicle-mounted unit stays, in OPM control, within the same range as in PPP applications.

With the comparisons undertaken here, however, it must be noted that exposure data related to the applied amount of active substance are assessed. During OPM control, as already explained above, clearly less active substance is applied per shift than with PPP applications. Therefore, the differences are smaller when considering the working-day exposure. As shown by comparative calculations, the exposure in OPM control remains, however, also in such a working-day context, higher than in PPP applications.

4.3.2 Bystanders

4.3.2.1 Total exposure

In Tab. 4.22, the bystanders' exposure is listed as belonging to the different measurement series. The dermal and air samples taken simultaneously during a measurement series are clearly assigned, whereby the order given in Tab. 3.8 and Tab. 3.9 is adhered to. The listed data are related to the applied amount of active substance. For inhalation exposure, the inhalation rate of an adult of 1.25 m^3/h was assumed.

Tab. 4.22 Total exposure of bystanders: quantified diflubenzuron related to the applied amount of active substance [mg/kg]. Overview of the dermal and air samples taken simultaneously according to Annex 2.

Task	Sample identifier (bystander)		Dermal exposure [mg/kg]						Sample identifier (bystander)		Inhalation exposure [mg/kg]	
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total			5 m	10 m
Vehicle-mounted sprayer Application of the Dimilin™ 80 WG suspension	VMS-application	dB-1	58.1	74.8	133	23.5	47.0	70.4	VMS-application	iB-1	< 0.06	0.07
		dB-2	21.8	48.8	70.6	2.00	1.59	3.59		iB-2	< 0.06	< 0.06
		dB-3	2.89	4.30	7.19	0.649	0.713	1.36		iB-3	0.07	0.05
		dB-4	8.37	13.0	21.4	0.461	0.358	0.819		iB-4	< 0.03	< 0.03
		dB-5	10.1	13.8	23.9	3.61	1.79	5.39		iB-5	0.06	< 0.06
		dB-6	30.4	30.0	60.5	20.0	14.2	34.1		iB-6	< 0.03	< 0.03
		dB-7	216	297	513	378	311	689		iB-7	0.07	< 0.06
		dB-8[a]	908	1200	2100	153	201	354		iB-8	0.24	0.19
		dB-9	58.3	72.8	131	56.2	69.4	126		iB-9	< 0.09	< 0.09
		dB-10	20.5	25.0	45.5	17.1	18.3	35.4		iB-10	0.10	0.10
		dB-11	1.09	0.627	1.72	0.112	0.222	0.335		iB-11	< 0.05	< 0.05
		dB-12	25.9	27.4	53.3	16.8	17.4	34.2		iB-12	0.10	< 0.05
		dB-13	10.4	16.6	27.0	3.95	5.87	9.82		iB-13	0.07	0.09
		dB-14	36.6	40.0	76.6	18.1	23.1	41.2		iB-14	< 0.09	< 0.09
		dB-15	72.3	85.5	158	58.1	51.4	110		iB-15	< 0.03	< 0.03

Tab. 4.22 (continued)

Task	Sample identifier (bystander)		Dermal exposure [mg/kg]						Sample identifier (bystander)		Inhalation exposure [mg/kg]	
			5 m upper segment	5 m lower segment	5 m total	10 m upper segment	10 m lower segment	10 m total			5 m	10 m
Hand-held sprayer Application of the Dimilin^{TM} 80 WG suspension	**HHS-application**	dB-1	4.33	4.64	8.97	4.21	3.41	7.62	**HHS-application**	iB-1	< 0.21	< 0.21
		dB-2	134	94.6	229	26.0	43.0	69.0		iB-2	0.07	0.10
		dB-3	14.1	19.7	33.8	14.9	15.5	30.3		iB-3	0.06	0.06
		dB-4	222	315	538	64.9	39.9	105		iB-4	2.96	2.58
		dB-5[b]	224	216	440	18.0	15.7	33.7		iB-5	3.20	1.09
		dB-6	92.7	112	205	212	213	425		iB-6	0.22	0.20
		dB-7	12.5	14.9	27.4	20.6	19.5	40.1		iB-7	0.09	0.13
		dB-8	61.2	74.0	135	2.02	0.863	2.88		iB-8	< 0.19	< 0.19
		dB-9	8.37	14.7	23.1	2.51	4.64	7.15		iB-9	0.30	0.16
		dB-10	0.202	0.534	0.737	0.170	0.171	0.341		iB-10	< 0.09	< 0.09
		dB-11	325	332	657	91.8	87.2	179		iB-11	0.59	0.42
		dB-12	481	334	815	244	157	401		iB-12	0.12	0.33
		dB-13	55.2	79.4	135	25.9	41.5	67.4		iB-13	< 0.18	< 0.19
		dB-14	148	58.9	207	58.9	41.3	100		iB-14	< 0.09	< 0.09
		dB-15	25.0	32.4	57.5	7.24	12.2	19.5		iB-15	< 0.10	< 0.10

[a]: The rack frame located at 5 m was blown over by the force of the spray jet, however, it was set up again after about 1 min.
[b]: The 5 m measuring equipment was set up at a distance of just 4.3 metres to the tree.

4.3.2.2 Correlation analysis

As regards the dermal exposure of bystanders, the same question arises as with the workers, i.e. as to how far dermal exposure correlates with inhalation.

When the absolute values of dermal and inhalation exposure of bystanders are displayed in a scatter diagram, a point cloud is obtained which allows no clear differentiation between the types of spray application as well as between the distances of 5 m and 10 m from the trees treated. A cluster marking reflects at best the tendency that Dimilin^{TM} 80 WG application with a hand-held sprayer results in higher inhalation exposures, though this tendency is not reflected in the dermal values (Fig. 4.33).

For the correlation analysis, the normal distribution of absolute measured values was checked using the Shapiro-Wilk test. On the basis of the - not given - normal distribution of data, the measured values were log10 transformed. The log10 transformed data obtained were normally distributed for the dermal exposure of bystanders. For inhalation exposure, a normal distribution of the log10 transformed values was only obtained for the measurement carried out during diflubenzuron application with the hand-held sprayer at a distance of 10 m. The Pearson correlation was only calculated for the dataset with the normally distributed air values (two-sided significance level). For these data, a moderate positive correlation (r=0.465) was obtained which was, however, not significant (IBM SPSS Statistics 22).

When the measured exposure levels are related to the amount of active substance applied in each case (see Section 4.2.1), the scatter diagram given in Fig. 4.34 is obtained. Due to the highly standardised tasks, particularly with regard to the amount of Dimilin^{TM} 80 WG suspension applied, a scatter diagram similar to that given in Fig. 4.33 is here obtained.

To summarise, it can be said that, for the bystanders the absolute measured values for dermal exposure do not correlate with those for inhalation exposure. As causes for the lack of correlation of the measured values are conceivable: the varying distance of the sampling set ups to the spray head of the respective spraying device, weather conditions, the size distribution of droplets in the spray mist as well as differences between direct spray jet exposure and exposure by indirectly blown spray mist.

Basically, the results for the exposure of bystanders can also be used in assessing exposure of workers not directly occupied with the biocide application. A conceivable task would for example consist in blocking off the danger zone. The recorded measurement data for the exposure of bystanders can thus also be used in an extended consideration of worker exposure.

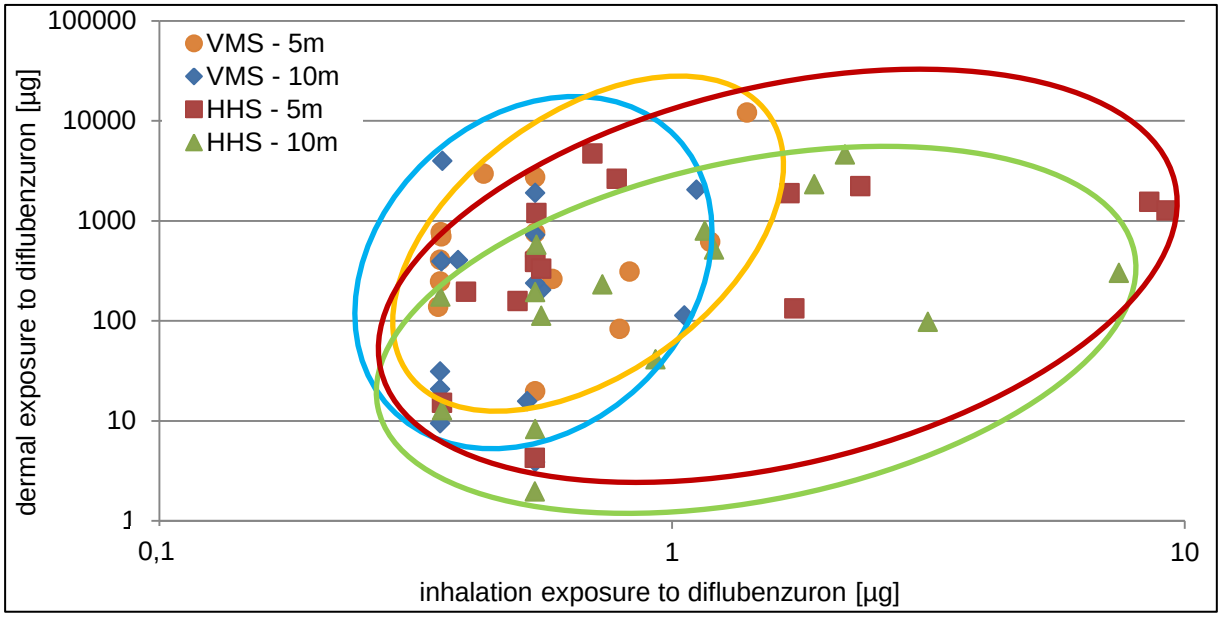

Fig. 4.33 Dermal exposure vs. inhalation exposure of bystanders at an inhalation rate of 1.25 m³/h; the data are given as absolute values in µg.

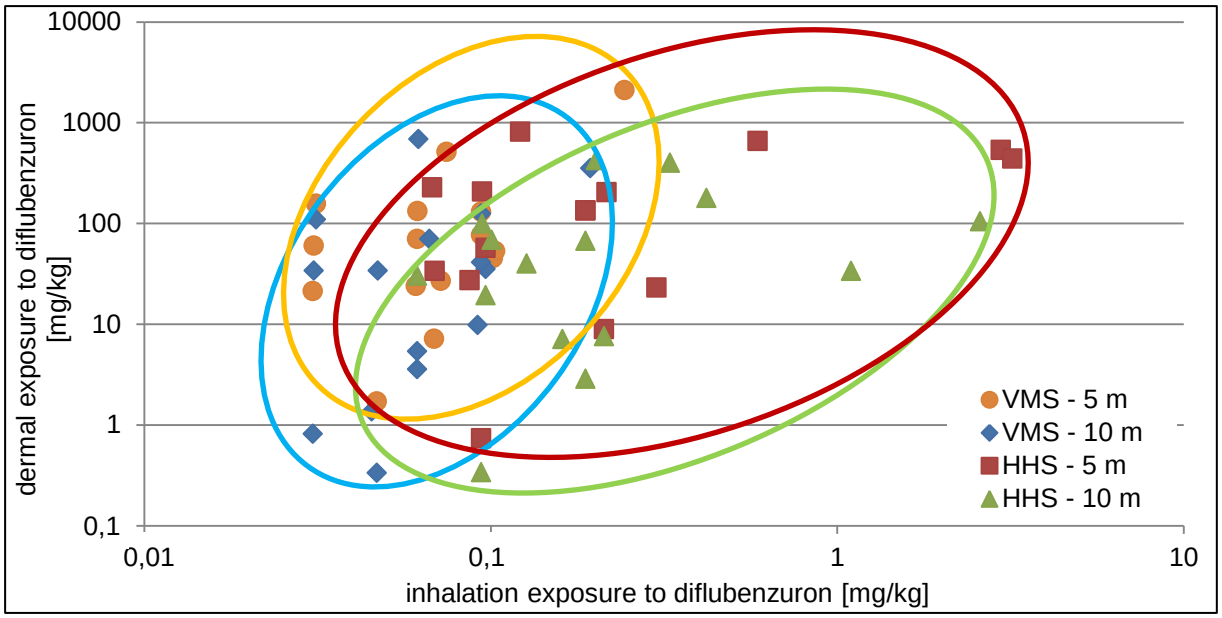

Fig. 4.34 Dermal exposure vs. inhalation exposure of bystanders at an inhalation rate of 1.25 m³/h; the data are related to the applied amount of active substance.

