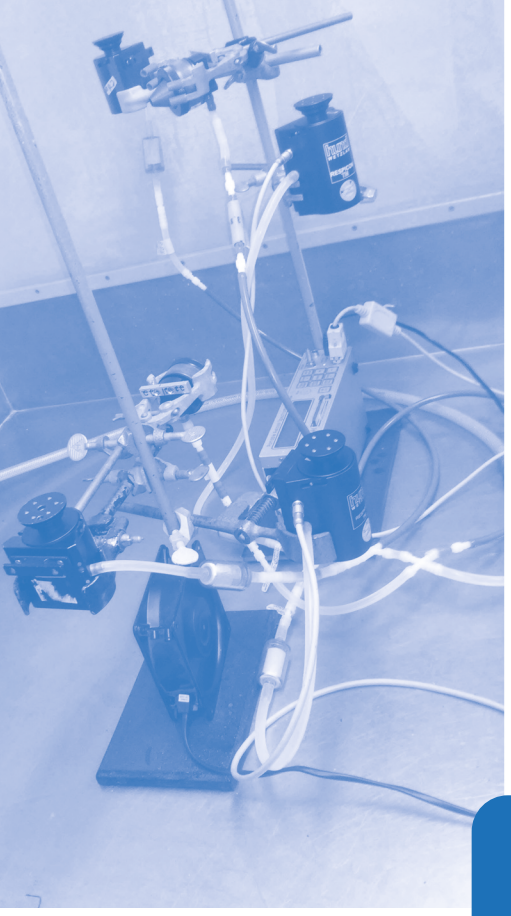

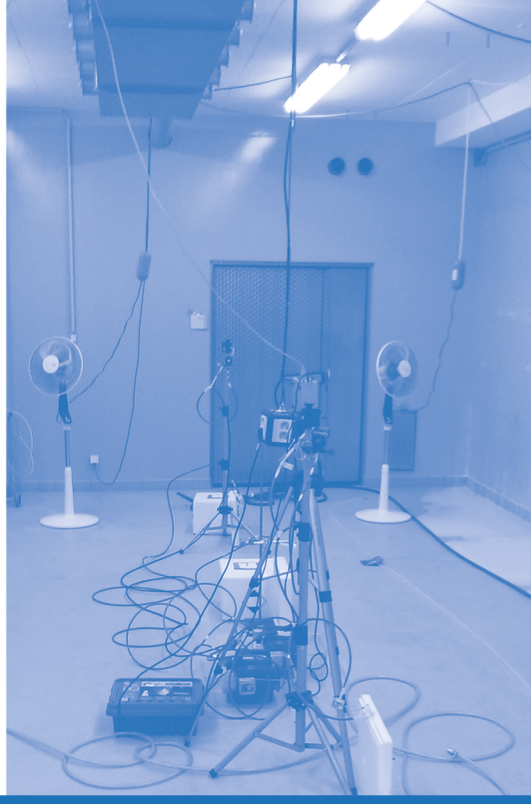

Human exposure to biocidal products: Measurement of inhalation and dermal exposure during the application of biocide foams

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Federal Institute for Occupational Safety and Health

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Human exposure to biocidal products: Measurement of inhalation and dermal exposure during the application of biocide foams

Abstract

At professional workplaces, biocidal products are applied by foaming techniques, among others. This project aimed at the development and assessment of a practical and easy-to-use assessment method, providing estimates of inhalation and dermal exposure towards non-volatile substances during foaming of biocidal products. The focus was set on the substance classes of pyrethroids and quaternary ammonium compounds (QACs) as two examples for non-volatile active substances which can be applied as either spray or foam.

The source strengths of the release of inhalable aerosols of the active substance and their deposition on surfaces were quantified in control chamber measurements carried out for representative foaming and spraying processes as well as biocidal formulations. The difference between foaming and spraying was demonstrated under controlled conditions. For the foaming processes the source strength data were parameterised and related to easily available process parameters. Finally, the data were classified into three release categories. A modified 2-box-dispersion model was used to predict the concentration of the inhalable aerosol from the source strength data for different exposure situations. Results obtained from the control chamber measurements and the model calculations were compared with data measured at workplaces in the field and at simulated workplaces.

The inhalable concentration of an active substance is smaller for foaming processes compared to related spraying procedures. This is in contrast to dermal exposure where there is no difference between foaming and spraying, because dermal exposure is dominated by direct contact and splashes rather than by aerosol deposition. Therefore, the measured values for the dermal exposure are in good agreement with predictions from the TNsG spray models of the methodology document used in regulatory contexts. These models are insufficiently applicable to inhalation exposure during foaming. Here, the inhalation exposure can be conservatively estimated by the developed, modified 2-box-model using the release categories as input data.

Key words

Biocides, foaming, aerosol formation, exposure, inhalation, dermal, exposure modelling

Arbeitsplatzbelastungen bei der Verwendung von Biozidprodukten: Messungen zur inhalativen und dermalen Exposition bei der Ausbringung von Biozidschäumen

Kurzreferat

An gewerblichen Arbeitsplätzen werden Biozidprodukte unter anderem mittels Schaumtechniken ausgebracht. In diesem Vorhaben wurde ein praxisnahes Verfahren zur Abschätzung der inhalativen und dermalen Exposition gegenüber nichtflüchtigen Bioziden beim Schäumen etabliert und bewertet. Hinsichtlich der Biozidwirkstoffe lag der Fokus auf den Substanzklassen der Pyrethroide und der quartären Ammoniumverbindungen (QAVs).

Im Einzelnen wurden die Quellstärken der Freisetzung einatembarer Wirkstoffaerosole und die aerosolbedingte Wirkstoffablagerung auf Oberflächen für repräsentative Schaum- und Sprühverfahren und Wirkstoffformulierungen in Modellraumuntersuchungen unter kontrollierten Randbedingungen bestimmt. Zudem wurden die Unterschiede bei vergleichbaren Verfahren zwischen Schäumen und Sprühen untersucht. Für die Schaumverfahren wurden die Quellstärken parametrisiert, auf zugängliche Prozessparameter zurückgeführt und im Hinblick auf die praktische Anwendung in drei Freisetzungskategorien eingeteilt. Diese Quellstärkeninformation wurde in einem angepassten 2-box-Modell zur Vorhersage der Exposition für unterschiedliche Expositionssituationen verwendet. Die Übertragbarkeit der Modellraumergebnisse und der Modellvorhersagen wurde anhand von Messungen an Arbeitsplätzen sowie nachgestellten Arbeitsplätzen bewertet.

Während die inhalative Exposition beim Schäumen gegenüber dem Sprühen geringer ist, ergeben sich für die dermale Exposition keine relevanten Unterschiede zwischen Schäumen und Sprühen. Grund dafür ist, dass die dermale Exposition vor allem auf Kontakte bei der Handhabung und auf Kontaminationen durch Spritzer und nicht auf Aerosolablagerungen zurückzuführen ist. Dementsprechend stimmen die dermalen Expositionsdaten gut mit den Daten der im Rahmen der Zulassung für Sprühprozesse verwendeten TNsG-Sprühmodelle des Methodologiepapiers überein. Auf die inhalative Exposition beim Schäumen sind diese Modelle nur unzureichend anwendbar. Hier erlaubt nunmehr das entwickelte, angepasste 2-box-Modell unter Verwendung der Freisetzungskategorien der verwendeten Schaumprozesse eine konservative Abschätzung der inhalativen Exposition.

Schlagwörter

Biozide, Schäumen, Aerosolbildung, Exposition, inhalativ, dermal, Expositionsmodellierung

1 Introduction

Recommended hygiene concepts include the use of foam instead of spray techniques for the application of biocidal products. The application is usually carried out manually by appropriately trained personnel. As part of the authorisation procedure for biocidal products, an assessment of the expected exposure of the user to the active substances and substances of concern contained in the product is required in order to evaluate the risks associated with the use of the products and, if necessary, to define risk mitigation measures. The present studies are limited to the consideration of non-volatile active substances. Examples are quaternary ammonium compounds (QACs) and pyrethroids. Foam application offers obvious advantages over spray application: Foaming is assumed to result in a longer exposure time of the active substances, which means that the surface dose of the active substance can be reduced compared to spraying techniques. In addition, foam application seems to have a lower release of aerosols compared to the alternative spray application, which could reduce both inhalation and dermal exposure compared to spray application. In contrast to the use of spraying techniques (e.g. KOCH et al., 2004, GARROD et al., 1998), there are no explicit measurement data or calculation models for foam application on the basis of which a reliable exposure estimate could be made.

In the case of the spraying techniques, there is a clear relationship between the process parameters and the formation of aerosols via the generated droplet size distribution of the spray mist. From this, different spraying techniques can be classified in terms of their exposure potential (source strength) to inhalable aerosols of active substances. Data on aerosol source strength can then be used in relevant deterministic modelling approaches such as ConsExpo, SprayExpo, etc. to estimate workplace exposure during application activities. For spray technologies, a validation of this approach is described by a comparison with workplace measurements by KOCH et al. (2012).

Alternatively, exposure estimates are made on the basis of collected workplace measurements parameterised and grouped according to typical active substance categories, workplace and process parameters. For the exposure assessment of a new application, it is assigned to a suitable group and, depending on the amount of data and variance, a suitable percentile of the measured concentrations in the group is used. However, the underlying workplace measurements are often already 20 years old. It is not clear in all cases whether these measured values still validly describe current workplaces.

Exposure assessment for foam application can principally follow analogues strategies:

1. Measurement and parameterisation of the release of active substances in model room experiments for the relevant foaming and application techniques; use of these source term informations in deterministic exposure modelling; validation of the results by comparison with exemplary measurements at workplaces.

2. Measurement of the release of aerosols containing the active substance during foaming and spraying under comparable conditions of use such as, for example, the operating pressure. Derivation of reduction factors for the foaming processes (compared to spraying) and their verification in exemplary measurements at

workplaces. Use of the database for spray applications to estimate exposure for the corresponding foam applications by applying the reduction factor.

3. Collection of a comprehensive data set of workplace concentrations for relevant workplace categories and foam application techniques. Grouping according to the relevant categories of active substances, process parameters and application scenarios analogue to spray application.

The first approach requires the experimental characterisation of the source strength as well as the development of an exposure model. Both are not available for foam application. However, slightly modified, existing deterministic models can be used in principle for exposure assessment for foam application when the corresponding source strength of the inhalable aerosol of active substance (given in mass of inhalable active substance per time) is determined under realistic conditions of use. The primary task is therefore a comprehensive characterisation of the aerosol source strength for the relevant foam application processes, the categorisation of the data under practical perspectives as well as a model validation based on measurements at selected workplaces.

In the second approach, common exposure-determining parameters must be found for foam and spray techniques, which allow for a direct comparison. This is based on the assumption that such a common set of parameters exists. For some application techniques based on the release of premixed foams from a nozzle, this is approximately the case. There are no such parameters for other techniques, for example propellant foams or handheld foam devices, where foaming takes place in a mixer downstream of the release nozzle. Therefore, the source strength database was expanded in the course of the project. A larger set of nozzle parameters was used for foaming techniques only, and the project work was shifted in direction of the first approach described above i.e. a more extensive characterisation of the source term.

The third approach cannot be carried out comprehensively within the time frame envisaged in the project. However, it is quite reasonable to merge the workplace data obtained in this study with data from other sources in a common database and to analyse the data according to the third of the above listed schemes.

At present it is not clear, however, whether dermal exposure can be directly related to the aerosol emission data. Exposure to splashes and contact to the active substance are important factors that may dominate dermal exposure compared to skin deposition of aerosolised active substance.

The report closely follows scheme #1 and is structured as follows:

The report starts with the chapters introduction and objectives followed by materials and methods. This chapter is divided into the description of the general concepts to achieve the project goals and the experimental procedures and set-up to measure the source strength and the exposure of the substances under consideration. Furthermore, the envisaged modelling approaches are described. The validation of the experimental methods for determination of aerosol release as well as for the analytical methods follow.

The results chapter contains the data on aerosol release measured for the foaming techniques and (to a smaller extent) the release for comparable spraying techniques. For foaming, these data are grouped and assigned to process categories. Next, the results on dermal and inhalation exposure determined at the selected workplaces are presented.

Chapter 6 contains the exposure modelling. In 6.1 a simple, deterministic model is presented which enables the estimation of inhalation exposure and the aerosol related part of the dermal exposure. This chapter contains also the comparison of model predictions with results of measurements at workplaces. In 6.2 a comparison of measured dermal and inhalation exposure with the TNSG predictions is carried out.

The final chapters are a summary and an outlook.

2 Objectives

The general objective is the development and assessment of a practical procedure to estimate the inhalation and dermal exposure to non-volatile subtances during foaming at commercial and industrial workplaces.

This is to be achieved by the following steps:

- Characterisation of the released aerosol of the active substance in view of inhalation and dermal exposure under realistic conditions of use for relevant foaming and spraying techniques.
- Development of a simple deterministic exposure model.
- Verification of the model based on measurements at representive workplaces.
- Determination of reduction factors to spray techniques for the cases with comparable process parameters.

3 Materials and methods

3.1 Concept for the characterisation of the release of active substances

A central objective of the project is the characterisation of the airborne release of active substances for health-relevant particle size fractions with special emphasis on the inhalable aerosol. Selected biocidal products and different application methods are considered. In particular, the process parameters controlling the release as well as the differences between foam and spray processes have to be quantified.

In order to assess the inhalation exposure, so-called release fractions are measured. They are defined as the ratio of the mass of active substance, $m^s_{r,t,i}$, released as aerosol in three health related size ranges defined in the DIN EN 481 standard (r: respirable, t: thoracic, i: inhalable) normalised to the total amount, M^s, of released active substance:

(3.1)

$$R^s_{r,t,i} = \frac{m^s_{r,t,i}}{M^s}.$$

The release fractions are required to determine the source related input parameters in exposure models to predict the exposure for the selected exposure and application scenarios. The values of the so-defined release fractions are independent of the mass fraction of the active substance in the foaming liquid. The source strength, S^s, relevant for exposure is calculated from the release fraction and the total mass flow rate of active substance, $\dot{M}^s$, of the foaming and spraying process, respectively:

(3.2)

$$S^s_{r,t,i} = \dot{M}^s \cdot R^s_{r,t,i}$$

The assessment of dermal exposure caused by skin deposition of the released aerosol is based on the deposition velocity, a quantity determining the mass flux towards the body surface. One has to distinguish between horizontal and vertical surfaces: $v^s_{dep,v}$ and $v^s_{dep,h}$. The deposition velocity does however not account for skin exposure caused by direct contact with the formulation or by splashes.

The determination of the released aerosol mass, $m^s_{r,t,i}$, is carried out by size resolved measurement of the concentration of the active substance. For this purpose, surface treatment of short duration is performed inside a control chamber (volume, V) under well stirred mixing conditions. The released aerosol mass is calculated from the concentration values, $c^s_{0;r,t,i}$, obtained immediately after termination of the treatment process by multiplication with the chamber volume:

(3.3)

$$m^s_{r,t,i} = c^s_{0;r,t,i} \cdot V$$

The deposition velocities of the active substance depend on the mass size distribution of the released aerosol. The deposition velocities are determined from measurements of the surface dose, $\rho^s_{v,h}$, of active substance deposited on pads placed in horizontal and vertical orientation inside the control chamber:

(3.4)

$$v^s_{dep,v,h} = \frac{\rho^s_{v,h}}{\bar{c}^s_i \cdot T_f}.$$

Here, $\bar{c}^s_i$, is the airborne concentration of the active substance averaged over the duration, T_f, of the release measurement.

The deposition velocities are overestimated since the measured inhalable concentration is smaller than the total concentration of the airborne active substance ($c^s_{tot} > c^s_i$) especially when coase particles are dominating the particle size distribution. Another overestimation of the deposition velocity, particularly on vertical surfaces, may be related to increased turbulence in the control chamber compared with the situation at workplaces.

3.2 Concept for the calculation of inhaled and deposited dose

The time averaged exposure concentration, $\bar{c}^s$[1], as well as the inhaled and dermal dose are calculated from the source strength of the released aerosol and the deposition velocities, together with parameters on size and geometry of the room, ventilation rate, particle losses on inner surfaces, and the exposure time, $T + T_r$. This is the sum of the duration of application, T, and an additional residence time, T_r, of the user inside the room.

The relevant parameters determining the exposure concentration are the source strength, $S^s_i(t)$, (with dimension kg/s) and the dilution function, $\chi(t)$, (with the dimension m^{-3}), describing the dispersion of the released substances in the indoor environment. For the inhaled dose the inhalation flow rate, Q_A , (with dimension m^3/s) is additionally required. The temporal concentration pattern, $c^s(t)$, for well stirred conditions and no additional residence tie T_r=0 [2] is given by;

(3.5)

$$c^s(t) = \int_0^t S^s_i(t') \cdot \chi(t - t')dt'$$

It is seen from Eq. 3.5 that the concentration at time, *t*, is determined by the sum from all source contributions of preceding times weighted by the dilution effect during the

[1] hereafter, $\bar{c}^s$, denotes the inhalabe concentration

[2] The case of non-zero residence, T_r, is treated in the Appendix.

time period $t - t'$. For a non-ventilated room of volume, V_R, and negligible particle losses the dilution function is given by $\chi(t) = 1/V_R$. Taking into account the loss rate $\Gamma = \gamma_e + \gamma_s$ caused by air exchange, γ_e, and particle deposition, γ_s, the dilution function reads: $\chi(t) = \exp(-\Gamma t)/V_R$.

The time averaged concentration and the inhaled dose are calculated from Eq. 3.5 by time integration:

(3.6)

$$\bar{c}^s = \frac{1}{T}\int_0^T c(t)\cdot dt = \frac{1}{T}\int_0^T \int_0^t S_i^s(t')\cdot\chi(t-t')dt'dt, \qquad D^{inh} = \bar{c}^s \cdot Q_A \cdot T.$$

Using Eq. 3.2 this can be expressed by the mass flow rate of the active substance, $\dot{M}^s$, and the release fraction of active substance, R_i^s, of the process under consideration

(3.7)

$$\bar{c}^s = \frac{R_i^s}{T}\int_0^T \int_0^t \dot{M}^s(t')\cdot\chi(t-t')dt'dt.$$

For constant mass flow rate, $\dot{M}^s$, during the entire duration of exposure, T (with T_r = 0), and a perfectly mixed, non-ventilated room of volume, V_R, and without any further particle losses due to deposition (1-box-model: $\chi = 1/V_R$) Eq. 3.7 yields:

(3.8)

$$\bar{c}^s = \frac{1}{2}\,\frac{R_i^s\cdot\dot{M}^s}{V_R}\cdot T = \frac{1}{2}\,\frac{R_i^s\cdot M^s}{V_R}, \qquad D^{inh} = Q_A\cdot\frac{1}{2}\frac{R_i^s\cdot M^s}{V_R}\cdot T,$$

where M^s is the total mass of sprayed or foamed active substance (in kg).

Taking the loss rate, Γ, into account ($\chi(t) = \exp(-\Gamma t)/V_R$), time integration of Eq. 3.6 yields:

(3.9)

$$\bar{c}^s = \frac{1}{\Gamma\cdot T}\left[1 - \frac{1}{\Gamma\cdot T}(1-\exp(-\Gamma\cdot T)\right]\cdot\frac{R_i^s\cdot M^s}{V_R},$$

This is Eq. 3.8 for a non-ventilated room, multiplied by a factor accounting for the loss of substance during the exposure duration, $\Gamma\cdot T$.

This can be generalised by introducing the dispersion function, $\bar{\kappa}$, describing the aerosol dispersion in the room:

(3.10)

$$\bar{c}^s = \bar{\kappa}\cdot\frac{R_i^s\cdot M^s}{V_R}.$$

In the modelling part of this project, approaches of the dispersion function, $\bar{\kappa}$, are developed for realistic exposure scenarios that go beyond the 1-box approach mentioned above.

(3.11)

$$\bar{\kappa} = 1/2 \text{ bzw. } \bar{\kappa} = 1/(\Gamma \cdot T)\,[1 - 1/(\Gamma \cdot T)\,(1 - \exp(-\Gamma \cdot T)]$$

and resulting in a conservative estimation of measured workplace concentrations.

The dermal dose to the body surface due to the deposition of the particles containing the active substance, subdivided into horizontal and vertical surfaces, is calculated from:

(3.12)

$$D^{derm} = \left(A_h \cdot v^s_{dep,h} + A_v \cdot v^s_{dep,v}\right) \cdot \int_0^T c(t) \cdot dt.$$

Here, the horizontal body surface, A_h, and the vertical surface, A_v, are treated separately due to different deposition velocities. Using Eq. 3.6 the dermal dose is given by:

(3.13)

$$D^{derm} = \frac{\left(A_h \cdot v^s_{dep,h} + A_v \cdot v^s_{dep,v}\right)}{Q_A} \cdot D^{inh}.$$

This value only accounts for the aerosol related dermal dose. Accidental splashes of the spray liquid or the foam as well as direct contact with contaminated surfaces (for example the foam gun) are not taken into account here.

Data on the total amount of used active substance as well as the process specific release rates are required for exposure assessment for a selected spraying or foaming scenario. The substance consumption is directly obtained from the concrete application. Release rates are supplied in tabular form and are arranged according to process categories. The establishment of this table is a central part of this study. The data serve as input in exposure modelling adopted to the specific scenario.

3.3 Experimental approach for the measurement of release rate and deposition of the active substance

3.3.1 General concept

The strategy to determine the initial concentration of the aerosolised substance ($c^s_{0;r,t,i}$ in Eq. 3.3) consists in the combination of the measurement of the time averaged concentration of the active substance, $\bar{c}^s_{r,t,i}$, and the detection of the temporal pattern of the aerosol concentration during the spraying/foaming process and a certain time period thereafter (total measurement period, T_m) inside a defined model room. Spatial aerosol homogeneity is assumed due to well stirred conditions established inside the model room. The process steps required are described in detail in Appendix 6 and

have been published in SCHWARZ and KOCH (2017). They are immediately applicable in small scale release experiments when a spray bottle or aerosol can is used. For large scale processes using foam and spray generators with high throughput the process had to be adjusted due to the required large dimensions of the control volume.

The release fraction of the non-volatile active substance under consideration was not detected directly but by using the non-volatile tracer substance caesium chloride that was added to the aqueous liquid formulation at a concentration of 0.1 % (w/w), comparable with the content of the active substances in the final formulation. The analytical detection of the tracer was carried out in all cases by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry). The conversion to the active substance can be perfomed using the ratio of the contents of caesium chloride and biocidal product in the formulation. This was verified experimentally as detailed in Chapter 4.2.3. In particular, this conversion can be applied to the total content of non-volatile substances, leading to the total aerosol release rate.

For a selected particle size fraction the expected temporal concentration pattern is presented in Fig. 3.1. It shows 4 consecutive applications characterised by the concentration peak, $c_{0,k}^{s}$ $(k = 1 \ldots 4)$, and the 1/e-decay time, τ. The τ-values are assumed to be identical for all applications carried out under the same conditions. The variations of the concentration peaks are due to possible variances in the product mass flow rate of sprayed/foamed biocidal product and variations in the application times. The measured quantities are the temporal pattern of the total aerosol concentration (see below), from which the relative heights of the concentration peaks and the 1/e-time are derived, and the time averaged concentration (indicated by the green bars) of the active substance or the tracer substance. The relative heights, α_k $(k = 1 \ldots 4)$, of the concentration peaks are expressed as $\alpha_k = c_{0,k}^{s}/c_{0,1}^{s}$. These ratios are equivalent of the corresponding ratios of the total aerosol to be determind by a particle concentration spectrometer since the fraction of active substance of the total aerosol mass remains constant. The total aerosol comprises all non-volatile components of the formulation and can also be determined using the tracer method and applying a corresponding conversion factor calculated form the ratio of the mass of all non-volatiles to the tracer mass.

The total content of non-volatiles was determined by pipetting a defined mass of the formulation on a surface and gravimetric measurement of the weight gain after evaporation of the volatiles at 80°C in a drying chamber. The following values were obtained for the biocidal products investigated in this study:

- QAC E: 11.4 % (n = 5)
- QAC F: 9.8 % (n = 5)
- QAC M: 11.6 % (n = 5)
- PER F: 6.7 % (n = 5)
- Insect foam F: 40 % (n = 3)[3]
- Wasp foam (B.1 und B.2): 15 % (n = 3)[3]
- Wasp spray B: 3.5 % (n = 3)[4]

[3] After 4 days at room temperature.
[4] After 30 days at 75 °C.

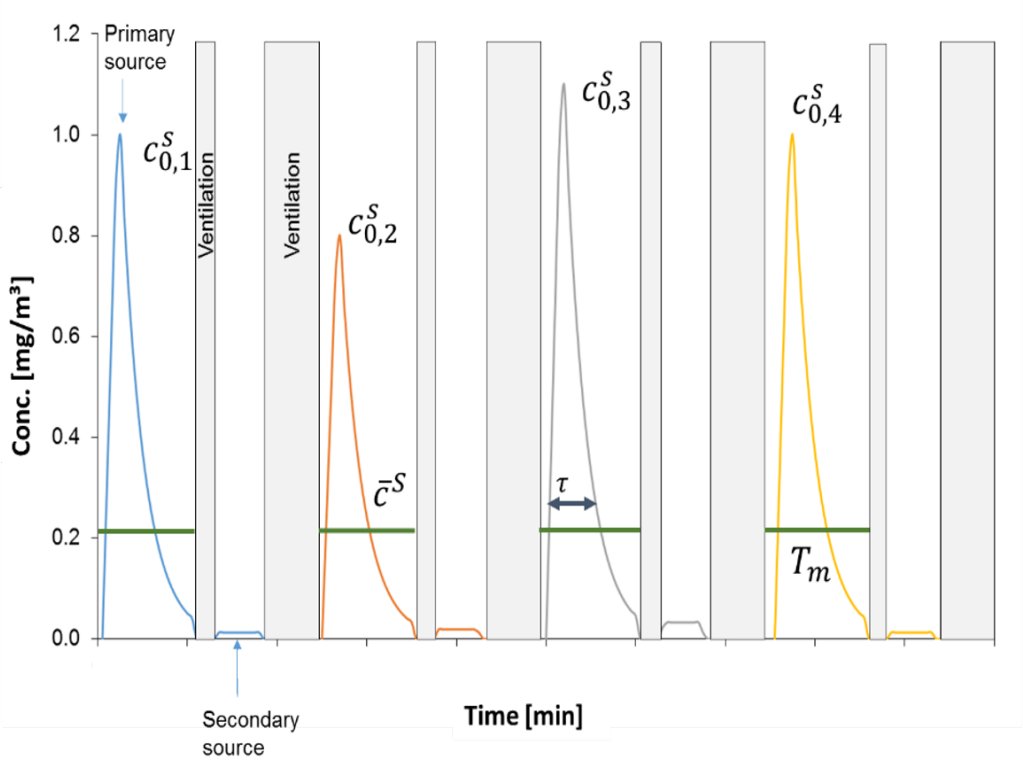


Fig. 3.1 Expected concentration pattern of the aerosol after four consecutive short spray or foam applications. The subscripts r, t, i are omitted here.

For N release actions and subsequent exponential concentration decrease characterised by the 1/e-time, τ, the time averaged concentration, $\bar{c}^S$, and the concentration peaks, $c^S_{0,k}$ $(k = 1 \ldots N)$, are related by:

(3.14)

$$\bar{c}^S = \frac{1}{N}\sum_{k=1}^{N} c^S_{0,k} \cdot \frac{\tau}{T_m}\left(1 - e^{-T_m/\tau}\right).$$

Using the experimentally determined relation

(3.15)

$$c^S_{0,k} = \alpha_k \cdot c^S_{0,1}$$

the initial concentrations, $c^S_{0,k}$, can be calculated from the measured time averaged concentration of the active substance, $\bar{c}^S$:

(3.16)

$$c^S_{0,k} = \bar{c}^S \cdot \frac{N \cdot \alpha_k}{\sum_{k=1}^{N} \alpha_k} \cdot \frac{\frac{T_m}{\tau}}{1 - e^{-\frac{T_m}{\tau}}}.$$

From this, the release fraction of each spraying or foaming action can be determined:

(3.17)

$$R_k^s = \frac{c_{0,k}^s \cdot V_R}{Q_l \cdot t_{s,k}}.$$

These equations are valid for all three health related size fractions. The subscripts (r, t, i) on the concentration symbols have been omitted for the sake of simplicity. V_R is the volume of the model room (control volume). The liquid flow rate is denoted by Q_l and $t_{s,k}$ are the durations of the four spray actions.

3.3.2 Model rooms and aerosol diagnostics

The release measurements were carried out in model rooms of different size, depending on the foaming/spraying technology investigated. Handheld spray and foam devices were characterised in a chamber of 1.5 m³ volume. For the analysis of sprays and foams released by propellant cans a 41 m³ room was used. Large scale disinfection devices were tested in a room of 158 m³ volume. Rapid aerosol homogenising was ensured by sufficient air turbulence generated by 1, 2 or, in case of the large room, 4 room ventilators. Details are described in Appendix 6.

The mass concentration of the inhalable fraction of the aerosolised active substance was measured from samples collected with the *Gesamtstaubprobenahmekopf* (GSP, following DIN EN481). In several tests, the thoracic and respirable fractions were collected in addition, using the Respicon®. The amount of tracer substance or active substance collected on the filters were analysed chemically to obtain the time averaged mass concentration, $\bar{c}^s$. In order to check for spatial homogeneity of the aerosol, two GSPs (F1 and F2) were used for sampling the inhalable aerosol. In 32 tests we used additionally two Respicons (R1, R2).

The temporal pattern of all three size fractions of the aerosol mass concentration was measured using the aerosol spectrometer Type 1.109 (Grimm). The relation of the peak heights, α_k, and the particle size specific decay times, $\tau_{r,t,i}$, were derived from the spectrometer data. The upper size limit of the aerosol spectrometer is 34 µm leading to an overestimating of the decay time of the inhalable fraction collected with the GSP. However due to the short sampling time of 10 minutes the error on the initial concentrations required to calculate the release fractions is small.This results in only small errors in exposure assessment since large particles with high settling velocities (7.5 cm/s for 50 µm-particles) contribute only little to the inhalation exposure.

In order to measure the particle deposition velocities vertical and horizontal deposition pads were placed in the large model room.

Foam and spray application was carried out according to the use in the industrial practice. During application and the subsequent sampling time the room ventilation was switched off.

Details of the model rooms and the release measurements are described in Appendix 6.

Fig. 3.2 Model rooms and instrumentation: small (1.5 m^3), medium (41 m^3), 2 × large (158 m^3). The circles indicate the sampling devices and, on the right photo, the deposition pads.

The data evaluation scheme is shown in App. Fig. 1. The measurement results described above as well as data on the foaming/spraying process are required to calculate the release fraction from Eq. Tab. 4.1. The flow rate, Q_l, was measured by weighing the liquid container before and after the test.

For the CsCl concentration determined analytically by ICP-MS we used the average values obtained from the devices placed at two separate positions: 2 × GSP + 1 × Respicon (if available). Thoracic and respirable concentrations were determined from one Respicon, only. The decay times related to the size fractions were extracted from regression analysis applied to semi-logarithmic plots of the concentration patterns. This was carried out for only one of the four release actions. Pre-test showed the validity for this (test V4 and V5). This is not the case for the relative peak heights. These values were derived for each peak from the first 5 minutes following the start point of the spraying action. A value of 1 was always assigned to the first peak.[5]

3.3.3 Chemical analysis

Sampling and subsequent analysis were shared between the project partners depending on their expertise: dermal exposure – FAU Erlangen-Nürnberg; inhalation exposure – Fraunhofer ITEM. This as well as different analytical equipment available at the two laboratories were the reason that for both groups of active substances, pyrethroids and QACs, two analytical methods each were implemented and validated (Appendix 2 to 5). The implementation of GC-MS based methods for the determination of dermal and inhalation exposure to pyrethroids was based on the VDI guideline 4301.

The ionic nature of QAC can result in long-lasting residence times of the analyte in the system causing unwanted interferences in analytical measurements. In order to circumvent this effect, in both laboratories analytical methods for the determination of the QAC sub-group of benzalkonium chloride (BAC) were set-up and validated based on the work of VAN BOXTEL et al. (2016). This method utilises the thermal instability of

[5] It was seen in the course of the project that the two GSP samplers were sufficient for an accurate determination of the release fractions. Therefore, the Respicon samplers were omitted. This opened more room to vary process parameters. Furthermore, for technical reasons sometimes only two instead of 4 release actions were feasible.

BAC. The thermal degradation product benzyl chloride can be quantified by head-space-GC-MS.

3.3.3.1 Pyrethroids – Inhalation exposure

The analytical method for the quantification of airborne pyrethroids and piperonyl butoxide (PBO) was based on the VDI guideline 4301 and the dissertation by ELFLEIN (2003). Briefly, analytes collected on glass fibre filters are quantified by GC-MS after solvent extraction. At Fraunhofer ITEM the method was validated for the analytes PBO, tetramethrin and phenothrin. To account and compensate for errors during sample preparation and analysis deuterated PBO (PBO-d9) was used as internal standard (ISTD). Method and validation parameters are detailed in the corresponding validation report (ITEM, 2018, 1).

Note:
In the course of the study a biocidal product containing permethrin and PBO was used. Filters were analysed for both substances. The VDI guideline 4301- Blatt 4 addresses the determination of both, PBO and permethrin, in indoor air. In the course of this study the implementation of this method was successfully achieved for the analytes PBO, tetramethrin and phenothrin at the laboratories of Fraunhofer ITEM. This method should therefore also be suitable for the quantification of permethrin, which was confirmed by a plausibility check using measurement data – the ratio between permethrin and PBO in the filter extracts was equal to the one of the application solution.

3.3.3.2 Pyrethroids – Dermal exposure

A sensitive and compound specific GC-MS method for the quantification of PBO and the pyrethroids tetramethrin, phenothrin, permethrin, cyfluthrin, cypermethrin and deltamethrin was set-up and validated based on the method implemented at Fraunhofer ITEM. Quantification was achieved in SIM mode (Single Ion Monitoring). Deuterated pyrethroids as internal standards (ISTD) are not commercially available; hence bifenthrin was used as ISTD. Tyvek material and cotton were used as sorbent during sample collection for the determination of dermal exposure. Method and validation parameters are detailed in the corresponding validation report (IPASUM, 2018).

During the sampling events 11–13 and 27 pyrethroids were applied by foaming (overalls 11, 12 and 27) and spraying (overall 13). Dermal exposure is presented via phenothrin as both the foam as well as the spray product contained this active substance, allowing direct comparison between those two application techniques. The wasp foam sprays B.1 and B.2 (insect foam), as well as wasp spray B contained either d-phenothrin (#13 and 27) or 1R-trans-phenothrin (#11 and 12). D-trans-phenothrin was used as analytical reference standard. In general phenothrin consists of equal amounts of the isomers 1R-cis-; 1R-trans-; 1S-cis- and 1S-trans phenothrin. D-phenothrin consists to more than 95 % of the R-isomers; a mixture of 1R-cis- and 1R-trans-isomers (approx. 89 % 1R-trans isomer). From an analytical point of view, it is assumed that all phenothrin isomers show the same MS response and that the corresponding isomers in the application products were quantified correctly.

The chromatograms showed always two phenothrin signals (m/z = 123). Both peaks were used for the quantification.

3.3.3.3 Quarternary ammonium compounds (benzalkonium chloride, BAC) – Inhalation exposure

Airborne benzalkonium chloride should be collected on PTFE filters and quantified directly by GC-MS. Following the work of VAN BOXTEL et al. (2016), no extraction steps should be necessary beforehand. The implementation and validation of this method was conducted at Fraunhofer ITEM. D7-benzyldimethyldecylammonium chloride was used as ISTD to account and compensate for any possible errors during sample preparation and analysis. Method and validation parameters are detailed in the corresponding validation report (ITEM, 2018, 2).

3.3.3.4 Quarternary ammonium compounds (benzalkonium chloride, BAC) – Dermal exposure

Tyvek material and cotton were used as sorbent during sample collection for the determination of dermal exposure. Quantification was achieved by GC-MS after sample extraction and using d7-benzyldimethyldodecylammonium chloride as internal standard. Method and validation parameters are detailed in the corresponding validation report (IPASUM, 2018).

3.3.3.5 Tracer – Caesium chloride (CsCl)

The tracer CsCl was quantified via the caesium isotope (^{133}Cs) using ICP-MS (X-Series II Termo Fisher Scientific) coupled to an ASX 520 autosampler (CETAC). As internal standards indium (^{115}In) and lutetium (^{175}Lu) were used, both at a concentration of 5 ppb.

Dilute hydrochloric acid (0.15 %) was used as extraction solvent (final extract volume: 25 mL). All chemicals were purchased from Carl Roth GmbH + Co KG.

Aqueos solutions and standards were prepared using deionised water (Synergy-UV, Millipore).

3.4 Biocide formulations

During the release measurements, the disinfection agents and insecticides given in Tab. 3.1 were used.

The active substances and/or added tracer used for chemical analysis are marked in italic letters. The first three products are available as ready-to-use pressurised cans. QAC containing products are available as aqueous solutions, which are further diluted with water prior to their use. CsCl is added to the final formulation at a mass concentration of 0.1 %. The release fraction listed later on in this report are due to the addition of the tracer independent of the concentration of active substance in the QAC based products. This allows a direct comparison of different foaming and spraying techniques in regard to their release of inhalable aerosols.

Tab. 3.1 Disinfectants and insecticides used for release measurements.

Product name	Active substance (-concentration) Manufacturer specifications	Non-volatile share in % (w/w)
Wasp spray B (Insect spray B)	*PBO (17.4 g/kg)*, Tetramethrin (4.05 g/kg), *d-Phenothrin (1 g/kg)*	No information
Wasp foam B.1; B.2 (Insect foam B.1, B.2)	Tetramethrin (B.1: 3.1 g/kg; B.2: 1.5 g/kg), *d-Phenothrin* *(B.1: 1.05 g/kg)* *Trans-R-Phenothrin* *(B.2: 1.5 g/kg)*	No information
Insect foam F	*Permethrin (28 g/L)** Pyrethrine (1 g/L)* *PBO (2 g/L)**	No information
QAC F	Product DDAC (33 g/kg)** *BAC (66 g/kg)***	Product 9.8 %
	Application solution *CsCl (0.1 %)*	Application solution (2 %) 0.20 %
QAC E	Product DDAC (33 g/kg)** *BAC (66 g/kg)***	Product 11.4 %
	Application solution *CsCl (0.1 %)*	Application solution (2 %) 0.23 %
QAC M	Product BAC (95 g/kg)**;#	Product 11.6 %
	Application solution *CsCl (0.1 %)*	Application solution (20 %) 2.32 %
PER F	Product Alpha-Cypermethrin (60 g/L)**	Product 6.7 %
	Application solution *CsCl (0.1 %)*	

PBO – Piperonyl butoxide; DDAC = Didecyldimethylammonium chloride; BAC – Benzalkonium chloride; CsCl – Caesium chloride

* density according to safety data sheet 0.9 g/mL. ** density of the concentrate: 1 g/mL. # N-Alkyl(C12-16)

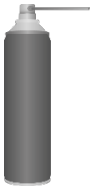
3.5 Application techniques

The application techniques considered for release characterisation should represent techniques used in practice. The selection was based on a questionnaire and direct contacts with the known manufacturers of foaming and spraying devices.

A rough classification was carried out according to the underlying mechanisms of foam generation, the mass flow rate of foam, the dimensions of the foam nozzle, and the operating pressure. A distinction can be made between processes that use a gaseous foaming agent, such as a propellant gas in propellant-based systems and processes in which the foam-forming formulation is mixed with air before or during its release through a nozzle. In processes that use low pressure in the range of 1–6 bar, the foaming air and liquid formulation are mixed in a storage tank or in a mixer in the feed line to the nozzle. Air and liquid flow rates can often be adjusted independently of each other. For most of the tests with this type of device, the volume flow rate of the foaming air was measured by means of a mass flow meter, which was inserted in the corresponding air supply line. Another group of foaming techniques is based on the Venturi principle. Here, water is supplied from the in-house water supply (pressure range 1–6 bar) or from a high-pressure device (>20 bar) and exits in a Ventury nozzle at high speed. According to the Bernoulli principle, air and foam-forming concentrate are sucked in and mixed with the water to generate the foam. This takes place in the foam guns shown, from which the foam is then released through the terminal round or rectangular nozzles.

It is assumed that aerosols during foaming and spraying are formed by mechanisms acting directly at the nozzle. They are determined by the outlet speed and the nozzle size and geometry. The technical design of the supply unit is of minor importance in this regard. The ratio of foam volume to liquid volume (foam expansion ratio) was assumed to be an additional parameter influencing aerosol formation during foaming. In this study, the foam expansion ratio was determined by weighing a measured volume of foam. (The value 1 g/cm³ was assumed for the density of the aqueous formulation.) The resulting technical boundary conditions such as the use of different foam nozzles, independent variation of the amount of foam air and liquid as well as the usability for spraying and foaming largely determined the choice of procedures. To ensure practical relevance, devices and nozzles were obtained from major manufacturers. Details on the devices and the nozzles used can be found in Tab. 3.2 and Tab. 3.3. In Tab. 3.3, all foam nozzles had oval shape, apart from the first three round-shaped nozzles. The nozzle cross sectional areas were calculated assuming an ellipse with dimensions of their semi-axis listed in the table. Their values vary by a factor of 26 for the processes with continuous release (beginning with the second row in Tab. 3.3), which means that a wide range of the mass flow rates of the biocide formulation is covered.

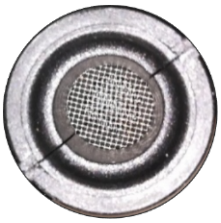
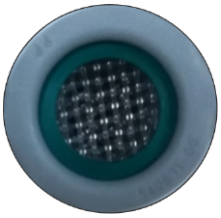
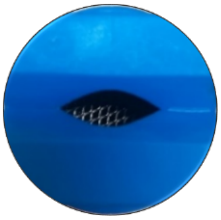
Tab. 3.2 Devices used in the release measurements in model rooms.

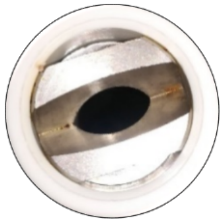
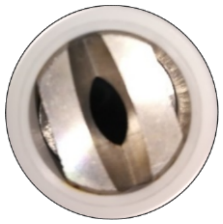
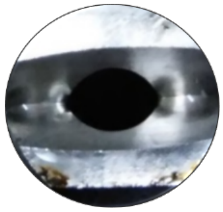
Device	Characteristics	
Insect foam B.1 and B.2 Insect spray B	Propellant as foaming agent, continuous release, foam and spray version	
Insect foam F	Propellant as foaming agent, continuous release	
Hand pump foamer and sprayer	Air injection, discontinuous release, foam and spray versions	 Spray device Foam device
Hand compression foamer and sprayer	Air injection, continuous release, foam and spray versions	 Hand compression device with spray and foam nozzle
Hand compression sprayer 2 (alternative)	Air injection, continuous release, spray version	 Sray nozzle 0.5 mm, 0.8 mm and 1.2 mm
Pressure foamer and sprayer P (1–3 bar)	Pressure 1–3 bar. Pressure at nozzle approx. 1.5 bar. Pre-mixing, use of different foaming cartridges, continuous release, foam and spray versions	

Tab. 3.2 (cont) Devices used in the release measurements in model rooms.

Device	Characteristics	
Pressure foamer B	Pre-mixing, ratio of air and liquid adjustable, total pressure smaller 6 bar, operated with different foam nozzles, continuous release	
Pressure foamer and sprayer G	Pre-mixing, ratio of air and liquid adjustable, total pressure smaller 6 bar, operated with 3 foam nozzles, continuous release, foam and spray versions	
Low pressure foam gun	Air injection in a venturi nozzle, operated with a water pump at 3 bar connected to a water tank filled with the aqueous tracer solution, continuous release	
High pressure gun	Air injection in a venturi nozzle, operated with high pressure booster, continuous release	

Tab. 3.3 Dimensions of the foam and spray nozzles.

Nr.	Device	Nozzle	Dimensions [mm]	Area [mm²]	
Foam nozzles					
1	Hand pump foamer		Ø 0.9; 2 × 1.2; Foam nozzle Ø 6	28.3	
2	Hand compression foamer	Foam nozzle G 3/8“	Foam nozzle Ø 11; 2 air nozzles 9 × 2.9	95	
3	Pressure foamer P	Universal foam nozzle	Foam nozzle Ø 9.8	75.4	
4	Pressure foamer P	Teejet TP 11006 VP with foam car-tridges: blue, black, red com-posed of 2, 3 and 4 flat disks	3.5 × 1.0	2.75	
5	High pressure foam gun	PA LS-10 foam gun	5.6 × 15.1	66.4	
6	Low pressure foam gun	Foam gun V8	Rectangular slit: 25 × 3 mm and side slits; release primar-ily via rectan-guar front slit	75	

Nr.	Device	Nozzle	Dimensions [mm]	Area [mm²]	
7	Pressure foamer G	50/200	12.5 × 6.3	61.9	
8	Pressure foamer G	65/150	11.1 × 5.9	51.4	
9	Pressure foamer G	50/100	9.4 × 4.7	34.7	
10	Pressure foamer B	H1/4U Veejet 4050	5.7 × 3.7	16.6	
11	Pressure foamer B	Fan nozzle A	7.0 × 5.1	28.0	
12	Pressure foamer B	Fan nozzle B	7.9 × 4.6	28.5	

Nr.	Device	Nozzle	Dimensions [mm]	Area [mm²]	
13	Pressure foamer B	Fan nozzle C	9.57 × 3.77	28.3	
14	Pressure foamer B	Fan nozzle D	11.16 × 3.0	26.3	
15	Pressure foamer B	Fan nozzle E	4.9 × 1.5	5.8	
16	Pressure foamer B	Fan nozzle F	5.8 × 1.8	8.2	
17	Pressure foamer B	Fan nozzle H	6.2 × 1.95	9.5	
18	Pressure foamer B	Fan nozzle J	7.47 × 2.7	15.8	

Nr.	Device	Nozzle	Dimensions [mm]	Area [mm²]	
19	Pressure foamer B	Fan nozzle K	9.8 × 2.7	20.8	
20	Pressure foamer B	Fan nozzle L	11.4 × 4.2	37.6	
Spray nozzles					
21	Hand compression sprayer 2	Spray nozzle 0.5 mm	Ø 0.5	0.2	
22	Hand compression sprayer 2	Spray nozzle 0.8 mm	Ø 0.8	0.5	
23	Hand compression sprayer 2	Spray nozzle 1.2 mm	Ø 1.2	1.1	
24	Hand compression sprayer	TPU 8002 PP	Length 1.5, center 0.5	0.589	

Nr.	Device	Nozzle	Dimensions [mm]	Area [mm²]	
25	Hand compression sprayer	XR 8002 VS	Length 1.0, center 0.45	0.353	
26	Hand compression sprayer	Regulat-ing nozzle	Ø 1.1	0.95	
27	Hand pump sprayer		Ø 0.15	0.02	
28	Pressure sprayer P	Teejet TP 11006 VP	3.5 × 1.0	2.75	
29	High pressure spray gun	VP 145 Vario Power Jet Full Control (soft)	Outer oval 7.9 × 3.4, innner Ø 1.05	21.1 (outer) 0.87 (inner)	
30	Pressure sprayer G	BSPT Washjet ¼ MEG 4030	4.2 × 2.35	7.8	

4 Validation

4.1 General approach (release measurements)

A measurement example to validate the basic assumptions on the concentration patterns and the evaluation procedure is shown in Fig. 4.1. Two foam applications of a 2 % aqueous solution of the biocidal product QAC F were carried out with the pressure foam device G. The application solution (with a BAC (benzalkonium chloride) content of 0.16 %[6]) was spiked with 0.1 % CsCl. The relative peak heights following the two foaming actions and the decay times of the concentration of the individual size fractions were measured from the total aerosol, independently from the active substances or the tracer. The peak height comparison is based on mean values (5 min = 300 s) of the concentrations after the start of the release (see below and Fig. 4.2). The decay times result from the slope of the linear regression of the semi-logarithmic plot of the concentration values (dashed lines in Fig. 4.1). The differences of the slope in the alveolar and inhalable fraction are due to the particle size dependence of deposition losses on the room surfaces and the rotor blades of the fans. During ventilation, the concentration decay is dominated by air exchange and, therefore, is the same for all three size fractions.

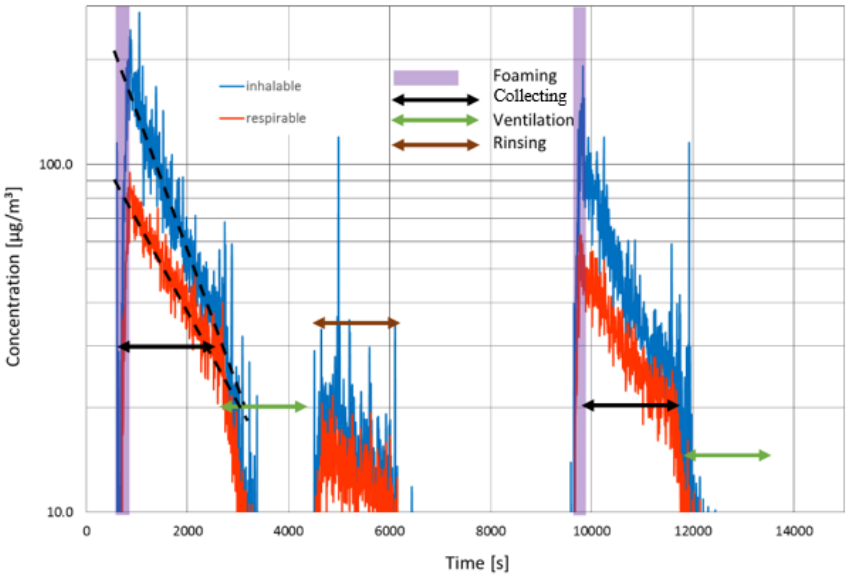


Fig. 4.1 The mass concentration time curves of the respirable (red) and inhalable (blue) aerosol fractions measured with the aerosol spectrometer during two foam applications and during rinsing of the foam with tap water using a fine droplet spray nozzle. (The thoracic fraction is not shown for clarity).

For this experiment, the corresponding data are shown in App. Tab. 1. The CsCl release fractions determined from both foam actions agree well.

The spectrometer signals during the rinsing action are due to the evaporating mist released by the spray nozzle. After evaporation of the droplets, a solid aerosol remains consisting of the salts dissolved in the tap water and other non-volatile impurities. This mainly respirable aerosol is detected in the spectrometer but does not contribute to the

[6] Analytically determined BAC- content: 80.4 g/kg

mean CsCl concentration because it was not collected during the washdown phase. A possible further aerosol source due to the bursting of the foam bubbles was not identified separately neither during ventilation (air exchange rate 8 h^{-1}) nor before rinsing. If present, this contribution has already decayed after the actual measurement phase (black double arrow) and can no longer be detected afterwards. In any case, this contribution is measured in addition to the direct spray-induced aerosol release during the measurement phases and is taken into account in the calculation of the aerosol release fraction. However, a separation of both contributions is not feasible.

An essential prerequisite for the release measurement procedure is the fast spatial homogenisation of the concentration in the model room. This is demonstrated in Fig. 4.2. With the start of foam application, the inhalable and respirable concentrations at fixed position 1 increase linearly, although the aerosol source (foam nozzle) is moved three times over the entire longitudinal extent of the room during the three-minute application. The linear increase in concentration can only occur when the aerosol is mixed in time scales small compared to the total application time. The high-frequency oscillations in the concentrations are due to the oscillating changes in direction of the fans. Further evidence of good internal mixing is the exponential decrease in concentration after the application.

The ratios of the slopes of the straight lines correspond to the ratios of the peak heights. In the two-minute time interval after the end of the application there is no significant drop in concentration, so that the relative peak height (rows 15–18 in App. Tab. 1) can be compared by averaging the concentration over the 5-minute period marked in green.

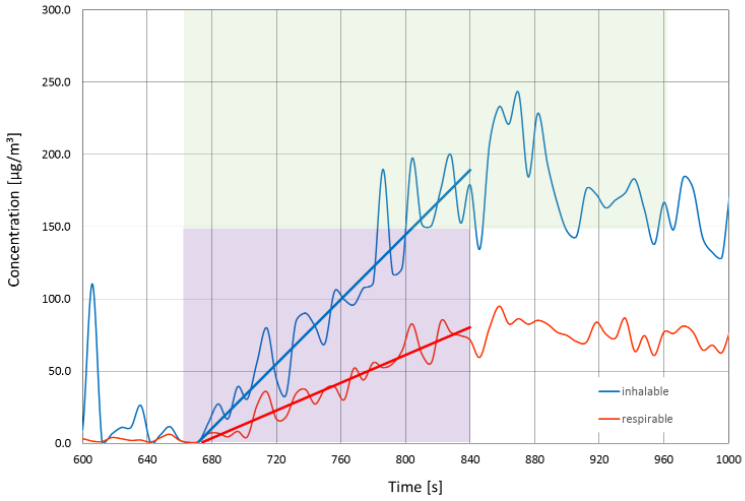


Fig. 4.2 Time pattern of the alveolar and inhalable fraction during the foam application phase and a short period afterwards. Measurements with the aerosol spectrometer. Marked in purple: Application period. Marked in green: Averaging period for the calculation of relative peak heights between individual application actions.

The time averaged tracer concentrations measured at both positions compare well, especially in the respirable and inhalable fractions, as the results in Fig. 4.1 show. The differences in the Respicon values in the thoracic fraction and the inhalable fraction are due to device specific particle losses in the virtual impactor of the Respicons. The evaluations according to App. Tab. 1 are always based on the mean values of the measurements at the two sampling positions.

Tab. 4.1 Time averaged CsCl concentration in µg/m³. i: GSP and Respicon; t and r: Respicon for two foam (V1 and V3) and one spray (V2) experiments performed.

Test #	Position 1				Position 2			
	i_GSP	i_Resp	t	r	i_GSP	i_Resp	t	r
	[µg/m³]				[µg/m³]			
V1	24.3	23.7	15.3	4.2	23.5	18.0	12.5	4.5
V2	66.5	61.1	43.1	13.7	66.6	51.9	35.8	14.9
V3	4.6	4.9	3.3	0.6	4.5	4.2	2.6	0.7

r: respirable, t: thoracic, i: inhalable

Aerosol release studies using small-scale spray and foam devices were conducted in previously validated control chambers of 1.5 and 41 m³ of volume, respectively (SCHWARZ and KOCH, 2017).

4.2 Validation of the tracer method

The determination of the release fractions of the non-volatile biocidal product substances, in particular of the QAC, is carried out indirectly by labelling the aqueous formulation with a tracer that can be detected sensitively with low background interference. Caesium chloride was chosen as tracer. CsCl has been extensively used as a marker substance in other contexts at ITEM.

4.2.1 Determination of caesiumchloride on mixed cellulose ester (MCE) filters

Sample filters (mixed cellulose ester, MCE) are processed by aqueous solvent extraction. The solution is then analysed by ICP-MS for its content of caesium. The method paramaters are the following:

Theoretical limit of quantification: (according to[7] DIN 32645)	0.025 µg/m³ (for an air sample volume of 0.21 m³ [8] and a liquid sample volume of 25 mL) 0.21 ng/mL (extraction volume: 25 mL)
Practical limit of quantification: (bottom calibration standard)	0.075 µg/m³ (for an air sample volume of 0.21 m³ [8] and a liquid sample volume of 25 mL) 0.5 ng/mL (sample volume (aq): 50 mL); 25 ng/filter

[7] For the calibration regime between 0.075 µg/m³ an 3 µg/m³ (0.5 ng/mL and 20 ng/mL in aqueous solution)

[8] Duration of sampling: 60 min at 3.5 L/min (sampling with GSP)

Recovery:	99.6 %, concentration 0.15 µg/m³ (n = 6; 1 ng/mL in filter extract)
	97.6 %, concentration 3 µg/m³ (n = 6; 1 ng/mL in filter extract)
Precision:	relative standard deviation < 1 % for a concentration range between 0.15 to 3 µg/m³ (n = 6)
Estimated expanded uncertainty[9]:	20 %

The method has an estimated expanded measurement uncertainty of 20 %. It is therefore suitable for the determination of airborne CsCl particles at the workplace according to DIN EN 482.

4.2.2 Limit of quantification

In the experiments, at least 320 liters of air are drawn through the sampling filters during 30 minutes for each application, and a 4-fold application (120 min 2.66 l/min, as volume flow rate of the Respicon). For this sample volume a limit of quantification for CsCl of 0.015 µg/m³ was determined for the entire procedure consisting of sample preparation and Cs measurement in the ICP-MS. The initial concentration, $c_{0,r,t,i}$, to be used for the calculation of the release fractions is larger than the average concentration, $\bar{c}^{s}$, by a factor of 2 due to the process-related decrease in concentration after the release, which can be seen from the comparison of the corresponding values in App. Tab. 1. For a room volume of 158 m³, this is equivalent to a limit of quantification for the released CsCl mass of 2 × 0.015 × 158 = 4.7 µg. For CsCl a mass fraction in the formulation of 0.1 %, the relationship between the limit of quantification for the measurement of the release fractions and the mass flow rate of the foam formulation during foam generation is shown in Fig. 4.3. The release fractions measured by the CsCl method and the limits of quantification must be converted for all non-volatile components according to their content in the formulation. The limit of quantification can be adapted to the requirements by selecting the experimental parameters such as release time, room volume, CsCl concentration in the formulation, etc. The limit of quantification can also be adapted to the requirements of the test. In the majority of the experiments, the sampling time could be reduced from 30 to 10 minutes. In addition, only 2 instead of 4 releases were carried out. This increases the limit of quantification for the measurement of the CsCl concentration by a factor of 6 to 0.09 µg/m³. However, the mean CsCl concentrations (of the inhalable fraction) actually measured in the release tests were significantly higher, except for three tests where the universal foam nozzle generating only very little aerosol was used, see Fig. 5.1 and the raw data tables (App. Tab. 15 – App. Tab.17).

[9] Calculation following; website: www.dguv.de/ifa/praxishilfen/praxishilfen-gefahrstoffe/software-berechnung-der-erweiterten-messunsicherheit-nach-ifa/index.jsp

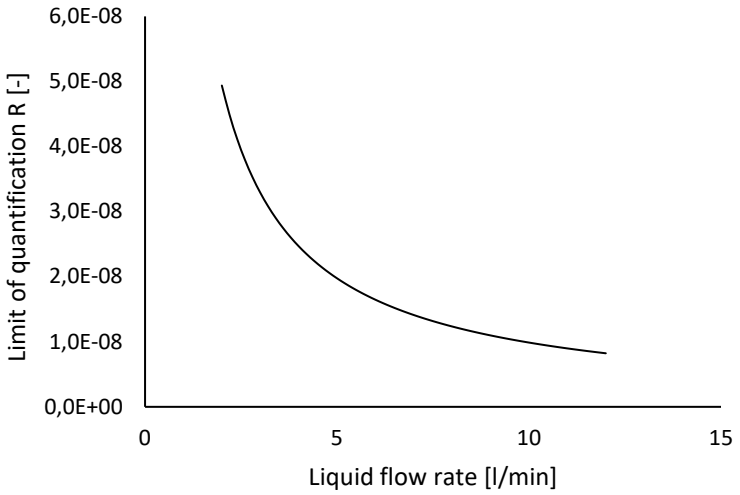


Fig. 4.3 Limit of quantification for the measurement of the release fractions as a function of the liquid flow rate using the CsCl method.

4.2.3 Comparison with the QAC analysis

The comparison between the analysis of the tracer and of the active substance was performed as part of a preliminary test during the development of QAC analytics.

An aqueous formulation containing 0.1 % CsCl and 0.3 % benzyldimethyl-alkyl(C_{8-18}) ammonium chloride (benzalkonium chloride, Sigma-Aldrich) was sprayed 4 times with application times of 2.5 min each. The released inhalable aerosol was sampled over the 4 applications and subsequent decay periods (approx. 30 min each) with CFC and GSP sampling units using teflon coated glass fiber filters (Pall GmbH, Dreieich, Germany). QAC and CsCl quantification were performed on the same filter. The CFC samplers were operated at an air sampling rate of 2 L/min and the GSP samplers at 3.5 L/min. On average, the aerosol content analyses of benzalkonium chloride and caesium chloride reflect the 3:1 mixing ratio in the formulation.

Tab. 4.2 Simultaneous analysis (CFC sampler) of benzalkonium chloride and caesium chloride in the released inhalable aerosol. Concentrations in µg/m³.

Test	Benzalkonium chloride	Cäsium chloride	Ratio
Filter 1	96.1	28.8	3.3
Filter 2	83.2	24.8	3.4
Filter 3	73.5	29.8	2.4
Filter 4	82.9	28.8	2.9
Average	**83.9**	**28.0**	**3.0**
STDEV	**8.1**	**1.9**	**0.5**

Another comparison between the active substance and the tracer substance was carried out in a foam application test with QAC F. The foam solution contained 0.1 % CsCl and 0.16 % BAC. Five filter samples of the aerosol released during foaming were analysed. The ratio of BAC content to CsCl content was determined to be 1.66 ± 0.11. Thus, the CsCl tracer method can be used to determine the release of non-volatile aerosol components for spraying as well as foaming.

4.3 Validation of the pyrethroid method

4.3.1 Characteristics of the pyrethroid method (inhalative)

Based on the dissertation by ELFLEIN (2003) and the VDI guideline 4301, an analytical method was established that allows determination of PBO, tetramethrin and phenothrin (mixture of isomers) after extraction from glass fiber filters by GC-MS (Appendix 2). The method has the capacity to include additional pyrethroids. For pyrethroids not covered by VDI standard 4301, cross-validation might be necessary. The method parameters are listed in the following section:

Theoretical limit of quantification: (noise + 10 × STDEV of noise)	PBO: 0.05 µg/m³ (for an air sample volume of 0.21 m³ and a liquid sample volume of 1 mL) Tetramethrin: 0.005 und 0.02 µg/m³ (Peak 2 und 1); (for an air sample volume of 0.21 m³ and a liquid sample volume of 1 mL) Phenothrin: 0.02 µg/m³ (for an air sample volume of 0.21 m³ and a liquid sample volume of 1 mL)
Practical limit of quanitification: (bottom calibration standard)	0.024 µg/m³ (for an air sample volume of 0.21 m³ and a liquid sample volume of 1 mL) 5 ng/mL (sample volume (liq): 1 mL)
Accuracy:	
PBO	91.4–115 %
Tetramethrin	82.1–112 %
Phenothrin	82.6–105 %
Precision:	
PBO	Rel. standard deviation: 1.3–13.4 %
Tetramethrin	Rel. standard deviation: 2.2–14.1 %
Phenothrin	Rel. standard deviation: 3.7–15.8 %

For the measurement range from 5 to 500 ng/mL (0.024 to 2.4 µg/m³); at a sample volume[8] of 0.21 m³ and a liquid sample volume of 1 mL.

Estimated expanded uncertainty[10]:	
PBO	32 %
Tetramethrin	34 %
Phenothrin	34 %

[10] Calculation according to IFA; website: www.dguv.de/ifa/praxishilfen/praxishilfen-gefahrstoffe/software-berechnung-der-erweiterten-messunsicherheit-nach-ifa/index.jsp

The method has estimated expanded measurement uncertainties for PBO, tetramethrin and phenothrin of 32 % and 34 % each. It is therefore suitable for the detection of these three analytes at the workplace according to DIN EN 13936. With regard to the accuracy, no correction factor is introduced, since no systematics was found with regard to under- or overdetection in the course of validation.

4.3.2 Characteristics of the pyrethroid method (dermal)

A measurement method to quantify potential dermal exposure to pyrethroids has been successfully developed and validated. To detect exposure during spraying or foaming of biocidal products containing pyrethroids, the method uses Tyvek coveralls and cotton gloves for sampling. The sampling media are extracted with acetone, and are analysed by GC-MS after adding an internal standard and exchanging the solvent. The analytical method allows the quantification of PBO, tetramethrin, trans-phenothrin, permethrin, cyfluthrin, cypermethrin as well as deltamethrin on tyvek and cotton material. The method parameters are listed in the following section for the analytes PBO, tetramethrin and phenothrin, the detailed method description and validation can be found in the corresponding validation report (IPASUM, 2018).

Theoretical limit of quantification: (following DIN 32645)	PBO: 1.75 µg/L
	tetramethrin: 1.69 µg/L
	trans – phenothrin: 1.23 µg/L
Glove:	0.2–0.3 µg/glove for PBO, tetramethrin and trans-phenothrin
Tyvek material:	0.1 ng/cm² für PBO, tetramethrin und trans-phenothrin
Accuracy:	
PBO	85.0–109 % (Tyvek); 97.9–105 % (cotton)
Tetramethrin	91.4–104 % (Tyvek); 85.7–97.0 % (cotton)
Phenothrin	91.4–113 % (Tyvek); 87.6–99.4 % (cotton)
Day to day precision:	
PBO	4.62–9.06 %
Tetramethrin	4.75–8.38 %
Phenothrin	3.17–4.02 %

For the measurement range 10–500 µg/L (precision, n = 8); 5–50 µg/L (accuracy, n = 3).

With regard to the accuracy, no correction factor is introduced, since no systematics with regard to under- or over-determination was identified during the validation. The measurement method developed for the determination of potential dermal pyrethroid exposure thus allows the selective and sensitive determination of the analytes at good limits of quantification of 1.23–1.75 µg/L. The precision data and also the data on relative recovery can be described as good, so that a practical and stable measurement method is available.

4.4 Validation of the QAC method (Benzalkonium chloride)

4.4.1 Characteristics of the benzalkoniumchloride method – inhalative

Based on the publication by VAN BOXTEL et al. (2016), an analytical method for the determination of airborne benzalkonium chlorides after collection on PTFE filters was implemented and validated at Fraunhofer ITEM (ITEM, 2018, 2). The method allows the determination of the benzalkonium chlorides via the sum parameter benzyl chloride, which is released during thermal treatment of the benzalkonium chlorides. After collection of the benzalkonium chlorides on PTFE filters, spiking with ISTD, and removal of residual solvent under a N_2 stream, the headspace above the filters can be sampled directly after heating and transferred to the GC-MS system for analysis. This approach avoids the expected analytical losses, carry-over and similar during sample preparation (e.g. liquid extraction) caused by the ionic nature of the benzalkonium chlorides.

In summary, the validation showed that it is not a model method with regard to compliance with defined acceptance criteria. Liquid spiking of PTFE filters as control standards for method validation is limited. This is clearly shown in the course of the validation. We found substantial variation of the measured values around the nominal value as well as a significant number of outliers. These observations were made during the precision and accuracy studies and analytical errors were excluded. The application of a CsCl-labeled QAC formulation in the model room and subsequent analysis of BAC and CsCl content from the same filters (n = 17) confirmed the suitability of the analytical method for filter samples obtained in the field. The actual mixing ratio of 1:1.6 for CsCl: QAC in the applied solution was confirmed by the analyses to be 1.6 ± 0.3.

The method is thus fit for purpose for the intended comparison between the inhalation exposure derived from release experiments in the model room with the experimentally determined exposure at the real workplace.

The method parameters are listed in the following section:

Theoretical limit of quantification: (noise + 10x STDEV of noise)	0.0095 µg/m³ (for an air sample volume[8] of 0.21 m³)
Theoretical limit of quantification: (bottom calibration standard)	2.4 µg/m³ (for an air sample volume[8] of 0.21 m³)
	0.5 µg/Filter
Accuracy:	95.2 bis 113 %[11]
Precision:	2.5 bis 22.8 %

For the measurement range form 0.5 to 6 µg/filter (2.4 bis 29 µg/m³); at a sample volume[8] of 0.21 m³.

Estimated expanded uncertainty[10]:	35 %

[11] Obvious outliers were discarded (see validation report, IPASUM, 2018)

The method has an expanded measurement uncertainty of 35 %. It is therefore, in accordance with DIN EN 13936, suitable for the detection of airborne BAC at the workplace.

With regard to the accuracy, no correction factor is introduced, since no systematics with regard to under- or overdetection was identified during the validation.

4.4.2 Characteristics of the benzalkoniumchlorid method – dermal

A measurement method for quantifying potential dermal exposure during the application of biocidal products containing BAC by spraying or foaming was developed and successfully validated. The method uses Tyvek coveralls and cotton gloves as sampling media, which are extracted with acetone. After addition of internal standards the extracts were dried and the dry residues were pyrolysed in crimped capped headspace vials. The benzyl chloride formed as a pyrolysis product is used to quantify the BAC content. The analytical method is a headspace GC-MS method based on the work of VAN BOXTEL et al. (2016). The detailed method description and validation can be found in the validation report (IPASUM, 2018).

Limit of quantification according to DIN 32645:	0.019 µg/Vial (2 µg/L)
Glove:	2 µg/glove (100 mL extraction liquidl)
Tyvek material:	1 ng/cm² (50 mL extraction liquid for 900 cm²)
Accuracy:	90.0–102 % (Tyvek) for the amount of analyte 0.12 to 0.6 µg/vial (n = 3); 95.9–105 % (cotton) for the amount of analyte 0.06 to 0.3 µg/vial (n = 3)
Precision:	2.62–6.12 % for the amount of analyte 0.1 to 5 µg/Vial (n = 8)

No correction factor is introduced with regard to accuracy, as no systematic approach to under- or over-detection was identified during validation. The headspace GC-MS method thus proves to be a specific and sensitive analytical method that allows the analytes to be determined without extensive extract purification and leads to a good limit of quantification of 0.019 µg of benzalkonium chloride/vial. The good precision data and the very good recovery rates show that the method is stable and suitable for practical use.

4.5 Summary

Within the scope of the project, two GC-MS based methods were developed and validated in the two laboratories for the determination of dermal and inhalation exposure to BAC and selected pyrethroids. The sample media for dermal exposure for both analyte groups were Tyvek material (full body coverall) and cotton (gloves).

PTFE-coated filters were used to collect the inhalable aerosol containing BACs and glass fiber filters were used for the pyrethroids. Due to the expected low concentration of inhalable active substance (here: BAC) at the workplace and in the model room investigations, a tracer method using CsCl was proposed and validated. The tracer method benefits from the high sensitivity of ICP-MS and the associated reduction in the limit of quantification.

5 Results

5.1 Investigations in the model rooms

Depending on the application, the release fractions of active substance were measured in either one of the three existing model rooms. The procedure followed for spraying and foaming is described in Appendix 6. Apart from the three pyrethroid containing products, the release fractions for all other products and application methods were quantified via chemical analysis of the tracer substance (CsCl).

5.1.1 Generic results

The values of the time averaged concentrations of inhalable active substance of the application tests in the model rooms after sampling with different devices are shown in Fig. 5.1 and Fig. 5.2. The corresponding data can be found in App. Tab. 11 of Appendix 8. The reference value for the inhalable aerosol size fraction is the GSP sampling device GSP1. The concentration values determined from the two inhalable samplers are nearly identical, indicating spatial homogeneity of the inhalable aerosol concentration in the model rooms. This is a prerequisite for determining the aerosol release fraction from the concentration according to Eq. 3.17. As expected, the uniform distribution is also realised in the smaller model rooms, as shown by the corresponding data points in Fig. 5.1.

The linear relationship also applies to the Respicon data. Fig. 5.2, however, shows that the Respicon 1 gives systematically lower values for for the inhalable concentration. This is due to device-specific losses of the extra-thoracic particles in the inlet head. The ratio of the respirable concentrations of R1 and R2 is on average 0.95 and for the thoracic fraction the ratio is 0.98.

For the evaluation of the model room experiments, the concentration of inhalable active substance is obtained from the mean values from GSP1 and GSP2 samples and (if available) from the R2 samples. Only the values of the R2 sampler are used to calculate the thoracic and respirable concentrations.

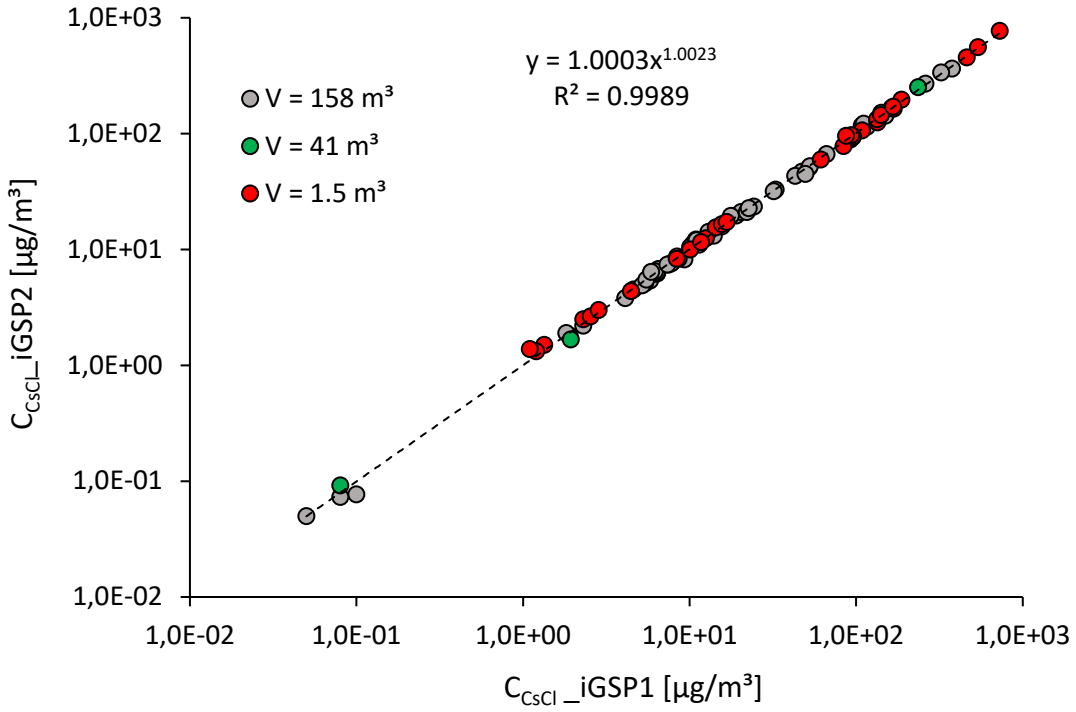


Fig. 5.1 Average CsCl concentrations for the release measurements in the model rooms determined from the two GSP sampling systems (GSP1 and GSP2) placed at different positions.

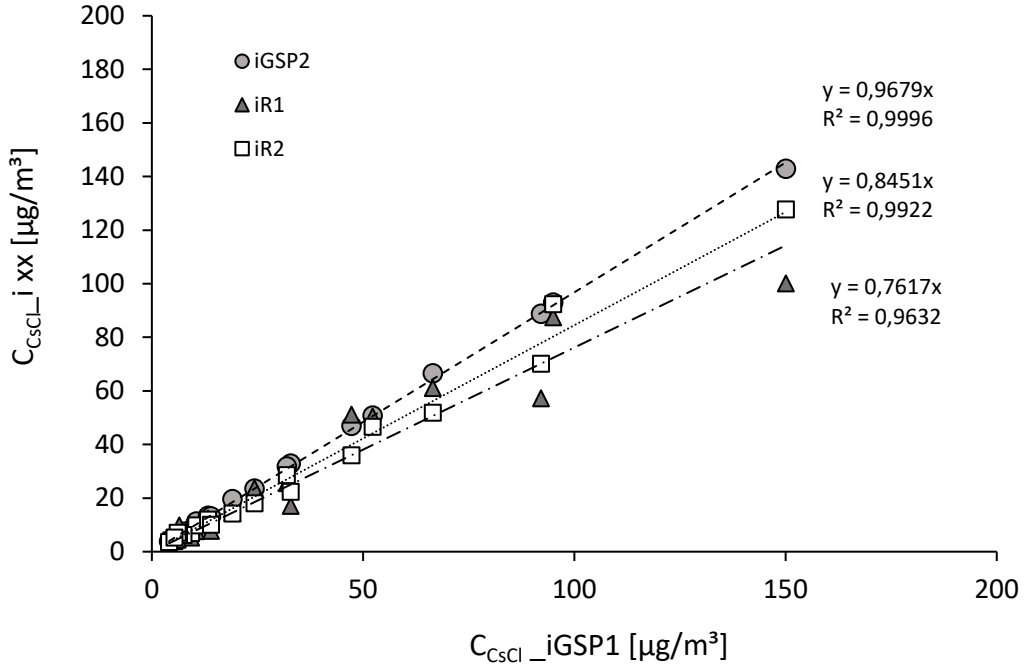


Fig. 5.2 Time averaged CsCl concentrations for the release measurements carried out in the large model room based on the sampling devices used, compared to the reference sampler GSP1.

Furthermore, for a total of 13 release tests in the large model room, deposition pads were exposed and their CsCl loading was evaluated. In each case, the mean values from the three horizontally and vertically arranged deposition pads were calculated. Using Eq. 3.4 the deposition velocities were calculated from these values. The concentration, $\bar{c}_i^s$, was based on the GSP and the R2 samples. The deposition velocity towards the horizontal pads depends significantly on the particle size, as it is mainly determined by the mechanism of sedimentation. The larger the extra-thoracic fraction of the aerosol, the higher is the value of the deposition velocity. The extra-thoracic fraction can be determined from the Respicon and GSP data according to Eq. 5.1.

(5.1)

$$\eta_{ext} = \frac{\bar{c}_i^s - \bar{c}_t^s}{\bar{c}_i^s}.$$

Fig. 5.3 shows the trend of increasing deposition velocities on horizontal surfaces, A_h, with the extra-thoracic fraction of the active substance aerosol. The aerosol deposition on vertically arranged surfaces, A_v, is significantly lower and does not depend on the particle size (see also Table 5.1).

The dermal dose accumulated during the time period, T, is calculated from:

(5.2)

$$D^{derm} = T \cdot \bar{c}_i^s \cdot \left(A_h \cdot v_{dep,h}^s + A_v \cdot v_{dep,v}^s\right).$$

Since both, the inhaled dose and the deposited dose are proportional to the aerosol concentration and the exposure duration their ratio is calculated from:

(5.3)

$$\frac{D^{inh}}{D^{derm}} = \frac{T \cdot \bar{c}_i^s \cdot Q_A}{T \cdot \bar{c}_i^s \cdot \left(A_h \cdot v_{dep,h}^s + A_v \cdot v_{dep,v}^s\right)} = \frac{Q_A}{A_h \cdot v_{dep,h}^s + A_v \cdot v_{dep,v}^s}.$$

Assuming a value of 2 m² for the body surface area (10 % horizontal, 90 % vertical), a conservative value of 0.95 cm/s for the horizontal and 0.2 cm/s for the vertical deposition velocity, and an inhalation flow rate of 1.25 m³/h, a value of 6.3 % for the ratio of inhaled to dermal dose. Even assuming a reduction factor of 10 through clothing, the calculated dermal dose effective on the skin surface is still greater than the inhaled dose. However, in this context, the different bioavailability of active substances of the two exposure pathways has to be taken into account. It should also be noted that dermal exposure through accidental contact with the biocidal product formulation during handling and splashes are not considered.

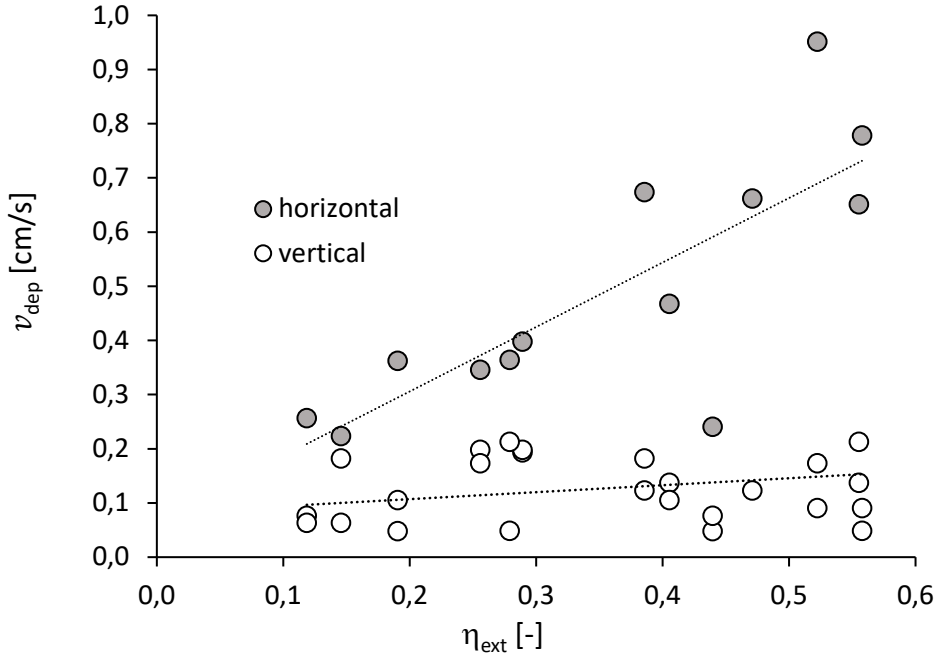


Fig. 5.3 Deposition velocity on horizontal surfaces (filled symbols) and vertical surfaces (open symbols).