5 Data compilation for the evaluation of biocides according to Regulation (EU) No.528/2012

In the field studies of 2014 and 2015, it was possible to collect detailed information on OPM control processes using vehicle-mounted sprayers and hand-held sprayers and to obtain valid data on the inhalation and dermal exposure of workers and bystanders. These data permit a modelling of exposure scenarios comparable with those investigated here, and can thus also be transferred to other active substances or products.
With the data obtained for the two types of spray application investigated, apart from OPM control, other spray applications can also be evaluated where devices comparable to those in this project are used and where there is a similar, i.e., nearly vertical, spray pattern. Similarly, the data on weighing out and portioning of the granules and on the cleaning of the equipment can also be transferred to other exposure situations where a similar exposure pattern is to be expected.
In this section the measured exposure levels are grouped according to tasks and application phases, and given with their empirical percentiles to facilitate the use of the data obtained from this project for the exposure assessment of biocidal products.

5.1 Workers

Where possible, the exposure level is related to the applied amount of active substance in mg/kg, such as also usual in exposure models for plant protection product applications. For this purpose, the level of inhalation exposure was calculated from the original measurement data assuming an inhalation rate of 1.25 m^3/h (ECHA 2013, ECHA 2015a).

Additionally, the input parameters for modelling the exposure estimate of OPM controls are emphasised.

However, should the application situation to be evaluated differ considerably from the procedures observed in this project, the input parameters discussed in this work need to be scrutinised. If, for example, large contiguous areas are treated, so that workers need to drive back and forth significantly less, or hand-held sprayers with a separate, possibly larger tank are used, which stands on the ground, considerably greater daily applied amounts might have to be assumed.

5.1.1 Weighing out and portioning of the granules

At the beginning of the spraying season, two of the three companies monitoredin this project weighed out and portioned the biocidal product available in the form of granules from larger packages. With one of the companies, two exposure measurements were carried out for this task. In this case the granules were taken from a cardboard barrel holding 20 kg with a measuring cup and poured into a plastic bag that was placed on kitchen scales. Accordingly, 240 g or 300 g (the suitable amount for a tank containing 800 L or 1000 L) were portioned into each bag.

Tab. 5.1 Exposure levels measured for the weighing out and portioning of the granular biocide. The given data are based on the handled (i.e. weighed out and portioned) amount of active substance in [mg/kg].

Weighing out and portioning of the granules			
Route of exposure	**n**	**Minimum [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	2	2.99	7.27
dermal exposure: body	2	0.722	1.11
inhalation exposure	2	0.022	0.070

For weighing out and portioning of the granules, 37 min (10 kg granules) in one case and 65 min (20 kg granules) in the other case were required. Tab. 5.1 shows the exposure levels measured during this task.

5.1.2 Spraying with vehicle-mounted sprayers

This task consists of three application phases

- "preparing the spray liquid",
- "application of the spray liquid" and
- "cleaning of the vehicle/ vehicle-mounted sprayer".

5.1.2.1 Preparation and application: description of tasks and measured values

The two application phases preparation and application were mostly measured together in the 2014 field study, the first of the two project years, i.e. each sampling began before preparation and ended after application. With the sampling in 2015, the dermal exposure of hands and body was recorded separately for the two application phases, i.e., the dermal samplers were changed after preparation of the spray liquid. Inhalation exposure was measured by personal air sampling throughout both application phases in both project years, however, in 2015 additional measurements were undertaken in the driver's cabin during application, which corresponded to inhalation exposure during application. An exclusive measurement of inhalation exposure during preparation was impossible for technical reasons (see Section 3.3.1.2).

In the data shown in Tab. 5.2, the datasets from the dermal measurements of 2015 have therefore been included twice, i.e., once for the two separate application phases and additionally once again together with the data from 2014 in the dataset for the combined preparation and application. Here, in each case, values for preparation and application belonging to one work process have been added and then included in the dataset. For the modelling of an exposure scenario, which includes both application phases, the combined dataset for preparation and application should be used due to the larger underlying data base.

For preparing the biocide from the water dispersible Dimilin^{TM} 80 WG used during the measurements, the granules were first of all poured into the strainer provided for this purpose. Thereafter, a hose is used to add water which is then mixed with the

product by starting the agitator installed in the tank. The data comprise different kinds of construction (see Section 3.1). Eleven datasets (five times both application phases together and six times preparation and application separate) were obtained with spray units having an 800 L or 1000 L spray tanks, into which the granules had to be added through the tank filler opening at the top. During this task, the worker had to lean against the tank while pouring in the preportioned granules stored in plastic bags. The water was then filled in with a hose attached to the lower side of the tank. With four datasets (with both application phases separately measured), granules (from preportioned paper sandwich bags) and water (through a hose) were filled in through the tank filler opening at the top of the 300 L tank, whereby the water was taken twice from a hydrant and twice from a 1000 L tank transported on the loading platform of the small truck. With one dataset (both application phases measured together) the granules were poured into a separate rear-mounted pre-mix tank, whereby in this case the water was then added to the tank by a hose through the tank filler opening at the top of the spray tank. The analysis of the exposure pattern shows that a considerable amount of the exposure occurring during activities involving the vehicle-mounted sprayers can be attributed to contact with contaminated surfaces (see Fig. 4.5 and Fig. 4.6 in chapter 4.1.1.1). For this reason, it can be assumed that the formulation type of the product only has a minor impact on the exposure level, so that the data can also be used for the modelling of liquid formulations, for example.

The application was carried out with the respective spray units, whereby mostly the full tank of spray liquid was applied during one measurement. As a full tank was generally sufficient for the treatment of trees at several application sites, the datasets also comprise the time necessary for driving from one site to the next. During spraying, the worker was located in the closed cabin of the vehicle. From here he steered the vehicle and controlled the spraying device, i.e., he turned spraying on/off and adjusted the spraying angle and, in case of the Dragone devices, also the spraying direction. The window of the cabin was usually closed. Only in rare occasions, the driver had to leave the cabin (see Annex 1 for details).

5.1.2.2 Preparation and application: input parameters

With the vehicle-mounted sprayers, preparation lasted as a rule only a few minutes. In contrast, application took 62-106 min for the 300 L spray tank and between 63 and 261 min for the 800 and 1000 L tanks. When considering the entire work shift, it is to be taken into account that apart from the actual application further tasks take place, for example discussing and coordinating the route to be taken, the donning of protective clothing etc.

Throughout the entire project duration it was found that it is mostly possible to apply two full tanks from a larger spray tank (800-1000 L) during an 8-hour work shift, for the smaller 300 L spray tank it is estimated that at most 6 tank contents can be applied during a shift. As realistic worst case, therefore, the application of 2000 L spray liquid per working day can be expected. The application is carried out on a daily basis over a period of up to 8 weeks per year.

5.1.2.3 Cleaning of the vehicle-mounted sprayers: description of tasks andmeasured values

At the end of the spraying season, which lasts several weeks, the vehicles (small trucks) and vehicle-mounted sprayers (including the spray tanks) were cleaned with a high-pressure cleaner and if necessary by hand with a cloth or brush from the still adhering or dried on residual spray liquid.

Although the dataset comprises only few data, hardly any comparable data in literature had been published for this task up to that time; known publications for cleaning procedures mostly involve exposure to the cleaning agent used and not exposure to the removed contamination.

As regards citing any exposure level during such cleaning procedures, no useful relationship to the applied amount of active substance can be provided as, in this particular case, the form of presentation is different to that of the application phases described previously. Here it is assumed that, in the course of the pest control season, due to a constantly recurring wetting of the surfaces, whereby in addition a part of the already adhering contamination is constantly being flushed off again, equilibrium is gradually arrived at, and an approximately constant contamination of the surfaces occurs. At the time of cleaning, all contaminations have become dried up, meaning that only the non-volatile ingredients of the original spray liquid are still available, reflecting the composition of the original product. The product used here is practically free of volatile ingredients, of which approximately 80 % is from the analysed active substance diflubenzuron and 20 % from other non-volatile ingredients; in a simplified way, this composition is also assumed for the contaminations. In order to derive, from the measured values determined in the cleaning process, a generally applicable presentation of the exposure level for modelling, an extrapolation was carried out from the analytically established amount of active substance onto the non-volatile amounts of spray liquid, i.e., the measured value was divided by 80 %. The given values therefore represent an exposure to the total contamination, which here consists of approximately 80 % of the active substance and 20 % of other non-volatile product ingredients. The exposure level is given in relation to time. In order to obtain from this, for modelling, the exposure to another (non-volatile) active substance and another product, the following calculation can be used:

$$E_{\mathrm{as}} = E_{\mathrm{F\ 2343}} \cdot \frac{c_{\mathrm{as}}}{100\% - c_{\mathrm{vm}}} = E_{\mathrm{F\ 2343}} \cdot \frac{c_{\mathrm{as}}}{c_{\mathrm{as}} + c_{\mathrm{nvm}}}$$

with:

E_{as}	exposure to the active substance in the product to be assessed
$E_{\mathrm{F\ 2343}}$	exposure determined in Project F 2343
c_{as}	concentration of the active substance in the product to be assessed
c_{vm}	concentration of volatile matter in the product to be assessed
c_{nvm}	concentration of non-volatile matter in the product to be assessed, with the exception of the active substance

5.1.2.4 Cleaning of the vehicle-mounted sprayers: input parameters

A total of three measurements at different sites were performed. The duration of the cleaning procedures was 7, 40 and 55 min. In the case of the short cleaning duration, the units were only coarsely washed with the high-pressure cleaner and manual wiping was not considered necessary. This explains the comparatively low exposure levels determined, which correspond to the minima listed for all exposure routes in Tab. 5.2.

Based on the observations made during the measurement periods and the conversations held with the workers, it can be assumed that thorough cleaning of a vehicle-mounted sprayer including spray tank and vehicle takes about 60 min, as a realistic worst-case assumption. Cleaning is carried out on a yearly basis.

Tab. 5.2 Vehicle-mounted sprayers: Exposure levels related to the amount of active substance applied [mg/kg], to the duration of the application [mg/min] or as a concentration in air [µg/m³].