Tab. 5.1 Data set for the determination of the vertical and horizontal deposition velocity by measuring the CsCl loading on the deposition pads.

Test	T_d [min]	η_{ext}	C_i [µg/m³]	Loading [µg/m²]		Flux density [µg/(m² min)]		Deposition velocity [cm/s]	
				hor	ver	hor	ver	hor	ver
V10	48	0.29	7.0	80.6	39.1	1.68	0.81	0.40	0.19
V11	51	0.26	12.9	136.4	78.2	2.67	1.53	0.35	0.20
V12	44	0.52	83.7	2101	383	47.75	8.70	0.95	0.17
V13	44	0.56	43.4	892	103.4	20.27	2.35	0.78	0.09
V15	48	0.28	140.2	1470	197	30.63	4.10	0.36	0.05
V16	48	0.56	12.4	231.9	75.8	4.83	1.58	0.65	0.21
V17	52	0.40	3.8	55.9	16.4	1.08	0.32	0.47	0.14
V18	46	0.19	6.3	63.0	18.3	1.37	0.40	0.36	0.11
V19	52	0.44	17.7	132.4	26.4	2.55	0.51	0.24	0.05
V20	46	0.12	6.5	45.8	13.6	1.00	0.30	0.26	0.08
V21	46	0.15	5.3	32.5	9.2	0.71	0.20	0.22	0.06
V22	44	0.39	93.4	1662	449	37.77	10.20	0.67	0.18
V23	44	0.47	49.9	872	162	19.82	3.68	0.66	0.12

hor: horizontal surfaces
ver: vertical surfaces

5.1.2 Release fractions (inhalable)

In the project, a total of 96 release experiments were carried out with different devices, operating parameters and biocidal product formulations. In 30 experiments, the formulation was also sprayed when the devices are envisaged for both, foam and spray application. Foaming and spraying were carried out under the same conditions as far as possible in order to enable a direct comparison. Reduction factors for the foam application in comparison to the spray application were derived in accordance with the project tender. The results for the QAC containing products were based on the analysis of CsCl. The data for insect foams B1 and B2, insect spray B and insect spray F were derived form the analysis of the active substances, including phenothrin and permethrin. A complete overview of all measurement results is given in Appendix 8.

The study focussed on the inhalable fraction of the released aerosol. The respirable and the thoracic size fraction were measured additionally in 23 tests carried out in the large model room, and 9 tests performed in the small scale control volume (1.5 m³) as well as 4 experiments in the medium size room (41 m^3).

Fig. 5.4 shows the inhalable release fraction for the foaming devices listed in Tab. 3.2. The data represent the release fractions for the intended use with the formulations QAC F, QAC E and QAC M representative for the QAC-containing formulations, the PER F as a representative of the insecticide alpha-cypermethrin, the insect foams with the active substance d-phenothrin as well as the insect foam F including the active substance permethrin. The standard deviations shown characterise the uncertainties that can occur during operation in practice. This includes the preparation of the solution by diluting the concentrate, the foam application procedure, inaccuracies in the pressure adjustment, fluctuations in the operation of the devices, the use of different foam cartridges for the pressure foamer P as well as the application of the two QAC formulations QAC E and F for the pressure foamer device G.

The relative standard deviation of the pressure foamer G data is, for example, approx. 53 % with a mean value of the inhalable release fraction of 0.02 %, as can be deduced from the values in Fig. 5.4. The errors in the filter analysis of the active substance is small, as is implicitly shown in Fig. 5.1. For the foam applications with the pressure foamer P it was found that the foam consistency can vary depending on the filling level of the device. In some cases, in the early phase of operation, the foam was very wet and the release looked more like a spray process. These situations were not taken into account in the calculation of the mean value for the applications with the Teejet TP 11006VP nozzle with the different foam cartridges. In the summarising Fig. 5.4, the foam disks were not evaluated separately. This applies to foaming with QAC F. The standard deviation shown by the corresponding error bar in Fig. 5.4 characterises these uncertainties. The relative standard deviation of the pressure foamer P data is thus up to 55 %.

The results for the high pressure and low pressure foam guns are in the range between 0.003 % and 0.02 %, similar to those of the pressure foamer G. This indicates that the nominal pressure is not a determinant for the aerosol release.

The two handheld devices used in this study show very different results. The hand pump foamer is characterised by a high aerosol potential with a release fraction of approx. 0.1 %. In contrast, the hand compression foamer releases much less aerosols

even below the release fractions of the propellant-based foam cans. The latter were expected to generate little aerosol because they produce very dry foams at low exit velocities.

The maximum value of 0.6 % for the average inhalable release fraction was measured for the pressure foamer operated with the PER F product. The tests of this combination may be of low relevance for the use in practice since it did not generate a foam. An additional foaming agent had to be added to the formulation. Furthermore, the liquid was not a solution but a suspension. The lowest value of 0.0003 % for the inhalable release fraction was measured when operating the pressure foamer P with the universal foam nozzle. The relatively wet foam flows out of the foam nozzle at a very low velocity compared to all other devices (see chapter 5.1.4).

The total span of the measured data of the inhalable release fraction is described by a factor of approx. 2000.

The information on the pressure must be regarded as a guidance, as it generally does not reflect the pressure conditions at the foam nozzle, but rather indicates different system pressures depending on the device. This helps the user to operate the device reproducibly. The specification of the pressure is generally not meaningful for the venturi foam nozzles.

For the devices envisaged also for a spray application by replacing the foam nozzle with a spray nozzle, comparative release studies were also carried out. The results of these tests are shown in Fig. 5.5.

Values of about 1 % were measured for the aerosol release fractions when using the high-pressure process, the pressure sprayer P using the Teejet nozzle and the hand compression sprayer 2. The formulation has little influence. This also applies to the values when using the hand compression sprayer, but at a slightly lower level of approx. 0.5 %. With the hand pump sprayer, the fan shape of the spray mist can be varied by turning the nozzle cap. When adjusting a wide fan significantly more aerosol is formed than with a narrow one. With the wide fan, the aerosol release rate is in the range of 10 %. The propellant gas based insect spray shows similarly high levels of the inhalable release fraction of active substance.

When spraying, the inhalable release fractions are generally higher than with foaming. Different reduction factors are derived form the release data for the individual processes (Fig. 5.6). In the case of propellant based pyrethroid products, there is a three orders of magnitude reduction (factor 2930) when foaming compared to spraying. This is mainly due to the high aerosol release values during spraying related to the very fine droplet size distribution that is usually present in propellant based spray systems. For the “large-scale” pressure foamer G, the aerosol release when foaming is reduced by a factor of 10 compared to spraying. The nozzle 50/200 (exit area approx. 8 times larger than that of the spray nozzle) was used for the foam application. For the high pressure gun, the reduction factor is 61. For the pressure device P, the reduction factors vary a lot, depending on the respective references. When using the fan nozzle with and without a foam cartridge, the reduction factors have values of 4 for the 20 % QAC M mixture and 26 for the formulation with QAC F. For the PER F formulation with foaming agent, a reduction factor of 2 was measured. There were problems with the homogeneity of the application solution during the application. However, when using

the universal foam nozzle in the pressure device P, which has a very low aerosol formation potential the exposure during foaming compared to spraying is reduced by almost a factor of 2600. The low foam exit velocity (see Chapter 5.1.4) leads to the rather inadequate foam quality. Therefore, this nozzle is rated unsuitable for foam application by professional users.

The hand compression device releases the foam also at a comparatively low velocity (see chapter 5.1.4), which leads to a low aerosol generation during foaming and thus to comparatively high reduction factors of a few hundred when compared to spraying. The differences result from the relation to the respective foam formulation. The reduction factor for the hand pump device is also variable, depending on whether a narrow (factor: 18) or wide fan (factor: 108) is used for spraying.

For all spray processes, the airborne release of non-volatile active substances depends very sensitively on the primary droplet distribution of the spray mist, which among others can also be related to the shape of the spray cone. Even small shifts in the primary droplet distributions lead to considerable changes in the aerosol release. Establishing a relationship between the droplet size distribution and the process parameters is rather difficult because of the complex dependencies. Likewise, when foaming under the same operating conditions, the release depends extremely on the choice of the appropriate foam nozzle. Therefore, a standardised comparison of the aerosol release between spray and foam applications cannot be related to characteristic process parameters such as the nominal pressure common to spraying and foaming. Therefore, more release measurements were carried out for the foam application compared to the spray application in order to cover a wider range of process parameters and device types for foaming which are relevant in practice. The overall data set obtained for foaming was intended to help finding possible relationships between the process parameters and the foam release and to try to classify the aerosol formation potential according to criteria of practical relevance.

The data on aerosol release are required for specifying the source strength in deterministic exposure modelling.

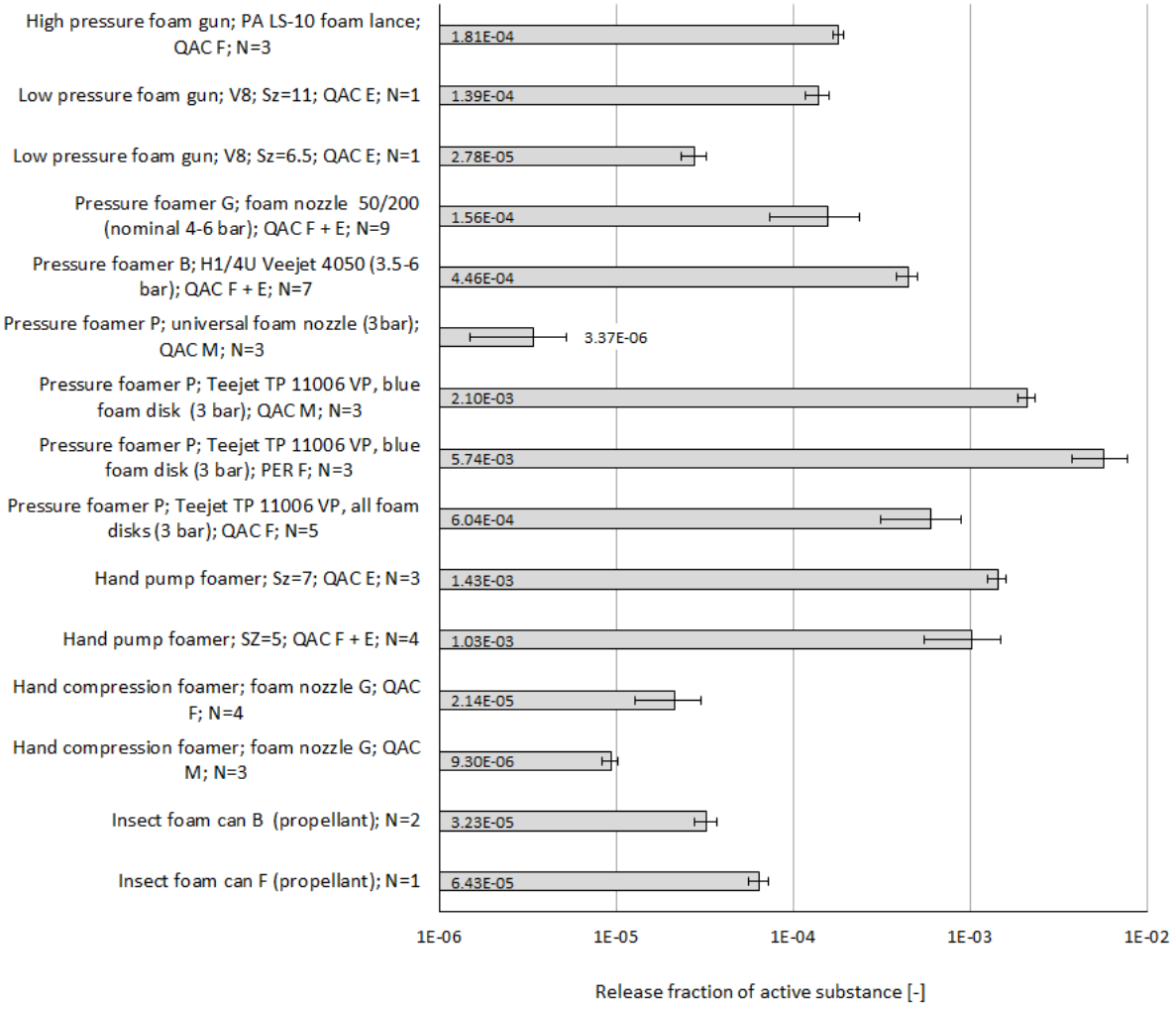


Fig. 5.4 Inhalable release fractions for foaming with devices used in practice. N is the number of tests. Each test comprises at least 2 release actions. For N > 1 the standard deviation was determined from the average release fractions of each test. For N = 1 the standard deviation is determined from the repetitions within the test.

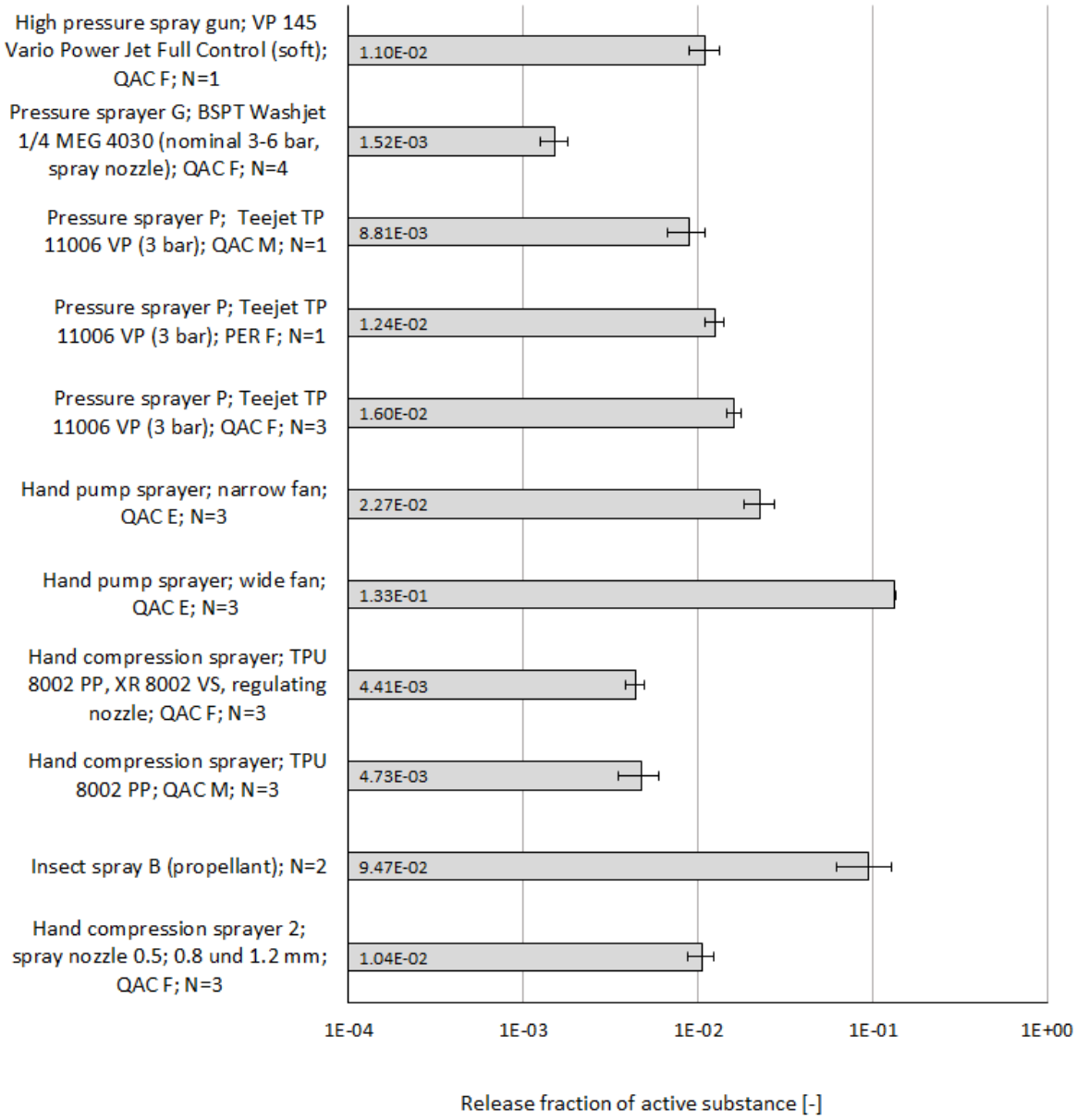


Fig. 5.5 Inhalable release fractions for spraying with the same devices as in Fig. 5.4. N is the number of tests. Each test comprises at least 2 release actions. For N > 1 the standard deviation was determined from the average release fractions of each test. For N = 1 the standard deviation is determined from the repetitions within the test.

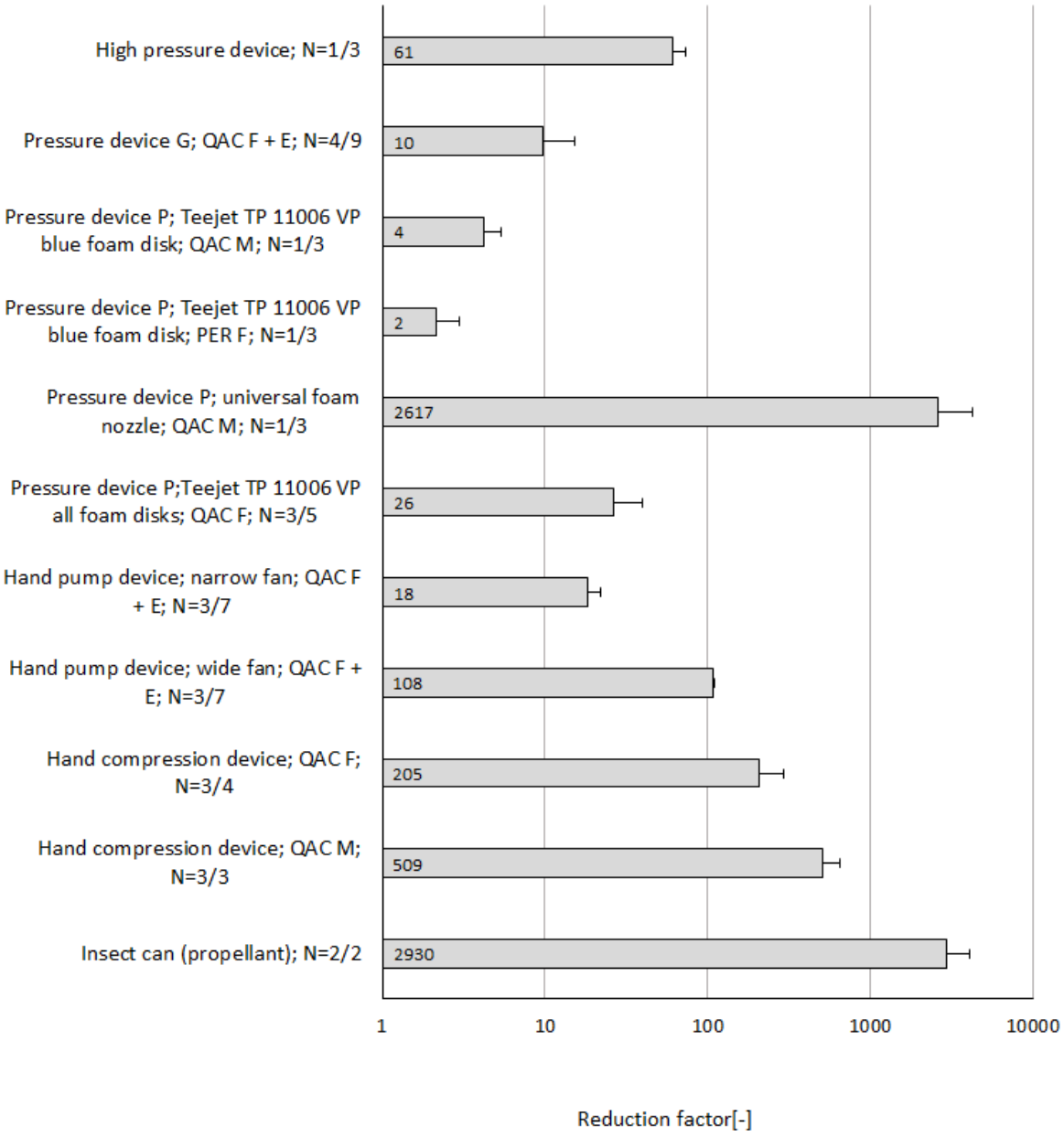


Fig. 5.6 Reduction factors for the release fraction calculated for tests for foaming and spraying carried out under comparable conditions.

5.1.3 Release fractions (thoracic and respirable)

In 31 model room experiments, the thoracic and the respirable release fraction were also measured using the Respicons. The results are summarised in the following two figures (Fig. 5.7, Fig. 5.8). The percentages of the respirable and thoracic release fraction of the inhalable fraction are shown in the figures. Because of the limited number of measurements, only mean values and standard deviations were given for the devices, irrespective of their operating conditions. The bars without error bars are single measurements. For both foaming and spraying, an average of more than 50 % of the released inhalable particles of active substance is attributed to the thoracic size regime. For respirable particles the differences between the devices are larger.

In addition to the cumulative thoracic and inhalable fractions, the values of the differences tracheo-bronchial (the difference between thoracic and respirable) and extra-thoracic (the difference between inhalable and thoracic) fractions are shown. The percentage of respirable, tracheo-bronchial and extra-thoracic fractions are required for concentration modeling using SprayExpo.

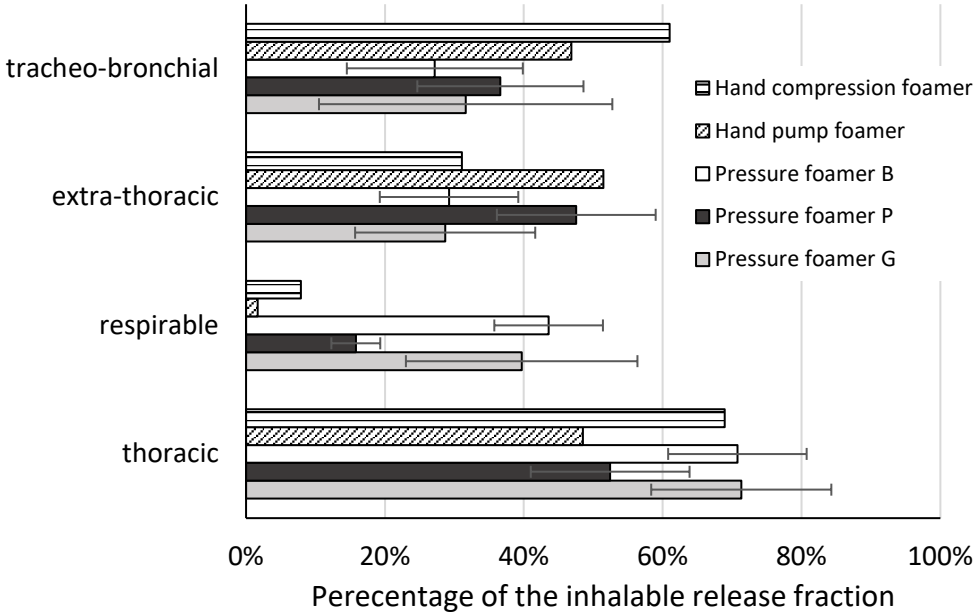


Fig. 5.7 Percentage of the inhalable release fraction attributed to thoracic and respirable particles as well as the difference tracheo-bronchial and extra-thoracic particles for foaming.

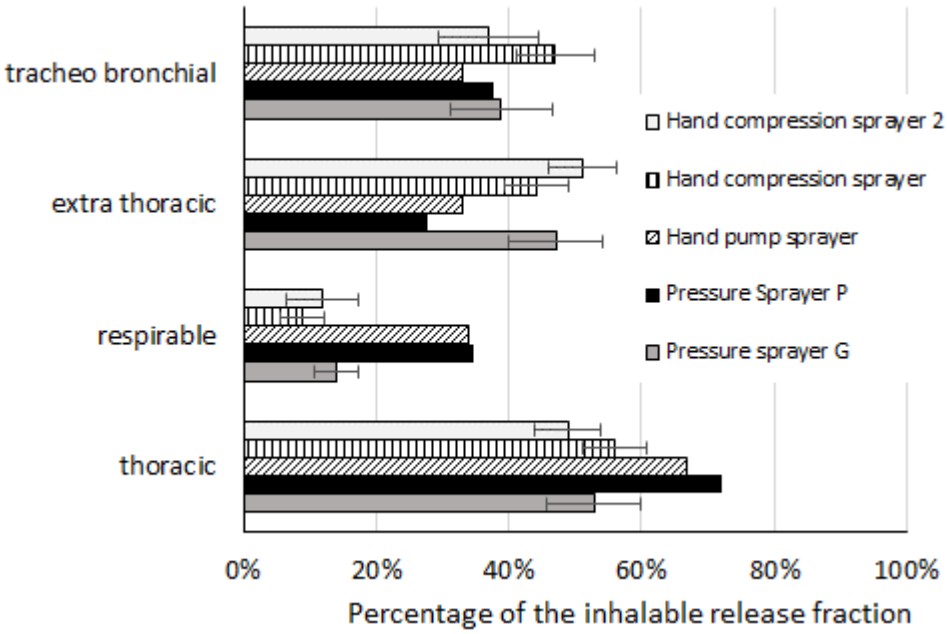


Fig. 5.8 Percentage of the inhalable release fraction attributed to thoracic and respirable particles as well as the difference tracheo-bronchial and extra-thoracic particles for spraying.

5.1.4 Parametrisation of the inhalable release fraction

It is hypothesised that aerosol formation occurs primarily at the interface between foam jet and air, which implies that the exit velocity of the foam stream leaving the nozzle and the dimensions of the nozzle should be process parameters influencing aerosol formation during foaming. This is illustrated in Fig. 5.9.

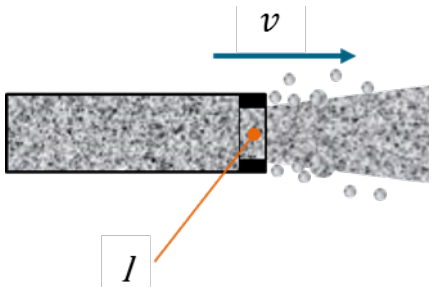


Fig. 5.9 Schematic drawing of the foam nozzle and illustration of the assumed aerosol release mechanisms. l is the circumference of the nozzle and v is the exit velocity.

Obviously, there should be a positive correlation with the exit velocity, v, and the surface area generated per volume of foam exiting the nozzle $\sim(1/l)$. Here, l is the circumferential length of the foam nozzle. This suggests that the release fractions correlate with the quantity v/l. Furthermore, the release fraction of active substance should depend on the concentration of active substance in the foam droplets. This is inversely proportional to the foam expansion ratio, E. The smaller the foam expansion ratio (= ratio of foam volume to liquid volume), the larger is the active substance concentration

in the foam for the same concentration of active substance in the formulation. This results in the following correlation:

(5.4)

$$R_i^s \sim v/(l \cdot E).$$

This hypothesis is supported by the data shown in Fig. 5.10. The corresponding numerical data are listed in Tab. 5.2.

The foam expansion ratios (foam volume/liquid volume) were determined by weighing a defined foam volume. From experiment V24 on, this was done for each experiment or a series of experiments carried out under the same boundary conditions. For the foam expansion ratios for tests performed earlier, new measurements of the expansion ratio were carried out or data from tests were used that were determined under the same boundary conditions.

The exit velocity was calculated from the sum of the air flow rate, Q_a , the flow rate of the formulation, Q_l, and the nozzle cross-sectional area, A. The air flow rate for the premixed foams was determined by means of a mass flow meter connected to the foam air supply line. The liquid volume flow rate was determined from the amount of formulation consumed during the release experiment.

Data from the devices based on the injection principle – high pressure nozzle, low pressure nozzle and hand compression device – are also included in the figure. The air volume flow rate in these devices could not be measured directly. Therefore, it was estimated from the foam expansion ratio and the flow rate of the liquid ($\tilde{Q}_a = (E-1) \cdot Q_l$). There is an average conversion factor between $\tilde{Q}_a$ and Q_a which was determined from experiments where the expansion ratio was measured by weighing and could also be calculated from the measured volumetric flow rates. An average correction factor of 0.60 (± 0.35) was obtained from all data except V40–V42 with extremely liquid foam. This factor was used for the estimation of the air flow rate in the injector nozzles: $Q_a = \tilde{Q}_a/0.6$. The values calculated in this way can only be a rough estimate, as the correction factors for the individual tests vary considerably. A detailed analysis shows a systematic decrease with increasing exit velocity.

The values for the inhalable release fraction of active substance cover a range of almost four orders of magnitude. The square gray dots in Fig. 5.10, belong to the tests V52–V54, carried out with the formulation of PER F combined with a foaming agent. As already mentioned, the formulation in these experiments was a suspension that precipitated partly to the bottom of the tank. The corresponding data points were not taken into account in the regression analysis. Likewise, the data point marked with a gray triangle (V60), was considered as an outlier and was discarded. A very low aerosol release of $1.3 \cdot 10^{-6}$ was measured here (close to the limit of quantification), which is due to the low exit velocity and the large nozzle dimensions. In addition, the value of the foam expansion ratio of 3 did not correspond to the visual impression. The value of the release fraction was well below the two values measured in experiments 61 and 62 of approx. $4 \cdot 10^{-6}$.

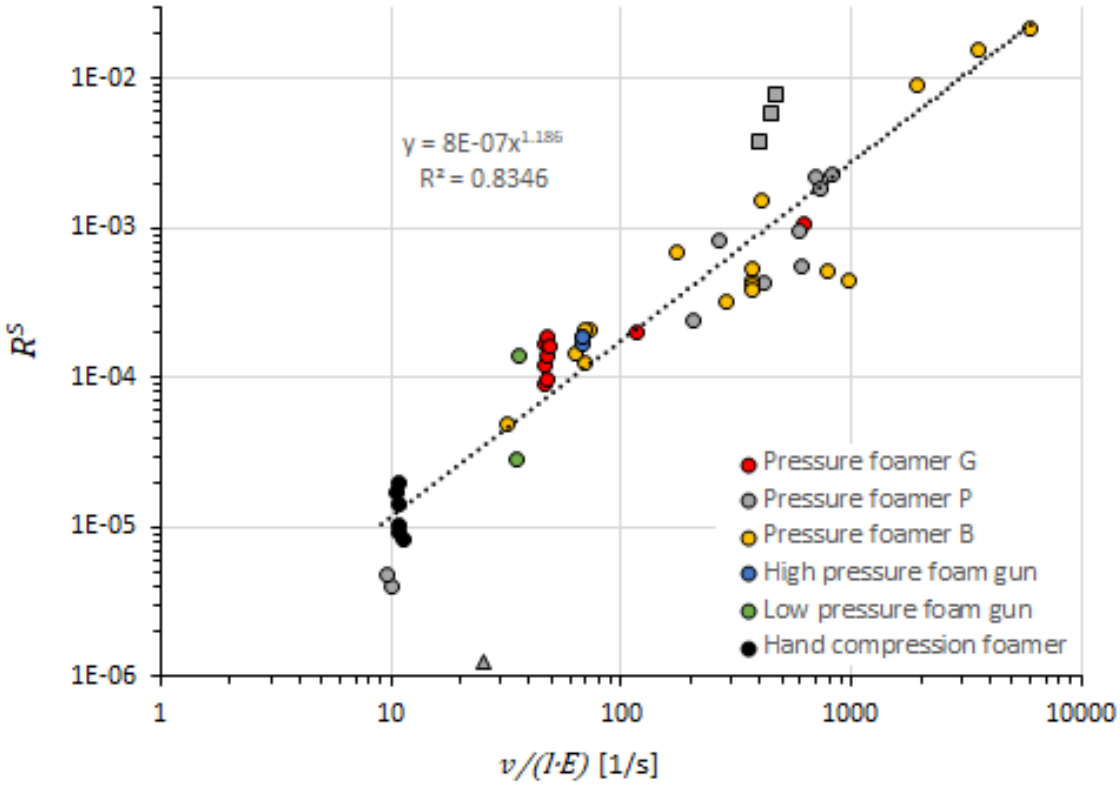


Fig. 5.10 Release fractions as a function of exit velocity, nozzle circumference and foam expansion ratio. The points result from the data for various nozzles, which were investigated in combination with the three pressure foam devices B, G and P as well as the high and low pressure foam guns in the large model room and hand compression foamer in the small room.

The volume flow rate of the foam air cannot be measured under practical field conditions. However, assuming the above relationship between the air flow rate, the foam expansion ratio, and the flow rate of the liquid formulation the release fraction can be correlated to parameters that are readily available.

The following relationship is obtained from Eq. 5.4:

(5.5)

$$R_i^s \sim \frac{v}{l \cdot E} = \frac{Q_a + Q_l}{A \cdot l \cdot E} \approx \frac{Q_l \cdot E}{A \cdot l \cdot E} = \frac{Q_l}{A \cdot l} \ .$$

This means that the foam release can be traced back to the formulation throughput and the nozzle geometry (cross sectional area, circumference). As mentioned above, the third step is an approximation only. Eq. 5.5 provides an educated guess of the existence of a relationship between the release fraction and the quantity $Q_l/(A \cdot l)$. This correlation is shown in Fig. 5.11. The tests with very low values of the foam expansion ratio of 2 and 3 (tests V40–V42), which were achieved with the very small Lechler nozzles, were not taken into account. In the case of these untypical wet foams, the conversion factor of air flow volume rate calculated from the expansion ratio and the measured flow rate was less than 0.1 instead of 0.6.

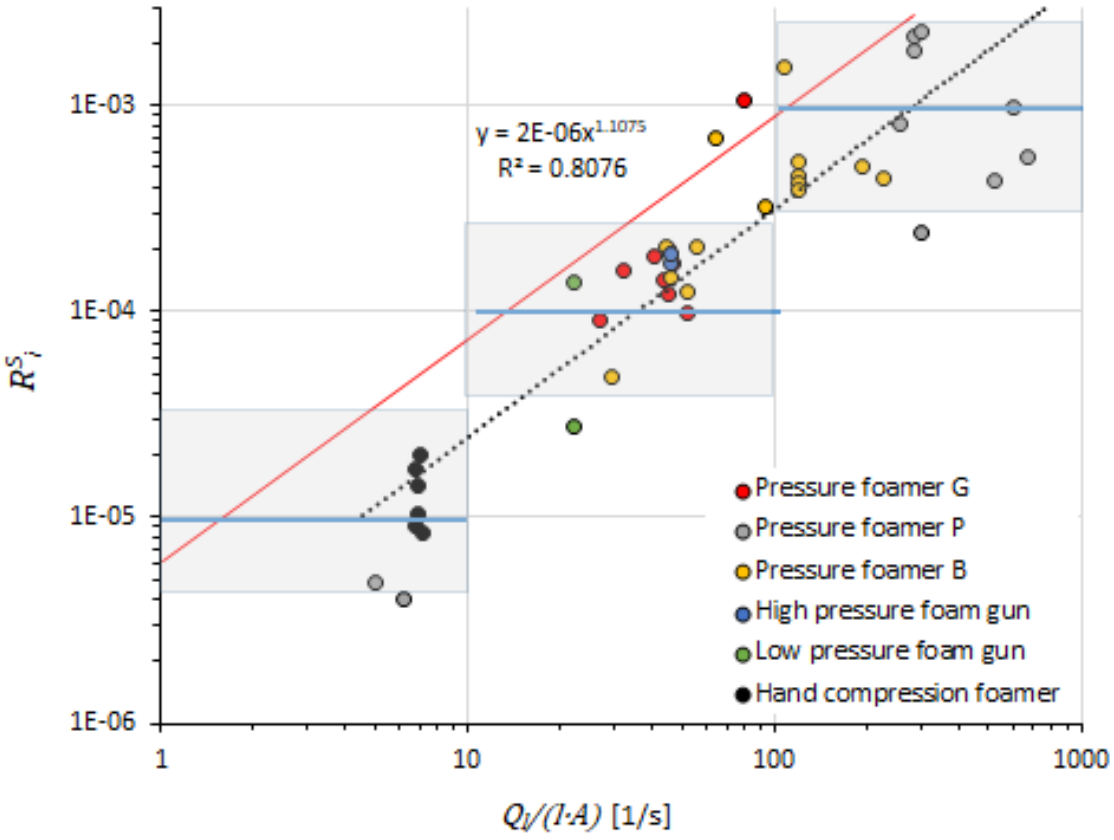


Fig. 5.11 Correlation between release fraction and a quantity derived from the nozzle geometry and the liquid throughput.

The regression coefficient is smaller than the one in Fig. 5.10, which is based on more precise process data. However, in Fig. 5.11 neither the foam expansion ratio nor the air flow rate must be determined. The liquid flow rate is easily determined from the consumption of liquid formulation and the application time. A practicable approach for a sufficiently conservative estimate of the exposure concentration would be the straight line in red:

(5.6)

$$R_i^s = 6 \cdot 10^{-6} \left(\frac{Q_l}{l \cdot A} \right)^{1.11} .$$

Another possibility of categorisation would be to select the three values marked in blue as values for the corresponding classes of the x-axis variable or to choose the ranges of values marked in grey.

This procedure can only be used for the continuously operating foam generation techniques based on air mixing. From the data set available, a release rate of $2 \cdot 10^{-3}$ can be associated to the hand pump foamer, and, for the propellant cans, a release fraction of $6 \cdot 10^{-5}$ can be applied.

The three release categories (1–3) are characterised by the values 10^{-3}, 10^{-4} and 10^{-5} (geom. mean) and a span of a factor of 10.

The pressure foamer P in combination with the fan nozzle Teejet 11006 VP and the pressure foamer B equipped with the standard nozzle H1/4U Veejet 4050 belong to class 1. The stationary devices with wide foam nozzles and high foam throughput such as the pressure foamer G as well as high and low pressure foam gun are assigned to class 2. Release class 3 covers devices with low throughput and comparatively wide foam nozzles such as the pressure foamer P with the universal foam nozzle (A = 75 m²) or the hand compression foamer with a nozzle of 95 mm² cross sectional area.

The hand pump foamer and the investigated propellant based foams (foam cans) belong to the classes 1 and 2 according to the measurements carried out.

A direct relationship between the release category and the nominal operating pressure of the process could not be found. In principle, the continuously operating foam processes are assigned to the categories via the process and nozzle parameters, liquid throughput, nozzle circumference and nozzle outlet area, which can be determined from the manufacturer's specifications.

Tab. 5.2 Data base for the corelation between aerosol release fraction and process parameters for the pre-mixed foaming systems. See also (Tab. 3.3).

Device	Test #	Q_a [l/min]	Q_l [l/min]	A [mm²]	l [mm]	v [m/s]	v/(l·E) [1/s]	Q_l/(l·A) [1/s]	E	R^s
Pressure foamer G	V7	112	5.2	61.9	31	31.6	46.6	45.1	21.8	1.2E-04
	V9	115	3.1	61.9	31	31.8	46.9	26.9	21.8	9.2E-05
	V10	113	6.0	61.9	31	32.1	47.3	52.0	21.8	9.7E-05
	V18	113	5.4	61.9	31	31.9	47.1	46.8	21.8	1.7E-04
	V20	115	5.0	61.9	31	32.3	47.7	43.3	21.8	1.4E-04
	V21	116	4.7	61.9	31	32.5	48.0	40.7	21.8	1.8E-04
	V30	120	3.7	61.9	31	33.3	49.2	32.1	21.8	1.6E-04
	V31	124	3.9	51.4	28	41.4	112.3	45.3	12.8	2.0E-04
	V32	122	3.9	34.7	23	60.5	616.7	80.2	4.2	1.1E-03
Pressure foamer P	V16	5.0	0.8	2.75	8	35.2	595.7	599.8	7.3	9.7E-04
	V17	3.0	0.3	2.75	8	20.3	266.4	254.9	9.4	8.2E-04
	V27	5.0	0.9	2.75	8	35.8	606.0	674.8	7.3	5.6E-04
	V28	4.0	0.7	2.75	8	28.5	414.6	524.9	8.5	4.3E-04
	V29	2.4	0.4	2.75	8	17.0	203.8	299.9	10.3	2.4E-04
	V52	5.4	0.2	2.75	8	34.0	466.5	150.0	9	*7.7E-03*
	V53	4.5	0.2	2.75	8	28.6	393.2	165.0	9	*3.7E-03*
	V54	5.2	0.2	2.75	8	32.9	451.5	165.0	9	*5.8E-03*
	V56	8.1	0.4	2.75	8	51.4	706.5	284.9	9	2.2E-03
	V57	9.4	0.4	2.75	8	59.4	816.5	299.9	9	2.3E-03
	V58	8.4	0.4	2.75	8	53.2	731.5	284.9	9	1.8E-03
	V60	8.7	1.8	75.4	31	2.3	25.1	13.0	3	*1.3E-06*
	V61	9.0	0.9	75.4	31	2.2	10.0	6.2	7	4.0E-06
	V62	10.0	0.7	75.4	31	2.4	9.6	5.0	8	4.9E-06

Device	Test #	Q_a [l/min]	Q_l [l/min]	A [mm²]	l [mm]	v [m/s]	v/(l·E) [1/s]	Q_l/(l·A) [1/s]	E	R^s
Pressure foamer B	V6	78	2.9	16.6	15	81.4	781.5	193.3	*6.9*	5.1E-04
	V8	40	1.4	16.6	15	41.7	287.4	93.3	*9.6*	3.8E-04
	V11	50	1.8	16.6	15	52.1	371.3	120.0	9.3	4.5E-04
	V19	56	3.4	16.6	15	59.8	965.7	226.6	4.1	4.4E-04
	V24	52	1.8	16.6	15	54.1	369.7	120.0	9.7	4.2E-04
	V25	52	1.8	16.6	15	54.1	369.7	120.0	9.7	5.4E-04
	V26	52	1.8	16.6	15	54.1	369.7	120.0	9.7	3.9E-04
	V36	48	1.8	28.0	19	29.6	73.3	55.6	21	2.1E-04
	V37	47	1.8	28.5	20	28.5	70.2	51.8	20	1.2E-04
	V38	47	1.8	28.3	23	28.6	50.3	46.4	20	1.5E-04
	V39	47	1.8	26.3	26	30.8	70.4	44.1	17	2.1E-04
	V40	45	1.7	5.8	11	134.8	5922.1	431.2	2	*2.1E-02*
	V41	45	1.7	8.2	13	94.9	3518.2	256.1	2	*1.5E-02*
	V42	46	1.8	9.5	14	84.3	1947.9	220.1	3	*9.1E-03*
	V43	46	1.8	15.8	18	50.4	408.2	107.6	7	1.5E-03
	V44	47	1.8	20.8	23	39.1	173.3	63.9	10	6.9E-04
	V45	47	1.8	37.6	27	21.6	32.1	29.6	25	5.0E-05
High pressure foam gun*	V48	33	6.5	66.4	36	9.8	68.4	45.6	4	1.9E-04
	V49	33	6.5	66.4	36	9.8	68.4	45.6	4	1.7E-04
	V49a	33	6.5	66.4	36	9.8	68.4	45.6	4	1.9E-04
Low pressure foam gun*	V50	51	5.6	75	56	12.7	34.8	22.2	6.5	2.8E-05
	V51	93	5.6	75	56	22.0	35.7	22.2	11	1.4E-04
Hand compression foamer*	KS10	19	1.4	95	35	3.5	11.4	7.2	9	8.5E-06
	KS11	18	1.3	95	35	3.3	10.7	6.7	9	9.2E-06
	KS12	18	1.4	95	35	3.4	10.9	6.9	9	1.0E-05
	KS28	13	1.4	95	35	2.5	10.8	6.9	6.8	1.4E-05
	KS29	13	1.3	95	35	2.5	10.6	6.7	6.8	1.7E-05
	KS30	13	1.4	95	35	2.6	10.9	7.0	6.8	2.0E-05

*The air flow rate of the ventury foam nozzles was estimated from the liquid flow rate, the measured foam expansion ratio and a correction factor.

5.2 Workplace measurements

Validation of the model (chapter 6) was performed for specific scenarios by conducting workplace monitoring campaigns. Dermal and inhalation exposure to non-volatile active substances of the application solution were monitored. Focus was directed towards pyrethroids in insecticides and BACs in disinfectants. Solely the spray or foam application process was sampled. Peripheral work before and after the application were not considered[12].

Potential dermal exposure to BAC and pyrethroids was captured using Tyvek® coveralls as whole body dosimeters. After the spray/foam application the Tyvek® coveralls were separated in 11 segments. Potential dermal exposure on the hands were monitored using cotton gloves as sample media. After extraction the analytes were quantified using (HS)-GC-MS analysis (chapter 3.3.3.2 and 3.3.3.4). Results regarding potential dermal exposure are given in chapter.

Inhalation exposure of the operators to BAC or pyrethroids during spray/foam applications was monitored using personal samplers. GSP samplers were operated at 3.5 or 10 L/min and analytes subsequently quantified by (HS)-GC-MS analysis (chapter 3.3.3.1 and 3.3.3.3). The low exposure during foaming compared to spraying hampered the quantification of BAC. Hence, where possible CsCl was spiked to the application solution, serving as tracer (0.1 % (w/w)). This way the limit of quantification could be lowered by a factor of 20 (BAC: 0.5 µg/filter; CsCl: 0.025 µg/filter). Results regarding inhalation exposure are given in chapter 5.2.1.

In total, 26 applications were monitored, comprising the application by i. professionals in actual workplace and simulated workplace settings (n = 6/6); ii. pest controllers in simulated workplace settings (n = 5); iii. operators in simulated workplace settings (n = 2) and simulated scenarios in model rooms (n = 7).

The applications of biocidal products involved 10 spraying and 16 foaming activities. BAC containing disinfectants were applied in 21 cases and in the remaining five events pyrethroid based pesticides. Tables in the Appendix 10 give an overview of workplaces monitored with corresponding parameters, considered active substance, application technique and the results regarding inhalation and potential dermal exposure (App. Tab. 18 to App. Tab. 27 in Appendix 10).

[12] For scenarios AP1–4, 9 and 10 the commonly encountered wiping of surfaces after their treatment was captured as well.

Tab. 5.3 Overview of monitoring campaigns – broken down into device categories and operator types[#]

Workplace monitoring	Simulation – Application by professional user	Simulation – Application by laboratory technician
Pressurised cans		
–	AP27 – Wasp control* by pest controller, indoors (foam application)	AP11, AP12 – Wasp control*, indoors (foam application)
	AP28 – insect control by pest controller, indoors (foam application)	AP13 – Wasp control*, indoors (spray application)
Handheld devices (small scale applications, e.g. tabletops)		
–	AP1, AP2 – Treatment of worktops by hygiene specialist (foam application)**	AP9 – Treatment of tabletops (foam application)**
–	AP3, AP4 –Treatment of worktops by hygiene specialist (sprayapplication)**	AP10 – Treatment of tabletops (spray application)**
Stationary devices – <3 bar (large scale applications, e.g. walls)		
AP18, AP20 – Surface disinfection in a sauna (foam application)	AP24, AP25 – surface treatment with an anti-mould product in a living room; application by a pest controller (foam application)	AP6 – Surface treatment in a model room (foam application)
AP19 – disinfection of the pool sides in an indoor swimming pool (spray application)	AP26 – surface treatment with an anti-mould product in a living room; application by a pest controller (spray application)	AP8 – Surface treatment in a model room (spray application)
Stationary devices – 3–6 bar (large scale applications, e.g. walls)		
–	–	AP5 – Surface treatment in a model room (foam application)
–	–	AP7 – Surface treatment in a model room (spray application)
High pressure devices – > 10 bar (large scale applications, e.g. disinfection of stables)		
AP15 – Disinfection of a hen house (fattening farm) (foam application)	AP14 – Disinfection of a pigsty (foam application)**	–
AP16 – Disinfection of a hen house (fattening farm) (spray application)	AP17 – Disinfection of a pigsty (spray application)**	–
AP21 – Disinfection of a pigsty (foam application)	–	–

[#] The conducted monitoring campaigns were numbered consecutively, AP1 to AP28. AP22 and AP23 were not assigned due to an inconsistency in the numbering.
* Treatment of mock-ups (e.g. wasp nest made of paper bag), **simulated workplace.

5.2.1 Dermal exposure

Within the framework of this research, in addition to inhalative exposure, potential dermal exposure was investigated by the foaming and spraying of QAC- or pyrethroid-containing biocidal products.

For this purpose, 26 coveralls and 30 pairs of gloves were obtained. In four workplaces at which disinfection by wiping was performed, gloves were changed after the foam or spray application of the biocidal product before commencing with wiping. At these workplaces, each person was sampled using one set of coveralls and two pairs of gloves; this explains the seeming discrepancy in the number of coveralls and gloves examined.

In the following sections, the measurement results for potential dermal exposure are presented and discussed. For this purpose, the absolute amount of analysed active substance on the individual coverall segments is given in µg (see App. Tab. 31), the exposure on the coveralls normalised to the amount of active substance applied in mg/kg (see App. Tab.32), and the exposure normalised to the amount of active substance applied and the relevant segment area are given in µg/(kg × cm²) (see App. Tab. 33). Supplemental information, including raw data on potential dermal exposure as quantified in the workplace measurements, are presented in Appendix 11.

5.2.1.1 Results – Potential dermal exposure on the coveralls

The absolute exposure levels on the coveralls (see App. Tab. 31) lie in the one-digit to five-digit µg-range. Mean coverall exposure amounted to 2420 ± 4490 µg (median: 492 µg; range: 1.78–15 700 µg). When evaluating exposure levels, it is important to consider that the applied amount of active substance varied widely during workplace measurements. Relating the exposure on the coveralls to the relevant amount of active substance applied (see App. Tab.32) yields mean exposures of 724 ± 1440 mg/kg (median: 65.1 mg/kg; range: 2.16–5400 mg/kg). The exposure normalised to the amount of active substance applied and to the corresponding coverall segment area can be similarly calculated (see App. Tab. 33) to be 23.9 ± 47.6 µg/(kg × cm²) (median: 2.15 µg/(kg × cm²); range: 0.071–178 µg/(kg × cm²)) (see also Tab. 5.4).)

Tab. 5.4 Potential dermal exposure on the coveralls by foaming and spraying of biocidal products (n = 26).

Exposure on the coveralls	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	2420 ± 4490	1.78	492	1700	13800	15700
Expsoure normalised to the amount of active substance applied [mg/kg]	724 ± 1440	2.16	65.1	346	3710	5400
Exposure normalised to the amount of active substance applied and the relevant coverall segment area [µg/(kg × cm²)]	23.9 ± 47.6	0.071	2.15	11.4	123	178

Disinfection by wiping was sampled at workplaces #1 to #4, #9, and #10, whereby the biocidal product was spread by wiping following application. At workplaces #1 to #4, work surfaces at a height of 90 cm were disinfected, while, at workplaces #9 and #10,

the treated tabletops were at a height of 75–80 cm. During the distribution of the biocidal product by wiping in applications #1–#4, the worker's forearms came into contact with the applied biocidal product as well as the still-wet work surfaces. This fact is reflected in Coveralls #1–#4 by the high exposure on the corresponding right-forearm segment of the coveralls, as the worker was right-handed (see App. Tab. 31). These coverall segments represent 77–92 % of total coverall exposure (see App. Tab. 42).

If it becomes necessary to separately determine the potential dermal exposure on these coveralls analogous to the gloves with regard to application and wiping, it is possible to include the exposure on the right forearm after wiping to the exposure on the remaining coverall segments after application as well as to the exposure on the entire set of coveralls after application and wiping. Through this procedure, the relatively high exposures may become distorted as a result of the process of wiping, not due to the data sets of coverall exposure by the simple foaming and spraying of the biocidal products (Tab. 5.5).

Tab. 5.5 Potential dermal exposured quantified on the coveralls.

Coverall No.	Absolute exposure [µg]	Exposure normalised to the amount of active substance applied [mg/kg]	Exposure normalised to the amount of active substance applied and the relevant coverall segment area [µg/(kg × cm²)]
1 (Application)[a]	205	394	–[c]
1 (Wiping)[b]	1810	3490	–[c]
1 (Application + Wiping)	2020	3880	128
2 (Application)[a]	33.2	329	–[c]
2 (Wiping)[b]	289	2860	–[c]
2 (Application + Wiping)	322	3190	105
3 (Application)[a]	65.9	431	–[c]
3 (Wiping)[b]	760	4970	–[c]
3 (Application + Wiping)	826	5400	178
4 (Application)[a]	73.7	679	–[c]
4 (Wiping)[b]	253	2330	–[c]
4 (Application + Wiping)	327	3010	99.5
5	55.6	3.34	0.110
6	127	27.4	0.904
7	383	20.0	0.659
8	34.2	26.7	0.883
9 (Application+ Wiping)	57.5	64.2	2.12
10 (Application + Wiping)	327	394	13.0
11	1.78	2.16	0.071
12	81.4	146	4.82
13	356	1070	35.2
14	1000	200	6.60
15	1370	11.9	0.393
16	1810	13.4	0.444
17	10800	81.5	2.69

Coverall No.	Absolute exposure [µg]	Exposure normalised to the amount of active substance applied [mg/kg]	Exposure normalised to the amount of active substance applied and the relevant coverall segment area [µg/(kg × cm²)]
18	752	66.0	2.18
19	637	9.83	0.325
20	325	28.5	0.941
21	7190	48.6	1.60
24	15700	83.4	2.75
25	2830	17.8	0.587
26	14800	149	4.93
27	600	842	27.8
28	147	21.3	0.703

[a] Coveralls without right forearm
[b] Only right forearm
[c] Areal presentation of results would not be meaningful

Tab. 5.6 and Tab. 5.7 present the exposure on the coveralls following application of the biocidal products (n = 24) as well as following application and wiping (n = 6).

Tab. 5.6 Potential dermal exposure on the coveralls following foaming or spraying of the biocidal products (n = 24) (application only, without #9, #10).

Exposure on the coveralls	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	2480 ± 4680	1.78	370	1480	14200	15700
Exposure normalised to the amount of active substance applied [mg/kg]	196 ± 291	2.16	57.3	232	818	1070
Exposure normalised to the amount of active substance applied and the relevant coverall segment area [µg/(kg × cm²)]	6.57 ± 9.71	0.071	1.89	7.78	27.1	35.2

Tab. 5.7 Potential dermal exposure on the coveralls following foaming or spraying of the biocidal products with handheld devices[a] (n = 6) (application and wiping, #1–#4, #9, #10).

Exposure on the coveralls	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	646 ± 717	57.5	327	701	1720	2020
Exposure normalised to the amount of active substance applied [mg/kg]	2660 ± 2060	64.2	3100	3710	5020	5400
Exposure normalised to the amount of active substance applied and the relevant coverall segment area [µg/(kg × cm²)]	87.8 ± 68.1	2.12	102	123	166	178

[a] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer

In workplace measurements 1–4, gloves were changed after application of the biocidal product, thereby allowing for the separate measurement of hand exposure by application or by wiping. In the following sections, the exposure on the coveralls will be evaluated accordingly for these measurements. For the process of wiping, the exposure on the right forearm is considered; for the application of the biocidal product, the exposure on the remaining coverall segments is considered (see Tab. 5.5). The data thus calculated is presented in Tab. 5.8. The difference in exposure after only application or only wiping is clearly evident here, and the median values vary by a factor of about 8.

Tab. 5.8 Potential dermal exposure on the relevant coverall segments following foaming or spraying of the biocidal product with handheld devices[a] (n = 4, #1–#4).

	Mean ± SD	**Minimum**	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Absolute exposure on the coverall segments [µg]						
Application[b]	94.4 ± 75.6	33.2	69.8	106	185	205
Wiping[c]	779 ± 728	253	524	1020	1660	1810
Exposure normalised to the amount of active substance applied [mg/kg]						
Application[b]	458 ± 153	329	412	493	642	679
Wiping[c]	3410 ± 1140	2330	3180	3860	4750	4970

[a] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer
[b] Coveralls without right forearm
[c] Only right forearm

5.2.1.2 Results – Potential dermal exposure on the gloves

App. Tab. 34 depicts the exposure on the gloves following foaming and spraying of the biocidal product. The table presents the absolute amount of active substance on the gloves in µg as well as the exposure normalised to the applied amount of active substance in mg/kg. For the calculation of the exposure related to the applied amount of active substance and the segment area [µg/(kg × cm²)], an area of 410 cm² per hand was used, in accordance with Recommendation 14 of the ECHA "Ad hoc Working Group on Human Exposure" ["Default human factor values for use in exposure assessments for biocidal products",12 June 2017].

The cotton gloves used were also measured, yielding an area of 600 cm^2 per glove, a value that even accounts for the short cuffs of the gloves. Because the coveralls were worn over the glove cuffs during workplace measurements, it is reasonable to utilise an area of 410 cm^2 per hand for normalising potential dermal exposure on the gloves.

Regarding the quantified exposure on the gloves (App. Tab. 34), the glove pairs in measurements #1 to #4, as well as in measurements #9 and #10, are especially conspicuous. For these applications, the biocidal product was applied for disinfection by wiping on small surfaces using handheld devices like hand pump foamer and sprayer as well as hand compression foamer and sprayer. Following application, the product was evenly spread by wiping. For generally small amounts of biocidal active substances, this type of application led to absolute exposures in the four- to five-digit µg

range. For the exposure data normalised to the amount of active substance applied, the difference compared to the exposure on the remaining glove pairs is even more evident.

When considering the simple foaming and spraying of the biocidal products, measurements #9 and #10 cannot be considered for the summary in Tab. 5.9, as the exposure on these gloves reflects both application and wiping.

Tab. 5.9 Potential dermal exposure on the gloves by foaming and spraying of biocidal products (application only, without #9, #10) (n = 24).

Exposure on the gloves	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	3440 ± 13900	0.295	210	1050	4320	68700
Exposure normalised to the amount of active substance applied [mg/kg]	101 ± 139	0.192	23.3	140	390	449
Exposure normalised to the amount of active substance applied and glove area [µg/(kg × cm²)]	123 ± 170	0.234	28.4	171	475	548

The absolute glove exposures given in Tab. 5.9 by simple application of the biocidal products vary substantially over six orders of magnitude. Mean glove exposure was about 3440 ± 13 900 µg (median: 210 µg; range: 0.295–68 700 µg). As in previous sections, it is important to consider the varying amounts of active substance applied during measurement when evaluating exposure levels. Normalising exposure levels – as with the coveralls – to the relevant applied amount of active substance yields mean exposures of 101 ± 139 mg/kg (median: 23.3 mg/kg; range: 0.192–449 mg/kg). Accordingly, the exposure normalised to the amount of active substance applied and to the glove area was calculated to be 123 ± 170 µg/(kg × cm²) (median: 28.4 µg/(kg × cm²); range: 0.234–548 µg/(kg × cm²)).

When considering the homogenous distribution of the biocidal product by wiping in addition to application, the glove exposure levels are considerably higher (n = 6). Considering only workplace measurements #1–#4, #9, and #10 yields a mean glove exposure of 19 300 ± 17 600 µg (median: 12 600 µg; range: 5550–52 800 µg). Relating exposure levels to the relevant applied amounts of active substance yields mean exposures of 59 500 ± 34 000 mg/kg (median: 64 800 mg/kg; range: 15 100–102 000 mg/kg). Accordingly, the exposure normalised to the amount of active substance applied and to the glove area was calculated to be 72 500 ± 41 500 µg/(kg × cm²) (median: 79 000 µg/(kg × cm²); range: 18 400–124 000 µg/(kg × cm²)) (see also Tab. 5.10).

Tab. 5.10 Potential dermal exposure on the gloves by foaming and spraying of biocidal products with handheld devices[a] (n = 6) (application and wiping, #1–#4, #9, #10).

Exposure on the gloves	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	19300 ± 17600	5550	12600	21500	45700	52800
Exposure normalised to the amount of active substance applied [mg/kg]	59500 ± 34000	15100	64800	82100	97000	102000
Exposure normalised to the amount of active substance applied and to the glove area [µg/(kg × cm²)]	72500 ± 41500	18400	79000	100000	118000	124000

[a] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer

The glove exposures quantified in workplaces #1 to #4 allow for separate evaluation following application and wiping activities. Tab. 5.11 summarises hand exposure after application of the biocidal product (n = 4) as well as exposure following distribution of the product by wiping (n = 4). Exposures are given here as absolute values, as values normalised to the amount of active substance applied, and additionally as values normalised to the area of both hands (820 cm^2).

Tab. 5.11 Potential dermal exposure on the gloves by foaming and spraying of biocidal products with handheld devices[a] (n = 4, #1–#4).

Exposure on the gloves	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure on the gloves [µg]						
Application	26.6 ± 20.7	7.62	25.0	42.0	47.4	48.7
Wiping	19700 ± 22300	5500	10300	22800	46800	52800
Exposure normalised to amount of active substance applied [mg/kg]						
Application	228 ± 225	19.9	222	408	441	449
Wiping	78400 ± 21100	50700	80700	87900	98800	102000
Exposure normalised to amount of active substance applied and glove area [mg/(kg*cm²)]						
Application	278 ± 274	24.3	271	497	538	548
Wiping	95600 ± 25700	61800	98400	107000	121000	124000

[a] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer

When reviewing the data presented in Tab. 5.11, it becomes clear that, when disinfecting by wiping, hand exposure primarily occurs through the spreading of the applied biocidal product by wiping. A factor of 350–400 lies between the median values. What begins to emerge is the clear effect that wiping leads to higher exposure levels on the gloves compared to the coveralls. (see Tab. 5.8).

5.2.1.3 Results – Potential total dermal exposure

Potential total dermal exposure can be calculated by summing up the measured exposure levels on the coveralls with those of the gloves. Tab. 5.12 presents these measured total exposure levels by foaming or by spraying. Absolute exposure is given in µg, and exposure normalised to the applied amount of active substance is given in mg/kg. The last column of Tab. 5.12 gives the percentage of hand exposure to total exposure (100 %).

For measurements #1 to #4, three different total exposure levels are given for each measurement: potential dermal exposure after simple application of the biocidal product; exposure after wiping; and finally, total exposure after both application and wiping.

Tab. 5.12 Potential total dermal exposure by foaming and spraying of biocidal products.

	Absolute exposure [µg]			**Exposure normalised to the amount of active substance applied [mg/kg]**			**Proportion of hand exposure to total exposure [%]**
Measurement	**Coveralls**	**Gloves**	**Total**	**Coveralls**	**Gloves**	**Total**	
1 (Application)	205[a]	10.3	**215**	394[a]	19.9	**414**	**4.80**
1 (Wiping)	1810[b]	52800	**54600**	3490[b]	102000	**105000**	**96.7**
1 (Application + Wiping)	2020	52800	**54800**	3880	102000	**105000**	**96.3**
2 (Application)	33.2[a]	39.7	**72.9**	329[a]	394	**723**	**54.5**
2 (Wiping)	289[b]	7870	**8150**	2860[b]	78000	**80900**	**96.5**
2 (Application + Wiping)	322	7900	**8230**	3190	78400	**81600**	**96.1**
3 (Application)	65.9[a]	7.62	**73.5**	431[a]	49.8	**480**	**10.4**
3 (Wiping)	760[b]	12700	**13500**	4970[b]	83300	**88300**	**94.4**
3 (Application + Wiping)	826	12800	**13600**	5400	83400	**88800**	**93.9**
4 (Application)	73.7[a]	48.7	**122**	679[a]	449	**1130**	**39.8**
4 (Wiping)	253[b]	5500	**5750**	2330[b]	50700	**53000**	**95.6**
4 (Application + Wiping)	327	5500	**5870**	3010	51100	**54100**	**94.4**
5	55.6	207	**263**	3.34	12.5	**15.8**	**78.9**
6	127	49.3	**176**	27.4	10.6	**38.0**	**27.9**
7	383	330	**713**	20.0	17.2	**37.1**	**46.2**
8	34.2	22.3	**56.5**	26.7	17.4	**44.1**	**39.4**
9 (Application + Wiping)	57.5	24400	**24500**	64.2	27300	**27300**	**99.8**
10 (Application + Wiping)	327	12500	**12800**	394	15100	**15400**	**97.4**
11	1.78	213	**215**	2.16	258	**261**	**99.2**
12	81.4	0.295	**81.6**	146	0.529	**147**	**0.361**
13	356	71.8	**428**	1070	215	**1280**	**16.8**

	Absolute exposure [µg]			Exposure normalised to the amount of active substance applied [mg/kg]			Proportion of hand exposure to total exposure [%]
Measurement	**Coveralls**	**Gloves**	**Total**	**Coveralls**	**Gloves**	**Total**	
14	1000	1180	**2180**	200	235	**435**	**54.1**
15	1370	297	**1660**	11.9	2.59	**14.5**	**17.9**
16	1810	95.9	**1910**	13.4	0.711	**14.1**	**5.02**
17	10800	1440	**12200**	81.5	10.9	**92.4**	**11.8**
18	752	1010	**1770**	66.0	88.9	**155**	**57.4**
19	637	12.4	**649**	9.83	0.192	**10.0**	**1.91**
20	325	305	**630**	28.5	26.7	**55.2**	**48.4**
21	7190	1460	**8650**	48.6	9.84	**58.4**	**16.8**
24	15700	68700	**84400**	83.4	364	**448**	**81.4**
25	2830	1890	**4720**	17.8	11.8	**29.6**	**40.0**
26	14800	4750	**19600**	149	47.8	**197**	**24.2**
27	600	82.3	**683**	842	115	**957**	**12.1**
28	147	427	**574**	21.3	62.0	**83.3**	**74.4**

[a] Coveralls without right forearm
[b] Only right forearm

In summary, workplace measurements should first be considered in which the biocidal product was exclusively applied (n = 24). Here, the absolute total exposure levels vary by over three orders of magnitude. Mean total exposure was calculated to be 5920 ± 17 400 µg (median: 639 µg; range: 56.5–84 400 µg). Because different amounts of active substance were applied in different measurements, total exposure was also calculated normalised to the relevant amount of active substance applied. This computation yielded mean exposure levels of 297 ± 374 mg/kg (median: 119 mg/kg; range: 10.0–1280 mg/kg).

Considering the proportion of hand exposure to total exposure, 36.0 ± 28.2 % (median: 33.7 %; range: 0.361–99.2 %) of the total exposure is found on the hands. This data is further summarised in Tab. 5.13.

Tab. 5.13 Potential total dermal exposure by foaming and spraying of biocidal products (n = 24) (application only, without #9, #10).

Total exposure	**Mean ± SD**	**Minimum**	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Absolute exposure [µg]	5920 ± 17400	56.5	639	1980	18500	84400
Exposure normalised to the amount of active substance applied [mg/kg]	297 ± 374	10.0	119	438	1100	1280
Proportion of hand exposure to total exposure [%]	36.0 ± 28.2	0.361	33.7	54.2	81.0	99.2

The following sections will summarise those total exposure levels which reflect sampler exposure for both the application of the biocidal product and its distribution by wiping (n = 6).

The absolute total exposure levels lie in the four- to five-digit µg range. On average, total exposure levels were calculated to be 20 000 ± 18 200 µg (median: 13 200 µg; range: 5870–54 800 µg). Exposure calculated normalised to the applied amount of active substance yielded mean exposure levels of 62 100 ± 35 800 mg/kg (median: 67 900 mg/kg; range: 15 400–105 000 mg/kg).

Considering the proportion of hand exposure to total exposure, 96.3 ± 2.12 % (median: 96.2 %; range: 93.9–99.8 %) of the total exposure is found on the hands. This data is further summarised in Tab. 5.14.

Tab. 5.14 Potential total dermal exposure by foaming and spraying of biocidal products with handheld devices[a] (n = 6) (application and wiping, #1–#4, #9, #10).

Total exposure	Mean ± SD	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure [µg]	20000 ± 18200	5870	13200	21700	47200	54800
Exposure normalised to the amount of active substance applied [mg/kg]	62100 ± 35800	15400	67900	87000	101000	105000
Proportion of hand exposure to total exposure [%]	96.3 ± 2.12	93.9	96.2	97.2	99.2	99.8

[a] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer

It becomes clear at this point that, in workplace measurements #1 to #4, #9, and #10, at which disinfection by wiping was performed, potential total dermal exposure is primarily determined by the exposure on the hands and forearms during the process of wiping.

5.2.1.4 Evaluation of the results

The evaluation of the results requires further categorisation of the obtained data. On one hand, the primary question stands as to whether foam or spray applications differ from one another in terms of potential dermal exposure. On the other hand, the secondary question remains as to whether the type of application device leads to differences in exposure levels.

Comparison between foaming and spraying

In order to compare the application types of foaming and spraying, the data sets by which only application was sampled must first be considered (n = 24). When dividing the data into foam application and spray application, no differences between the application types can be detected, neither in the absolute exposure [µg], nor in the exposure normalised to the amount of active substance applied [mg/kg], nor in the exposure which is additionally normalised to the relevant segment areas [µg/(kg × cm²)]. This observation holds equally true for exposure on the coveralls, as well as for exposure on the gloves and for total exposure.

Fig. 5.12 shows the box-plot diagram of the samplers' exposure levels normalised to the amount of active substance applied and to the relevant areas of the sampling media. Box-plot diagrams of the absolute exposure or of the exposure normalised to the amount of active substance applied can be found in the Appendices App. Fig. 13 and App. Fig.14. The relevant data for foam and spray applications is summarised in App. Tab. 35 to App. Tab. 37.

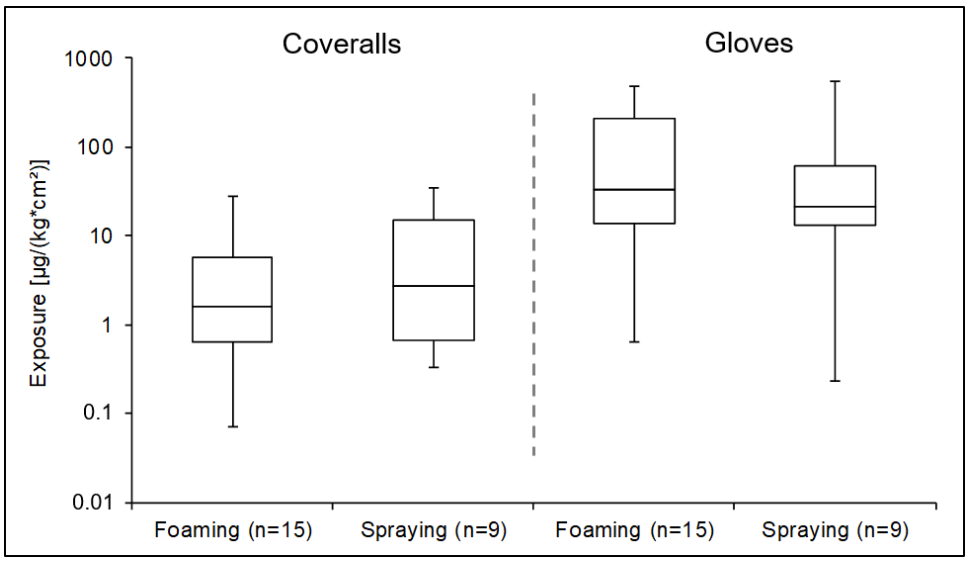


Fig. 5.12 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application only, without #9, #10). The figure shows samplers' exposure normalised to the amount of active substance applied and to the relevant area of the sampling media [µg/(kg × cm²)].

Additionally, measurements in which both application and wiping were sampled allow for evaluation regarding the type of application. The relevant box-plot diagrams are presented in Fig. 5.13 to Fig. 5.15, and the corresponding data for foaming and spraying applications is summarised in Tab. 5.15 to Tab. 5.17.

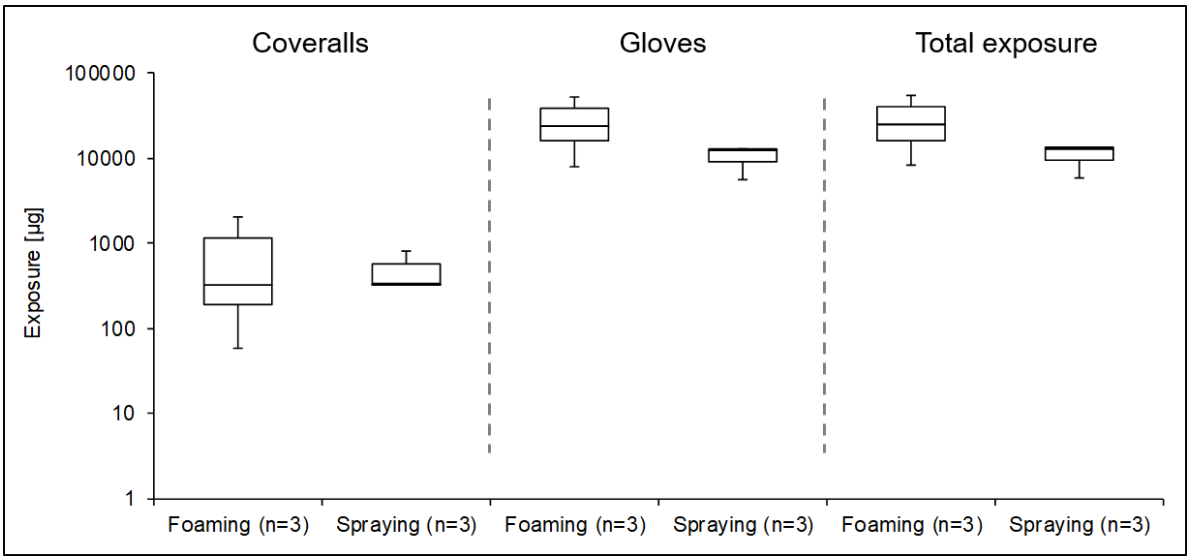


Fig. 5.13 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application and wiping, #1–#4, #9, #10). The figure shows the samplers' absolute exposure [µg].

Tab. 5.15 Absolute exposure on samplers after foaming or spraying of biocidal products [µg] (application and wiping, #1–#4, #9, #10). Evaluation per application type.

	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Absolute exposure on the coveralls [µg]					
Foam (n = 3)	57.5	322	1170	1850	2020
Spray (n = 3)	327	327	577	776	826
Absolute exposure on the gloves [µg]					
Foam (n = 3)	7900	24400	38600	50000	52800
Spray (n = 3)	5550	12500	12600	12700	12800
Absolute total exposure [µg]					
Foam (n = 3)	8230	24500	39600	51800	54800
Spray (n = 3)	5870	12800	13200	13500	13600

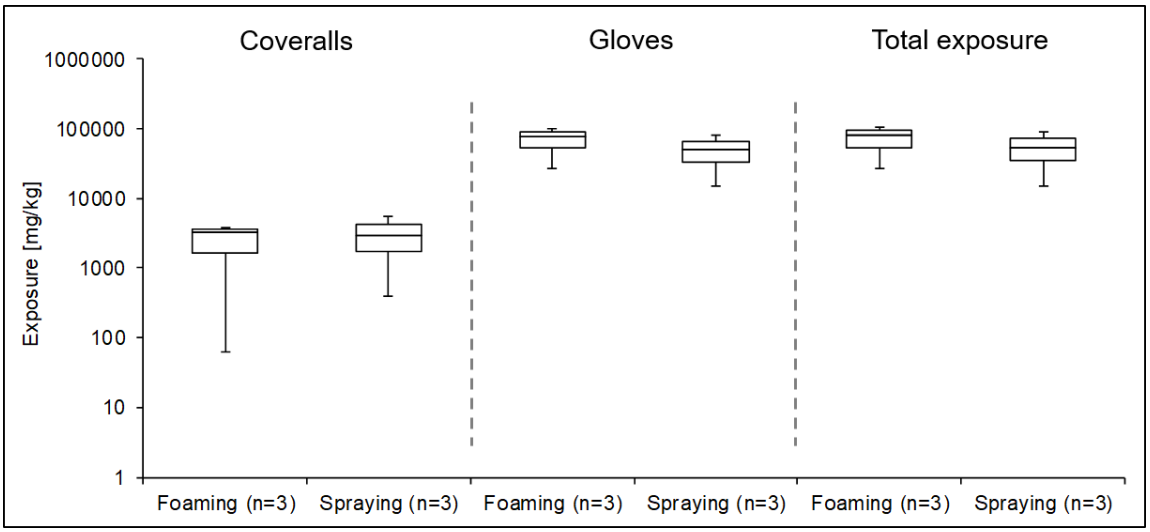


Fig. 5.14 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application and wiping, #1–#4, #9, #10). The figure shows the samplers' exposure normalised to the amount of active substance applied [mg/kg].

Tab. 5.16 Samplers' exposure normalised to the applied amount of active substance after foaming or spraying of biocidal products [mg/kg] (application and wiping, #1–#4, #9, #10). Evaluation per application type.

	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Exposure normalised to the applied amount of active substance on the coveralls [mg/kg]					
Foam (n = 3)	64.2	3190	3540	3810	3880
Spray(n = 3)	394	3010	4210	5160	5400
Exposure normalised to the applied amount of active substance on the gloves [mg/kg]					
Foam (n = 3)	27300	78400	90000	99300	102000
Spray (n = 3)	15100	51100	67300	80200	83400
Total exposure normalised to the applied amount of active substance [mg/kg]					
Foam (n = 3)	27300	81600	93500	103000	105000
Spray(n = 3)	15400	54100	71500	85300	88800

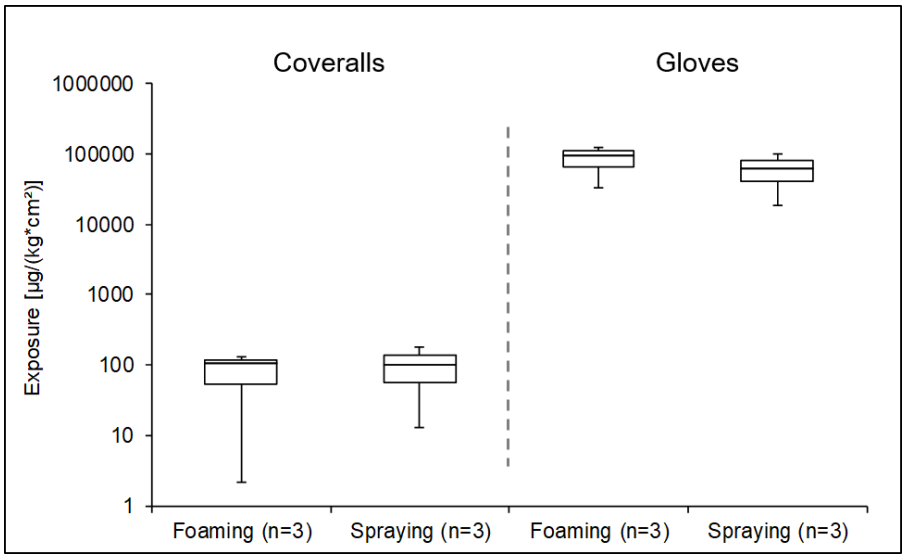


Fig. 5.15 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application and wiping, #1–#4, #9, #10). The figure shows the samplers' exposure normalised to the amount of active substance applied and to the relevant area of the sampling media [µg/(kg × cm²)].

Tab. 5.17 Samplers' exposure normalised to amount of active substance applied and exposure normalised to the relevant area of the sampling media after foaming or spraying of biocidal products [µg/(kg × cm²)] (application and wiping, #1–#4, #9, #10). Evaluation per application type.

	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Exposure normalised to the amount of active substance applied and to the area of the coveralls [µg/(kg × cm²)]					
Foam (n = 3)	2.12	105	117	126	128
Spray (n = 3)	13.0	100	139	170	178
Exposure normalised to the amount of active substance applied and to the area of the gloves [µg/(kg × cm²)]					
Foam (n = 3)	33300	95600	110000	121000	124000
Spray (n = 3)	18400	62400	82000	97800	102000

In the measurements in which both the application of the biocidal product and its distribution by wiping were sampled, there is no evident difference between application types. Neither the coveralls nor the gloves show a recognisable difference in exposure following application by foaming or by spraying.

The heightened exposure on the gloves is, however, clearly recognisable, and can be ascribed to the process of wiping (Fig. 5.13 and Fig 5.15).

In principle, it is not surprising that there is no significant difference to be seen when comparing the application types of foaming and spraying. With regard to dermal exposure, such a difference between application types would only be prevalent with aerosol deposition. In real-world measurements, high exposure levels on the coveralls and

gloves can mainly be ascribed to direct contact with biocidal products, contaminated application devices, or recently treated surfaces.

In order to conceive the potential dermal exposure caused by aerosol deposition, the following sections will only consider the five least exposed coverall segments. Using the data from App. Tab. 33, which provides exposure normalised to the area per kilogram of active substance applied, the exposure levels of each of the five least exposed segments – with the differing areas of each segment taken into account – are investigated. The „dermal exposure levels by aerosol deposition“ thus calculated are sorted by application type and presented as box-plot diagram in Fig. 5.16. In this depiction, a difference clearly arises between foaming and spraying applications, and the medians vary by a factor of 3.8. The data for this box-plot diagram are summarised in Tab. 5.18.