Preparation						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	12	0.439	25.9	60.8	185	276
dermal exposure: body	10	0.133	6.17	9.50	17.5	19.9
inhalation exposure		not determined separately				
Application						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands [a]	12	0.829	5.86	16.1	51.5	67.4
dermal exposure: body	12	0.417	6.27	7.97	10.4	11.0
inhalation exposure [a]	12	0.002	0.005	0.006	0.010	0.014
Preparation and application [b]						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	16	3.15	36.1	58.2	105	112
dermal exposure: body	16	1.87	10.4	15.8	38.8	74.9
inhalation exposure [a]	16	0.002	0.006	0.026	0.052	0.068
Cleaning of the vehicle-mounted sprayer [c]						
Route of exposure	**n**	**Minimum**	**Median**	**75th percentile**	**95th percentile**	**Maximum**
dermal exposure: hands	3	0.03 mg/min	1.36 mg/min	-	-	2.92 mg/min
dermal exposure: body	3	0.13 mg/min	0.36 mg/min	-	-	0.80 mg/min
inhalation exposure [a]	2[d]	2.06 µg/m³	-	-	-	2.07 µg/m³

[a] An inhalation rate of 1.25 m³/h was assumed.

[b] Dataset includes values from measurements in which the two application phases (preparation and application) have been measured together, as well as added contributions from the above-listed separate measurements of both application phases.

[C] For cleaning of the vehicle-mounted sprayers, the exposure to all non-volatile constituents of the used biocidal product is indicated.

[d] One of the three values measured is not considered in this dataset, because it was below the limit of quantification which, in this case, was very high (3.71 mg/m^3) due to the unusually short sampling time of 7 minutes; the calculated concentration in air for this measurement was 4.55 µg/m^3.

5.1.3 Spraying with hand-held sprayers

The use of the hand-held sprayers can be divided into the application phases

- “preparation or transfer the spray liquid“,
- “application of the spray liquid“ and
- “cleaning of the spraying equipment“ (cleaning of the spraying equipment was not measured within this project)

5.1.3.1 Preparation and/or transfer and application: description of tasks and measured values

The filling of the spray tank is carried out using two different methods. The term “preparation“ is here used for preparation of the spray liquid from the granular biocidal product. Here, the granules were taken with a measuring spoon from a plastic bag holding approximately 300 g and poured into the strainer set in the filling opening of the HHS-spray tank. Subsequently, the spray tank was filled up with water.
On the other hand, the term “transfer” means the pouring of ready-to-use spray liquid, for example from a canister. The canister had previously been filled using a hose from the spray tank of the vehicle-mounted sprayer.
For application, as a rule, the full volume of the tank (12 L) was sprayed at a single application site. This volume lasted for at least one or two very large or several small oak trees. In the first field study in 2014, the exposure levels were determined during the application of two full tanks for all routes of exposure, i.e., the datasets comprise the preparation (in two cases the transfer instead) and the application of two full tanks of 12 L each.
In the 2015 field study, procedure and measurement strategy were somewhat refined. For example, the tanks were filled with already prepared spray liquid instead of preparing it. In addition, the dermal samplers for the hands were changed each time after transfer and after application of a 12 L full tank, so that the exposure of the hands for both application phases could be recorded separately; measurement of both inhalation and dermal exposure of the body continued as before, involving both preparation and application of two full tank volumes.

Tab. 5.3 shows the results of these measurements related to the amount of active substance applied, in each case in mg/kg. The values for “preparation and application” comprise a complete procedure (preparation and application of 2 x 12 L spray liquid each), in the same way the values for “transfer and application” comprise a complete process, containing the values listed separately for “transfer” and “application”. The values for “preparation/transfer and application” comprise in turn all values for both procedures and also contain the values previously listed. For the assessment of corresponding biocidal products, the authors suggest assuming that both procedures are performed in pest control measures so that, as a rule, the last mentioned, summarised values should be used for this purpose.

5.1.3.2 Preparation and application: input parameters

As the application of the spray liquid using the vehicle-mounted sprayer is considerably more efficient than using the hand-held sprayer in terms of effort and duration, the latter was only used when using a vehicle-mounted unit was impossible

due to local conditions (fencing off, no treated roadway to the application site). Accordingly, the hand-held sprayer was used for a maximum of a few hours per day. Application of a tank volume of 12 L lasted approximately 10-20 min including preparation of the spray liquid. At maximum, the application of four full tanks at one site was observed; this lasted in total approximately one hour. From a purely mathematical point of view it could be concluded that 32 full tanks can be applied during an 8-hour shift. However, it must be taken into account that the filled unit is very heavy (11 kg dead weight, in addition to 12 kg spray liquid and a certain amount of gasoline, together therefore approximately 25 kg). A continuous application of the biocide with this unit without extended breaks can already be excluded due to the physical exertion involved. In addition, throughout the whole project, no sites were visited, at which such an extended use of these units would have been useful; driving times to reach the different application sites are always necessary, which always involves a change of protective gloves and protective suits.

The authors are therefore of the opinion that a single worker who exclusively uses the hand-held sprayer in OPM control, could apply, during an 8-hour shift, a maximum of 16 full tanks of 12 L each. On the basis of a realistic worst case assumption, therefore, the application of a volume of approximately 200 L spray liquid per working day can be assumed. The application is carried out on a daily basis over a period of up to eight weeks.

Tab. 5.3 Hand-held sprayers: Exposure levels related to the amount of active substance applied [mg/kg].

Transfer						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	16	27.8	102	150	273	395
Application						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	16	17.4	58.3	78.6	124	128
Transfer and application						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands [a]	18	64.1	187	264	442	521
dermal exposure: body	10	166	427	831	1200	1320
inhalation exposure [b]	10	0.094	0.13	0.21	0.24	0.25
Preparation and application						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	8	599	1440	1950	7080	9560
dermal exposure: body	8	753	2910	4920	10700	11800
inhalation exposure [b]	8	0.35	1.05	2.00	3.82	3.91
Preparation/ transfer and application [c]						
Route of exposure	**n**	**Minimum [mg/kg]**	**Median [mg/kg]**	**75th percentile [mg/kg]**	**95th percentile [mg/kg]**	**Maximum [mg/kg]**
dermal exposure: hands	18	90.4	475	1328	3550	9560
dermal exposure: body	18	166	963	2580	9160	11800
inhalation exposure [b]	18	0.09	0.24	0.73	3.70	3.91

[a] Data includes two values that have been measured over two application cycles, including both application phases. In addition, from the exposure heights listed above, the two application phases associated with the same of the 16 measured processes were added up and inserted into this dataset.

[b] An inhalation rate of 1.25 m³/h was assumed.

[C] This dataset is a combination of the "transfer and application" and the "preparation and application" datasets listed above. The exposure heights of two consecutive application cycles, at which at the same time a single coverall was measured, were added up. This dataset represents 18 operations, in which two tank fillings were transferred or prepared and then applied, with the values for the three exposure pathways referring to the same process.

5.2 Bystanders

On exposure to the spray mist, the dermal absorption through the skin and the inhalation of the spray mist must be taken into account. Both routes are accounted for in the test design as regards bystanders, in which the dermal exposure is measured using vertically fixed Tyvek^{TM} sheets and the inhalation exposure using stationary air samplers. The measurement time lasted as long as the application, but at least for a minimum of 15 min.

As maximum, a direct exposure to the spray mist can last for the entire time period of application (including the time it takes until the spray mist has not yet settled). In reality, however, it can be assumed that, in most cases, bystanders are only exposed during a fraction of treatment time, as they would move out of the spray mist area. A risk assessment assuming exposure during the entire application therefore constitutes the worst case.

Generally, a difference is made between the exposures of adults and children. This is due to different body weight, different body surface area and respiration volume. This difference was accounted for in the study design by cutting the Tyvek^{TM} sheets into lower and upper segments. The lower segment corresponded to approximately the total body surface of a six to ten year old child, both segments together to approximately the total body surface of an adult (ECHA 2013). For the inhalation route no difference was made regarding physical height. The sample head of the pump was, at a height of 1.50 m, at the average adult breathing zone height. The effect of sampling at 1.50 m for the exposure estimate of a child is considered negligible. The segments as well as the air samplers were - insofar as possible on site - located in the direction of the drifting spray mist, in each case at a distance of 5 m and 10 m from the treated tree/ tree row in order to determine the maximum possible exposure.

Evaluation of the data is carried out separately for the application type used. In the two years together, 15 measurements for Dimilin^{TM} 80 WG application with the vehicle-mounted unit and 15 measurements for application with the hand-held sprayer were performed. Regarding the depositions on the segments used for dermal sampling, it is noticeable that the measured values with both types of application clearly deviate by a factor of up to 1000. This is explained by the different conditions on site (wind force, wind direction, thermics, access to the trees, etc.) and the applied amount of Dimilin^{TM} 80 WG (treatment duration, dilution, etc.), and reflects the normal variation obtained in such a treatment. The variation in the air samples is smaller, particularly during application with the vehicle-mounted sprayer. The level of air exposure measured does not correlate with the duration of the measurement or the treatment, respectively. The maximum treatment duration was 55 min for the vehicle-mounted sprayer and 53 min for the hand-held sprayer. On average, the treatment duration with the vehicle-mounted unit, however, was clearly shorter than with the hand-held sprayer.

The exposure levels following application with the vehicle-mounted sprayer and the hand-held sprayer are within the same order of magnitude. Generally, the dermal exposure decreases as the distance to the treated tree increases. The 95th percentiles determined for diflubenzuron were, taking into account all measured

values for the vehicle-mounted sprayer, 3263 µg (5 m) and 1349 µg (10 m) for the lower segment as well as 5702 µg (5 m) and 2619 µg (10 m) for the total Tyvek^{TM} sheet. For the hand-held sprayer, the 95th percentiles of all measured values were 1425 µg (5 m) and 1323 µg (10 m) on the lower segment as well as 3253 µg (5 m) and 2995 µg (10 m) on the total Tyvek^{TM} sheet. For the exposure estimate of an infant (1-2 years) which, when compared with a child, has a body surface smaller by a factor of 1.9 (ECHA 2013), mathematical values of 1717 µg (5 m) or 710 µg (10 m) for the vehicle-mounted sprayer and 750 µg (5 m) or 696 µg (10 m) for the hand-held sprayer would be obtained. Approximately half of the measurements obtained from the charged filters of the air sampling are below the limit of quantification. If, for these measurements, the quantification limit is used as assessment value, 95th percentiles of 0.60 µg (5 m) and 0.52 µg (10 m) for application with the vehicle-mounted unit and 4.2 µg (5 m) and 2.1 µg (10 m) for application with the hand-held sprayer are obtained, respectively. By correction of these values (flow rate of the pump: 10 L/min) for the inhalation rate of a child (1.32 m^3/h or 22 L/min; ECHA 2013) or adult (1.25 m^3/h or 20.8 L/min, ECHA 2013), exposure levels of 1.3 µg (5 m) and 1.1 µg (10 m) are obtained for a child and 1.2 µg (5 m) and 1.1 µg (10 m) for an adult per spray application for the vehicle-mounted sprayer. For the hand-held sprayer, values of 9.2 µg (5 m) and 4.7 µg (10 m) for a child and 8.7 µg (5 m) and 4.4 µg (10 m) for an adult are obtained. For an infant (inhalation rate: 1.26 m^3/h or 21 L/min, ECHA 2013), exposure levels of 1.3 µg (5 m) and 1.1 µg (10 m) for the vehicle-mounted unit and 8.8 µg (5 m) and 4.5 µg (10 m) for the hand-held sprayer are obtained.