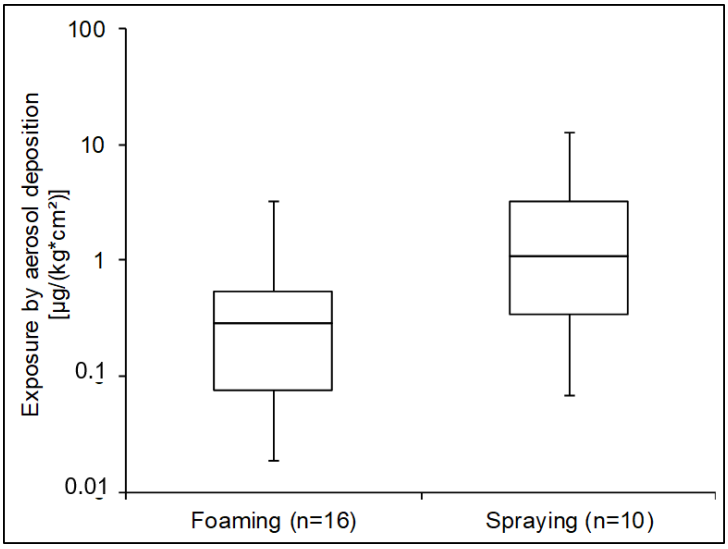


Fig. 5.16 Box-plot diagram of “dermal exposure levels by aerosol deposition.” The figure shows exposure normalised to the amount of active substance applied and to the relevant segment area for the five least exposed coverall segments [µg/(kg × cm²)].

Tab. 5.18 Exposure normalised to the amount of active substance applied and to the relevant segment area for the five least exposed coverall segments [µg/(kg × cm²)]. Evaluation per application type.

Exposure normalised to the amount of active substance applied and to the relevant segment area [µg/(kg × cm²)]	**Minimum**	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Foam (n = 16)	0.019	0.286	0.539	1.82	3.28
Spray (n = 10)	0.067	1.10	3.24	8.86	12.9

In order to ensure that the differences in aerosol deposition are commensurate with the individual measurements, the data is directly compared for which the application in question was carried out once by foaming and once by spraying. Application via

handheld devices[13] is colour-coded in shades of blue, application with pressurised cans is coded in shades of red, and application via devices for large-scale applications is coded in shades of green. Fig. 5.17 shows the data sets with logarithmically scaled axes. Excluding Coveralls #14 and #17, the individual measurements show a recognisable increase in dermal exposure by aerosol deposition when the biocidal product is applied by spraying rather than by foaming.

That Coveralls #14 and #17 show no increase in potential dermal exposure for the least exposed coverall segments in the comparison between foaming and spraying application may be explained by the fact that measurements 14 and 17 comprised disinfecting a small pigsty which was divided into smaller sections with gridded fencing. The biocide user had to move the fencing and had a lot of direct contact with already-treated surfaces. The numerous structures also presented the risk that large sections of the sampler coveralls could be homogenously contaminated by backsplash of the application solution.

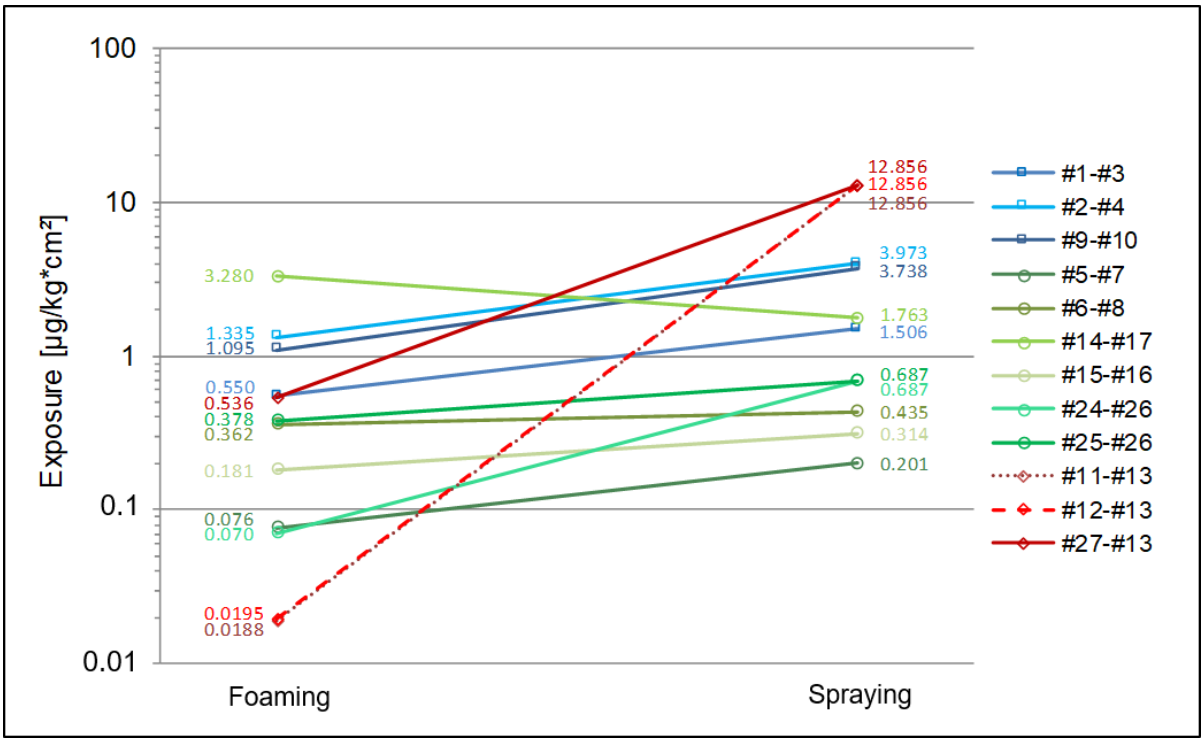


Fig. 5.17 "Dermal exposure levels by aerosol deposition" – direct comparison of the measurements. The figure shows exposure normalised to the amount of active substance applied and to the relevant segment area of **the five least exposed** coverall segments [µg/(kg × cm²)].

Fig. 5.17 shows a grouping of data sets depending on application device, which can be more clearly recognised in the box-plot diagram shown in Fig. 5.18.

[13] Handheld devices: hand pump foamer and spray (bottles) as well as hand compression foamer and sprayer

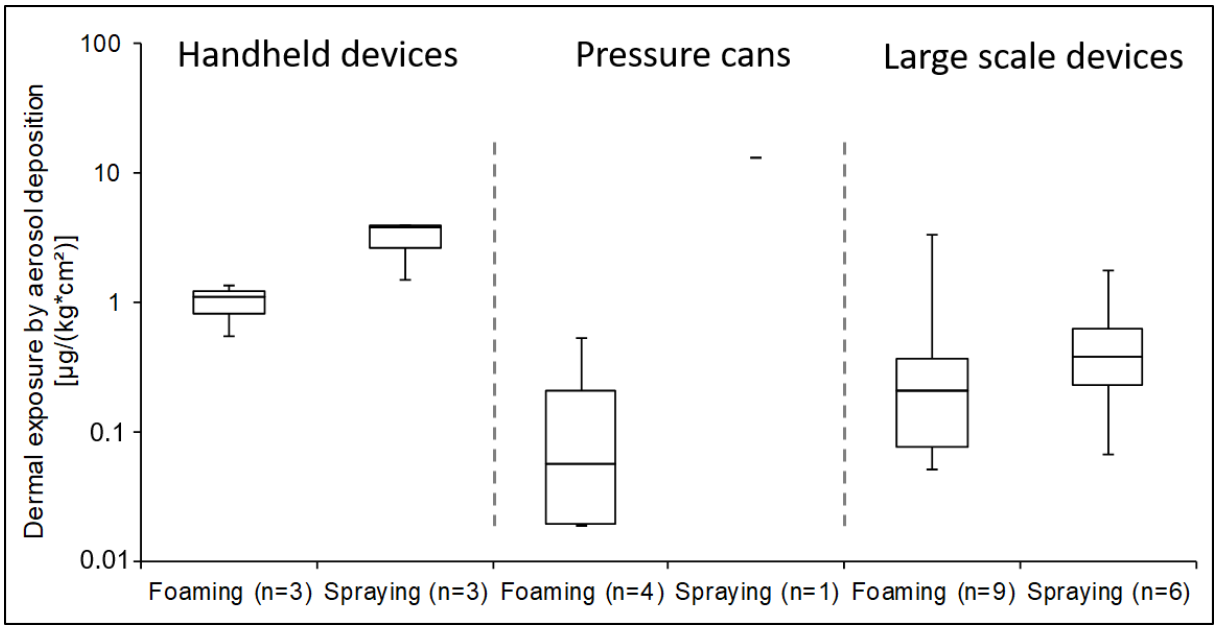


Fig. 5.18 Box-plot diagrams of "dermal exposure levels by aerosol deposition" in different device types. The figure shows exposure normalised to the amount of active substance applied and to the relevant segment area for the five least exposed coverall segments [µg/(kg × cm²)].

Comparison of application devices

When the measurement results (application only) are classified into handheld devices (hand pump foamer or sprayer (bottles) as well as hand compression foamer and sprayer; operating pressure < 3 bar with a volumetric capacity of less than 2 L), pressurised cans (propellant cans for application by foaming or spraying), and stationary or semi-stationary devices (devices for large-scale applications; operation pressure 3–6 bar as well as high pressure, each with a volumetric capacity greater than 2 L), it is possible to recognise differences when considering absolute exposure [µg], exposure normalised to the applied amount of active substance [mg/kg], as well as exposure additionally normalised to the relevant segment areas [µg/(kg × cm²)]. This difference is graphically clarified by the box-plot diagrams for exposure normalised to the applied amount of active substance in [mg/kg], as shown in Fig. 5.19, as well as in the additional box-plot diagrams in the Appendix (App. Fig. 15 and App. Fig. 16). The numerical values for application with different device types are summarised in App. Tab. 39 to App. Tab. 41.

The compiled exposure values normalised to the amount of active substance applied (Fig. 5.19) are highest both for the coveralls and for the gloves following application with handheld foam and spray devices, followed by pressurised cans and devices for large-scale application. In the graphical representation of absolute exposure (App. Tab. 15), the higher exposure levels of the coveralls and gloves after large-scale application was clearly evident, which can be primarily attributed to the large applied amounts of active substance.

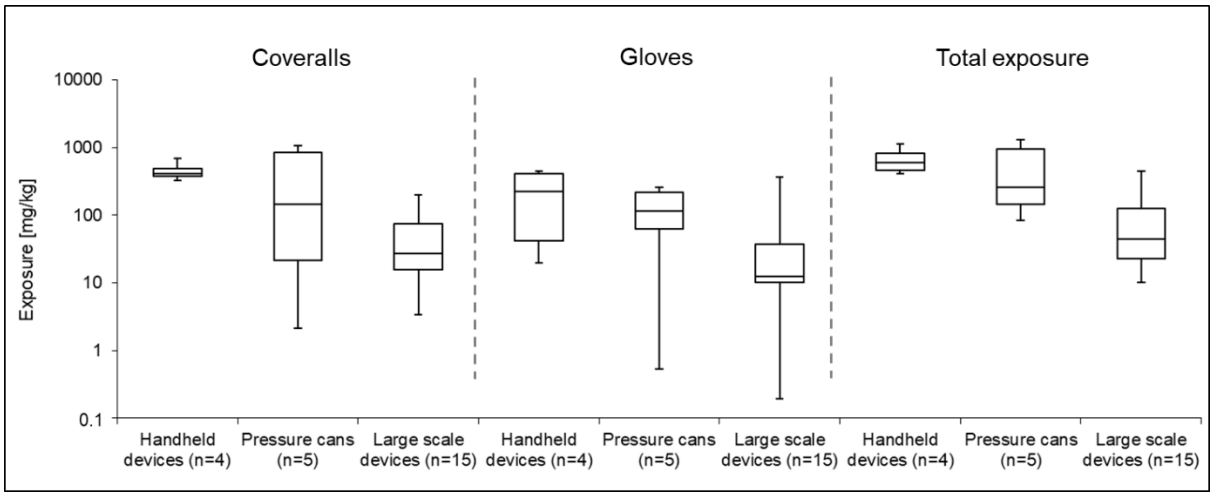


Fig. 5.19 Box-plot diagrams of potential dermal exposure after foaming or spraying of biocidal products (application only). The figure shows samplers' exposure normalised to the applied amount of active substance [mg/kg] due to application with different application devices.

Exposure patterns on the coveralls

In order to recognise exposure patterns and focal points on the coveralls, the quantified amounts of active substance on the individual coverall segments were divided by the area of the corresponding segment and by the amount of active substance applied. The values thus calculated, given in units of µg/(kg × cm²), were averaged for each individual application type and used in this way for graphical representation (Fig. 5.20). In Fig. 5.20, minimally exposed areas of the body are shown in green; moderately exposed areas of the body are shown in yellow; and highly exposed areas of the body are shown in red.

Appendix 11 shows a table (App. Tab. 43) with the data used for the figure shown below and a detailed discussion of exposure patterns is given.

For handheld devices[14], the high exposure levels of the forearms and of the breast/stomach area were especially notable. From these focal points of exposure, it is clear that the treated surfaces were at about the height of the user's hips or stomach, and that the biocide user stood in front of the surface in question. It is further evident that, when wiping by hand, the forearms primarily came into contact with the biocidal product. There was no noticeable difference between application by foaming and spraying in this case.

During application with pressurised cans for foaming and spraying, the forearms are also highly exposed. These measurements showed that the coverall was more heavily exposed after spraying the biocidal product compared to foaming. The numerical values seen in App. Tab. 42 and App. Tab. 43 also indicate the precipitation of spraying mists onto the user (#13) by way of high exposure levels on the coverall hood and

[14] Handheld devices: hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer

upper arms; moderate exposure levels on the breast, stomach, and back; and relatively low exposure levels on the legs.

The usage of foaming and spraying devices for large-scale application clearly shows homogenous but relatively low exposure on the coveralls. A difference between foaming and spraying applications could not be observed. A tendency towards lower exposure levels was shown on the hood, forearms, and back when compared to the breast/stomach area and the lower legs. When comparing different application devices, it is important to consider that, with devices for large-scale application, much larger amounts of active substance are applied, which is not reflected by the data presented in Fig. 5.20.

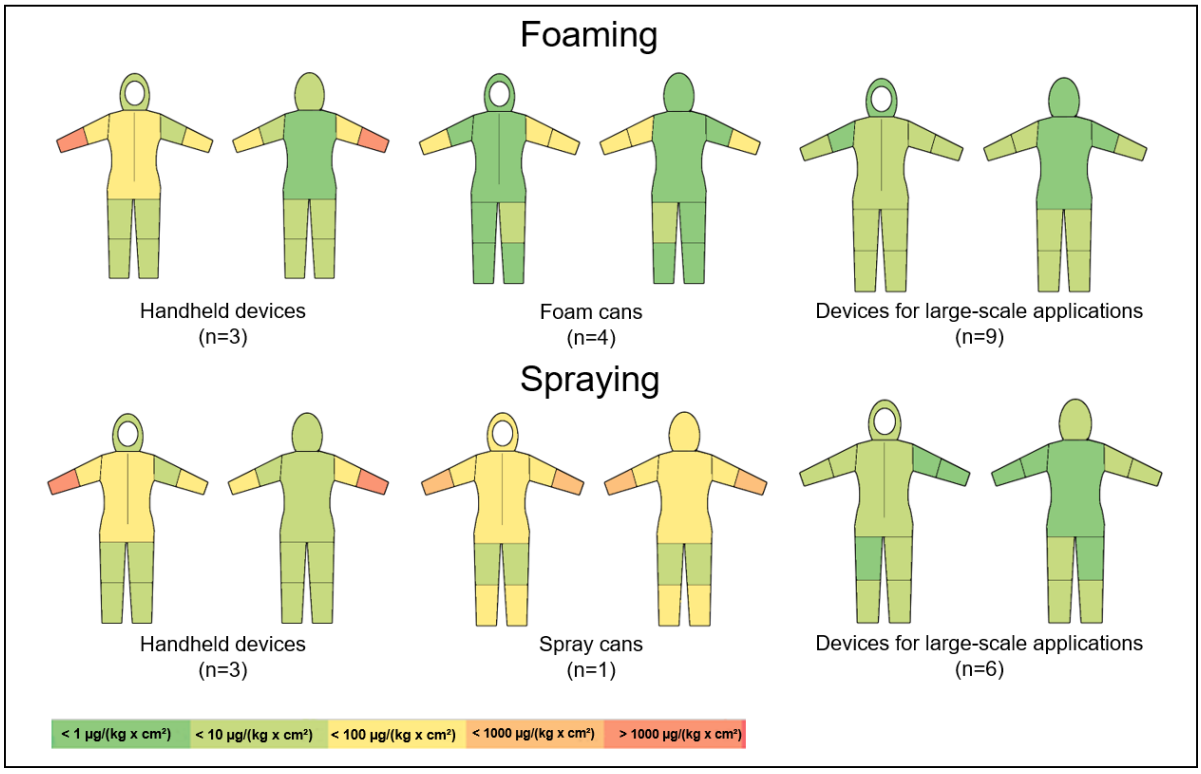


Fig. 5.20 Exposure patterns on the coveralls. This figure is based on the exposure levels normalised to the corresponding segment area and to the amount of active substance applied. The areas of the body were colour-coded according to the given scale.

5.2.2 Inhalation exposure

Fig. 5.21 and Fig. 5.22 give an overview of the inhalation exposure data gathered for foam and spray application scenarios in the scope of the conducted workplace monitoring campaigns. The figures show the inhalation exposure [µg/m³] normalised to the amount of applied active substance or tracer [µg/(m³ × g)]. The application devices were divided in 5 device categories. Propellant cans (pressurised cans), handheld devices (hand pump foamer and sprayer as well as hand compression foamer and sprayer), stationary low pressure devices with a nominal vessel pressure of < 3 bar and/or 3–6 bar and stationary high pressure devices.

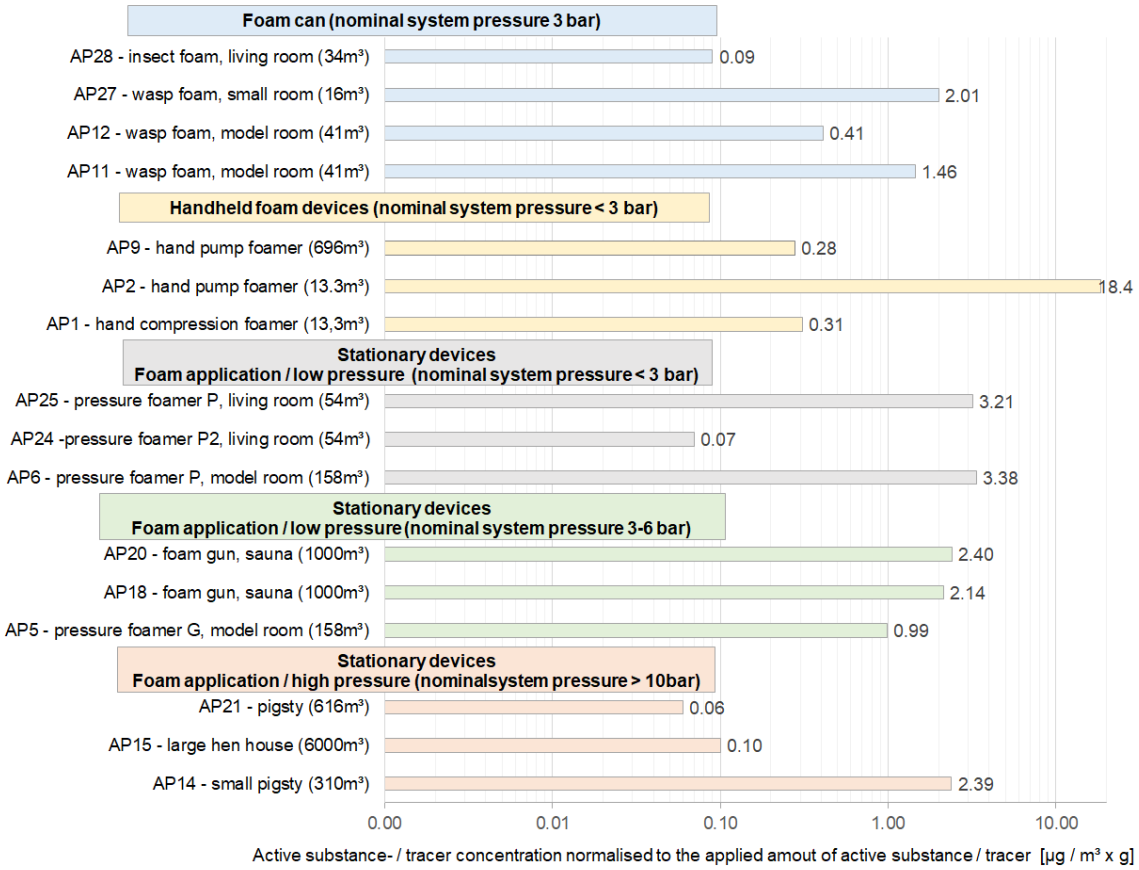


Fig. 5.21 Foam applications – Inhalation exposure at sampled workplaces (AP14, AP15, AP18 and AP20: measurement data were below the limit of quantification. For those the figure gives the limit of quantification. The figure shows rounded values.

Within the individual device categories for foam spray applications variations between the min. and max. exposure values were also observed. In the category of pressurised cans a factor of 22 between min. and max. value was determined, whereas for the handheld devices this factor was 66. Across all device groups this factor was 307. This finding is an indication for the diversity of the foam spray applications and hence the corresponding inhalation exposure of the operator. The highest inhalation exposure, normalised to the applied amount of active substance/tracer, was observed for scenario AP2 (18.4 µg/(m³ × g)), where a hand pump foamer was used.

Within the device categories good agreement was observed for the inhalation exposure, provided that similar process parameters were applied. Applications with pressurised cans are to name as one example. AP28 and AP12 involved the use of a nozzle for precise application, resulting in a small spray angle. AP27 and AP11 on the other hand, were mainly conducted without use of such a nozzle and consequently with a wider spray angle in place. In the category of devices with a vessel pressure of 3–6 bar intended for large-scale applications, similar exposure data were observed for AP18 and AP20. In both cases, a low pressure foam gun was used. The same applies for AP6 and AP25. Here, the same type of device (pressure foam equipment) including the same nozzle, was used; once in a model room and once in the living room of a house.

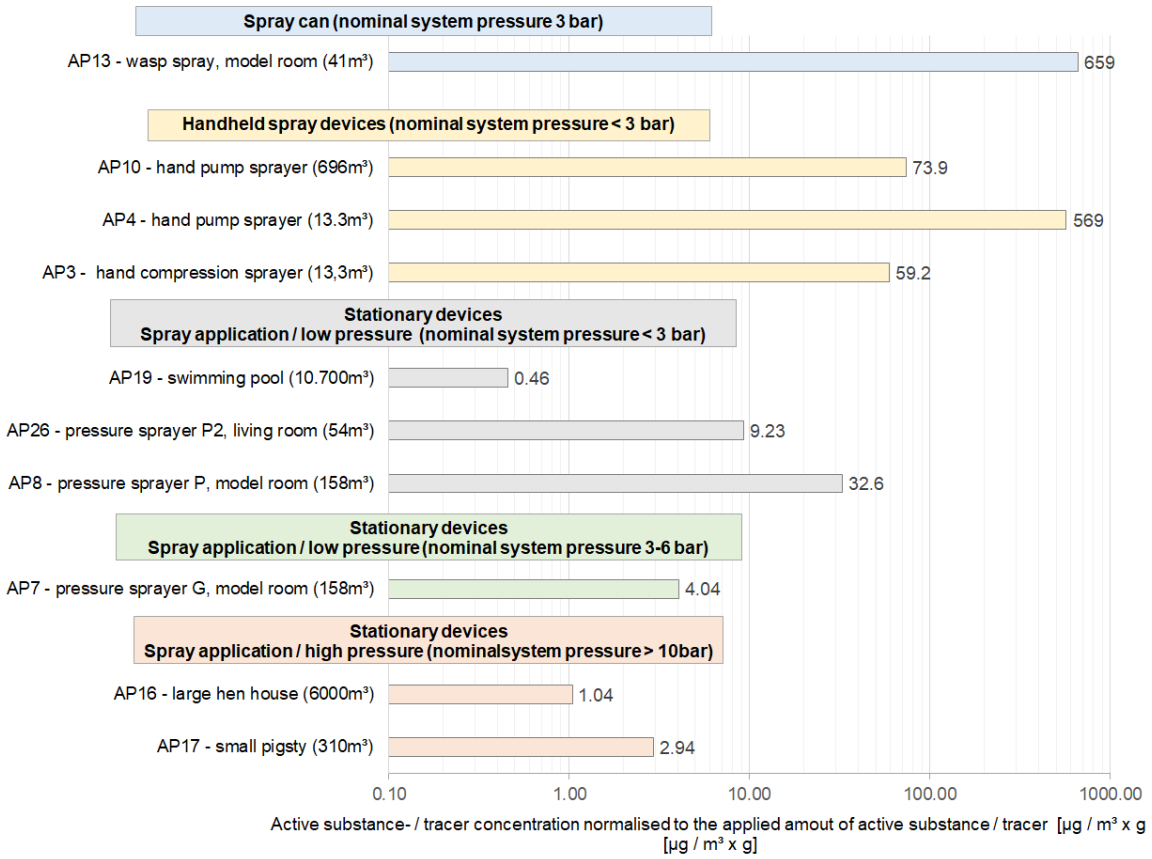


Fig. 5.22 Spray application – inhalation exposure data at workplaces. The figure shows rounded values.

Within the individual device categories for spray application variations between the min. and max. exposure values were also observed. In the category of stationary high pressure devices the factor was 3 and for stationary low pressure devices 77. Across all device groups this factor was 1430. The data provide a first indication for a possible differentiation of the device categories in applications with particularly high or low exposure. Normalising exposure concentration to the amount of applied active substance or tracer showed that large scale applications within the categories of < 3 bar, 3–6 bar and high pressure devices tend to result in lower inhalation exposure, than small-scale applications within either of the respective device categories.

Following the approach described in chapter 5.2.1.4, a reduction factor (RF) of 17 between spray and foam application was calculated based on the respective median values, 21 µg/(m³ × g) and 1.23 µg/(m³ × g). Such a general reduction factor across all device categories, however, does not sufficiently reflect the RMM potential (RMM: risk mitigation measure) of changing from spraying to foaming.

In instances, where a direct comparison between spraying and foaming was possible the corresponding reduction factors varied between 1–1607, covering more than three orders of magnitude (Fig. 5.23). These RFs show that the median based RF of 17 is a good estimate for only 3 out of 12 investigated scenarios (AP8 vs AP25; AP8 vs AP6 and AP16 vs AP15 with an RF of 10). For three scenarios (RF = 1–4) it represents a clear overestimation and for the remaining 6 scenarios a clear underestimation (RF = 31-1607).

The 12 reduction factors given here, result from direct comparisons between activity driven spray and foam applications (e.g. wasp control or surface treatment, Tab. 5.3), where similar device techniques[15] were used; e.g. pressurised cans: spray can vs foam can, stationary devices: device P without vs with foam cartridge. Selection of spray and foam nozzles was made according to the recommendations given by the manufactures. The determination of the reduction factors was achieved by means of (partly) simulated workplace scenarios (App. Tab. 18 – App. Tab. 27). This way, variability in exposure concentration attributable to different operators and/or locations could be excluded. At actual workplaces such circumstances will rarely apply when addressing the RMM efficiency of changing from spraying to foaming. On the contrary, additional sources of variation are most likely to be found in the field such as application of different devices, nozzles and other process parameters; hampering the comparison between spraying and foaming and therefore the deduction of a reduction factor, if not even rendering it impossible.

A comparison of reduction factors obtained at standardised conditions in model rooms support that observation (Fig. 5.6). For example the reduction factor obtained with device P during investigations in model rooms ranged between 2–2617. These variations are mainly explained by the nozzle geometry; small outlet surface vs large outlet surface (RF 4 (flat fan nozzle[16]/flat fan nozzle[16] with blue foam cartridge) vs RF 2617 (flat fan nozzle[16]/universal foam nozzle[17])). During simulated workplace scenarios (AP8 and6, applications in a model room), where in both instances the same flat fan nozzle was used, a reduction factor of 10 was determined. This RF was confirmed by a foam application conducted by a pest controller (AP25) using the same device configuration in comparison to the spraying scenario AP8 (simulated workplace in a model room). This shows, that reduction factors determined by simulated application scenarios in model rooms are also applicable for real workplaces as long as the same device configurations are used. However, a comparison between workplaces 26 and 25 (spraying vs foaming) showed a reduction factor of only 3. Here, a comparison was made between the pressure device P2 in conjunction with a standard hollow cone nozzle and the pressure device P equipped with a flat fan nozzle and a foam cartridge upstream. It has to be mentioned that the application with the device P was done using a compressor which kept the systemic pressure at a constant value throughout the entire application duration. The required systemic pressure, when using device P2, was set by manual pumping. The application of the biocidal product led to a decrease of the systemic pressure, making repeated manual pumping necessary to adjust for the pressure loss. Hence, application with device P2 were not conducted at constant vessel pressure. Comparison of spray and foam applications with device P2 (AP26 vs AP24), where a hollow cone spray nozzle and the universal foam nozzle[17] were used, a reduction factor of 132 was determined. In this device category reduction factors from 3 to 132 were obtained, depending on the selected nozzle and foam generation technique (foam cartridge vs screen nozzle).

[15] Exception: Comparison AP26 vs AP25. AP26: Pressure sprayer/foamer P2 with hollow cone nozzle (spray); System pressure was build up by manual pumping. Vessel pressure was not constant during application. AP25: Pressure sprayer/foamer P, foam cartridge and flat fan nozzle, System pressure was build up using a compressor. Vessel pressure was constant during application.
[16] Outlet area: 2.75 mm²; TeeJet 100 06 VP
[17] Outlet area: 75.4 mm²; universal foam nozzle

The impact of the nozzle geometry on the reduction factor was also observed in the device category of trigger sprays (hand sprayer). This was demonstrated as a result of applying different spray angles in the course of the investigations run in model rooms (Fig. 5.6). During spraying an application with a small fan spray jet resulted in a lower reduction factor (RF 18) than an application with a broad fan spray jet (RF 108). Data gathered during workplace sampling campaigns where the same biocidal product was applied with handheld spray and foam devices showed reduction factors of 31 to 264. Again, this divergence is most likely attributable to the set spray angles.

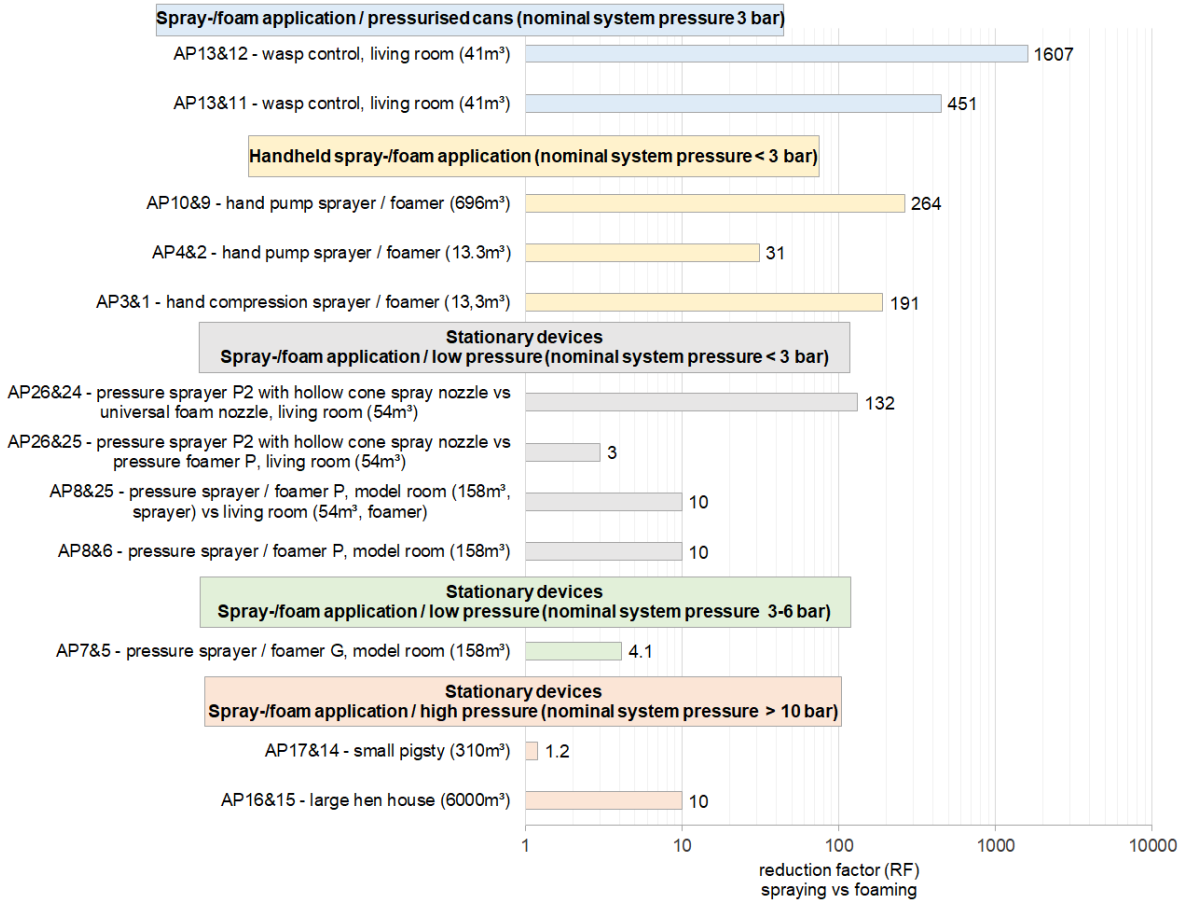


Fig. 5.23 Sampling at (simulated) workplaces: Deduction of reduction factors for spray vs foam applications by direct comparison. Rounded values are given.

For all spray vs foam applications considered in this study a reduction of the inhalation exposure was observed (Fig. 5.23). In 9 out of the 12 cases shown above the inhalation exposure during foaming was at least 10 times lower than during the corresponding spray applications. A special exception were AP14 (foaming) and AP17 (spraying). Here, a surface area of min. 215 m² was treated with a high pressure device in a sty (310 m³). Inhalation exposure amounted to < 2.39 µg/(g*m³) (AP14) and 2.94 µg/(g*m³) (AP17) respectively. The use of a high pressure device in such a small room could be considered overly ambiguous. As a result changing from spraying to foaming might not result in the expected reduction of inhalation exposure.

Overall, the qualitative observation was made that changing from spraying to foaming can be considered a risk mitigation measure regarding inhalation exposure, if applied correctly. A general reduction factor or a reduction factor specific for a device category could not be identified.

An assessment of the foaming techniques regarding their efficiency as risk mitigation measures based on for example historic spraying data is considered difficult. This is due to the fact that not always sufficient data are available to select an adequate reference value for the comparison. Including more application scenarios would not provide further insight on reduction factors and hence was not pursued.

5.2.3 Discussion and conclusion – Inhalation vs dermal exposure

Based on the few data points the qualitative conclusions was drawn that changing from spraying to foaming will reduce inhalation as well as dermal exposure caused by aerosols. Data for dermal hand exposure were not considered for the following observations. The observed trend was not as pronounced for dermal exposure as it was for inhalation exposure; as is indicated by the corresponding median values for the determined reduction factors (3.8 vs 17). As already mentioned in the previous chapters, the prediction of a generally applicable reduction factor is not favoured due to the diversity of the applications themselves, the devices and the individual behaviour of the operator.

Exposure estimates for potential inhalation exposure can be based on parameters such as exit velocity of the product at the nozzle and nozzle geometry (see chapter 6). Exposure prediction for potential dermal exposure is hampered due to the occurrence of accidental events such as contact with treated surfaces or application solution as well as their frequency. Dermal exposure solely based on the active substance being present as aerosol (equals inhalation dose D^{inh}) can be predicted using equation 3.13 (chapter 3.2; or equation 5.3 in chapter 5.1.1). In this study Tyvek® coveralls with a 'body surface area' of max. 30 000 cm² were used for the determination of potential dermal exposure. It is assumed that approx. 10 % of overall surface (here: 3 000 cm²) are horizontal deposition areas ($\mathrm{A_w}$) for the airborne non-volatile active substance. The remaining 90 % (27 000 cm²) are vertical areas ($\mathrm{A_s}$) where deposition of the airborne active substance can take place. The deposition velocities on vertical and horizontal areas, $v_{dep,s} = 0.2\ \mathrm{cm/s}$ and $v_{dep,w} = 0.95\ \mathrm{cm/s}$, were deduced from experiments conducted in model rooms (the highest value each, also see Fig. 5.3). Assuming an inhalation volume flow, Q_A, of 347 cm³/s[18], the inhalation dose corresponds to 4.2 % of the dermal dose.

(5.7)

$$\frac{D^{inh}}{D^{derm}} = \frac{Q_A}{(A_h \cdot v_{dep,h}^{s} + A_v \cdot v_{dep,v}^{s})} = 0.042$$

In the event that beside the airborne active substance other sources are contributing to dermal exposure, e.g. contact to treated surfaces or the application solution, the

[18] Inhalation volume flow = breathing rate (default value: professional user in biocidal product process): 1.25 m³/h

term $\frac{D^{inh}}{D^{derm}}$ will decrease according to the contribution of this secondary exposure source.

For the corresponding spray and foam applications sampled at workplaces the ratio between the inhalation and dermal exposure doses were determined and are shown in Fig. 5.24 (top). In all cases, but three individual exceptions, all dermal exposure was well above the postulated value derived from equation 5.3 (red line). In the latter, aerosols (c^{inh}) are assumed to be the only exposure source. Hence, those data show that dermal exposure is mainly caused by diffuse secondary sources, such as direct contact with the active substance via treated surfaces (e.g. AP1–4 where due to wiping of the treated surfaces considerable exposure of the lower arms with the active substance was found; App. Tab. 43) or splashes.

In regard to dermal exposure, the hood of the coverall is considered as a segment least likely to be affected of random events, with exposure to the aerosolised active substance being the main source. Applying equation 5.3 to the hood (horizontal area: 201 cm²; vertical area: 1060 cm²; values were measured) the inhalation dose corresponds to 86 % of the dermal dose ($\frac{D^{inh}}{D^{derm}} = 0.86$). Following this approach some events match well with the postulated value (red line in Fig. 5.24; bottom).

However, there are also cases in which the dermal exposure is clearly below or also clearly above this value. There is no indication of a logical pattern.

An alternative method to demonstrate a possible connection between dermal and inhalation exposure is the presentation of the absolute values in µg in a scatter plot.

In Fig. 5.25 the total exposure to the active substance measured for the coveralls is plotted against the inhalation doses, for an assumed breathing rate of 1.25 m³/h, for all investigated foam and spray applications. The value of 1.25 m³/h corresponds to an elevated respiratory volume at workplaces (10 m³ in 8 hours) [Hartwig und MAK Commission 2017] and should therefore represent the worst case scenario for inhalation exposure. The foam and spray applications are colour coded. The dermal exposure of the five least affected coverall segments (extrapolated to the overall surface area of the coverall) was plotted against the inhalation exposure (Fig. 5.26). It is assumed that this way the contribution of diffuse secondary exposure sources, which can make up a considerable part of the dermal exposure, are eliminated as far as possible. In comparison to Fig. 5.25 this should lead to a better correlation as the dermal exposure should be dominated by aerosol deposition when applying this approach.

After logarithmic transformation of the data in Fig. 5.25 a linear correlation with a correlation coefficient of $R^2 = 0.357$ is obtained and for the data Fig. 5.26 a linear correlation with $R^2 = 0.6896$ (Fig. 5.27).