These measurement data can now be entered into a risk assessment for bystanders. From these external exposure data, systemic exposure has to be calculated. For diflubenzuron, a dermal absorption of 75 % and an absorption from inhalation of 100 % are assumed. Additionally, use of light clothing (penetration 50 %) is assumed, which reduces exposure to 50 % of the body surface (corresponds approximately to the part of the trunk in relation to the total body surface). Subsequently, the systemic exposure is normalised to the body weight, and dermal and inhalation exposure are added up to make up total exposure. The total exposure is then compared with the toxicological reference value for an acceptable exposure level (AEL). For this estimate, the body weight of an infant is 10 kg, that of a child 23.9 kg and that of an adult 60 kg. The acute AEL for diflubenzuron of 0.13 mg per kg body weight and day is used as reference value because exposure to the spray mist during application occurs only once per year. Taking into account the exposure from contaminated surfaces would make a risk assessment for repeated (medium-term) exposure considering the corresponding $AEL_{medium\text{-}term}$ necessary.

The results of the risk assessment for bystanders during acute exposure to diflubenzuron are given in Tab 5.4 and Tab. 5.5. The acute reference value is not exceeding the measured values for the distances at 5 m and 10 m both for application with a vehicle-mounted sprayer and with a hand-held sprayer on the basis of the 95th percentiles. This means that acute exposure of bystanders presents no risk when adhering to a minimum distance of 5 m. Therefore, no additional measures for the protection of bystanders must be taken. Nevertheless, in the context of good professional practice and preventive health measures, care is to be taken that no persons are present in direct proximity to the application site during spraying and drying of the spray coating.

Tab. 5.4 Bystander exposure and capacity utilisation of AEL_{acute} during application of diflubenzuron using a vehicle-mounted sprayer (95^{th} percentile).

	Distance [m]	Measured value dermal [µg] 95^{th} percentile	Measured value dermal corrected (75 % dermal absorption) [µg] 95^{th} percentile	Measured value inhalation corrected (100 % inhalation absorption) [µg] 95^{th} percentile	systemic exposure dermal [mg/kg BW]	systemic exposure inhalation [mg/kg BW]	AEL_{acute} [%]
Infant	5	1717	1288	1.26	0.097	0.00013	74.4
	10	710	533	1.09	0.040	0.00011	30.8
Child	5	3263	2447	1.32	0.077	0.00006	59.1
	10	1349	1012	1.14	0.032	0.00005	24.5
Adult	5	5702	4277	1.25	0.053	0.00002	41.1
	10	2619	1964	1.08	0.025	0.00002	18.9

Tab. 5.5 Bystander exposure and capacity utilisation of AEL_{acute} during application of diflubenzuron using a hand-held sprayer (95^{th} percentile).

	Distance [m]	Measured value dermal [µg] 95^{th} percentile	Measured value dermal corrected (75 % dermal absorption) [µg] 95^{th} percentile	Measured value inhalation corrected (100 % inhalation absorption) [µg] 95^{th} percentile	systemic exposure dermal [mg/kg BW]	systemic exposure inhalation [mg/kg BW]	AEL_{acute} [%]
Infant	5	750	562	8.82	0.042	0.00088	33.1
	10	696	522	4.48	0.039	0.00045	30.5
Child	5	1425	1068	9.24	0.034	0.00039	26.1
	10	1323	992	4.70	0.031	0.00020	24.1
Adult	5	3253	2440	8.73	0.031	0.00015	23.6
	10	2995	2246	4.44	0.028	0.00007	21.7

6 Summary and outlook

The aim of the investigations described here was to determine the potential dermal and inhalation exposure of workers during control of the oak processionary moth by spraying. In addition, a possible exposure of bystanders was investigated.

Data acquisition/ determination of exposure

For determining exposure, a procedure was developed and validated within this project for the quantification of dermal exposure to diflubenzuron using coveralls made of polyethylene material (Tyvek^{TM}), cotton gloves as well as Tyvek^{TM} sheets. Directly following the pest control operation, the coveralls were cut up into 21 segments and the Tyvek^{TM} sheets into two segments. To determine dermal exposure, the dosimeters exposed to Dimilin^{TM} 80 WG or the separate segments were extracted. The extract was analysed using PCI-GC-MS in the SIM mode after sample clean up. The determination of inhalation exposure was carried out both by personal and stationary air sampling, whereby the respirable dust fraction was measured. The filters were extracted and the extracts analysed using HPLC-UV.

The methods developed and validated in the context of the investigations allow a reliable and reproducible determination of the potential dermal and inhalation exposure, such as found in chemical OPM control by spraying. With these methods, in 2014 and 2015, pest control companies were monitored by measurements during the application of diflubenzuron containing insecticides. By this, for the first time, data on the exposure of workers and bystanders were recorded.

In total, during this period, three companies engaged in pest control were monitored during biocide application with vehicle-mounted sprayers and hand-held sprayers, whereby eight workers were sampled performing different tasks. To determine the dermal exposure of workers, 51 coveralls and 85 pairs of gloves as well as 65 air samples (stationary or personal air sampling) were taken on professional users.
The inhalation and dermal exposure of bystanders was also recorded during biocide application with vehicle-mounted sprayer or hand-held sprayer whereby, for each type of application, 15 samplings at distances of 5 m and 10 m from the treated tree/group of trees were carried out. Accordingly, in the field studies, 60 datasets for Tyvek^{TM} sheets were obtained for dermal exposure and 60 stationary air samplings were made to determine the exposure of bystanders.

The measurement results on workers´ exposure have been systematically compiled and evaluated with regard to the type of spray application and task. The data for the exposure of bystanders were evaluated regarding the type of application and the distance from the treated tree/group of trees. The valid data obtained in this way can be used for product authorisation at national and European level in the assessment of spray applications and are important in assessing the risk of bystanders on acute exposure to diflubenzuron.

In this project, dermal and inhalation exposure resulting from the following tasks have been investigated:

- weighing and portioning of Dimilin^{TM} 80 WG granules
- preparation or transfer of Dimilin^{TM} 80 WG suspension for vehicle-mounted sprayers and hand-held sprayers,
- application of Dimilin^{TM} 80 WG suspension with vehicle-mounted sprayers and hand-held sprayers
- cleaning of the vehicles/ vehicle-mounted sprayers at the end of the spray season.

Workers

Dermal exposure (coverall and gloves) of the workers during weighing out and portioning of Dimilin^{TM} 80 WG granules was determined twice and was 8.39 and 3.71 mg per kg active substance handled, respectively. In this task, especially the hands (84 % of total dermal exposure) and to a lesser extent the remaining body, were exposed to diflubenzuron during the task. On average, the inhalation exposure of the workers during this task was 0.05 mg/kg.

After biocide application with a vehicle-mounted sprayer, dermal exposure of the workers was in a two-digit mg/kg range. The median exposure during preparation and application of Dimilin^{TM} 80 WG suspension was 50.8 mg/kg (95th percentile: 186 mg/kg; n=16), whereby especially the preparation of the spray liquid (median: 37.5 mg/kg; 95th percentile: 112 mg/kg; n=10) and to a lesser extent the application of the spray liquid (median: 13.5 mg/kg; 95th percentile: 60.6 mg/kg; n=12), contributed to the total exposure. Again, especially the hands contributed to the exposure, making up 80 % of the total dermal exposure. The calculated median for inhalation exposure is, for the preparation and application of Dimilin^{TM} 80 WG suspension, 0.006 mg/kg (95th percentile: 0.052 mg/kg; n=16).

In the case of biocide application with the hand-held sprayer, the total dermal exposure of workers was in the four-digit mg/kg range. The median for total dermal exposure in preparation/transfer and application of Dimilin^{TM} 80 WG suspension was 1520 mg/kg (95th percentile: 13900 mg/kg; n=18) whereby, for the preparation and application task, markedly higher total doses were found (median: 4900 mg/kg; 95th percentile: 16500 mg/kg; n=8) than for the transfer and application task (median: 695 mg/kg; 95th percentile: 1530 mg/kg; n=10). The question as to whether this difference between preparation and application or transfer and application actually is caused by the task, or is mainly based on interindividual differences of the workers, could not be clarified conclusively.

After biocide application with the hand-held sprayer, twice as much diflubenzuron was found on the coveralls than on the gloves, which reflects the direct spray mist exposure of the workers during this type of Dimilin^{TM} 80 WG application. The high dermal exposures determined when working with the hand-held sprayer were also found with the inhalation data. The median for inhalation exposure was 1.05 mg/kg (95th percentile: 3.82 mg/kg; n=8) for preparation and application and 0.13 mg/kg (95th percentile: 0.24 mg/kg; n=10) for transfer and application.

During cleaning procedures, both vehicles and vehicle-mounted sprayers were cleaned using high-pressure equipment. Thereby, the workers were subjected to a total dermal exposure that was between 0.131 and 2.67 mg/min task duration (n=3). It was found that a more thorough cleaning of the equipment resulted in a higher exposure of the workers, and that this, in addition, especially occurred on the hands when manual cleaning with a brush or cloth was performed (17 % of the total dermal exposure was found on the hands without additional manual cleaning; 63 % on the hands with additional cleaning using a brush; 89 % on the hands with additional cleaning using a cloth). Inhalation exposure by workers during cleaning work was between 0.04 and <0.10 µg/min (n=3).

Bystanders

When measuring bystanders' exposure, considerable differences in the measured values were obtained both for dermal and inhalation exposure. In the case of dermal exposure, Dimilin^{TM} 80 WG exposure decreased between the Tyvek^{TM} sheets placed at a distance of 5 m and those placed at 10 m, both when using the vehicle-mounted sprayer and when using a hand-held sprayer. Thus, the median values decreased from 60.5 mg/kg to 34.2 mg/kg (95th percentile: from 990 mg/kg to 455 mg/kg) after application with a vehicle-mounted sprayer, or from 135 mg/kg to 40.1 mg/kg (95th percentile: from 704 mg/kg to 408 mg/kg) after application with the hand-held sprayer. With regard to the inhalation measurements, a decrease of diflubenzuron exposure occurred only in the 95th percentiles. Exposure declined from 0.15 mg/kg to 0.13 mg/kg after application with a vehicle-mounted sprayer and from 3.03 mg/kg to 1.54 mg/kg after application with the hand-held sprayer.

Generally, the great differences in the determined bystander exposure data indicate highly variable exposure situations. Possible influencing factors are, apart from the weather (adverse wind, changing of wind direction), the number and arrangement of the treated trees (individual trees, groups of trees or tree rows), the passing of the spray vehicle at different distances from the trees and samplers (vehicle-mounted sprayer) or the movement pattern of the pest control operators around the treated tree/group of trees (hand-held sprayer).

A risk assessment for bystanders for acute exposure to diflubenzuron was carried out using the quantified dermal as well as inhalation exposure data. The acute reference value, which was derived for the active substance diflubenzuron during active substance approval, is not exceeded, neither on application with a vehicle-mounted unit, nor when using a hand-held sprayer on the basis of the 75th and 95th percentiles of the measured values for distances of 5 m and 10 m; the acute exposure of bystanders therefore presents no risk on adherence to a minimum distance of 5 m. Consequently, no additional measures for the protection of bystanders must be taken here. In the context of good professional practice and preventive health measures, however, care is to be taken that no one is in direct proximity to the application site during spraying and drying of the spray coating.

Comparison with exposure levels in PPP applications

The spray applications occurring during OPM control with biocidal products differ considerably from application scenarios with partly identical application equipment/sprayers in the PPP field.

A comparison of the data recorded in this project with exposure data from agriculture shows that markedly higher dermal exposures occur in the control of the oak processionary moth using spray applications. The exposure levels (related to the amount of active substance applied) resulting from the application with vehicle-mounted sprayers are approximately 10fold (body) or 50-100fold (hands) higher than the exposure levels quantified in agriculture. 10- to 20fold higher exposure levels of body and hands (again related to the amount of active substance applied) were found to result from biocide application with the hand-held sprayer when compared to PPP. The inhalation data measured are for both spray application types in a comparable order of magnitude to those in the PPP field. This initial direct comparison was undertaken on the basis of exposure levels related to the applied amount of active substance; however, in the assessment of these figures, the amount of active substance applied per working day must also be taken into account. In the course of the investigations, it was found that, during OPM control, markedly less active substance is applied per working day than in corresponding PPP applications, which presumably is mainly due to the fact that no large continuous areas, but rather individual trees or smaller groups of trees are treated. For this reason, a certain amount of the actual working time is required for driving to the different sites of application. Due to the smaller amounts of active substance that are applied on a working day, the differences found have to be put into perspective when relating to a work shift. Nevertheless, also this consideration indicates a clearly higher exposure of the workers in OPM control than in the corresponding PPP applications. Due to the large differences in potential dermal exposure, therefore, an assessment in the biocides framework based on the exposure models established in the field of plant protection would be fraught with great uncertainties.

Conclusion

Because of the previous inadequate database, the generation of valid data on the potential dermal and inhalation exposure during OPM control with biocides has become indispensable. For the investigated workplaces and the use profiles recorded, comprehensive data for the assessment of dermal and inhalation exposure of workers and bystanders were thus obtained by using validated measurement methods. With the measured values recorded, a database is now available allowing an exposure evaluation of workers and bystanders during the control of the oak processionary moth by spray applications with vehicle-mounted and with hand-held sprayers and an exposure estimation to approve biocidal products at national and European level.

The exposure data determined, on a long-term basis also constitute a solid foundation for an improvement in occupational protective measures and therefore help in reducing the health risk from biocide application using spray techniques.

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Annex 1 Workers: Description of application situations and tasks

Weighing out and portioning of Dimilin™ 80 WG granules

Weighing-dO-1, dG-1, ip-1 and is-1 (measurement series 1)

Standing at a table, using household scales, a 20 kg package of Dimilin™ 80 WG was weighed and portioned in 240 g bags (see Fig. 3.6). With a measuring cup, Dimilin™ 80 WG was taken from the large 20 kg cardboard barrel and filled into small (in part already used) plastic bags. Thereby visible dust formation occurred. As required, the worker reached into the plastic bag and Dimilin™ 80 WG was taken out again with a measuring spoon. The bags were sealed with a wire/clip and placed in / thrown into an empty cardboard barrel causing dust formation. Finally, the granules scattered over the table were wiped off it using paper tissues into the left hand and thrown to the plastic bags in the cardboard barrel.

Weighing-dO-2, dG-2, ip-2 and is-2 (measurement series 2)

Standing at a table, using household scales, 10 kg Dimilin™ 80 WG were weighed and portioned into 300 g bags. With a measuring cup, the Dimilin™ 80 WG was taken from the large 20 kg cardboard barrel and weighed out (Fig. 3.7). Thereby visible dust formation occurred. If there were too many granules in the measuring cup, these were taken off with a measuring spoon. The granules were filled into plastic bags which were placed on the table next to the scales. After portioning of about 10 bags, they were sealed with a wire clip. At the end of the task, the 300 g bags were put into an empty cardboard barrel. The barrel was sealed, the scales were cleaned and the table swept with a brush.

Vehicle-mounted sprayer: Preparation of the Dimilin™ 80 WG suspension

VMS-preparation-dO-1 and dG-1 (measurement series 11)

The coverall VMS-preparation-dO-1 and the pair of gloves VMS-preparation-dG-1 were worn when preparing the Dimilin™ 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A.

VMS-preparation-dO-2 and dG-2 (measurement series 12)

The coverall VMS-preparation-dO-2 and the pair of gloves VMS-preparation-dG-2 were worn when preparing the Dimilin™ 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A.

VMS-preparation-dO-3 and dG-3 (measurement series 13)

The coverall VMS-preparation-dO-3 and the pair of gloves VMS-preparation-dG-3 were worn when preparing the Dimilin™ 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A. The bag with the portioned biocide was passed by a colleague.

VMS-preparation-dO-4 and dG-4 (measurement series 14)

The coverall VMS-preparation-dO-4 and the pair of gloves VMS-preparation-dG-4 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A.

VMS-preparation-dO-5 and dG-5 (measurement series 15)

The coverall VMS-preparation-dO-5 and the pair of gloves VMS-preparation-dG-5 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A.

VMS-preparation-dO-6 and dG-6 (measurement series 16)

The coverall VMS-preparation-dO-6 and the pair of gloves VMS-preparation-dG-6 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A.

VMS-preparation-dO-7 and dG-7 (measurement series 17)

The coverall VMS-preparation-dO-7 and the pair of gloves VMS-preparation-dG-7 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure for company C described in Section 3.1. For preparing the spray liquid, water was taken from a hydrant. The worker did not put the hood of his coverall on.

VMS-preparation-dO-8 and dG-8 (measurement series 18)

The coverall VMS-preparation-dO-8 and the pair of gloves VMS-preparation-dG-8 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure for company C described in Section 3.1. For preparing the spray liquid, water was taken from the 1000 L tank. The worker did not put the hood of his coveralls on.

VMS-preparation-dO-9 and dG-9 (measurement series 19)

The coverall VMS-preparation-dO-9 and the pair of gloves VMS-preparation-dG-9 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure for company C described in Section 3.1. For preparing the spray liquid, water was taken from the 1000 L tank. The worker did not put the hood of his coverall on.

VMS-preparation-dO-10 and dG-10 (measurement series 20)

The coverall VMS-preparation-dO-10 and the pair of gloves VMS-preparation-dG-10 were worn when preparing the Dimilin^{TM} 80 WG suspension. Preparation of the spray liquid agreed with the procedure for company C described in Section 3.1. For preparing the spray liquid, water was taken from a hydrant. The worker did not put the hood of his coverall on.

VMS-preparation-dG-11 (measurement series 21)

The pair of gloves VMS-preparation-dG-11 was worn when preparing the Dimilin™ 80 WG suspension. Preparation of the spray liquid agreed with the procedure described in Section 3.1 for company A. This time, the worker wore no coverall.

Vehicle-mounted sprayer: Application of the Dimilin™ 80 WG suspension

VMS-application-dO-1, dG-1.1, dG-1.2 and ip-1 (measurement series 3)

The coverall VMS-application-dO-1 was worn during checking and adjustment of the nozzles as well as during the entire application. The pair of gloves VMS-application-dG-1.1 was worn during checking and adjustment of the nozzles and during the first 64 min of application, the pair of gloves VMS-application-dG-1.2 during further application. Personal air sampling VMS-application-ip-1 was performed on the entire work process. Manual adjustment to the nozzle was made a several times to optimise the spray mist.

VMS-application-dO-2, dG-2.1, dG-2.2 and ip-2 (measurement series 4)

The coverall VMS-application-dO-2 was worn during adding of water (2x) as well as during both applications. The pair of gloves VMS-application-dG-2.1 was worn during the first adding of water with the hose and during the first application. The pair of gloves VMS-application-dG-2.2 when water was added for the second time with the hose and during the second application. Personal air sampling VMS-application-ip-2 was performed during the entire work process (adding of water, application, adding of water, and application).

VMS-application-dO-3, dG-3 and is-4 (measurement series 11)

The coverall VMS-application-dO-3 and the pair of gloves VMS-application-dG-3 were worn during application of the Dimlin™ 80 WG suspension. Stationary air sampling VMS-application-is-4 was performed during the entire work process in the driver's cabin.

VMS-application-dO-4, dG-4 and is-5 (measurement series 12)

The coverall VMS-application-dO-4 and the pair of gloves VMS-application-dG-4 were worn during application of the Dimlin™ 80 WG suspension. In the driver's cabin of the Unimog, the worker took off the hood of the coverall. Stationary air sampling VMS-application-is-5 was performed during the entire work process in the driver's cabin.

VMS-application-dO-5, dG-5 and is-6 (measurement series 13)

The coverall VMS-application-dO-5 and the pairs of gloves VMS-application-dG-5 were worn during application of the Dimlin™ 80 WG suspension. To telephone while underway, the worker dismounted from the Unimog and was leaning during this time with his seat/back against the accompanying vehicle, which had also stopped.

Stationary air sampling VMS-application-is-6 was performed during the entire work process in the driver's cabin.

VMS-application-dO-6, dG-6.1, dG-6.2 and is-7 (measurement series 14)

The coverall VMS-application-dO-6 and the pair of gloves VMS-application-dG-6.1 and VMS-application-dG-6.2 were worn during application of the Dimlin^{TM} 80 WG suspension. In the driver's cabin of the Unimog, the worker took the hood of the coverall off. After 52 min he helped with filling of the spray liquid from the tank of the vehicle-mounted sprayer into a 20 L canister. After this, the gloves were changed. Stationary air sampling VMS-application-is-7 was performed during the entire work process in the driver's cabin.

VMS-application-dO-7, dG-7 and is-8 (measurement series 15)

The coverall VMS-application-dO-7 and the pair of gloves VMS-application-dG-7 were worn during application of the Dimlin^{TM} 80 WG suspension. To telephone while underway, the worker dismounted from the Unimog and was leaning during this time with one hand against the stopped Unimog. Stationary air sampling VMS-application-is-8 was performed during the entire work process in the driver's cabin.

VMS-application-dO-8, dG-8 and is-9 (measurement series 16)

The coverall VMS-application-dO-8 and the pair of gloves VMS-application-dG-8 were worn during application of the Dimlin^{TM} 80 WG suspension. Stationary air sampling VMS-application-is-9 was performed during the entire work process in the driver's cabin.

VMS-application-dO-9, dG-9 and is-10 (measurement series 17)

The coverall VMS-application-dO-9 and the pair of gloves VMS-application-dG-9 were worn during application of the Dimlin^{TM} 80 WG suspension. The worker did not put the hood of his coverall on. He additionally wore a breathing mask. The window of the Unimog driver's cabin was temporary open during application. While underway, the driver descended once in order to pick up a traffic sign that had been knocked over. Stationary air sampling VMS-application-is-10 was performed during the entire work process in the driver's cabin. The sampling pump failed after 70 min.

VMS-application-dO-10, dG-10 and is-11 (measurement series 18)

The coverall VMS-application-dO-10 and the pair of gloves VMS-application-dG-10 were worn during application of the Dimlin^{TM} 80 WG suspension. The worker did not put the hood of his coverall on. He additionally wore a breathing mask. Stationary air sampling VMS-application-is-11 was performed during the entire work process in the driver's cabin.

VMS-application-dO-11, dG-11 and is-12 (measurement series 19)

The coverall VMS-application-dO-11 and the pair of gloves VMS-application-dG-11 were worn during application of the Dimlin^{TM} 80 WG suspension. The worker did not

put the hood of his coverall on. He additionally wore a breathing mask. Stationary air sampling VMS-application-is-12 was performed during the entire work process in the driver's cabin.

VMS-application-dO-12, dG-12 and is-13 (measurement series 20)

The coverall VMS-application-dO-12 and the pair of gloves VMS-application-dG-12 were worn during application of the Dimlin™ 80 WG suspension. The worker did not put the hood of his coveralls on. He additionally wore a breathing mask. Stationary air sampling VMS-application-is-13 was performed during the entire work process in the driver's cabin.

VMS-application-is-1, is-2 and is-3 (company A)

To monitor inhalation exposure during spray application, sampling devices were placed on the loading platform of the pickup. These measurements represent the worst case for the spray liquid application.