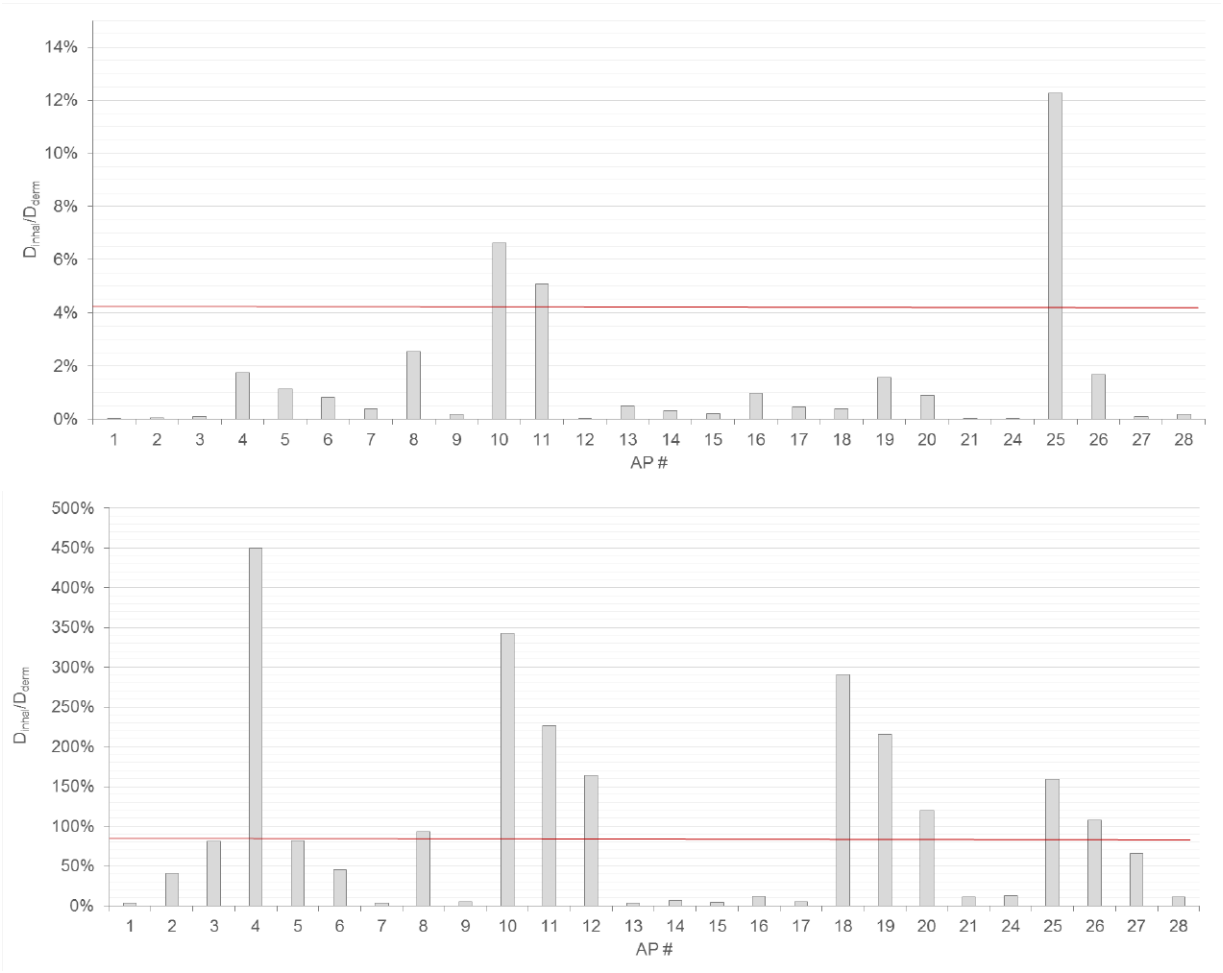


Fig. 5.24 Calculated theoretical dermal exposure; assuming it is only caused by deposition of the airborne active substance on the entire coverall (top) and the hood (bottom), which is less likely to be affected by random exposure events. The calculations are based on equation 5.3 and the data regarding potential dermal exposure given in App. Tab. 31. (Data for AP14, AP15, AP18 and AP20 were below the limit of quantification. For this figures it was calculated with the limits of quantification.)

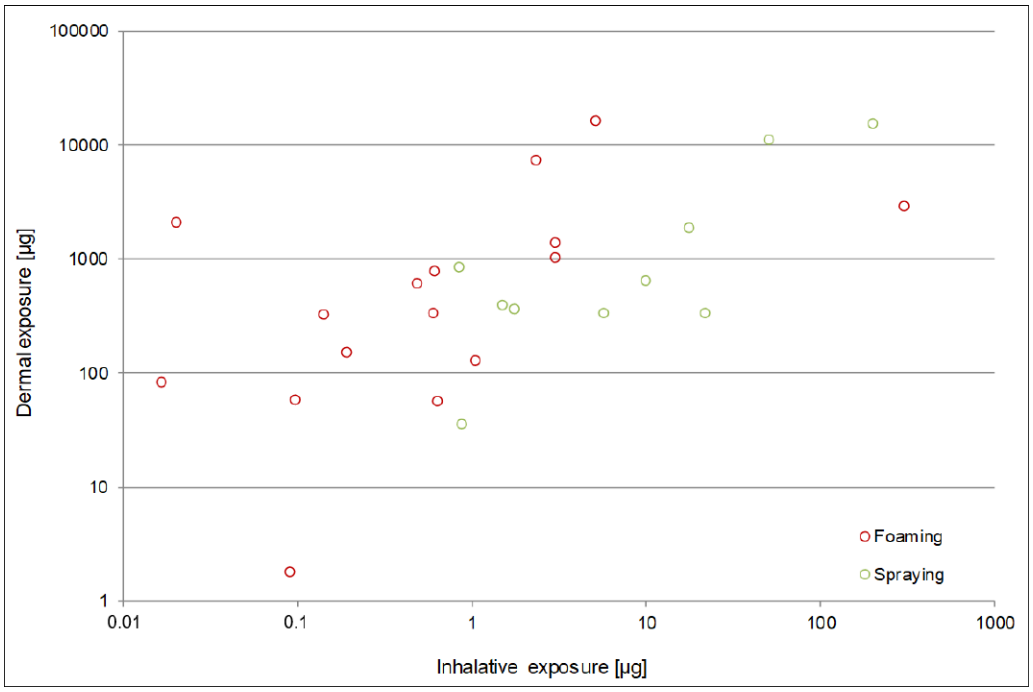


Fig. 5.25 Dermal exposure (coveralls) vs inhalation exposure for an assumed breathing rate of 1.25 m³/h. The data are given as absolute values in µg.

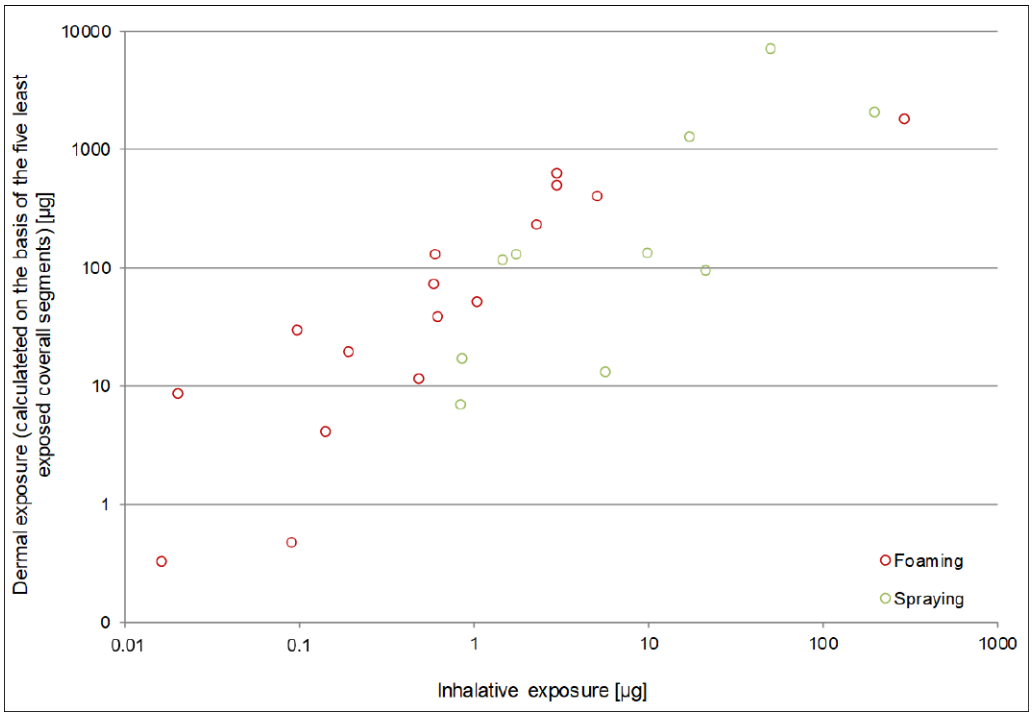


Fig. 5.26 Dermal exposure vs inhalation exposure for an assumed breathing rate of 1.25 ³/h. The dermal exposure of the five least affected coverall segments was extrapolated to the overall ‘body surface’ of the coverall. All data are given as absolute values in µg.

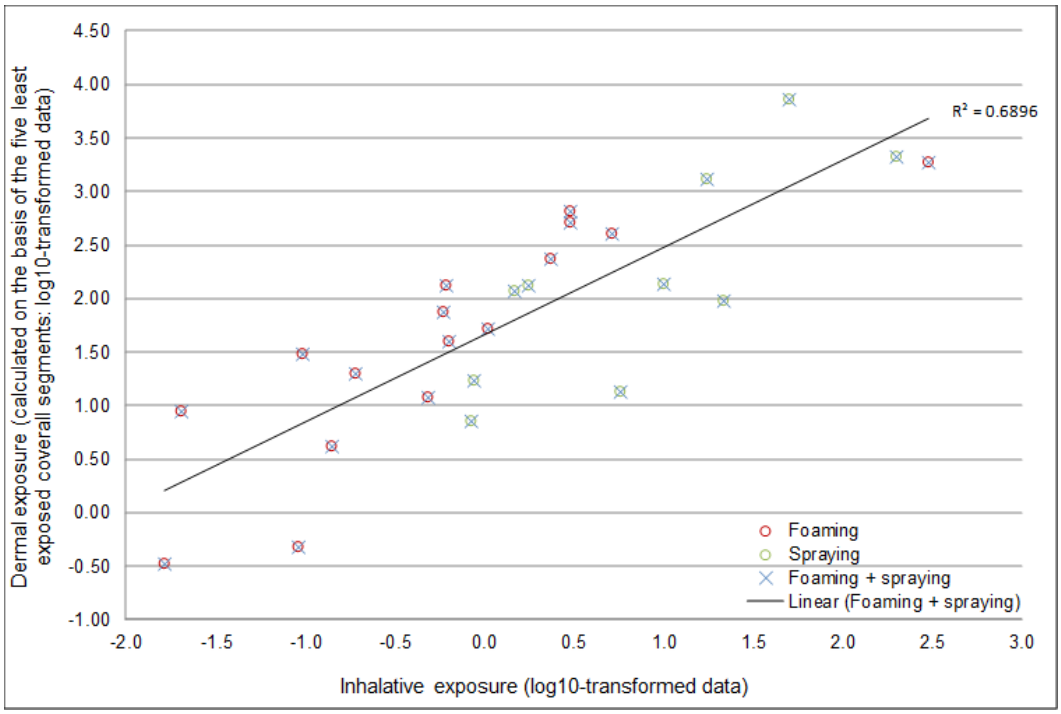


Fig. 5.27 Dermal exposure vs inhalation exposure for an assumed breathing rate of 1.25 m³/h. The dermal exposure of the five least affected coverall segments was extrapolated to the overall 'body surface' of the coverall. All data have been logarithmically transformed.

In summary, it can be concluded that based on inhalation exposure or corresponding estimates based on theoretical assumptions, no reliable predictions of dermal exposure can be made. Potential dermal exposure is determined by the application device, the individual behaviour of the operator and therefore also by random contamination events. These factors are also relevant for inhalation exposure; for example the positioning of the operator to the 'aerosol cloud'. However, their impact on the overall exposure is lower than for dermal exposure, where direct contact with the application solution often exceeds the contribution of the aerosol deposition considerably.

Regarding occupational health and safety the obtained exposure data can serve, long-term, as a first data base for the implementation of occupational safety measures in the area of biocidal product applications.

6 Modelling

6.1 Deterministic modelling (inhalative)

6.1.1 Modelling approach

The exposure modeling follows the scheme shown in Fig. 6.1. The objective is the deterministic calculation of the time averaged exposure concentration or frequency distribution of the concentration to be used in exposure assessment of an active substance or substance of concern. The underlying scenario suggests suitable, relevant foaming techniques and the specifics of the formulation containing the active substance to be marketed. The release fraction of active substance characterising the foaming technology as well as application specific information such as the typical surface dose required for the biocidal effect determine the source strength in a deterministic modelling. Additional input parameters required for concentration modelling are derived from the specific exposure scenario.

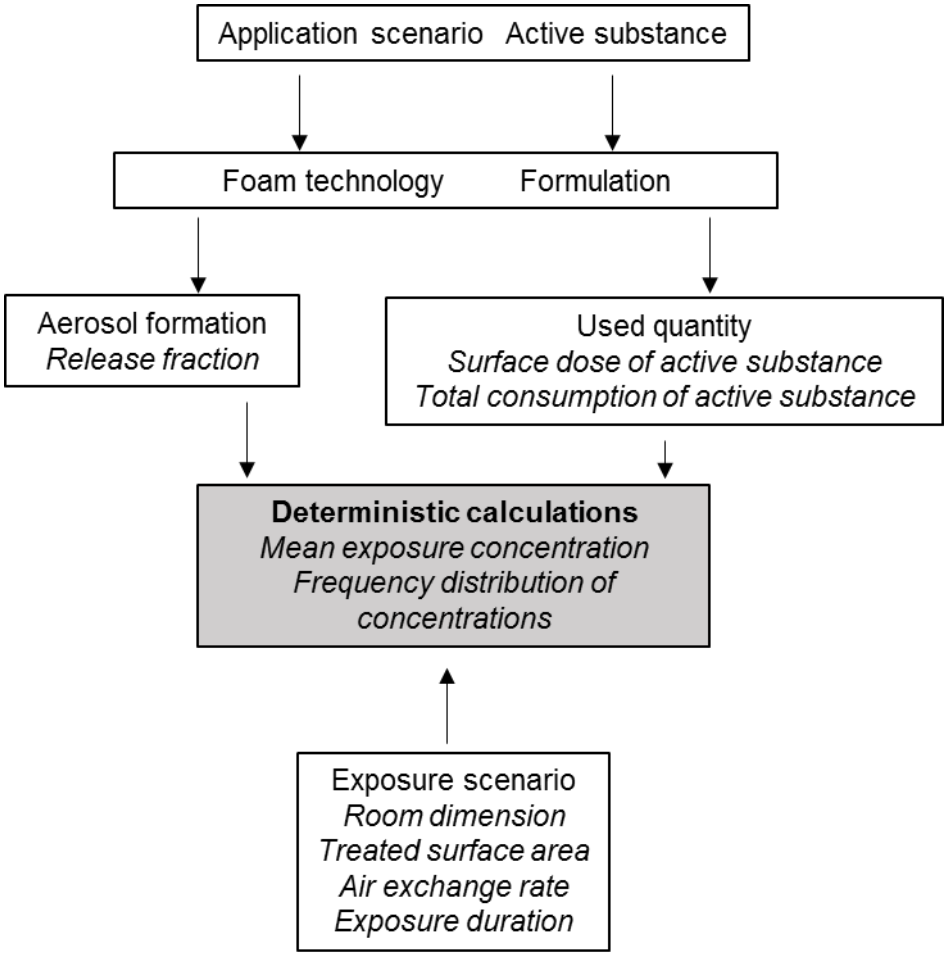


Fig. 6.1 Schematics for modelling the exposure concentration of non-volatile active substances during foam application.

The parameters of the model can be taken from so called fact sheets or there are distributions within specific value ranges. In this case, frequency distributions of the

concentration are calculated. The area requirement in professional kitchens depends on the number of daily customers and covers the range between 80 and 260 m^2 for a room height of 3 m [19]. The surface area to be treated should be proportional to this range of values. The quantities of active substance required are also subject to variation depending on quality and quantity of the surface contamination. For the QAC F, for example, the recommended dilution for the concentrate of the active substance in the final application solution is between 0.5 and 2 %.

The modeling approaches listed below apply for indoor application of biocidal products, only. The ConsExpo and SprayExpo models introduced for spray application, for example, could be used for calculating the concentration by making appropriate adjustments to the input modules. The source strength of active substance, $S^s = \dot{M}^s \cdot R^s$, (Eq. 3.2) is the determining parameter. This combines the aerosol formation potential of the foam process, characterised by the release fractions, $R^s_{r,t,i}$, with the mass flow rate, $\dot{M}^s$, of active substance typical for the application under consideration. The exposure situation of the foam user can be described in principle by a near field contribution close to the source and a far field contribution remote from the source. The near field exposure is independent of global parameters such as the room size or the air exchange rate and is related to the spatial connectivity between source and receptor. The development of the SprayExpo model is mainly based on this fact. In the case of foam applications, the source and receptor are usually not stationary, but move in space according to the progress of the application. The contribution to the exposure of the user remote from the source results from the (homogeneous) distribution of the released active substance inside the room. The contribution away from the source is independent of the position of the user, but depends on the time after the start of the foam application. For very large rooms, the far field contribution is negligible and the user's exposure is determined by the local aerosol cloud at the location of the foam application. In contrast, for small rooms the distinction between near field and far field is blurred, because the aerosol mixing time in the room is short.

6.1.1.1 Simple box-models

Following this arguments, simple 1-box and 2-box approaches for exposure modelling are employed as a first approximation. Instantaneous mixing of the released active substance aerosols in the entire room volume (1-box model) is assumed, or, for the 2-box model, mixing without losses occurs over a period, T_M, in a personal control volume, V_P. In the complementary period T-T_M thereafter, the aerosol is completely mixed in the entire volume, V_R (see Fig. 6.2). It is assumed here that the duration of exposure corresponds to the duration of use. The case of an additional residence time, T_r, after the application is dealt with in Appendix 9.

[19] Fachkommission Gebäude- und Betriebstechnik: Planung und Bau von Küchen und Kantinen; HIS Hochschul-Informations-System GmbH, Hannover1988

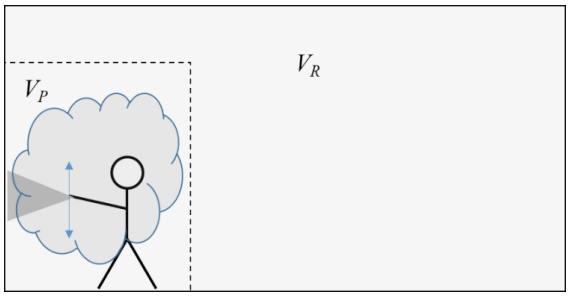


Fig. 6.2 2-box-exposure model. The position of the control volume, V_P, is connected with the user.

Because of complete mixing in the two control volumes, Eq. 3.5 can be used for the calculation of the concentration. Taking into account the air exchange and particle settling losses to surfaces in the room characterised by the loss rate, $\Gamma = \gamma_e + \gamma_s$, the dilution function is given by:

(6.1)

$$\chi(t) = \begin{cases} \frac{1}{V_P} & for\ t < T_M \\ \frac{1}{V_R} \cdot e^{-\Gamma t} & for\ t \geq T_M \end{cases} = \frac{1}{V_R} \cdot \begin{cases} \frac{V_R}{V_P} & for\ t < T_M \\ e^{-\Gamma t} & for\ t \geq T_M \end{cases}, \quad \Gamma = \gamma_e + \gamma_s$$

Fig. 6.3 shows examples of temporal concentration patterns for a near field volume of 10 m³ and a mixing time of 6 s. Near field and far field contributions can be identified from the plots. Without losses, there is a linear increase in concentration with time since a constant amount of active substance, $\dot{M}^s$, is fed into the room per time unit. This approach applies when there is no air exchange ($\gamma_e = 0$) and the exposure time is sufficiently small that settling losses can be neglected: $\gamma_s T \rightarrow 0$. The near field contribution dominates for large rooms. For small rooms, the far field contribution determines the concentration after a short time period. This is valid also for a ventilated room.

The time averaged concentration is calculated by inserting the dilution function into Eq. 3.7 and carrying out the time integration. For a continuous and constant foam release over the entire time period one obtains:

(6.2)

$$\bar{c}^s = R_i^s \cdot M^s \cdot \frac{1}{V_R} \cdot \bar{\kappa}(V_R/V_P\ , T_M, T, \Gamma).$$

The exposure concentration is easily calculated from the release fraction and the consumption of active substance, M^s, characterising the foaming process, and a dimensionless factor, $\bar{\kappa}$, resulting from the exposure scenario and the model. In this modelling approach the quantities determining $\bar{\kappa}$ are the parameters of the two box model: V_R , V_P, T_M, T and Γ. The full equation is given in Appendix 9. For a non-ventilated room and neglecting setting losses, the factor $\bar{\kappa}$ takes the value of $\bar{\kappa} = 1/2$ for the 1-box model ($V_P = V_R$). The time averaged concentration is directly related to the entire inhalable mass of active substance released into the room $R_i^s \cdot M^s$ by:

(6.3)

$$\bar{c}^S = \frac{1}{2} \cdot (R_i^S \cdot M^S)/V_R.$$

The factor 1/2 is a direct consequence of the linear concentration increase with time in case of continuous release (see Appendix 9 for a ventilated room). Fig. 6.4 and Fig. 6.5 show that this approach is comparable with the 2-box model for small rooms and long exposure duration. Otherwise, the figures demonstrate the dominance of the near field contribution for large rooms and short exposure times. The choice of the value of 10 m³ for the near field volume is based on the scenario of surface spraying using the pressure foamer P, G, B and foam gun and assuming a base area of 2 × 2 m² and a height of 2.5 m. The short mixing time of 6 s results from the fact that the personal volume is rapidly filled due to the dynamics of the moving source[20]. Air exchange and settling losses are effective for long application time periods and small room volumes.

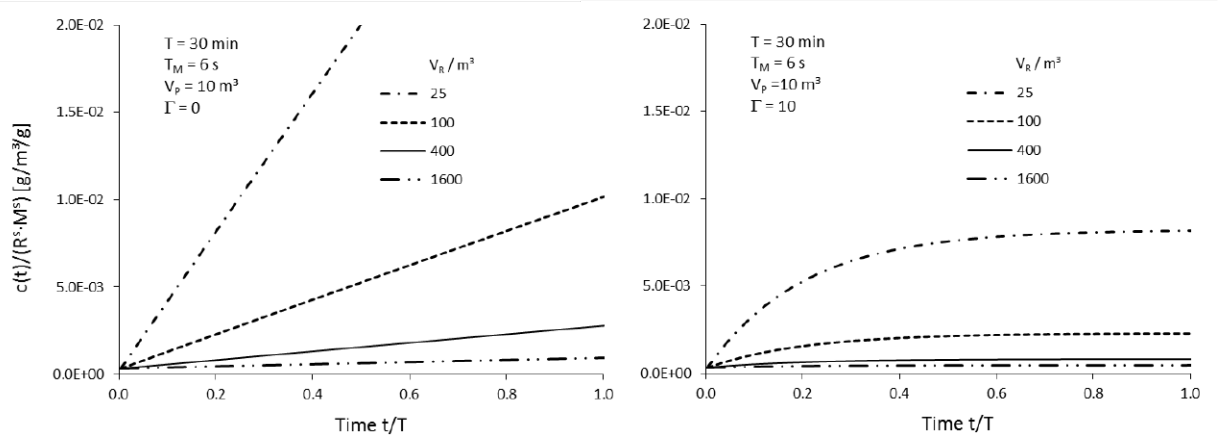


Fig. 6.3 Concentration patterns of inhalable active substance normalised to the total mass of released inhalable active substance ($t > T_M$).

[20] The values result by comparison with calculations carried out with SprayExo (see below)

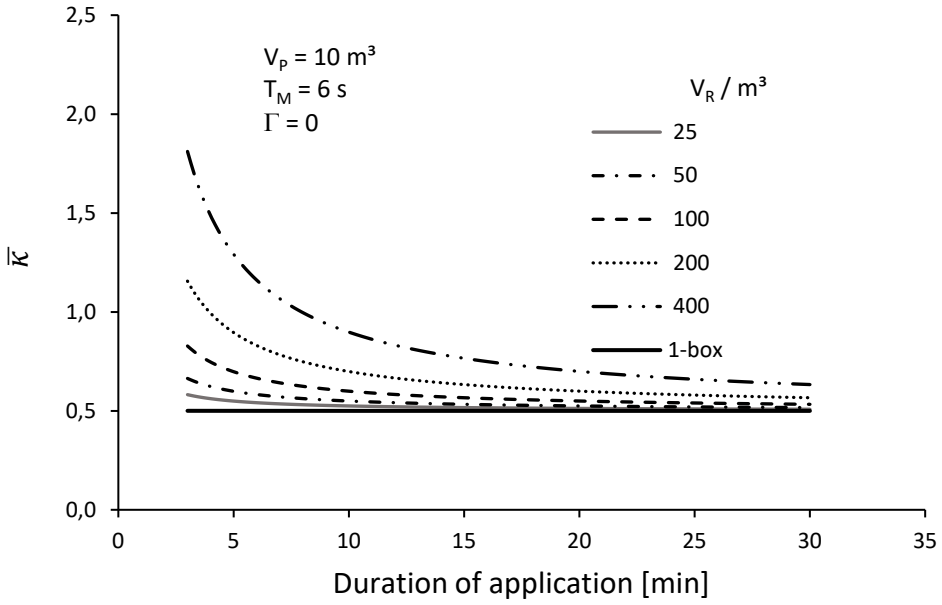


Fig. 6.4 The 2-box model factor $\overline{\kappa}$ as function of the room size and the duration of exposure. Losses by air exchange and settling are neglected. The limiting cases of 0.5 corresponds to the 1-box model.

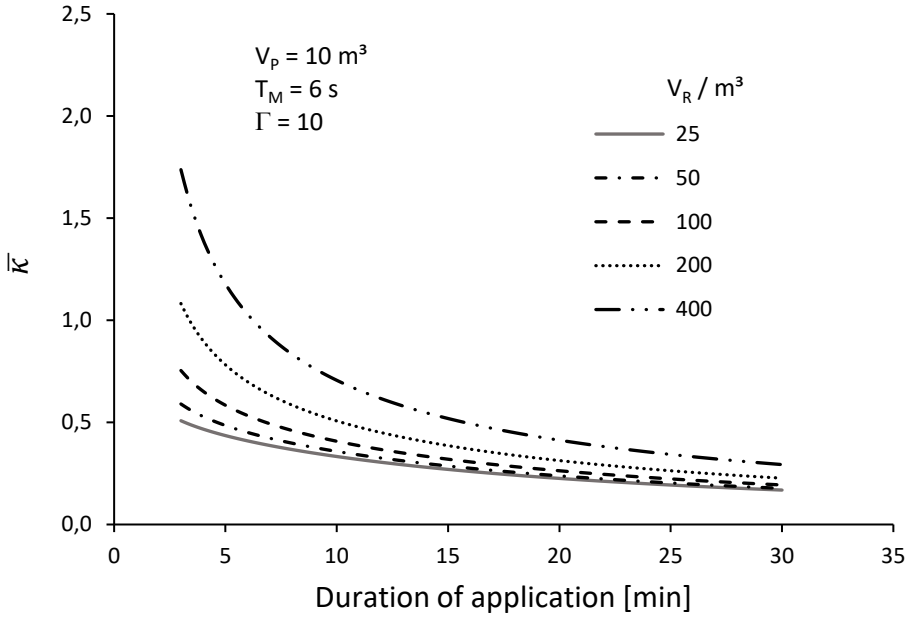


Fig. 6.5 $\overline{\kappa}$-values for the 2-box model and a loss rate of 10 h^{-1}.

For a sufficient efficiency of the biocidal product, the required active substance surface dose, ρ^s, is the key factor. Together with the surface F to be treated it determines the consumption of active substance:

(6.4)

$$M^s = \rho^s \cdot F.$$

The duration, T, of application results from the mass flow of liquid formulation, Q_l, and the concentration of active substance in the liquid $c^{s,l}$:

(6.5)

$$T = \frac{M^s}{Q_l \cdot c^{s,l}} = \frac{\rho^s}{c^{s,l}} \cdot \frac{F}{Q_l}.$$

The time averaged concentration is obtained from Eq. 6.2:

(6.6)

$$\bar{c}^s = R_i^s \cdot \rho^s \cdot \frac{F}{V_R} \cdot \bar{\kappa}(V_R / V_P, T_M, T, \Gamma).$$

This is a central relationship in exposure modelling. The influence of the foaming technology and the biocidal requirements are quantified by the parameters R_i^s und ρ^s. The application scenario enters the model via F/V_R and $\bar{\kappa}(V_P/V_R, T_M, T, \Gamma)$. In the most simple case: $\bar{\kappa} = 1/2$ (1-box model neglecting losses; $\Gamma T \to 0$).

Some of the parameters are interrelated. For example, a high liquid concentration of active substance ín the final formulation is recommended when a high surface dose is demanded: $\rho^s \sim c^{s,l}$. Large areas are generally treated with high throughput devices: $F \sim Q_l$. This means that the durations of application are comparable within an order of magnitude, even for very different secenarios. Typical values cover the range of 3 < T < 15 min per application. A similar statement can be made regarding the ratio of treated surface area to room volume: F/V_R. Particularly for room surface disinfection such as stable disinfection or building protection (wood protection) the treated surface area, F, should be proportional to the room volume, V_R. Variations of realistic values of the loss rate in the range1.5 < Γ < 20 [1/h] cause variations in $\bar{\kappa}$ within a factor of 2.

6.1.1.2 Spray-Expo

The SprayExpo model, developed for spray applications, can also be used for foam application. Only minor modifications are required. The droplet size distribution has to be replaced by the size dependence of the release fraction of the active substance. The modified input specifications are marked in yellow in Fig. 6.6.

The mass flow rate of the released non-volatile aerosol of the active substance is considered as the source term. Consequently, a percentage of 100 % is used to characterise the product as well as an extremely low value for the vapour pressure. The corresponding numerical values to be used in the input masks are 99.9 % for the concentration of active non-volatile substance in the liquid formulation and 10^{-5} hPa for the vapour pressure.

In a very conservative approach, the inhalable aerosol release can be assigned to the particle size fraction smaller than 5 µm. This is conservative in the sense that for this particle size range the influence of settling on the mean concentration will be small during the exposure durations relevant in practice. To be less conservative, the Respicon data for the release fractions from Table 6.1 can be used. They provide size-resolved information on the respirable, thoracic and inhalable fraction. After averaging

over all size resolved data available, the contribution to the respirable (< 5 µm), tracheo-bronchial (5–10µm) and extra-thoracic size regime is roughly 1/3. The latter results from the difference between the inhalable and the thoracic fraction and can be restricted to the particle size range 10–20 µm for a conservative calculation of the inhalation exposure.

In order to avoid the calculation of wall deposition of droplets a large value of 2 cm is used for the nozzle diameter.

Tab. 6.1 Particle size released based on the data shown in Fig. 5.7.

	Paricle size regime		
	10–20 µm	**5–10 µm**	**0–5 µm**
Ave. contribution	0.32	0.34	0.34
Stand. dev.	0.13	0.13	0.18
Variance	0.41	0.39	0.54

The source strength of aerosolised active substance, S_i^s to be inserted in Fig. 6.7 is calculated from the total mass flow rate of active substance, $\dot{M}^s$, in µg/s and the release fraction, R_i^s:

(6.7)

$$S_i^s = R_i^s \cdot \dot{M}^s$$

Dose and concentration output are given in ng and ng/m³ (Fig. 6.8).

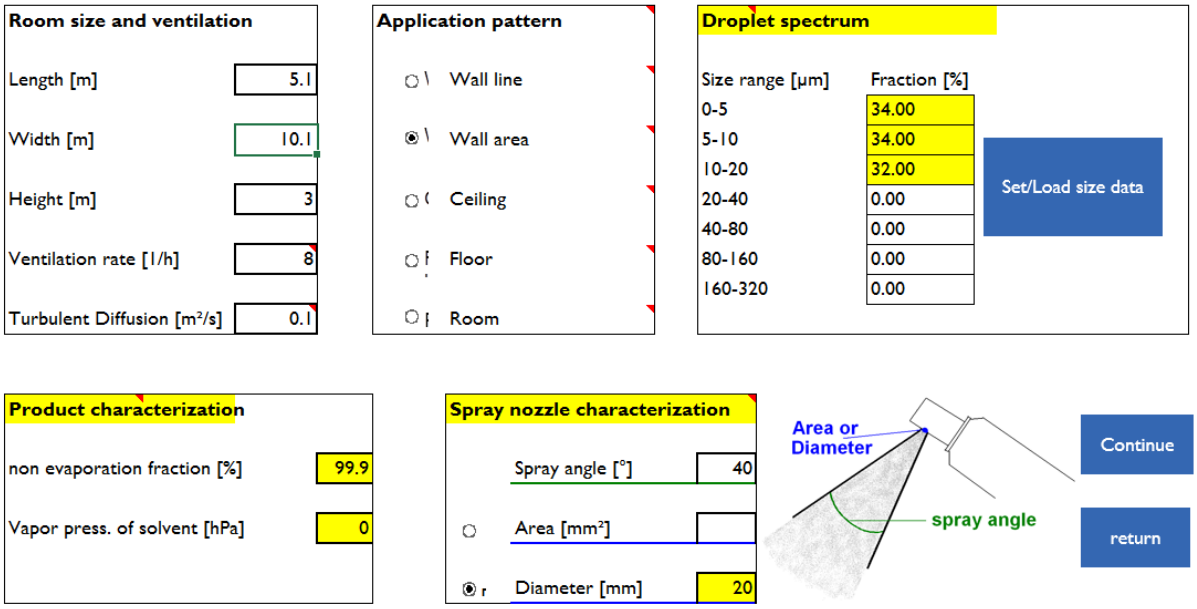


Fig. 6.6 Modified input mask of SprayExpo used for foams.

Application pattern
Wall area

Room size and ventilation

Length [m]	5.1
Width [m]	10.1
Height [m]	3
Ventilation rate [1/h]	8
Turbulent Diffusion [m²/s]	0.1

Droplet spectrum

Size range [µm]	Fraction [%]
0-5	34
5-10	34
10-20	32
20-40	0
40-80	0
80-160	0
160-320	0

Product characterization

non evaporation fraction [%]	99.9
Vapor press. of solvent [hPa]	0

Spray nozzle characterization

Diameter [mm]	20
Spray angle [°]	40

Application pattern - Wall area

	Begin [m]	End [m]	max. height [m]	Time [s]	Source strength [µg/s]
W1	1	9	3	240	13.4
W2	1	3	3	0	0
W3	1	9	3	0	0
W4	1	3	3	0	0

Distance

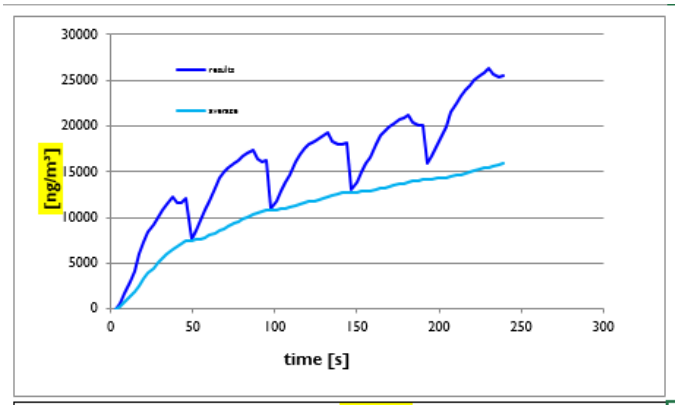
Sprayer to wall	Nozzle to wall [m]
1.5	0.5

Calculation

Time resolution: 1
High Low

- Inhalation exposure (total)
- Inhalable fraction
- Thoracic fraction
- Respirable fraction
- Dermal exposure

Fig. 6.7 Input mask for the application parameters (wall spraying).



Inhaled dose	6.34E+02	ng
Time ave. concentration	1.59E+04	ng/m³

time [s]	c [ng/m³]	gew. Mittelwert
6	541.421	270.711
12	2935.99	1298.22
17	5965.8	2539.9
23	8327.34	3858.8
29	10037	5012.17
35	11493.8	6033.98
40	11658.4	6873.42
46	12034	7494.91
52	8484.6	7554.08
58	10831.3	7828.06
63	13262.2	8251.33
69	14897.4	8777.9
75	15862.2	9305.63
81	16643.4	9816.66
86	17285.4	10304.2
92	16113.4	10677.5
98	11020.8	10849.4

Fig. 6.8 Results output (table truncated at 98 s).

A comparison between the results of SprayExpo calculations for the wall area mode and the 1-box and 2-box-models was carried out. SprayExpo was used to calculate the time averaged concentration of the inhaled active substance. The source strength was set to a fixed value of 10 µg/s, typical for disinfection of stables. Room size, duration of application, turbulent diffusion constant as well as loss rates (two values) were varied. The concentrations were normalised using Eq. 3.10, resulting in the dispersion function, $\bar{\kappa}$. The ratio between this value and the value from the 1-box result:

(6.8)

$$\bar{\kappa}_{1\_box} = 1/(\Gamma \cdot T)\,[1 - 1/(\Gamma \cdot T)\,(1 - \exp\,(-\Gamma \cdot T)],$$

are displayed in Fig. 6.9. Settling was neglected ($\Gamma = \gamma_e$).

The $\bar{\kappa}$-ratios are grouped according to the durations of application. Increasing the duration implies an increase in consumed mass leading to the same surface dose in all simulated scenarios.

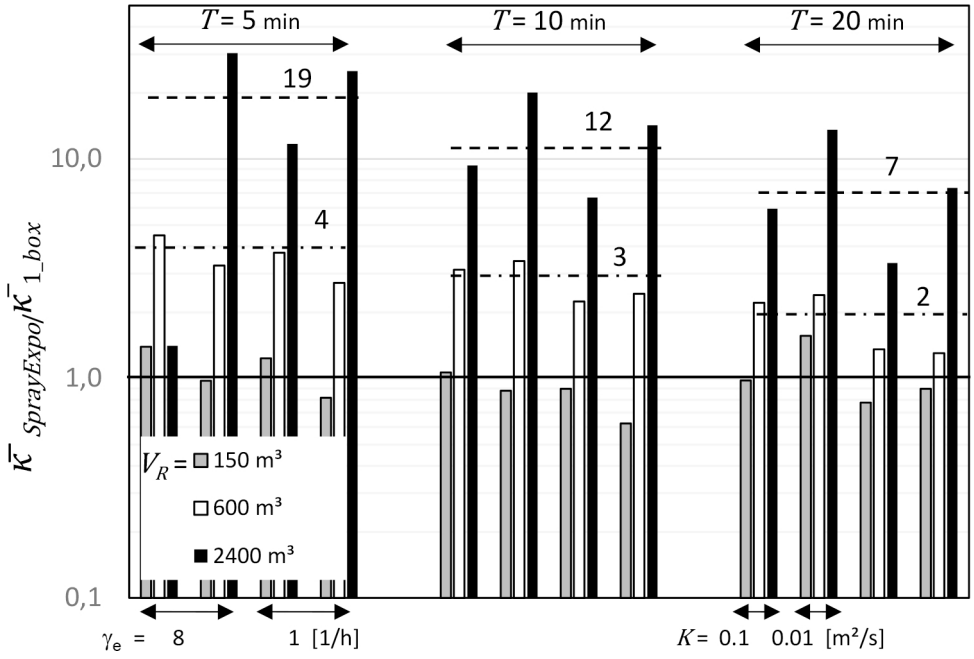


Fig. 6.9 $\bar{\kappa}$-ratios from SprayExpo calculations. Parameters varied: duration of application, T, room volume, V_R, air exchange rate, γ_e, and turbulent diffusion constant, K.

The room volume and the duration of application are the parameters determining the deviations of the results obtained using SprayExpo from those obtained using the 1-box model. For small rooms (150 m³) the exposure concentration is predicted sufficiently well by the 1-box model. The ratio between the $\bar{\kappa}$-values is approximately one. Larger volumes require correction factors. Their values are indicated in Fig. 6.9 at the dashed lines for V_R = 2400 m³ and dash dotted lines for V_R = 600 m³.

Similar investigations were carried out with the 2-box model. As shown in Appendix 9, for $T_r = 0$ and $\Gamma = \gamma_e$ the dispersion function, $\bar{\kappa}$, is given by:

(6.9)

$$\bar{\kappa} = \left[\frac{V_R}{V_P} \cdot \frac{T_M}{T}\left(1 - \frac{1}{2} \cdot \frac{T_M}{T}\right) + \frac{1}{\Gamma T}\left\{1 - \frac{1}{\Gamma T}(1 - e^{-\Gamma T})\right\}\right].$$

For the 2-box model the SprayExpo comparison was carried out for values of V_P = 10 m³ and T_M = 0.1 min. Fig. 6.10 shows smaller deviations in the results of the two models compared (2-box and SprayExpo) to the 1-box considerations, in particular for scenarios with higher values of the turbulent diffusion constant, K. No correction factors are recommended for the 2-box model.