Vehicle-mounted sprayer: Preparation and application of the Dimilin™ 80 WG suspension

VMS-preparation-application-dO-1, dG-1.1, dG-1.2, dG-1.3 and ip-1 (measurement series 5)

The coverall VMS-preparation-application-dO-1 was worn during general activities before preparing the Dimilin™ 80 WG suspension, during preparation and application of the Dimilin™ 80 WG suspension and during adjustment of the nozzles. The worker came into contact with the nozzles from his right shoulder as well as with the spray tank with his upper thighs and stomach. The pair of gloves VMS-preparation-application-dG-1.1 was worn during work prior to preparing the spray liquid, the pair of gloves VMS-preparation-application-dG-1.2 while preparing the spray liquid and adjusting the nozzles, and the pair of gloves VMS-preparation-application-dG-1.3 during application. Personal air sampling for VMS-preparation-application-ip-1 was performed during the entire work process.

VMS-preparation-application-dO-2, dG-2.1, dG-2.2 and ip-2 (measurement series 6)

The coverall VMS-preparation-application-dO-2 was worn during preparation and application of the Dimilin™ 80 WG suspension. The pair of gloves VMS-preparation-application-dG-2.1 was worn while preparing the spray liquid, and the pair of gloves VMS-preparation-application-dG-2.2 during application. Personal air sampling VMS-preparation-application-ip-2 was performed during the entire work process.

VMS-preparation-application-dO-3, dG-3 and ip-3 (measurement series 7)

The coverall VMS-preparation-application-dO-3 and the pair of gloves VMS-preparation-application-dG-3 were worn during preparation and application of the Dimilin™ 80 WG suspension. While filling the tank with water, the worker leaned against the vehicle-mounted unit with his hands. Personal air sampling VMS-preparation-application-ip-3 was performed during the entire work process.

VMS-preparation-application-dO-4, dG-4 and ip-4 (measurement series 8)

The coverall VMS-preparation-application-dO-4 and the pair of gloves VMS-preparation-application-dG-4 were worn during preparation and application of the Dimilin^{TM} 80 WG suspension. The worker's hood, shoulders and upper back touched the Unimog and his hands the filling level indicator. Personal air sampling VMS-preparation-application-ip-4 was performed during the entire work process.

VMS-preparation-application-dO-5, dG-5 and ip-5 (measurement series 9)

The coverall VMS-preparation-application-dO-5 was worn during preparation and application of the Dimilin^{TM} 80 WG suspension. While preparing the spray liquid, the worker removed the strainer already containing the Dimilin^{TM} 80 WG 3-4 times, as the water supply was not sufficient. During application, the worker dismounted from the vehicle in order to speak with a cyclist who had ridden through the spray jet and was standing during this time in the just applied spray mist. The tank was not sprayed empty; approximately 600 L of the prepared 1000 L spray liquid remained in the tank. The pair of gloves VMS-preparation-application-dG-5 was only worn when preparing the spray liquid. Personal air sampling VMS-preparation-application-ip-5 was performed during the entire work process.

VMS-preparation-application-dO-6, dG-6.1, dG-6.2, dG-6.3 and ip-6 (measurement series 10)

The coverall VMS-preparation-dO-6 and the pair of gloves VMS-preparation-dG-6.1, VMS-preparation-dG-6.2 and VMS-preparation-dG-6.3 were worn during weighing out of Dimilin^{TM} 80 WG granules and when preparing the spray liquid. The worker opened and closed the hydrant, opened the small plastic container, weighed out the granules on the loading platform of the pickup into a beaker using kitchen scales, opened the lid of the pre-mix tank, poured the biocide into the pre-mix tank and flushed out the beaker. By adding water, the Dimilin^{TM} 80 WG was preslurried in the mixing tank and then flushed into the large spray tank (in each case 2x). The worker followed the tractor in the accompanying vehicle during application. The coverall VMS-preparation-dO-6 was worn during weighing out (2x), adding the Dimilin^{TM} 80 WG to the pre-mix tank (2x), mixing (2x) as well as in the accompanying vehicle during application (2x). Pair of gloves VMS-preparation-dG-6.1 was worn during first weighing out, first adding to the pre-mix-tank and first mixing, pair of gloves VMS-preparation-dG-6.2 in the accompanying vehicle during the first application, and pair of gloves VMS-preparation-dG-6.3 during second weighing out, second adding to the pre-mix tank, second mixing as well as in the accompanying vehicle during the second application. Personal air sampling VMS-preparation-application-ip-6 was performed during the entire work process.

VMS-preparation-application-ip-7 (measurement series 11)

Personal air sampling VMS-preparation-application-ip-7 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The dermal samplers VMS-preparation-dO-1 and

VMS-application-dO-3 with the respective gloves, as well as the stationary air sampling VMS-application-is-4 belong to this measurement.

VMS-preparation-application-ip-8 (measurement series 12)

Personal air sampling VMS-preparation-application-ip-8 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The dermal samplers VMS-preparation-dO-2 and VMS-application-dO-4 with the respective gloves belong to this measurement.

VMS-preparation-application-ip-9 (measurement series 13)

Personal air sampling VMS-preparation-application-ip-9 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in **Tab. 3.8** in brackets behind the sampling time given. The worker dismounted from his vehicle part of the time to make a telephone call. The dermal samplers VMS-preparation-dO-3 and VMS-application-dO-5 with the respective gloves belong to this measurement.

VMS-preparation-application-ip-10 (measurement series 14)

Personal air sampling VMS-preparation-application-ip-10 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The worker dismounted during sampling to fill a canister with spray liquid from the VMS-tank. The dermal samplers VMS-preparation-dO-4 and VMS-application-dO-6 with the respective gloves belong to this measurement.

VMS-preparation-application-ip-11 (measurement series 15)

Personal air sampling VMS-preparation-application-ip-11 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The worker dismounted from his vehicle part of the time to make a telephone call. The dermal samplers VMS-preparation-dO-5 and VMS-application-dO-7 with the respective gloves belong to this air sampling.

VMS-preparation-application-ip-12 (measurement series 16)

Personal air sampling VMS-preparation-application-ip-12 was performed during the entire work process (preparation and application of the Dimilin^{TM} 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The sampling pump failed after 69 min. The dermal samplers VMS-preparation-dO-6 and VMS-application-dO-8 with the respective gloves belong to this air sampling.

VMS-preparation-application-ip-13 (measurement series 17)

Personal air sampling VMS-preparation-application-ip-13 was performed during the entire work process (preparation and application of the Dimilin™ 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The sampling pump failed after 74 min. The window of the Unimog driver's cabin was open part of the time during application. While underway, the driver descended once in order to pick up a traffic sign that had been knocked over. The dermal samplers VMS-preparation-dO-7 and VMS-application-dO-9 with the respective gloves belong to this air sampling.

VMS-preparation-application-ip-14 (measurement series 18)

Personal air sampling VMS-preparation-application-ip-14 was performed during the entire work process (preparation and application of the Dimilin™ 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The dermal samplers VMS-preparation-dO-8 and VMS-application-dO-10 with the respective gloves belong to this air sampling.

VMS-preparation-application-ip-15 (measurement series 19)

Personal air sampling VMS-preparation-application-ip-15 was performed during the entire work process (preparation and application of the Dimilin™ 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The dermal samplers VMS-preparation-dO-9 and VMS-application-dO-11 with the respective gloves belong to this air sampling.

VMS-preparation-application-ip-16 (measurement series 20)

Personal air sampling VMS-preparation-application-ip-16 was performed during the entire work process (preparation and application of the Dimilin™ 80 WG suspension). The time needed for the preparation of the spray liquid is given in Tab. 3.8 in brackets behind the sampling time. The dermal samplers VMS-preparation-dO-10 and VMS-application-dO-12 with the respective gloves belong to this air sampling.

Hand-held sprayer: Preparation and application of the Dimilin™ 80 WG suspension

HHS-preparation-application-dO-1, dG-1.1, dG-1.2 and ip-1 (measurement series 22)

The coverall HHS-preparation-application-dO-1 was worn during preparation and application of the Dimilin™ 80 WG suspension. The pair of gloves HHS-preparation-application-dG-1.1 was worn while preparing the spray liquid and the pair of gloves HHS-preparation-application-dG-1.2 during application. During application there were repeated problems with the hand-held sprayer, and the spray tank was not sprayed empty. Gasoline was refilled. Personal air sampling HHS-preparation-application-ip-1 was performed during the entire work process.

HHS-preparation-application-dO-2, dG-2 and ip-2 (measurement series 23)

The coverall HHS-preparation-application-dO-2 and the gloves HHS-preparation-application-dG-2 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-2 was performed during the entire work process.

HHS-preparation-application-dO-3, dG-3 and ip-3 (measurement series 24)

The coverall HHS-preparation-application-dO-3 and the gloves HHS-preparation-application-dG-3 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-3 was performed during the entire work process.

HHS-preparation-application-dO-4, dG-4 and ip-4 (measurement series 25)

The coverall HHS-preparation-application-dO-4 and the gloves HHS-preparation-application-dG-4 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-4 was performed during the entire work process.

HHS-preparation-application-dO-5, dG-5 and ip-5 (measurement series 26)

The coverall HHS-preparation-application-dO-5 and the gloves HHS-preparation-application-dG-5 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-5 was performed during the entire work process.

HHS-preparation-application-dO-6, dG-6 and ip-6 (measurement series 27)

The coverall HHS-preparation-application-dO-6 and the gloves HHS-preparation-application-dG-6 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-6 was performed during the entire work process.

HHS-preparation-application-dO-7, dG-7 and ip-7 (measurement series 28)

The coverall HHS-preparation-application-dO-7 and the gloves HHS-preparation-application-dG-7 were worn during preparation and application of the Dimilin™ 80 WG suspension. At the first preparation, the spray tank was ¾ full, and only water was added. At the second filling, spray liquid was prepared from granules, and gasoline was also refilled. Personal air sampling HHS-preparation-application-ip-7 was performed during the entire work process.

HHS-preparation-application-dO-8, dG-8 and ip-8 (measurement series 29)

The coverall HHS-preparation-application-dO-8 and the gloves HHS-preparation-application-dG-8 were worn during preparation and application of the Dimilin™ 80 WG suspension. Personal air sampling HHS-preparation-application-ip-8 was performed during the entire work process.

Hand-held sprayer: Transfer and application of the Dimilin™ 80 WG suspension

HHS-transfer-application-dO-1, dG-1 and ip-1 (measurement series 30)

The coverall HHS-transfer-application-dO-1 and the gloves HHS-transfer-application-dG-1 were worn during transfer and application of the Dimilin™ 80 WG suspension. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. Repeated problems with the spray unit occurred. Personal air sampling HHS-transfer-application-ip-1 was performed during the entire work process. During sampling it was very windy, and spray drift was visible.

HHS-transfer-application-dO-2, dG-2 and ip-2 (measurement series 31)

The coverall HHS-transfer-application-dO-2 and the gloves HHS-transfer-application-dG-2 were worn during transfer and application of the Dimilin™ 80 WG suspension. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. Personal air sampling HHS-transfer-application-ip-2 was performed during the entire work process. During sampling it was very windy, and spray drift was visible.

HHS-transfer-application-dO-3, dG-3.1 to dG-3.4 and ip-3 (measurement series 32)

The coverall HHS-transfer-application-dO-3 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-3.1 and HHS-transfer-application-dG-3.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-3.2 and HHS-transfer-application-dG-3.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. During the second filling of the hand-held sprayer and the second application the worker had put off his hood. Personal air sampling HHS-transfer-application-ip-3 was performed during the entire work process.

HHS-transfer-application-dO-4, dG-4.1 to dG-4.4 and ip-4 (measurement series 33)

The coverall HHS-transfer-application-dO-4 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-4.1 and HHS-transfer-application-dG-4.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-4.2 and HHS-transfer-application-dG-4.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. The worker did not have the hood of his coverall on. Personal air sampling HHS-transfer-application-ip-4 was performed during the entire work process.

HHS-transfer-application-dO-5, dG-5.1 to dG-5.4 and ip-5 (measurement series 34)

The coverall HHS-transfer-application-dO-5 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-5.1 and HHS-transfer-application-dG-5.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-5.2 and HHS-transfer-application-dG-5.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. Personal air sampling HHS-transfer-application-ip-5 was performed during the entire work process.

HHS-transfer-application-dO-6, dG-6.1 to dG-6.4 and ip-6 (measurement series 35)

The coverall HHS-transfer-application-dO-6 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-6.1 and HHS-transfer-application-dG-6.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-6.2 and HHS-transfer-application-dG-6.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. During the second filling of the hand-held sprayer and the second application the worker had put the hood of his coverall off. Personal air sampling HHS-transfer-application-ip-6 was performed during the entire work process.

HHS-transfer-application-dO-7, dG-7.1 to dG-7.4 and ip-7 (measurement series 36)

The coverall HHS-transfer-application-dO-7 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-7.1 and HHS-transfer-application-dG-7.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-7.2 and HHS-transfer-application-dG-7.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. Personal air sampling HHS-transfer-application-ip-7 was performed during the entire work process.

HHS-transfer-application-dO-8, dG-8.1 to dG-8.4 and ip-8 (measurement series 37)

The coverall HHS-transfer-application-dO-8 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-8.1 and HHS-transfer-application-dG-8.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-8.2 and HHS-transfer-application-dG-8.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. At the second filling of the hand-held sprayer and the second application the worker had not put on the hood of his coverall all the time. Personal air sampling HHS-transfer-application-ip-8 was performed during the entire work process.

HHS-transfer-application-dO-9, dG-9.1 to dG-9.4 and ip-9 (measurement series 38)

The coverall HHS-transfer-application-dO-9 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-9.1 and HHS-transfer-application-dG-9.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-9.2 and HHS-transfer-application-dG-9.4 in each case during the application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. Personal air sampling HHS-transfer-application-ip-9 was performed during the entire work process. Sampling was carried out in a slight drizzle.

HHS-transfer-application-dO-10, dG-10.1 to dG-10.4 and ip-10 (measurement series 39)

The coverall HHS-transfer-application-dO-10 was worn during transfer and application of the Dimilin™ 80 WG suspension (two full tanks). The gloves HHS-transfer-application-dG-10.1 and HHS-transfer-application-dG-10.3 were in each case worn during transfer of the spray liquid, the gloves HHS-transfer-application-dG-10.2 and HHS-transfer-application-dG-10.4 in each case during application of the spray liquid. Spray liquid was transferred from the spray tank of the vehicle-mounted sprayer to the tank of the hand-held sprayer with a canister. The worker did not take the hood of the coverall on. Personal air sampling HHS-transfer-application-ip-10 was performed during the entire work process.

Cleaning of the vehicles/ vehicle-mounted sprayers

Cleaning-dO-1, dG-1 and ip-1 (measurement series 40)

The coverall cleaning-dO-1 and the gloves cleaning-dG-1 were worn during cleaning of the Unimog and both vehicle-mounted sprayers. The cleaning procedures were carried out at a car wash site using an industrial high-pressure cleaner. The driver's cabin, the loading platform, the drop-sides and both vehicle-mounted sprayers were washed down using the high-pressure cleaner, scrubbed using soap and a brush and again washed clean with clear water. The worker also climbed onto the loading platform of the Unimog, whereby his stomach and buttocks came into contact with the Unimog/the vehicle-mounted sprayer. Personal air sampling Cleaning-ip-1 was performed during the entire work process.

Cleaning-dO-2, dG-2 and ip-2 (measurement series 41)

The coverall cleaning-dO-2 and the gloves cleaning-dG-2 were worn during cleaning of the Unimog and one vehicle-mounted sprayer. The cleaning procedures were carried out using a Kärcher™ high-pressure cleaner. The driver's cabin, the loading platform, the drop-sides and the vehicle-mounted unit were washed down using the high-pressure cleaner. The worker was careful to keep his distance from the vehicle and the vehicle-mounted unit (1-1.5 m). The underfloor was cleaned sideways and from below, the water mist from the high-pressure cleaner was blown approximately 6 m in wind direction. The worker did not climb onto the loading platform. Personal air sampling cleaning-ip-1 was performed during the entire work process.

Cleaning-dO-3, dG-3 and ip-3 (measurement series 42)

The coverall cleaning-dO-3 and the gloves cleaning-dG-3 were worn during cleaning of the Unimog and one vehicle-mounted sprayer. Cleaning work was carried out with a commercial Kärcher^{TM} K2 Kompakt. The driver's cabin, the loading platform, the drop-sides and the vehicle-mounted sprayer were washed down with the high-pressure cleaner, the underfloor was cleaned sideways from below, whereby a distance of approximately 1 m from the vehicle or the vehicle-mounted unit was adhered to. The rebound of the high-pressure cleaner hit his coverall. The Unimog and the vehicle-mounted sprayer were cleaned partly from a ladder, partly from the loading platform. After this, some surfaces were once more cleaned manually using a cloth. Personal air sampling cleaning-ip-3 was performed during the entire work process.

Cleaning-is-1 (measurement series 40), is-4 (measurement series 41) and is-7 (measurement series 42)

The stationary air sampling was carried out front right of the driver's cabin during the entire work process simultaneously to the personal air sampling cleaning-ip-1 to ip-3. Apart from the typical exposure of the workers due to rebounding water/dirty water from the vehicle, the stationary set up also measured possible spray drift.

Cleaning-is-2 (measurement series 40), is-5 (measurement series 41) and is-8 (measurement series 42)

The stationary air sampling was carried out back right of the loading platform during the entire work process simultaneously to the personal air sampling cleaning-ip-1 to ip-3. Apart from the typical exposure of the workers due to rebounding water/dirty water from the vehicle, the stationary set up also measured possible spray drift.

Cleaning-is-3 (measurement series 40), is-6 (measurement series 41) and is-9 (measurement series 42)

The stationary air sampling was carried out middle left, next to the vehicle mounted sprayer during the entire work process simultaneously to the personal air sampling cleaning-ip-1 to ip-3. Apart from the typical exposure of the workers due to rebounding water/dirty water from the vehicle, the stationary set up also measured possible spray drift.

Annex 1, Tab. 1 Overview of the measurements performed: assignment of the measurement series according to tasks.

Measurement series	Dermal		Inhalation		Year	Company
	Overall	**Gloves**	**Personal**	**Stationary**		
1	weighing-dO-1	weighing-dG-1	weighing-ip-1	weighing-is-1	2014	A
2	weighing-dO-2	weighing-dG-2	weighing-ip-2	weighing-is-2	2015	A
3	VMS-application-dO-1	VMS-application-dG-1.1 VMS-application-dG-1.2	VMS-application-ip-1		2014	A
4	VMS-application-dO-2	VMS-application-dG-2.1 VMS-application-dG-2.2	VMS-application-ip-2		2014	B
5	VMS-preparation-application-dO-1	VMS-preparation-application-dG-1.1 VMS-preparation-application-dG-1.2 VMS-preparation-application-dG-1.3	VMS-preparation-application-ip-1		2014	A
6	VMS-preparation-application-dO-2	VMS-preparation-application-dG-2.1 VMS-preparation-application-dG-2.2	VMS-preparation-application-ip-2		2014	A
7	VMS-preparation-application-dO-3	VMS-preparation-application-dG-3	VMS-preparation-application-ip-3		2014	A
8	VMS-preparation-application-dO-4	VMS-preparation-application-dG-4	VMS-preparation-application-ip-4		2014	A
9	VMS-preparation-application-dO-5	VMS-preparation-application-dG-5[a]	VMS-preparation-application-ip-5		2014	A
10	VMS-preparation-application-dO-6	VMS-preparation-application-dG-6.1 VMS-preparation-application-dG-6.2 VMS-preparation-application-dG-6.3	VMS-preparation-application-ip-6		2014	B
11	VMS-preparation-dO-1	VMS-preparation-dG-1	VMS-preparation-application-ip-7		2015	A
	VMS-application-dO-3	VMS-application-dG-3		VMS-application-is-4		
12	VMS-preparation-dO-2	VMS-preparation-dG-2	VMS-preparation-application-ip-8		2015	A
	VMS-application-dO-4	VMS-application-dG-4		VMS-application-is-5		

[a]: The gloves VMS-preparation-application-dG-5 were only worn while preparing the Dimilin™ 80 WG suspension.

Annex 1, Tab. 1 (continued) Overview of the measurements performed: assignment of the measurement series according to tasks.

Measurement series	Dermal		Inhalation		Year	Company
	Overall	**Gloves**	**Personal**	**Stationary**		
13	VMS-preparation-dO-3	VMS-preparation-dG-3	VMS-preparation-application-ip-9		2015	A
	VMS-application-dO-5	VMS-application-dG-5		VMS-application-is-6		
14	VMS-preparation-dO-4	VMS-preparation-dG-4	VMS-preparation-application-ip-10		2015	A
	VMS-application-dO-6	VMS-application-dG-6.1 VMS-application-dG-6.2		VMS-application-is-7		
15	VMS-preparation-dO-5	VMS-preparation-dG-5	VMS-preparation-application-ip-11		2015	A
	VMS-application-dO-7	VMS-application-dG-7		VMS-application-is-8		
16	VMS-preparation-dO-6	VMS-preparation-dG-6	VMS-preparation-application-ip-12		2015	A
	VMS-application-dO-8	VMS-application-dG-8		VMS-application-is-9		
17	VMS-preparation-dO-7	VMS-preparation-dG-7	VMS-preparation-application-ip-13		2015	C
	VMS-application-dO-9	VMS-application-dG-9		VMS-application-is-10		
18	VMS-preparation-dO-8	VMS-preparation-dG-8	VMS-preparation-application-ip-14		2015	C
	VMS-application-dO-10	VMS-application-dG-10		VMS-application-is-11		
19	VMS-preparation-dO-9	VMS-preparation-dG-9	VMS-preparation-application-ip-15		2015	C
	VMS-application-dO-11	VMS-application-dG-11		VMS-application-is-12		
20	VMS-preparation-dO-10	VMS-preparation-dG-10	VMS-preparation-application-ip-16		2015	C
	VMS-application-dO-12	VMS-application-dG-12		VMS-application-is-13		

Annex 1, Tab. 1 (continued) Overview of the measurements performed: assignment of the measurement series according to tasks.