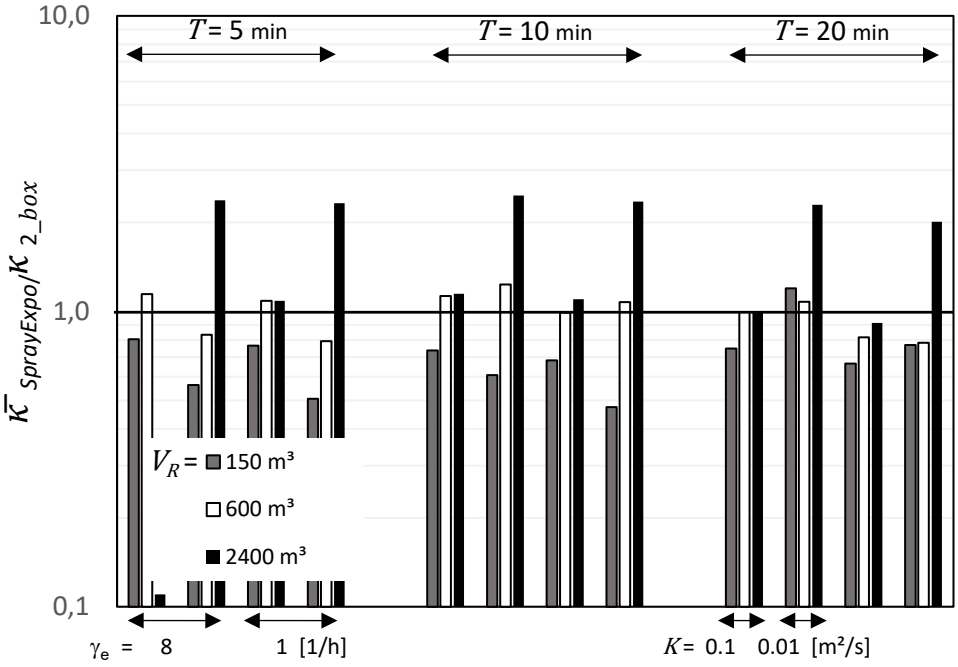


Fig. 6.10 $\bar{\kappa}$-ratios from SprayExpo calculations. Parameters varied: duration of application, T, room volume, V_R, air exchange rate, γ_e, and turbulent diffusion constant, K.

6.1.2 Comparison of the prediction of the deterministic models with measurements at workplaces and assessment

The comparison between model predictions and measurement results at workplaces is carried out with the 1-box model and the 2-box model where the parameters V_P = 10 m³ and T_M = 0.1 min are used as determined from the comparison with SprayExpo. The calculations with the 1-box and the 2-box-model were performed separately for the three size ranges: respirable, tracheo-bronchial and extra-thoracic to take particle size dependent settling into account. Representative diameter of 3, 7 and 14 µm, respectively, were used in the three regimes. This corresponds to settling velocities of v_s = 0.3, 0.15 and 0.59 cm/s (HINDS, 1999) and settling loss rates $\gamma_s = v_s/H$

of 0.3, 1.5 und 5.9 h^{-1} assuming a room height of H = 3.6 m[21]. The results of the separate size regimes were multiplied with the weights of 0.34, 0.34 and 0.32 (corresponding to the average Respicon results obtained in the release tests) and were subsequently added. The workplace scenarios were also modelled with SprayExpo and compared with measurement data.

The analytical models are simple enough to be used in case studies in practice. They also allow to calculate frequency distributions of the exposure concentration when the variances of the model parameters are taken into account. The comparison was carried out for those workplace measurements with foams for which the measured concentration values were above the limit of quantification. The techniques used and the analytes measured are listed in Table 6.2. For the simulated workplaces in the model room and other workplace investigations carried out at ITEM, caesium chloride was added to the QAC foam formulations. The comparison was based on the CsCl analysis. In all other cases, the active substance was measured.

The model parameters and the results of model calculations and measurements are listed in Tab. 6.3. The inhalable release fractions of the active substances of the foaming technologies used are taken from Fig. 5.4.

In all but two workplace investigations the duration of exposure was identical with the duration of foaming ($T_r = 0$). For AP1 and AP2 the deposited foam was distributed evenly on the surface by wiping. This post processing lasted much longer than the foaming actions. No aerosol release was assumed to take place during post processing. The influence of the additional residence time was taken into account by analytical formulas in the 1- and 2-box models (see Appendix 9) and they were specified in the input mask of SprayExpo (Fig. 6.7).

The comparison between measurement results and model predictions is shown in Fig. 6.11. The data were analysed by power law regression. For the 1-box model the Pearsons regression coefficient is slightly smaller than for the other two models. In SprayExpo a value of 0.1 m²/s was chosen for the turbulent diffusion constant. This relatively high value is related to turbulence generation caused by the foaming impulse and additional mixing by the movements of the user. The 2-box-model and SprayExpo simulation tend to be slightly more conservative. Mean values of the case specific conversion factors (measurement/model) as well as their minimum and maximum values are listed in Tab. 6.4. Although the average values are close to 1, the deviations of the individual values can be quite large. They cover a factor of 32 for the 1-box model and a factor of 29 for the 2-box-model and SprayExpo. A part of the variances is related to variances in the model source term via the release fractions. They are a factor of 4.3 and 4.0, respectively for the pressure foamers G and P (using QAC F and QAC E) as derived from the results of the model room experiments. At workplaces with high pressure foaming, the devices were similar to the device used in model room but not identical. This causes additional uncertainty.

[21] For all workplace measurements the settling loss rates were taken into account in the same way although the size distribution were probably quite different. This is also the view of chosing a single high value of the room height. The loss rate $\gamma_s = v_s/H$ implies a conservative estimation of the exposure,

Tab. 6.2 List of foam technologies and analytes used at the workplaces investigated. For AP14, AP15, AP18 and AP20 the concentration values were below the limit of quantification. These values were discarded.

Test	**Device**	**Analyte**
AP1	Hand compression foamer	CsCl
AP2	Hand pump foamer	CsCl
AP5	Pressure foamer G, foam nozzle 50/200	CsCl
AP6	Pressure foamer P, Teejet 110 06VP with foam cartridge	CsCl
V33-V35	Pressure foamer B, H1/4U Veejet 4050	CsCl
AP9	Hand pump foamer	CsCl
AP11	Insect foam B.2	Phenothrin
AP12	Insect foam B.2	Phenothrin
AP21	High pressure foam gun with high pressure booster	BAC
AP24	Pressure foamer P2, universal foam nozzle	CsCl
AP25	Pressure foamer P, Teejet 110 06VP with foam cartridge	CsCl
AP27	Insect foam B.1	Phenothrin
AP28	Insect foam F	Permethrin

Tab. 6.3 Comparison between model and measurement results obtained for the workplace scenarios investigated. When there was no forced ventilation an natural exchange rate of $\boldsymbol{\gamma_e = 0.1}$ h^{-1} was assumed. In AP21 (stable with open doors) we used a value of $\boldsymbol{\gamma_e = 5}$ h^{-1}.

	V_R	R_i^s	M^s	γ_e	T	T_r	$\frac{R_i^s \cdot M^s}{V_R}$	$\frac{R_i^s \cdot M^s}{T}$	$\kappa_{1\text{-box}}$	$\kappa_{2\text{-box}}$	$C_{1\text{-box}}$	$C_{2\text{-box}}$	$C_{SprayExo}$	Measure-ment
	m³	–	kg	1/h	min	min	kg/m³	µg/s			µg/m³	µg/m³	µg/m³	µg/m³
AP1	13.3	2.14E-05	3.25E-04*	8	1	5	5.23E-10	1.16E-01	0.59	0.69	0.3	0.4	0.4	0.1
AP2	13.3	1.43E-03	6.30E-05*	8	0.55	3.12	6.77E-09	2.73E+00	0.70	0.89	4.7	6.0	5.3	1.2
AP5	158	1.56E-04	1.04E-02*	8	1.83	0	1.03E-08	1.48E+01	0.45	1.29	4.6	13.3	9.2	10.3
AP6	158	6.04E-04	2.90E-03*	8	3.2	0	1.11E-08	9.12E+00	0.42	0.90	4.6	10.0	9.1	9.8
V33	158	4.46E-04	7.20E-03*	8	4	0	2.03E-08	1.34E+01	0.40	0.79	8.2	16.1	15.8	5.8
V34	158	4.46E-04	7.20E-03*	8	4	0	2.03E-08	1.34E+01	0.40	0.79	8.2	16.1	15.8	10.4
V35	158	4.46E-04	1.44E-02*	8	8	0	4.06E-08	1.34E+01	0.33	0.53	13.5	21.5	23.7	13.1
AP9	696	1.43E-03	5.60E-04*	2.3	19	0	1.15E-09	7.02E-01	0.33	0.69	0.4	0.8	0.8	0.2
AP11	41	3.23E-05	8.24E-04**	0.1	3.6	0	6.49E-10	1.23E-01	0.48	0.59	0.3	0.4	0.4	1.2
AP12	41	3.23E-05	5.57E-04**	0.1	3.4	0	4.39E-10	8.82E-02	0.48	0.60	0.2	0.3	0.3	0.2
AP21	616	1.81E-04	1.48E-01***	5	11	0	4.35E-08	4.06E+01	0.34	0.89	14.6	38.8	36.5	9.3
AP24	54	3.37E-06	1.02E-03*	0.1	20	0	6.37E-10	2.86E-02	0.40	0.42	0.3	0.3	0.3	0.7
AP25	54	6.04E-04	8.40E-03*	0.1	31	0	9.40E-08	2.73E+00	0.36	0.38	34.0	35.6	32.8	27.0
AP27	16	3.23E-05	7.10E-04**	0.1	20	0	1.43E-09	1.91E-02	0.40	0.40	0.6	0.6	0.5	1.4
AP28	34	6.43E-05	6.90E-03****	0.1	20	0	1.30E-08	3.70E-01	0.40	0.41	5.2	5.4	5.0	0.6

* values for CsCl **values für phenothrin *** values for BAC **** values for permethrin according to the third column of Tab. 6.2

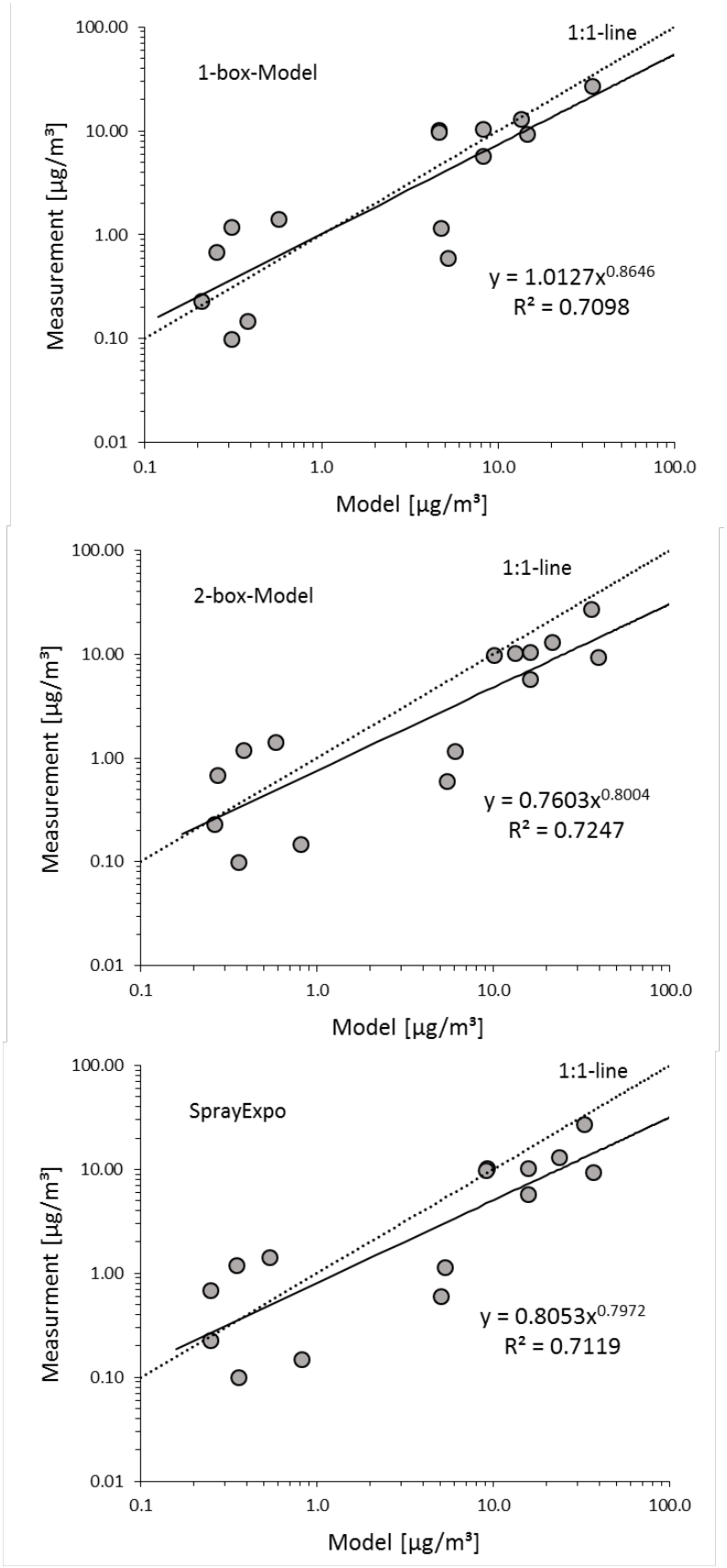


Fig. 6.11 Comparison between measurement and model prediction for the workplace investigations.

Tab. 6.4 Conversion factors between results of measurements and model prediction.

	1-box	2-box	SprayExpo
Mean	1.34	0.95	1.03
Minimum	0.12	0.11	0.12
Maximum	3.89	3.14	3.43

The SprayExpo and the 2-box model deliver almost identical results. This can also be seen from Fig. 6.12, where results of the 2-box model and the SprayExpo simulation were compared. As expected, the results correlate well, because the model parameters T_M and V_P of the 2-box model were derived from simulations by comparison with SprayExpo in the wall area mode. These simulations are obviously also representative for the actual workplace scenarios that differ from these calculations.

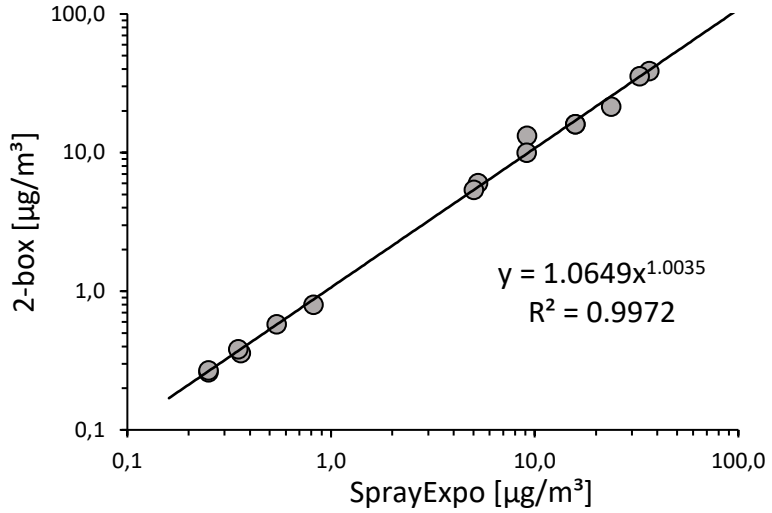


Fig. 6.12 Comparison of results from SprayExpo and the 2-box model.

Based on the available data and taking into account the uncertainties, the use of the simple analytical models for estimating the inhalable concentration of the active substance is appropriate.

In Section 5.1.4, a correlation between the release fractions and easily available process parameters was discussed, and the release fractions were classified in three categories specified by values that correspond to the blue lines in Fig. 5.11. These fixed values of the release fraction are assigned to the corresponding value ranges on the x-axis. They are approximately the geometric mean value of the data points. If the category specific values are used for R_i^S in the two analytical models, the correlation shown in Fig. 6.13 between measurement results and model predictions is obtained. On average, the 2-box model provides a conservative estimate of the inhalable concentration of the active substance, however, with a relatively large variance.

In summary, the 2-box model using release categories for a practicable source characterisation allows for a conservative estimate of the concentration of inhalable active substance as well as the corresponding inhaled dose. The contribution of the aerosol

to dermal exposure can also be derived from the concentration and Eq. 3.13. To be conservative, values of 0.95 cm/s for the deposition velocity on horizontal body surfaces and 0.2 cm/s for the deposition velocity on vertically aligned surfaces are used.

The input parameters of the model are the release fraction associated with the foam process, the amount of active substance consumed, the room volume, the loss rate due to air exchange, as well as the duration of the application and an additional residence time. The particle deposition can also be taken into account, provided information on the size distribution of the released active substance is available.

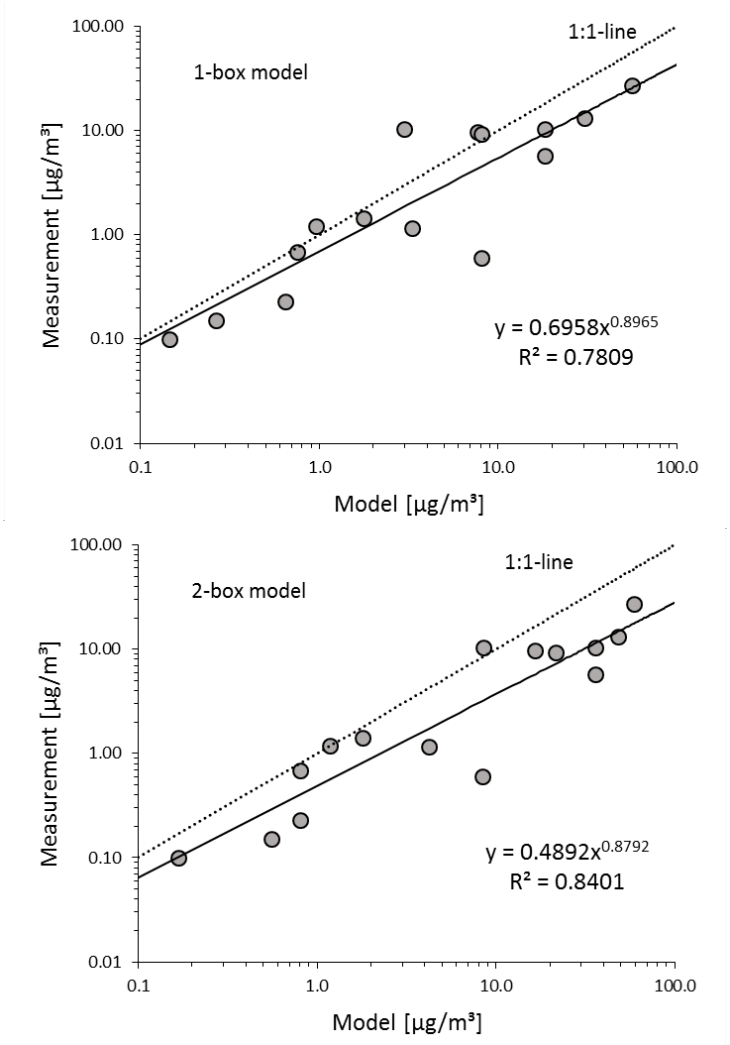


Fig. 6.13 Comparison between results of model calculations and measurements at workplaces when using the release categories from Fig. 5.11 for source term characterisation.

Tab. 6.5 Conversion factors between measurement and model calculation for the analytical models using the release categories as input.

	1-box	2-box
Mean value	0.85	0.51
Minimum	0.07	0.07
Maximum	3.48	1.21

The advantage of the analytical models is that variances of the model parameters, such as the variance of the release categories, active substance quantities or the typical range of values of air exchange rates, etc. can be easily incorporated into the calculations. The parameter values and their distribution can be stored in product- or application specific files and a frequency distribution of the concentration can be generated from them. Percentiles of the distribution can then be used for generalised conservative estimation of the exposure concentration. These analyses would have to be based on an inventory of the application- or substance-specific value ranges of the process parameters.

6.2 Comparison using TNSG-Models

6.2.1 Dermal exposure

In order to compare this project's compiled data on potential dermal exposure by the foaming and spraying of biocidal products with the indicative values for spray applications given in the guideline "Biocides Human Health Exposure Methodology" (ECHA 2015, BHHEM), the data was normalised to the mass of product solution applied per minute [mg/min]. The individual data sets were each allocated to an appropriate spray model and grouped. The corresponding normalised and grouped data is summarised in Tab. 6.6 to Tab. 6.11.

For application via handheld devices and devices for large-scale application, the data sets on potential dermal exposure for both application types were aggregated, as there were no significant differences between foaming and spraying applications present; both the measured value range and the 50th percentile are given. For pressurised cans, however, a difference between foaming and spraying is clearly indicated by the data, conclusively ruling out the possibility of aggregation.

The ECHA spray models used for comparison were assigned by application pressure. No appropriate model could be found for handheld devices (hand pump foamer and sprayer (bottles), hand compression foamer and sprayer), or pressurised foam and spray cans, as the indicative values based on the publication by POPENDORF et al. (1995) could not be realised. Data for stationary application devices with < 3 bar were compared with TNSG Spray Model 1, data for stationary application devices with 3–6 bar were compared with TNSG Spray Model 2, and finally, data for high-pressure application devices (> 10 bar) were compared with TNSG Spray Model 3.

The workplace data compiled within the framework of this project display an adequate level of consistency with the data given in the individual models of the ECHA guidelines.

Tab. 6.6 Handheld devices: potential dermal exposure by product amount [mg] or product amount per minute [mg/min] (application only, #1–#4).

Hand pump foamer and sprayer (bottle) as well as hand compression foamer and sprayer (< 3 bar) – application only						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
1	Foam	1.00*	128	6.47	128	6.47
2	Foam	0.55*	20.7	24.8	37.7	45.1
3	Spray	1.00*	41.2	4.76	41.2	4.76
4	Spray	1.28*	46.1	30.5	36.0	23.8
				Range	36.0–128	4.76–45.1
				50th perc.	39.4	15.1

* simple duration of application without wiping

Tab. 6.7 Handheld devices: potential dermal exposure by product amount [mg] or product amount per minute [mg/min] (application and wiping, #1–#4, #9, #10).

Hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer (< 3 bar) – application and wiping						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
1	Foam	6.00*	1260	33000	210	5500
2	Foam	3.67*	201	4940	54.8	1350
9	Foam	19.0*	35.9	15200	1.89	803
3	Spray	4.50*	516	7970	115	1770
4	Spray	4.45*	204	3470	45.9	779
10	Spray	17.0*	205	7810	12.0	459
				Range	1.89–210	459–5500
				50th perc.	50.4	1074

* the given duration of exposure includes both biocidal product application and wiping

Tab. 6.8 Stationary devices (< 3 bar): potential dermal exposure by product amount [mg] or product amount per minute [mg/min].

Stationary devices (< 3 bar)						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
6	Foam	3.20	79.4	30.8	24.8	9.62
24	Foam	20.0	792	3460	39.6	173
25	Foam	31.0	142	94.6	4.59	3.05
8	Spray	1.00	21.4	13.9	21.4	13.9
19	Spray	16.0	374	7.29	23.4	0.456
26	Spray	12.0	747	239	62.2	19.9
				Range	4.59–62.2	0.456–173
				50th perc.	24.1	11.8
Spray Model 1 (BHHEM 2015)				Range	0.63-692	12–181
				50th perc.	24.5 (102 measured values)	31 (5 measured values)

Tab. 6.9 Stationary devices (3–6 bar): potential dermal exposure by product amount [mg] or product amount per minute [mg/min].

Stationary devices (3–6 bar)						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
5	Foam	1.83	34.7	130	18.9	70.7
18	Foam	5.85	1270	1710	217	292
20	Foam	5.20	548	514	105	98.8
7	Spray	0.92	240	206	261	225
				Range	18.9–261	70.7–292
				50th perc.	161	162
Spray Model 2 (BHHEM 2015)				Range	2.30–36300	13.9–273
				50th perc.	45 (55 mea-sured values)	35 (6 measured values)

Tab. 6.10 Stationary devices (> 10 bar): potential dermal exposure by product amount [mg] or product amount per minute [mg/min].

Stationary devices (> 10 bar, high-pressure devices)*						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
15	Foam	12.0	2730	595	228	49.6
21	Foam	12.0	9720	1970	810	164
16	Spray	5.00	3630	192	726	38.4
17	Spray	5.83	8150	1090	1400	187
				Range	228–1400	38.4–187
				50th perc.	768	107
Spray Model 3 (BHHEM 2015)				Range	0.880–1240	21.7–119
				50th perc.	103 (27 measured values)	76 (6 measured values)

* Measurement #14 was not considered, because the concentration of active substance in the applied product failed to meet the requirements

Tab. 6.11 Pressurised cans (usually 3 bar, max. 8 bar): potential dermal exposure by product amount [mg] or product amount per minute [mg/min].

Pressurised cans (usually 3 bar, max. 8 bar)						
Measure-ment	Application type	Duration of exposure [min]	Exposure by product amount [mg]		Exposure by product amount per minute [mg/min]	
			Coveralls	Gloves	Coveralls	Gloves
11	Foam	3.63	1.19	142	0.326	39.0
12	Foam	3.43	54.2	0.197	15.8	0.057
27	Foam	20.0	572	78.4	28.6	3.92
28	Foam	20.0	5.24	15.3	0.262	0.763
13	Spray	0.38	356	71.8	929	187
			Foam (Range)		0.262–28.6	0.057–39.0
			Spray		929	187

6.2.2 Inhalative exposure

For inhalation exposure, the comparison is made using the measured mass concentration, C^s, of active substance or CsCl and the droplet aerosol concentration, C^T, calculated from the content, $c^{s,l}$, of active substance or CsCl in the formulation:

(6.10)

$$C^T = \frac{C^s}{c^{s,l}}.$$

The comparison for the spray applications is shown in Tab. 6.12. Here, the pump sprays were arbitrarily grouped into the pressure category < 3 bar, although the spray pressure cannot be specified.

The workplace concentrations determined in this project fall within the concentration ranges of spray models 1 and 2 assigned to the corresponding application. Model 3 used for high-pressure application by means of a single-substance spray nozzle significantly underestimates the concentrations measured in this study. This is due to the fact that model 3 is essentially based on measurements taken when spraying viscous dye formulations (antifouling products). Here, a very coarse spray droplet size distribution can be assumed, which leads to a low exposure concentration to inhalable aerosols. When spraying aqueous solutions, a finer spray mist with much higher exposure potential can be assumed.

Formally, the comparison can also be made for the foam applications. This can be found in Tab. 6.13. For the measurements assigned to spray models 1 and 2, the measured values are at the lower limit of the value range of the TNSG models; clearly below the corresponding median values. For the high pressure foam applications, the measured exposure concentrations are higher than the median value of spray model 3 for the high pressure spray application.

Tab. 6.12 Comparison droplet aerosol concentration at workplaces with TNSG model predictions (spray application).

Measurement	Device	Nom. pressure [bar]	C^T [mg/m³]	TNSG Model range; 50 %/75 %-percentile [mg/m³]
4	Hand pump sprayer	–	38.6	Spray model 1 0.2–631 104; 130
10	Hand pump sprayer	–	38.3	
3	Hand compression sprayer	<3	5.7	
8	Pressure sprayer P; fan nozzle (Teejet 110 06VP)	<3	26.1	
19	Battery operated pressure sprayer (2bar); pool area	<3	15.9	
26	Pressure sprayer P2; standard hollow cone nozzle; appartment	<3	49.9	
7	Pressure sprayer G; spray nozzle 30/40 (fan nozzle)	3–6	48.5	Spray model 2 0.98–813

Measure-ment	Device	Nom. pres-sure [bar]	C^T [mg/m³]	TNSG Model range; 50 %/75 %-percentile [mg/m³]
				20; 76
16	Spray application, high pressure; large chicken stable	>10	287.8	Spray model 3 0.04–79.4 6.6; 17.3
17	Spray application, high pressure; small pig stable	>10	197.7	
13	Insect spray B	3	220	Spray model 1 0.2–631 104; 130

Tab. 6.13 Comparison droplet aerosol concentration at workplaces with TNSG model predictions (foam application).

Measure-ment	Device	Nom. pres-sure	C^T [mg/m³]	TNSG Model 50 %/75 %-percentile
2	Hand pump foamer	–	1.16	Spray model 1 0.2–631 104; 130
9	Hand pump foamer	–	0.15	
1	Hand compression foamer	<3	0.10	
6	Pressure foamer P; fan nozzle (Teejet 110 06VP) with foam cartridge; large model room	<3	9.81	
24	Pressure foamer P2; universal foam nozzle; appartment	<3	0.69	
25	Pressure foamer P; foaming (black cartridge); Teejet 110/08 VP, appartment	<3	26.95	
5	Pressure foamer G; foam nozzle 50/200 (fan nozzle), large model room	3–6	10.32	Spray model 2 0.98–813 20; 76
18	Foam dispensing head (pressure of water supply), sauna area	3–6	<64.55 (<LOQ)	
20	Foam dispensing head (pressure of water supply), sauna area	3–6	<46.44 (<LOQ)	
V33	Pressure foamer B; H1/4U Veejet 4050	3–6	5.80	
V34	Pressure foamer B; H1/4U Veejet 4050	3–6	10.40	
V35	Pressure foamer B; H1/4U Veejet 4050	3–6	13.10	
21	High pressure foam gun, pig stable	>10	23.32	Spray model 3 0.04–79.4 6.6; 17.3
14	High pressure foam gun, small pig stable	>10	<800 (<LOQ)	
15	High pressure foam gun, large chicken stable	>10	<24.49 (<LOQ)	
11	Insect foam B.2	3	0.80	Spray model 1 0.2–631 104; 130
12	Insect foam B.2	3	0.15	
27	Insect foam B.1	3	1.36	
28	Insect foam F	3	0.02	

7 Summary

The following objectives should be achieved in the project:

- Characterisation of release parameters for active substances relevant for inhalation and dermal exposure during the application of biocidal foams as well as the spray application of biocidal products for practical technologies and substance classes.
- Development of a simple deterministic prediction model for inhalation.
- Verification of the model using representative measurements at workplaces.
- Determination of reduction factors between spraying and foaming when meaningful comparison criteria are available

The main project results are summarised as follows:

Inhalation exposure:

A comprehensive data set characterising the aerosol release for relevant foaming techniques was generated. For this purpose, so-called release fractions were determined in model room measurements. The variation of easily measured process parameters in the foaming processes allowed a categorisation of the release fractions.

It was found that for the frequently used premixed systems, the aerosol release is determined by the dimension of the nozzle, characterised by its circumference, l, the exit velocity, v, and to the foam expansion ratio, E, in the combination $v/(l \cdot E)$. Regression analysis of the measured data reveals a nearly linear dependence of the release fraction on this parameter combination (R^2 = 0.83). The relation between foam expansion ratio and air and liquid flow rates (Q_a, and Q_l) results in an approximate correlation of the release fraction with the quantity $Q_l/(l \cdot A)$, where A is the cross-sectional area of the nozzle exit. Thus, the aerosol release is related to process parameters that can be easily determined experimentally. Different possibilities have been suggested for classifying the release potential of a process:

1. Use of the correlation obtained from the data set: $R^s = 2 \cdot 10^{-6} \cdot (Q_l/(l\,A))^{1.1}$
2. Determination of the release fraction from a conservative perspective in ana-lysing the data set: $R^s = 6 \cdot 10^{-6} \cdot (Q_l/(l\,A))^{1.1}$
3. Assignment of the process to one of three release categories with values for the release fraction of 10^{-5}, 10^{-4}, and 10^{-3} for $(Q_l/(l\,A))$ between 1 and 10, 10 and 100, and 100 and 1000 [1/s], respectively. Based on the measurements, the pressurised cans and hand pump foamer (bottles) used are assigned to categories 2 and 1, respectively.[22]

These parameters are used as input variables for the deterministic models for estimating the inhalation exposure to inhalable aerosols. Simple 1- and 2-box models or

[22] The generalization of this order should be verified by further investigations.

SprayExpo simulations were used, which were adapted accordingly for foam application. The quality of the developed prediction models was verified using data collected at the workplaces. The foam devices and methods used in the workplace measurements corresponded to those used in the model room measurements. The investigations showed that the 2-box model, using the release categories assigned to the foam devices, conservatively predicts the concentrations measured at the workplaces within one order of magnitude.

A comparison with the TNSG spray models, which are classified according to the spray pressure, is questionable, because an unambiguous pressure assignment of the foam processes, which influences the aerosol formation, is hardly possible. If a formal assignment to the TNSG models is made according to the nominal pressures of the foam processes, the concentration values for the foam measurements for models 1 and 2 lie at the lower end of the value ranges of the TNSG models. For the high-pressure foam applications, the values are in the range of the concentration values listed in TNSG model 3 for the spray application.

The exposure concentration for foaming is generally lower than for spraying. However, a generally valid reduction factor with regard to inhalation exposure between spray and foam application could not be determined for the equipment categories in focus.

The exposure data and modeling results for foam application obtained in this project can also serve in the long term as an initial data basis for establishing improved occupational safety measures in the field of foaming biocidal products.

Dermal exposure:

In contrats to inhalation exposure, no significant difference was found between spray and foam application for dermal exposure. The reason was seen in the fact that the potential dermal exposure is determined by the equipment technology, the individual behaviour of the user and thus also by the occurrence of random contamination events such as splashes and direct contact. When only the segments of the coverall were considered, where dermal exposure was mainly due to aerosol deposition, a reduction factor of 3.8 was found between the two modes of application.

A simple prediction model was not developed for dermal exposure within the project. A comparison of the dermal data obtained in the project with the measurement data published in the BHHEM method paper shows a good agreement for the stationary devices considered as well as the high-pressure applications. The data collected for product application with handheld devices and pressurised cans could not be assigned to a suitable spray model.

8 Outlook

The comprehensive theoretical and practical findings on the inhalation and dermal exposure of workers during the application of biocidal foams will finally be processed in order to use them in the regulatory context i.e. biocidal product approvals for risk assessment of human health. Furthermore, the model development will be included in the upcoming project F2467 “Modular model approaches for exposure assessment for risk assessment at the workplace in the context of chemical safety” of the Federal Institute for Occupational Safety and Health.

Regarding the practical application of deterministic modeling, it is suggested to expand the database of release fractions. The categorisation of the hand pump foamers and the propellant foam cans, whose release fraction cannot be attributed to the described process parameters, is currently based only on measurements with a few selected individual devices. Here, additional investigations with an extended range of devices are necessary for a statistical validation of the proposed categorisation. Furthermore, it would be useful for the verification of the proposed 2-box model to obtain additional data of the active substance concentration at workplaces with large room volumes (> 1000 m^3), because especially in these scenarios the separation of personal exposure volume (near-field exposure) and room volume (far-field exposure) made in the 2-box model can be verified.

References

DIN EN 481: Arbeitsplatzatmosphäre; Festlegung der Teilchengrößenverteilung zur Messung luftgetragener Partikel. Berlin: Beuth Verlag 1993

DIN EN 482: Exposition am Arbeitsplatz – Allgemeine Anforderungen an die Leistungsfähigkeit von Verfahren zur Messung chemischer Arbeitsstoffe. Berlin: Beuth Verlag 2015

DIN EN 13936: Exposition am Arbeitsplatz – Messung eines als Mischung aus luftgetragenen Partikeln und Dampf vorliegenden chemischen Arbeitsstoffes – Anforderungen und Prüfverfahren. Berlin: Beuth Verlag 2014

ECHA: Guidance on the Biocidal Products Regulation Volume III Human Health – Part B Risk Assessment, Version 2.3, October 2015.

ELFLEIN, L. (2003): Entwicklung von validierten Analysemethoden zur Bestimmung von Innenrauminsektiziden und –akariziden. Dissertation. Universität Hannover Fachbereich Chemie. 2003

EMA Guideline: EMEA/CHMP/EWP/192217/2009 (www.ema.europa.eu/docs/en_GB/document_library/Scientific_guideline/2011/08/WC500109686.pdf)

GARROD A.N.I.; RIMMER, D.A.; ROBERTSHAW, L.; JONES, T.: Occupational exposure through spraying remedial pesticides, Ann. Occup. Hyg., 42:159-165. 1998

HINDS, W.C. (1999): Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles, 2nd Edit., John Wiley ISBN: 978-0-471-19410-1

IPASUM Arbeitsplatzbelastungen bei der Verwendung von Biozidprodukten: Messungen zur inhalativen und dermalen Exposition bei der Ausbringung von Biozidschäumen, 1. Zwischenbericht zum Projekt F2366, 2018

ITEM (1) F2366 – Arbeitsplatzbelastungen bei der Verwendung von Biozidprodukten: Messungen zur inhalativen und dermalen Exposition bei der Ausbringung von Biozidschäumen. Analyseverfahren zur Bestimmung ausgewählter Pyrethroide nach Luftprobenahme auf Glasfaserfiltern, Validierungsbericht, 2018

ITEM (2) F2366 – Arbeitsplatzbelastungen bei der Verwendung von Biozidprodukten: Messungen zur inhalativen und dermalen Exposition bei der Ausbringung von Biozidschäumen Analyseverfahren zur Bestimmung von Benzalkoniumchloriden nach Luftprobenahme auf PTFE-Filtern, Validierungsbericht, 2018

KOCH, W.; BERGER-PREIß, E.; BOEHNKE, A.; KÖNNEKER, G.; MANGELSDORF, I.: Arbeitsplatzbelastungen bei der Verwendung von Biozid-Produkten Teil 1: Inhalative und dermale Expositionsdaten für das Versprühen von flüssigen Biozid-Produkten, Dortmund: Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. 2004

KOCH, W.; BEHNKE, W.; BERGER-PREIß, E.; KOCK, H.; GERLING, S.; HAHN, S.; SCHRÖDER, K.: Validation of an EDP assisted model for assessing inhalation

exposure and dermal exposure during spraying processes. Dortmund: Bundesanstalt für Arbeitsschutz und Arbeitsmedizin. 2012

SCHWARZ, K.; KOCH, W.: Thoracic and Respirable Aerosol Fractions of Spray Products Containing Non-Volatile Compounds. J. Occup. Environmen. Hyg. 14:831-838. 2017

VAN BOXTEL, N.; WOLFS, K.; PALACIN, M. G.; VAN SCHEPDAEL, A.; ADAMS, E.: Headspace gas chromatography based methodology for the analysis of aromatic substituted quaternary ammonium salts. J. Chromatogr. A, 1476:105-113. 2016

VDI-Richtlinie 4301-Blatt 4: Messen von Innenraumluftverunreinigungen, Messen von Pyrethroiden und Piperonylbutoxid in Luft. VDI/DIN-Handbuch Reinhaltung der Luft Band 5: Analysen- und Messverfahren II. Düsseldorf: Verein deutscher Ingenieure e.V. 2016

List of symbols

r,t,i	Subscripts for the respirable, thoracic and inhalable size fraction	–
A	Cross sectional area of nozzle exit	mm²
$A_{h,v}$	Body surface (horizontal/vertical)	m^2
α_k	Ratio of the peak heights (normalised to the first release action)	
BAC	Benzalkonium chloride	
c	Aerosol mass concentration	µg/m³
$\bar{c}^s$	Average mass concentration of active substance (measurements in model rooms)	
$c_{0,k}^s$	Concentration peaks of active substance (measurements in model rooms)	
$c^{s,l}$	Content of active substance in the formulation	kg/kg
C^T	Calculated droplet mass concentration at the workplace	
C^s	Average concentration of active substance at the workplace	
Cs	Caesium	
CsCl	Caesium chloride	
$D^{derm/\,inh}$	Dermal, inhalation dose	µg
DDAC	Didecyldimethylammonium chloride	
F	Treated surface area	m²
GC-MS(D)	Gas Chromatography – Mass Spectrometry (Detection)	
GSP	Gesamtstaubprobenahmegerät (DE), inhalable sampling device	
E	Foam expansion ratio	–
HS	Headspace	
HS-GC-MS	GC-MS: Gas Chromatography – Mass Spectrometry and Headspace-Sample System	
γ_e	Loss rate by air exchange	1/h
γ_s	Loss rate by particle settling/deposition	1/h
Γ	Loss rate	1/h
k	Index for the release action during a test	
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry	
ISTD	Internal standard	
κ	Dispersion function	
MCE	Mixed Cellulose Ester	
M^s	Total mass of applied active substance	kg
$\dot{M}^s$	Mass flow rate of active substance	kg/s

m^s	Release mass of the inhalable active substance (measurements in model rooms)	µg
$\dot{M}_i^s$	Mass flow rate of the inhalabe active substance	µg/s
m/z	Mass to charge ratio	
N	Number of release actions	
PBO	Piperonylbutoxide	
PTFE	Polytetrafluorethylene	
QAC	Quaternary ammonium compounds	
QC-Standard	Quality Control-Standard	
Q_A	Inhalation volume flow rate	l/min
Q_l	Liquid volume flow rate	l/min
Q_a	Foam air volume flow rate	l/min
R^s	Release fraction of active substance	–
ρ^s	Surface dose of active substance	kg/m²; µg/m²
SIM	Single Ion Monitoring	
STDV	Standard deviation	
SIM	Single Ion Monitoring	
S^s	Source strength of aerosolised active substance	kg/s
t	time	min
$t_{s,k}$	Duration of individual spray/foam actions in the model room tests	min
T	Duration of application	min
T_m	Sampling duration during each spray/foam action in the model room	min
T_M	Aerosol residence time in the personal control volume	min
T_r	Residence time in the room	min
τ	Concentration decay time after the spray/foam action	min
v	Exit velocity	m/s
$v_{dep,h/v}^s$	Deposition velocity of active substance (horizon-tal/vertical)	cm/s
l	Nozzle circumference	mm
V_P	Personal control volume (2-box model)	m³
V_R	Volume of the model room, workplace	m³
χ	Dilution function	1/m³

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Appendices

Appendix 1 Data evaluation sheet

App. Tab. 1 Excel evaluation scheme of the release measurements. Input data are process data (shaded gray), data derived from measurements with the aerosol spectrometer (shaded green) and results of the chemical analysis of active substance (shaded yellow). The remaining values are results of calculations according to Eqs. 3.16 and 3.17. Example of 2 release actions (foaming)

Room volume	V	m³	158		
Liquid flow rate	Q	kg/min	9.00		
Number of spraying/foaming actions	N	–	2.00		
Duration of spraying/foaming	$t_{s,k}$				
1		min	3.00		
2		min	2.17		
3		min			
4		min			
Duration of spray action	$t_{s,k}$	min	30		
			Size fractions		
			i	t	r
Decay time	τ	min	15.6	20.0	29.0
rel. peak heghts	α_k				
1		–	1	1	1
2		–	0.62	0.63	0.68
3		–			
4		–			
Summe			1.62	1.63	1.68
Ave. concentration (CsCl)	$\bar{c}^S_{r,t,i}$	µg/m³	23.90	13.90	4.35
Initial concentration (CsCl)	$c^S_{0,k;r,t,i}$				
1		µg/m³	66.46	32.93	8.31
2		µg/m³	41.20	20.75	5.65
3		µg/m³			
4		µg/m³			
Release fraction (CsCl)	R^S	–			
1		–	**3.9E-07**	**1.9E-07**	**4.9E-08**
2		–	**3.3E-07**	**1.7E-07**	**4.6E-08**
3		–			
4		–			
Mean value		–	**3.6E-07**	**1.8E-07**	**4.7E-08**
Max. deviation		–	**5.6E-08**	**2.5E-08**	**2.9E-09**

Appendix 2 Standard operating procedure – Analytical method for the determination of selected pyrethroids after sampling on glass fibre filters

Introduction/objective

This operating procedure describes the extraction of the substances piperonyl butoxide (PBO), tetramethrin and phenothrin from glass fibre filters and their subsequent quantification by means of gas chromatography and mass spectrometric (GC-MS). The method is based on the dissertation by ELFLEIN (2003) and VDI Guideline 4301 Sheet 4 (2016).