Measurement series	Dermal		Inhalation		Year	Company
	Overall	**Gloves**	**Personal**	**Stationary**		
21		VMS-preparation-dG-11			2014	A
22	HHS-preparation-application-dO-1	HHS-preparation-application-dG-1.1 HHS-preparation-application-dG-1.2	HHS-preparation-application-ip-1		2014	A
23	HHS-preparation-application-dO-2	HHS-preparation-application-dG-2	HHS-preparation-application-ip-2		2014	A
24	HHS-preparation-application-dO-3	HHS-preparation-application-dG-3	HHS-preparation-application-ip-3		2014	A
25	HHS-preparation-application-dO-4	HHS-preparation-application-dG-4	HHS-preparation-application-ip-4		2014	A
26	HHS-preparation-application-dO-5	HHS-preparation-application-dG-5	HHS-preparation-application-ip-5		2014	A
27	HHS-preparation-application-dO-6	HHS-preparation-application-dG-6	HHS-preparation-application-ip-6		2014	A
28	HHS-preparation-application-dO-7	HHS-preparation-application-dG-7	HHS-preparation-application-ip-7		2014	A
29	HHS-preparation-application-dO-8	HHS-preparation-application-dG-8	HHS-preparation-application-ip-8		2014	A
30	HHS-transfer-application-dO-1	HHS-transfer-application-dG-1	HHS-transfer-application-ip-1		2014	A
31	HHS-transfer-application-dO-2	HHS-transfer-application-dG-2	HHS-transfer-application-ip-2		2014	A
32	HHS-transfer-application-dO-3	HHS-transfer-dG-3.1 HHS-transfer-dG-3.3 --- HHS-application-dG-3.2 HHS-application-dG-3.4	HHS-transfer-application-ip-3		2015	A
33	HHS-transfer-application-dO-4	HHS-transfer-dG-4.1 HHS-transfer-dG-4.3 --- HHS-application-dG-4.2 HHS-application-dG-4.4	HHS-transfer-application-ip-4		2015	A

Annex 1, Tab. 1 (continued) Overview of the measurements performed: assignment of the measurement series according to tasks.

Measurement series	Dermal		Inhalation		Year	Company
	Overall	**Gloves**	**personal**	**Stationary**		
34	HHS-transfer-application-dO-5	HHS-transfer-dG-5.1 HHS-transfer-dG-5.3 HHS-application-dG-5.2 HHS-application-dG-5.4	HHS-transfer-application-ip-5		2015	A
35	HHS-transfer-application-dO-6	HHS-transfer-dG-6.1 HHS-transfer-dG-6.3 HHS-application-dG-6.2 HHS-application-dG-6.4	HHS-transfer-application-ip-6		2015	A
36	HHS-transfer-application-dO-7	HHS-transfer-dG-7.1 HHS-transfer-dG-7.3 HHS-application-dG-7.2 HHS-application-dG-7.4	HHS-transfer-application-ip-7		2015	A
37	HHS-transfer-application-dO-8	HHS-transfer-dG-8.1 HHS-transfer-dG-8.3 HHS-application-dG-8.2 HHS-application-dG-8.4	HHS-transfer-application-ip-8		2015	A
38	HHS-transfer-application-dO-9	HHS-transfer-dG-9.1 HHS-transfer-dG-9.3 HHS-application-dG-9.2 HHS-application-dG-9.4	HHS-transfer-application-ip-9		2015	A
39	HHS-transfer-application-dO-10	HHS-transfer-dG-10.1 HHS-transfer-dG-10.3 HHS-application-dG-10.2 HHS-application-dG-10.4	HHS-transfer-application-ip-10		2015	A
40	Cleaning-dO-1	Cleaning-dG-1	Cleaning-ip-1	Cleaning-is-1 Cleaning-is-2 Cleaning-is-3	2014	A
41	Cleaning-dO-2	Cleaning-dG-2	Cleaning-ip-2	Cleaning-is-4 Cleaning-is-5 Cleaning-is-6	2015	C
42	Cleaning-dO-3	Cleaning-dG-3	Cleaning-ip-3	Cleaning-is-7 Cleaning-is-8 Cleaning-is-9	2015	A

Annex 2 Bystanders: Description of application situations

Vehicle-mounted spray unit: Application of Dimilin™ 80 WG suspension

VMS-application-dB-1 and iB-1 (company A)

The bystanders VMS-application-dB-1 and iB-1 were placed downwind next to a group of trees (three trees). The worker drove past once with the vehicle-mounted sprayer.

VMS-application-dB-2 and iB-2 (company A)

The bystanders VMS-application-dB-2 and iB-2 were placed downwind between the trees of a single sided alley of trees (approximately 20 trees). The worker drove past once with the vehicle-mounted sprayer.

VMS-application-dB-3 and iB-3 (company A)

The bystanders VMS-application-dB-3 and iB-3 were placed downwind between the trees of an alley (approximately 30 trees on the one, four trees on the other side). The worker drove past twice with the vehicle-mounted sprayer, the first time spraying in the direction of the bystanders, the second time spraying the opposite side of the alley.

VMS-application-dB-4 and iB-4 (company A)

The bystanders VMS-application-dB-4 and iB-4 were placed downwind between the trees of a single sided alley of trees. The spray mist drifted away from the bystanders. The worker drove past twice with the vehicle-mounted sprayer, spraying in the direction of the bystanders each time.

VMS-application-dB-5 and iB-5 (company A)

The bystanders VMS-application-dB-5 and iB-5 were placed downwind between the trees of a single sided alley of trees (approximately twelve trees). The worker drove past once with the vehicle-mounted sprayer.

VMS-application-dB-6 and iB-6 (company B)

The bystanders VMS-application-dB-6 and iB-6 were placed downwind between the trees of an alley. The spray mist was still notable at a distance of 40 m. The worker drove past twice with the vehicle-mounted sprayer, spraying once in the direction of the bystanders and once towards the opposite side of the alley.

VMS-application-dB-7 and iB-7 (company A)

The bystanders VMS-application-dB-7 and iB-7 were placed downwind between the trees of a single sided alley of trees (approximately 30 trees). The worker drove past once with the vehicle-mounted sprayer.

VMS-application-dB-8 and iB-8 (company A)

The bystanders VMS-application-dB-8 and iB-8 were placed downwind next to a group of trees. The Tyvek^{TM} sheets were spray jet completely. Due to the force of the spray jet, the frame rack at 5m distance, which however set up again after approximately one minute. The worker drove past once with the vehicle-mounted sprayer.

VMS-application-dB-9 and iB-9 (company A)

The bystanders VMS-application-dB-9 and iB-9 were placed downwind next to a group of trees (three trees). The worker drove past once with the vehicle-mounted sprayer. The spray mist was applied rather above the sheets.

VMS-application-dB-10 and iB-10 (company A)

The bystanders VMS-application-dB-10 and iB-10 were placed downwind between the trees of a single sided alley of trees (approximately 20 trees). The worker drove past once with the vehicle-mounted sprayer. The spray mist was applied rather high, depositing diffusely onto the sheets.

VMS-application-dB-11 and iB-11 (company A)

The bystanders VMS-application-dB-11 and iB-11 were placed downwind between the trees of an alley (approximately 30 trees on one side, four trees on the other). The worker drove past twice with the vehicle-mounted sprayer, spraying the first time in the direction of the bystanders and the second time spraying the opposite side of the alley. The spray mist was blow diffusely onto the sheets.

VMS-application-dB-12 and iB-12 (company A)

The bystanders VMS-application-dB-12 and iB-12 were placed between the trees of a single sided alley of trees. The worker drove past twice with the vehicle-mounted sprayer, spraying both times in the direction of the bystanders. The wind direction changed; when driving past for the first time the wind was blowing toward the sheep, driving past the second time wind was blowing away from the sheets. The worker applied the spray liquid rather high up into the treetops.

VMS-application-dB-13 and iB-13 (company A)

The bystanders VMS-application-dB-13 and iB-13 were placed between the trees of a single sided alley of trees (approximately 30 trees in two rows). The worker drove past twice with the vehicle-mounted sprayer and sprayed both times in the direction

of the bystanders. The wind direction was changing, blowing the spray mist diffusely onto the sheets (visible deposition rather at 5 m distance than at 10 m).

VMS-application-dB-14 and iB-14 (company A)

The bystanders VMS-application-dB-14 and iB-14 were placed between downwind the trees of a single sided alley of trees (approximately twelve trees). The worker drove past once with the vehicle-mounted sprayer. The spray mist was blown diffusely onto the sheets.

VMS-application-dB-15 and iB-15 (company A)

The bystanders VMS-application-dB-15 and iB-15 were placed between the trees (four rows of trees, approximately 30-40 trees). The wind direction was changing. The worker drove past three times with his vehicle-mounted sprayer and sprayed three times in the direction of the sheets. The spray mist was blown onto the sheets.

Hand-held sprayer: Application of the Dimilin^{TM} 80 WG suspension

HHS-application-dB-1 and iB-1 (company A)

The bystanders HHS-application-dB-1 and iB-1 were placed downwind next a lone tree located. The worker had problems in starting the hand-held sprayer.

HHS -application-dB-2 and iB-2 (company A)

The bystanders HHS-application-dB-2 and iB-2 were placed downwind between the trees of a single sided alley of trees (approximately 20 trees).

HHS -application-dB-3 and iB-3 (company A)

The bystanders HHS-application-dB-3 and iB-3 were placed downwind next to a group of four trees.

HHS -application-dB-4 and iB-4 (company A)

The bystanders HHS-application-dB-4 and iB-4 were placed downwind next to a single tree.

HHS -application-dB-5 and iB-5 (company A)

The bystanders HHS-application-dB-5 and iB-5 were placed downwind next to a single tree. The bystanders, who should have been placed at a distance of 5 m, were at a distance of 4.3 m.

HHS -application-dB-6 and iB-6 (company A)

The bystanders HHS-application-dB-6 and iB-6 were placed downwind next to a group of trees (three trees).

HHS -application-dB-7 and iB-7 (company A)

The bystanders HHS-application-dB-7 and iB-7 were placed mostly downwind next to several tees (two large and several small trees. The wind direction was changing.

HHS -application-dB-8 and iB-8 (company A)

The bystanders HHS-application-dB-8 and iB-8 were placed downwind next to a single tree. The spray mist was diffusely blown onto the sheets, rather onto the 5 m sheet.

HHS -application-dB-9 and iB-9 (company A)

The bystanders HHS-application-dB-9 and iB-9 were placed between the trees of a single sided alley of trees (approximately 20 trees). The wind direction was changing. The spray mist was diffusely blown onto the sheets.

HHS -application-dB-10 (company A)

The bystander HHS-application-dB-10 was placed between the trees of a single sided alley of trees (approximately 20 trees). The wind direction was changing. The spray mist was diffusely blown onto the sheets. The application was partly performed at a larger distance than 5 to 10 m from the bystanders (subsequent measurement HHS-application-dB-9 and iB-9).

HHS -application-dB-11 and iB-11 (company A)

The bystanders HHS-application-dB-11 and iB-11 were placed downwind next to a single tree. The 5 m sheet was for a short time directly in the spray jet, otherwise the spray mist was diffusely blown onto the sheets.

HHS -application-dB-12 and iB-12 (company A)

The bystanders HHS-application-dB-12 and iB-12 were placed downwind next to a group of trees (two trees). The spray mist was diffusely blown onto the sheets.

HHS -application-dB-13 and iB-13 (company A)

The bystanders HHS-application-dB-13 and iB-13 were placed downwind next to a single tree. The spray mist was diffusely blown onto the sheets.

HHS -application-dB-14 and iB-14 (company A)

The bystanders HHS-application-dB-14 and iB-14 were placed downwind next to a group of trees (four trees). The 5 m sheet was for a short time directly in the spray jet. Light drizzle was falling during sampling.

HHS -application-dB-15 and iB-15 (company A)

The bystanders in HHS-application-dB-15 and iB-15 were placed upwind between trees (two large and several small trees). One large tree was in front of and one behind the bystanders. The spray mist was blown very diffusely on the sheets, rather from the backside.