Procedure

Principle of the method

Glass fibre filters are extracted with ethyl acetate in an ultrasonic bath. After concentration of the extracts, the analytes (PBO, tetramethrin, phenothrin) are quantified by GC-MS using PBO-d9 as internal standard (ISTD).

Instruments and materials

- GC-MS coupling (for example: Agilent 7890A/5975C with HPChemStation and autosampler)
- Eppendorf pipettes (various sizes)- Volumetric flasks (1 and 10 mL)- tweezers
- Analytical balance (Sartorius, Research RC 210S)
- Ultrasonic bath (Bandelin SONOREX or Omnilab)
- Concentration workstation (TurboVap II from Zymark or Biotage) including glasses
- Beakers
- Autosamplervials (2 mL, amber glass; Agilent Technologies)
- Aluminium foil
- Glass fibre filter (37 mm; Whatman or similar)

Chemicals and solvents

- Ethyl acetate (short: EtAc; e.g. SupraSolv, Merck, Darmstadt, Germany).
- Piperonyl butoxide (abbreviation: PBO, e.g. Pestanal®, Sigma-Aldrich, product number: 45626)
- Piperonyl butoxide-d9 (short: PBO-d9, e.g. Sigma-Aldrich, product number: 73879)
- Tetramethrin (Pestanal®, e.g. Sigma-Aldrich, product number: 45681)
- Phenothrin (Pestanal®, e.g. Sigma-Aldrich, product number: 36193)

Solutions

Standard solutions:

Analyte standard solution 1

Tetramethrin
The pure substance (approx. 10 mg) is weighed out exactly and dissolved in 10 mL ethyl acetate. The final analyte concentration is determined by the weight and the purity of the substance (see e.g. the manufacturer's certificate of analysis).
The solution is prepared using a suitable balance and volumetric flask.

Example: 8.70 mg tetramethrin (purity: 98.3 %) is weighed out exactly and dissolved in 10 mL ethyl acetate. This results in an analyte concentration of 0.855 mg/mL.

Phenothrin
The pure substance (approx. 10 mg) is weighed out exactly and dissolved in 10 mL ethyl acetate. The final analyte concentration is determined by the weight and the purity of the substance (see e.g. the manufacturer's certificate of analysis).
The solution is prepared using a suitable balance and volumetric flask.

Example: 8.40 mg phenothrin (purity: 94.4 %) are accurately weighed and dissolved in 10 mL ethyl acetate. This results in an analyte concentration of 0.793 mg/mL.

Piperonylbutoxid (PBO)
The pure substance (approx. 10 mg) is weighed out exactly and dissolved in 10 mL ethyl acetate. The final analyte concentration is determined by the weight and the purity of the substance (see e.g. the manufacturer's certificate of analysis).
The solution is prepared using a suitable balance and volumetric flask.

Example: Es werden 8,98 mg Piperonylbutoxid (Reinheit: 98,6 %) genau abgewogen und in 10 mL Ethylacetat gelöst. Daraus resultiert eine Analytkonzentration von 0,885 mg/mL.

Analyte standard solution 2
Standard solutions 1 (tetramethrin, phenothrin and PBO) are diluted to an analyte mixed standard with a nominal concentration of the individual analytes of 10 µg/mL in ethyl acetate.
The solution is prepared using suitable pipettes and volumetric flasks.

Example: Ethyl acetate is added to a volumetric flask, the standard solutions 1 are added according to the following pipetting scheme (App. Tab. 2) and the flask is filled up to the mark with ethyl acetate.

App. Tab. 2 Analyte – standard solution 2 (mixed standard; 10 µg/mL): Pipetting scheme

Analyte	Volume Analyte-Standard solution 1 [µL]	Volume ethyl acetate [mL]
Tetramethrin	116.9	Mix in 10 mL
Phenothrin	126.1	
PBO	112.9	

Analyte – standard solution 3
The analyte standard solution 2 is diluted 1:10 in ethyl acetate. The concentration of the individual analytes in the solution was 1 µg/mL.
The solution is prepared using suitable pipettes and volumetric flasks.

Example: Fill 2 mL of ethyl acetate in a 10 mL volumetric flask, then add 1 mL of the analyte standard solution 2 and fill the flask up to the mark with ethyl acetate.

Internal standard (ISTD) – Solution 1
PBO-d9 is used as ISTD. The pure substance (10 mg; purity: 100 %) is supplied in an ampoule, which is opened and the substance is dissolved in 2 mL ethyl acetate. The final ISTD concentration is 5 mg/mL.
The solution is prepared using suitable pipettes and volumetric flasks.

Internal standard (ISTD) – Solution 2
The ISTD solution 1 is diluted 1:500 in ethyl acetate. For this purpose, approx. 5 mL ethyl acetate is placed in a 10 mL volumetric flask, 20 µL of ISTD solution 1 is added and then the flask is filled up to the mark with ethyl acetate. The concentration of ISTD solution 2 is therefore 10 µg/mL.
The solution is prepared using suitable pipettes and volumetric flasks.

Solutions for calibration:

Matrix
All calibration and blank value solutions are prepared in filter matrix.

For this purpose, the respective filters are cut into pieces, placed in a 50 mL beaker and extracted in an ultrasonic bath for 5 min after the addition of 10 mL ethyl acetate. The supernatant is transferred to a 250 mL Turbo-Vap glass. The extraction step is then repeated twice more. Concentration of the combined extracts to approx. 0.5 mL is carried out in a concentrator (Turbo-Vap II) at 40 °C wash bath temperature. The concentrated extract is then filtered through an Eppendorf pipette tip grafted with glass wadding into a 1 mL volumetric flask. The final volume is adjusted to 1 mL with ethyl acetate.
For the preparation of the calibration and blank value solutions, for example, 20 filters are individually processed in this way and finally combined to form a matrix.

Calibration solutions
Nine calibration solutions are prepared by appropriate dilutions of the analyte standard solutions 2 and 3 in matrix (App. Tab. 3). The calibration standards cover a concentra-

tion range from 5 to 500 ng/mL. It has proven useful to further subdivide this concentration range, for example 5–100 ng/mL and 100–500 ng/mL, to ensure sufficient linearity of the calibration function.
The standards are prepared using suitable microlitre syringes and volumetric flasks.

App. Tab. 3 Information on the preparation of calibration solutions.

Concentration [ng/mL]	Prepared-matrix volume [µL]	Analyte-Standard-solution/volume [µL]	ISTD-solution 2 [µL]	Final volume [mL]
5	985	*3*/5	10	1
10	980	*3*/10	10	1
25	965	*3*/25	10	1
50	985	*2*/5	10	1
100	980	*2*/10	10	1
200	970	*2*/20	10	1
300	960	*2*/30	10	1
400	950	*2*/40	10	1
500	940	*1*/50	10	1

QC-solutions (control solutions)

QC solutions are used to control the calibration and are integrated both at the beginning and at the end of a sample sequence. In the case of extensive sample sequences, it is useful to implement QC solutions at regular intervals in the sample sequence.

Glass fibre filters are prepared for three concentration levels, 7.5; 100 and 450 ng/filter. For this purpose, the filters are spiked with 7.5, 10 and 45 µL of the analyte standard solution 2, respectively. Each filter is also spiked with 10 µL of ISTD solution 2. The filters prepared in this way are then processed as described under “Sample preparation”. The final extract volume is 1 mL, resulting in the following extract concentrations for the QC standards

- QCLow: 75 ng/mL
- QCMed: 100 ng/mL
- QCHigh: 450 ng/mL.

The standards are prepared using suitable microlitre syringes and volumetric flasks.

Sample preparation

For sample preparation, the respective filters are cut into pieces, placed in a 50 mL beaker and extracted in an ultrasonic bath for 5 min after adding 10 mL ethyl acetate. The supernatant is transferred to a 250 mL Turbo-Vap glass. The extraction step is then repeated twice more. The combined extracts are concentrated to approx. 0.5 mL in a concentrator (Turbo-Vap II) at 40 °C water bath temperature. The concentrated extract is then filtered through an Eppendorf pipette tip grafted with glass wadding into a 1 mL volumetric flask. The final volume is adjusted to 1 mL with ethyl acetate.

The processing of the filters should take place promptly after sampling. The storage of the filter samples should not exceed the following periods (“Storage stability – filter matrix”) should not exceed:

- 8 days at 7–12 °C
- 24 h at room temperature.

Storage of sample extracts at –20 °C should not exceed 7 days for tetramethrin, while in the case of phenothrin and PBO sample extracts can be stored for up to 14 days under the specified storage conditions.

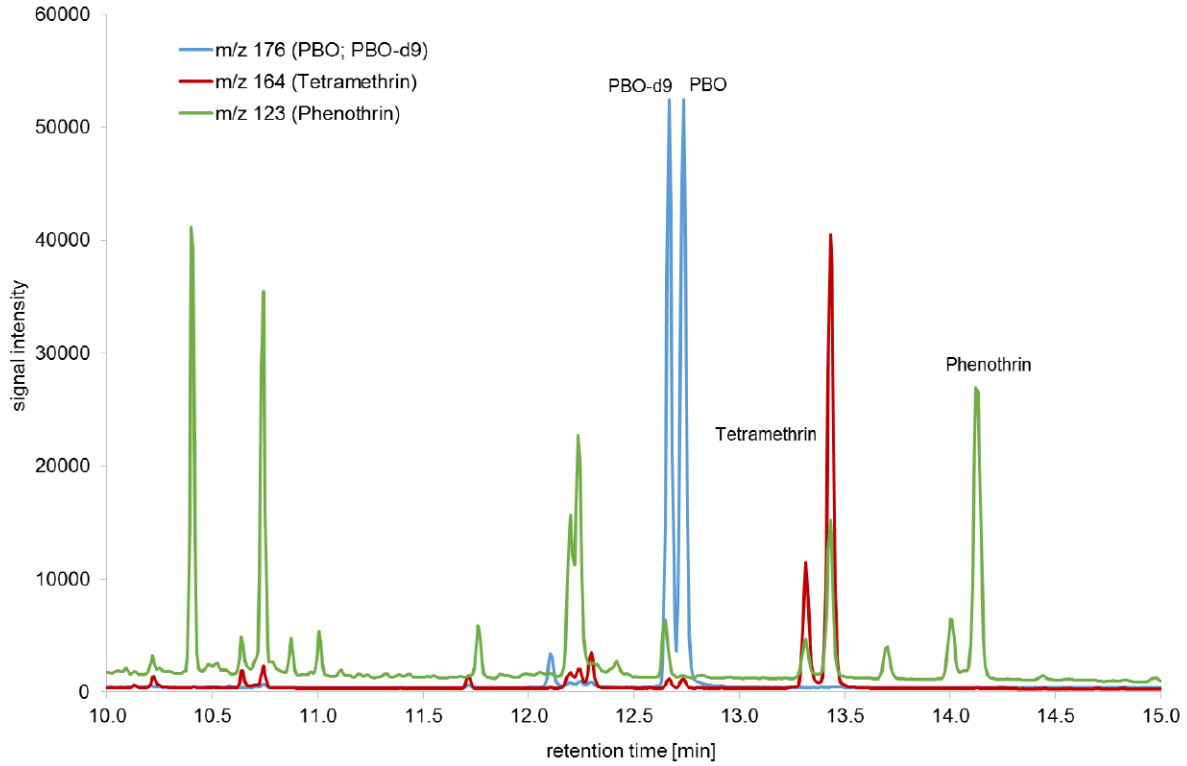
GC-MSD-measurement

The parameters and settings of the GC-MS method are listed in App. Tab. 4. Chromatographic traces of a 100 ng/mL standard are shown as examples for PBO, PBO-d9, tetramethrin and phenothrin in App. Fig. 1. Tetramethrin is quantified by the sum of the two isomers at 13.32 and 13.44 min. For phenothrin, several isomers are also available; quantification is based on the signal-strongest peak at 14.14 min.

App. Tab. 4 GC-MS: Parametes and values

Parameter	Value
GC-System	z. B. Agilent 7890A
Injection	Pulsed/Splitless
Injector – temperature	250 °C
Injektion volume n	2 µL
Separation column	HP-5, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm
Carrier gas	Helium, 1.4 mL/min
Temperature programme	Start: 60 °C (1 min) 40 °C/min to 240 °C (0 min) 10°C/min to 280 °C (20 min)
MS – System (MS)	Agilent 5975C
Transfer line – temperatuer	280 °C
Detector – temperature	230 °C
Measuring mode	Single Ion Monitoring (SIM)

Analyte	Quantification (quantifier ion/target ion) (m/z)	Qualification (qualifier ion) (m/z)	Retention time [min]
PBO-d9	176.1	149	12.68
PBO	176.1	149	12,74
Tetramethrin	164.0	123.0	13.32 und 13.44
Phenothrin	123	183	14.14



App. Fig. 1 Chromatographic traces for PBO, PBO-d9, tetramethrin and phenothrin of a 100 ng/mL standard.

Sample analysis

The samples are measured on a calibrated GC-MSD system. Before analysing the sample, a calibration check is performed by analysing at least one control standard. To check the validity of the measurement data, at least one (QC) standard of known concentration is additionally recorded at the end of the sample sequence. In the case of long sample sequences, it makes sense to run (QC) standards not only at the beginning and end, but also periodically within a sample sequence.

Evaluation of the measurement results

The retention times of the individual analytes (PBO, tetramethrin, phenothrin) can be taken as examples from the sample chromatogram in App. Fig. 1. The baseline, peak identification and peak separation performed by the analysis software must be checked and, if necessary, corrected manually.

Enter the respective absolute mass of the deuterated standard (ISTD; PBO-d9) in ng/mL into the analysis software.

With the aid of the analysis software, the result for the analytes is calculated on the basis of the calibration and displayed in ng/mL.

Criteria of acceptance

Based on the internal requirements (based on the EMA Guideline) for analytical methods at Fraunhofer ITEM, the following acceptance criteria are applicable for this method:

- For each analyte, the experimentally determined concentration should not deviate more than ± 15 % from the nominal concentration. For the lowest calibration point, the deviation in trueness shall not be greater than ± 20 %.

  The investigated concentration range should be covered by 5 calibration standards. The aim is to achieve a regression coefficient (R^2) of 0.99.

Documentation

The raw data are the printouts of the quantification results generated by the analysis software. For further processing, the data are transferred to an Excel spreadsheet. In addition to the analysis results, this table should contain information on the following points:

- Sample type
- Sample ID
- Sample Material
- GC-MSD File Name
- Date of analysis
- For solids Weighing
- Extraction volume
- Information on dilution
- Information on sample volume for GC-MSD measurement

Characteristics of the procedure

Limits of quantificationn
The theoretical limits of quantification were calculated as follows and are given in App. Tab. 5 below:

Limit of quantification = noise + 10x STDV of noise.

However, since these parameters vary depending on the instrument as well as its current performance (e.g. degree of contamination), the practical determination limit for all analytes was raised to 5.0 ng/mL (= lowest calibration point).

App. Tab. 5 Limits of quantification.

	Limit of quantification [ng/mL]
PBO	1.2
Tetramethrin	Peak 1: 4.1 Peak 2: 1.1
Phenothrin	3.7

Accuracy (In-series)
The accuracy of the analytical method determined during validation was between 91 and 115 % for PBO; between 82 and 112 % for tetramethrin and between 83 and 105 % for phenothrin. The acceptance criteria (± 15) applied at Fraunhofer ITEM were not met in all cases. The findings of 82 and 83 % for tetramethrin and phenothrin were one-off minor deviations carried out as part of the validation for correctness (in-series). These are considered as non-critical.

For the observed deviations from the acceptance criteria, an analytical error (e.g. pipetting error) was excluded. No repetition of the corresponding tests was performed, as this could falsify the performance or the working range of the method. It is suggested to pay special attention to tetramethrin and phenothrin during sample analysis.

Precision (In-series)
The precision of the analytical method determined during validation was between 1.3 and 13.4 % for PBO, between 2.8 and 14.1 % for tetramethrin and between 3.7 and 15.8 % for phenothrin. The acceptance criteria (± 15) applicable at Fraunhofer ITEM were not met in all cases for phenothrin. The determined precision of 15.8 % for phenothrin was a unique result, which is considered as uncritical in the context of the overall project.

For the observed deviations from the acceptance criteria, an analytical error (e.g. pipetting error) was excluded. No repetition of the corresponding tests was performed, as this could falsify the performance or the working range of the method. It is suggested to pay special attention to phenothrine during sample analysis.

Storage stability – filter matrix
As part of the validation, the storage stability for PBO, tetramethrin and phenothrin on glass fibre filters was investigated at A: 7–12 °C and B: at room temperature.

A: Storage stability at 7–12 °C
The storage stability at 7–12 °C was investigated over a period of 8 days. The mean recoveries were between 95 and 116 % for PBO, between 90 and 112 % for tetramethrin and between 90 and 104 % for phenothrin. The 116 % for PBO was due to an outlier in the sample series. The storability of glass fibre filters loaded with the three analytes is given at 7–12 °C for a period of 8 day.

B: Storage stability at room temperature
Since immediate cooling of the sampling medium (here: glass fibre filters) cannot always be guaranteed during air sampling, the storability of PBO, tetramethrin and phenothrin on glass fibre filters was investigated at room temperature over a period of 24 hours.

The mean recoveries were 115 % for PBO, 117 % for tetramethrin and 110 % for phenothrin. Sufficient storage stability of glass fibre filters loaded with the three analytes is given at room temperature for a period of 24 hours.

Storage stability – extract
The storage stability of filter extracts was investigated over a period of 2 weeks at –20 °C as part of the validation. Extract stability was not given for tetramethrin, as shown by mean recoveries of 116 to 125 % after 1 week and 123 to 130 % after

2 weeks. Mean recoveries after 2 weeks of 89 to 102 % for PBO and 98 to 112 % for phenothrin proved the extract stability for these two analytes.

Quality assurance measures

Calibration check
The calibration of the GC-MS system should be checked at regular intervals. Calibration standards should be included in the measurement series at the beginning and after completion of a measurement series. In the case of large measurement series, the calibration should also be checked within the measurement series using control standards (e.g. after every 10th chromatography run). The acceptance criteria listed under “Acceptance criteria” apply here (accuracy: ± 15 % of the nominal concentration; exception: smallest calibration standard: ± 20 % of the nominal concentration.

Appendix 3 Standard operating procedure: Measurement method for the determination of potential dermal exposure by the application of pyrethroid-containing biocidal products

Usage of polyethylene coveralls and cotton gloves for the collection of dermal exposure data of workers

General

Polyethylene coveralls and cotton gloves were used as whole-body dosimeters for the collection of dermal exposure data during spraying or foaming of active substance containing biocidal products.

Samplers

- Coveralls made of polyethylene material (DuPont® Tyvek® Classic Expert Model CHF5; Chemical Protection Coverall Category III, Types 5B and 6B; Arbeitsschutz-Express GmbH, Leipheim, Germany)

- Cotton gloves (Carex® cotton-jersey gloves, medium-heavy, lined, white, per STANDARD 100 by OEKO-TEX® (Size: 12 or 14) Trebes+Henning Handschuhe und Arbeitskleidung GmbH & Co. KG, Brieselang, Germany)

Collection of dermal exposoure data using polyethylene coveralls and cotton gloves

- Tyvek® whole-body coveralls, Tyvek® booties, and cotton gloves are made available by study personnel.

- With the assistance of study personnel, workers first put on Tyvek® booties followed by the coveralls, after which the booties are removed. This course of action prevents the contamination of the coveralls' interior by soiled work shoes.

- The gloves are put on.

- During sample collection, the type and duration of each activity, as well as any observed contamination events, are recorded in the surveillance sheet.

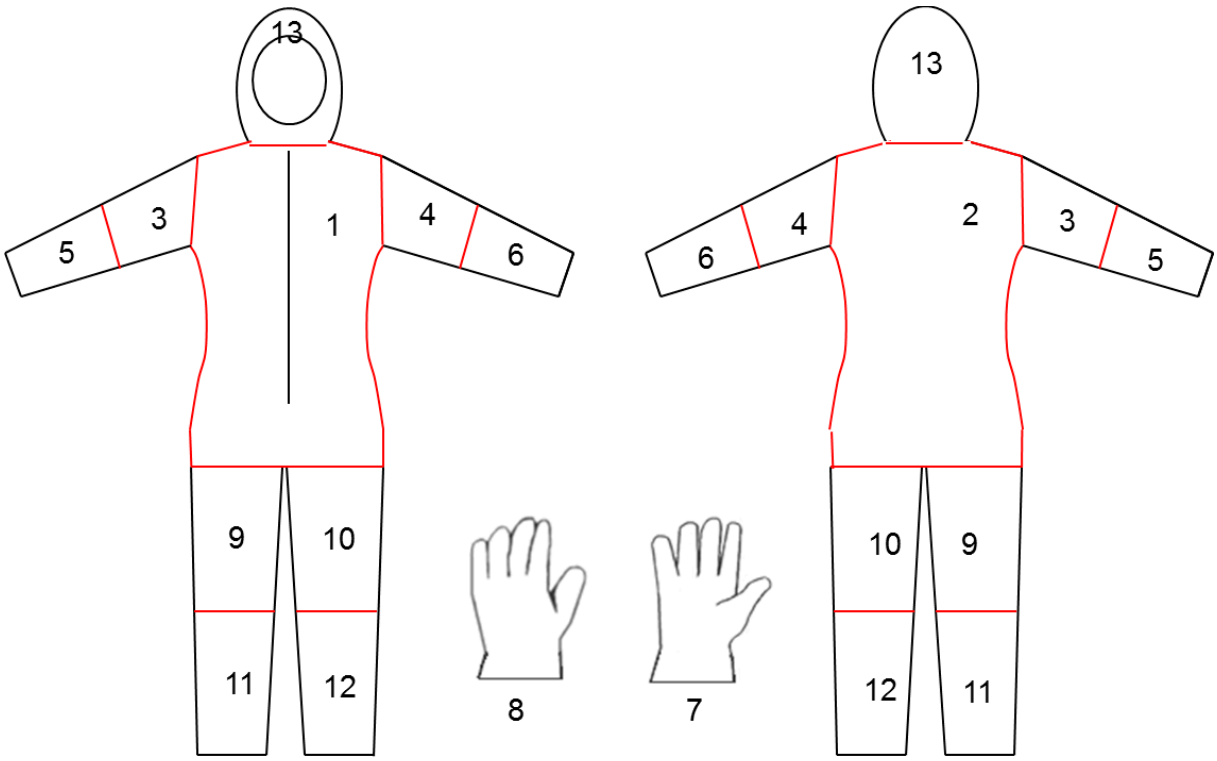
- Study personnel assist workers in the removal of their gloves.

- With the assistance of study personnel, workers first put on Tyvek® booties and remove the coveralls, after which the booties are removed. This course of action prevents the contamination of the coveralls' interior by soilied work shoes.

- The coveralls are disassembled into eleven segments according to the given cutting pattern (App. Fig. 2).

- The Tyvek® coverall segments and the non-segmented gloves are folded with the contaminated sides facing inward, wrapped in aluminium foil, placed in labelled polyethylene storage pouches, and stored during the field study at 6 °C.

- Following transport into the laboratory, the samplers are stored at −20 °C until processing.



App. Fig. 2 Cutting pattern for the disassembly of the coveralls into eleven segmets. Cutting guidance is indicated in red.

Determination of the piperonyl butoxide (PBO) or pyrethroid content in charged polyethylene or cotton materials by GC-MS

The analytes are extracted from the sampler material using acetone, whereby the samples are intensly shaken for five minutes on a horizontal shaker (200 min^{-1}). Following solvent exchange, the analytes are quantified using bifenthrin as an internal standard.

Equipment, chemcials, and sampler materials

For the determination of PBO and pyrethroids, a 7890A gas chromatograph (Agilent Technologies) with an autosampler and a 5975C mass spectrometer (Agilent Technologies) are used. The column utilised is an HP-5MS-UI-0.25 µm column (60 m × 0.250 mm; Agilent Technologies). PBO, tetramethrin, *trans*-phenothrin, and permethrin are measured in EI mode; and the remaining analytes are measured in NCI mode.

Gas chromatography

Capillary column:	HP-5MS-UI
Stationary phase:	(5 %-phenyl)-methylpolysiloxane
Length:	60 m
Inner diameter:	0.250 mm
Film thickness:	0.25 µm

Column temperature:	Initial temperature of 90 °C for 1 min; increase at a rate of 40 °C/min to 130 °C for 0 min; increase at a rate of 10 °C/min to 280 °C for 0.1 min; increase at a rate of 30 °C/min to 300 °C for 13 min
Carrier gas:	Helium 5.0 Flow rate: 1 mL/min
Injection volume:	1.2 µL

Mass spectrometry

Ionisation type:	EI
Source temperature:	230 °C
Quadrupole temperature:	150 °C
Detection mode:	Selected Ion Monitoring (SIM)
Dwell time:	50 ms or 100 ms
Solvent delay:	18 min
Ionisation type:	NCI
Reactant gas:	Methane
Source temperature:	150 °C
Quadrupole temperature:	150 °C
Detection mode:	Selected Ion Monitoring (SIM)
Dwell time:	50 ms or 100 ms
Solvent delay:	18 min

Laboratory equipment and materials

- Horizontal shaker
- Nitrogen evaporator
- Laboratory bottles with screw thread (Eppendorf 100, 500 or 1000 mL)
- 100- or 500-mL graduated cylinders
- Variable pipettes (10–100 µL; 100–1000 µL) (Fa. Eppendorf, Germany)
- 1 µm syringe filters
- GC vials (amber glass) with screw tops

Chemicals

- Piperonyl butoxide (PBO), tetramethrin, *trans*-phenothrin, bifenthrin (e.g. LGC Standards GmbH, Wesel, Germany)
- Permethrin, cyfluthrin, cypermethrin, deltamethrin (e.g. Dr. Ehrensdorfer, Wesel, Germany)
- Acetone for analysis (e.g. Fa. Merck)
- Toluol for analysis (e.g. Fa. Merck)

Extraction of PBO and pyrethroids from polyethylene or cotton materials

- The sampling material is, if necessary, further disassembled and the volume of the extracting agent is adjusted to match the amount of material. During this process, up to 6 g of Tyvek® material is extacted with 50 mL of acetone and up to 20 g of Tyvek® material is extracted with 100 mL of acetone. Gloves are extracted with 100 mL of acetone.

- The materials are placed in glass bottles and the corresponding volumes of acetone are added.
- The well-sealed glass bottles are intensely shaken for five minutes on a horizontal shaker.
- From the extraction containers, 1 mL of the acetone extract is withdrawn as a sample as well as 20 mL as a retention sample.
- The withdrawn 1 mL extracts are mixed with the deuterated internal standard and with 90 µL of toluol and blown down under a nitrogen stream to 100 µL.
- After adding 900 µL of toluol, the extracts are filtered using syringe filters and the filtered extracts are measured by GC-MSD.
- A sampler blank as well as a reagent blank are included in each analytical run.

App. Tab. 6 Selected ion monitoring (SIM technique) GC-EI-MS:

Analyte	**Retention time [min]**	**Quantifier [*m/z*]**	**Qualifier [*m/z*]**
PBO	19.518	176	149
Tetramethrin	20.018; 20.115	123	164
Bifenthrin (ISTD)	20.099	181	165
trans-Phenothrin	20.565; 20.661	123	183
Permethrin	22.334; 22.507	183	163

App. Tab. 7 Selected ion monitoring (SIM technique) GC-NCI-MS:

Analyte	**Retention time [min]**	**Quantifier [*m/z*]**	**Qualifier [*m/z*]**
Tetramethrin	19.921; 20.018	331.1	165.1
Bifenthrin (ISTD)	19.994	386.1	241
Cyfluthrin	23.055; 23.170; 23.368	206.9	170.9
Cypermethrin	23.629; 23.766; 23.944	206.9	170.9
Deltamethrin	27.341	296.8	78.9

For evaluation, the peak areas of the analytes are normalised to that of bifenthrin in order to compensate for fluctuations in the GC-MSD system.

Appendix 4 Standard operating procedure – Analytical method for the determination of benzalkonium chlorides after air sampling on PTFE filters

Introduction/Purpose of this operating procedure

This operating procedure describes the analysis of benzalkonium chloride after air sampling on PTFE filters by means of gas chromatography and mass spectrometric detection (GC-MSD). The method is based on the publication by VAN BOXTEL et al. (2016).

Procedure

Principle of the method

Benzalkonium chloride (BAC) consists of a mixture of alkylbenzyldimethyl-ammonium chlorides, where the alkyl chain lengths can be composed of C_8; C_{10}; C_{12}; C_{14}; C_{16} and C_{18} carbon atoms.

The ionic nature of the benzalkonium chlorides can lead to a long-lasting retention of the substances in the analysis system in the case of direct application (e.g. liquid injection), which in turn can cause memory effects on subsequent analytical measurements. To prevent this effect, an analytical method for the determination of benzalkonium chlorides was set up and validated based on the work of VAN BOXTEL et al. (2016). This method makes use of the thermal instability of the benzalkonium chlorides and the benzyl chloride released in the process, which can be quantified using headspace (HS)-GC-MS. This procedure does not allow alkyl chain length-specific quantification of the individual benzalkonium chlorides. In the context of this project, the determination of the benzalkonium content via the sum parameter benzyl chloride is sufficient, since toxicological aspects are not addressed here, but the focus is on the comparison of the aerosol release spray vs. foam application.

After sampling, the PTFE filter is transferred to a headspace (HS) vial. Deuterated (d7) benzyldimethyldecylammonium chloride is added to the benzyl residue as an internal standard (ISTD). The solvent, which is introduced by spiking with the ISTD, is removed in the nitrogen stream, the vial is closed and heated at 170°C. The benzyl chloride released in the process is quantified by HS-GC-MS.

Instruments and materials

- GC-MSD coupling Agilent 6890/5973 with HPChemStation and autosampler with headspace feeding system (Gerstel MPS) (or similar device)
- Eppendorf pipettes (various sizes)
- Volumetric flasks (1 and 10 mL)
- Tweezers
- Analytical balance (e.g. Sartorius, Research RC 210S)
- Drying oven
- Vacuum chamber (e.g. Supleco)
- Headspace vials with silicone PTFE septa (20 mL, e.g. Agilent Technologies)
- PTFE filter (Zefluor™, e.g. PALL))

Chemicals and solvents

- Methanol (Chromasolv, Honeywell)
- Benzyldimethyldecylammonium chloride-d7 (HPC Standards GmbH, product number: 674610)
- Benzalkonium chloride (short: BAC, Sigma-Aldrich, product number: 12060)

Solutions:

Benzalkonium chloride (analyte) – stock solution
The pure substance (approx. 150 mg) is weighed exactly and dissolved in 10 mL methanol. The final analyte concentration is determined by the weight and the purity of the substance.

The solution is prepared using a suitable balance and volumetric flask.

Example: 148.70 mg benzalkonium chloride (purity: 95 %) are accurately weighed and dissolved in 10 mL methanol. This results in an analyte concentration of 14.1 mg/mL.

Benzalkonium chloride (analyte) – standard solution 1
The stock solution is diluted with methanol to a nominal concentration of 100 µg/mL.

The solution is prepared using suitable pipettes and volumetric flasks.

Example: Fill methanol in a volumetric flask (10 mL), add 67.2 µL of the stock solution and fill the flask up to the mark with methanol.

Benzalkonium chloride (analyte) – standard solution 2
The stock solution is diluted with methanol to a nominal concentration of 1 mg/mL.

The solution is prepared using suitable pipettes and volumetric flasks.

Example: Fill methanol in a volumetric flask (1 mL), add 67.2 µL of the stock solution and fill the flask up to the mark with methanol.

Internal standard (ISTD) – stock solution
Benzyldimethyldecylammonium chloride-d7, with deuterated benzyl group, is used as internal standard. The pure substance (e.g. 10 mg; purity: e.g. 91.6 %) is dissolved in 10 mL methanol. In this case the final ISTD concentration is 0.92 mg/mL.

The solution is prepared using a suitable balance and volumetric flasks.

Internal standard (ISTD) – solution 1
The ISTD stock solution is diluted 1:10 in methanol. For this purpose, approx. 5 mL of methanol is filled in a 10 mL volumetric flask, 1 mL of the ISTD stock solution is added and then the flask is filled up to the mark with methanol. The concentration of ISTD solution 1 is therefore 92 µg/mL.

The solution is prepared using suitable pipettes and volumetric flasks.

Calibration and control standards:

Calibration standards
Calibration standards are prepared by spiking PTFE filters cut in two halves. One PTFE filter half is transferred to a 20 mL HS vial and the corresponding analyte and ISTD solution is added according to the pipetting scheme in App. Tab. 8. In this way, benzalkonium chloride quantities of 0.5 to 6 µg are covered. The filter halves prepared in this way are then processed as described under "Sample preparation".

The solution is prepared using suitable pipettes.

App. Tab. 8 Pipetting scheme – calibration standards.

Nominal amount [µg]	ISTD-solution 1 [µL]	BAC-solution 2 [µL]
0.5	10	0,5
1.0	10	1
2.0	10	2
3.0	10	3
4.0	10	4
5.0	10	5
6.0	10	6

Control standards (QC-standards)
QC standards are prepared in the same way as calibration standards by spiking 1/2 PTFE filters. For this purpose, the filter halves are spiked with 1.0, 2.5 or 5.0 µL of the analyte standard solution 2. Each filter half is also spiked with 10 µL of ISTD solution 2. This results in the following three QC levels:

- QCLow: 1.0 µg/half filter
- QCMed: 2.5 µg/half filter
- QCHigh: 5.0 µg/half filter.

The half filters prepared in this way are then processed as described under point "Sample processing".

The solution is prepared using suitable pipettes and volumetric flasks.

Sample processing

The methanol applied to the filter halves[23] by spiking (only the ISTD in the case of real samples) is removed in a nitrogen stream (30 min). The HS vials are sealed with silicone PTFE septa and incubated for 60 min at 170 °C in a drying chamber. The benzalkonium chloride in the samples treated in this way is then quantified via the released benzyl chloride by means of HS-GC-MSD (App. Tab. 9).

[23] Entire fiters can also be used.

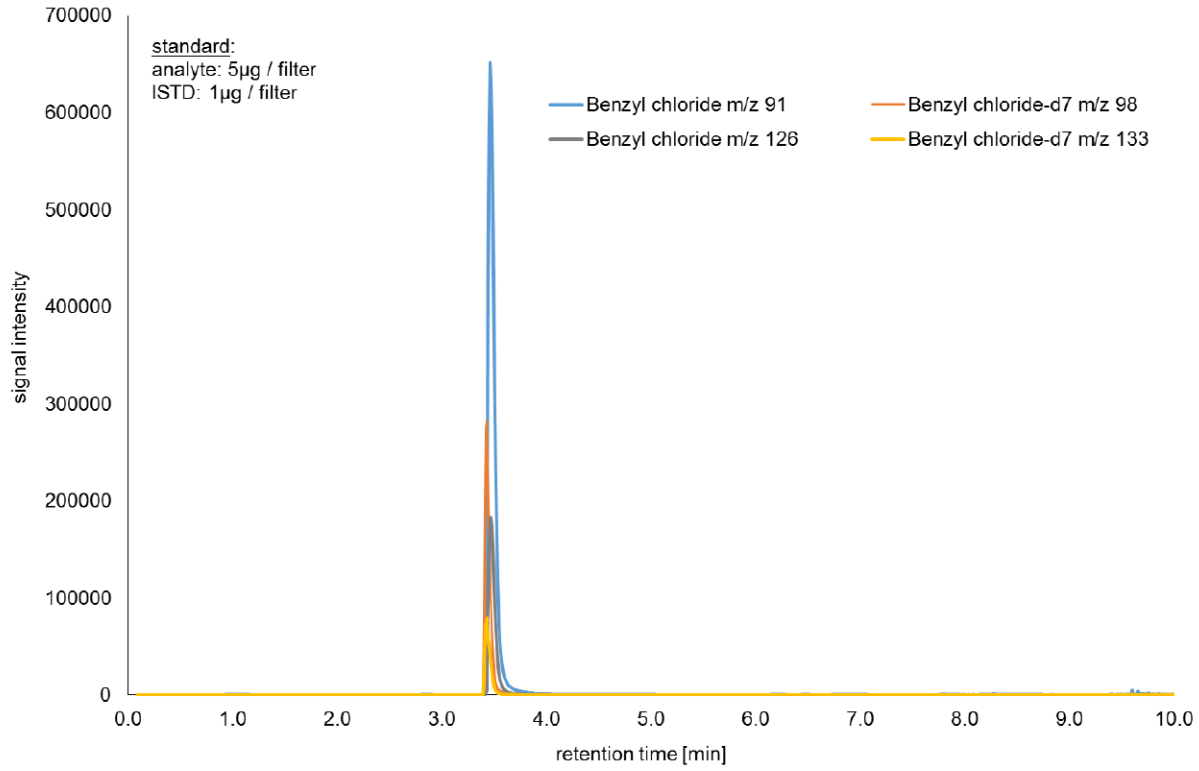
HS-GC-MSD-measurement

The parameters and settings of the HS-GC-MS method are listed in App.Table 9. Chromatographs of a 5 µg/half filter standard for benzyl chloride and benzyl chloride-d7 are shown as examples in App. Fig. 3.

App. Tab. 9 HS-GC-MSD: parameters and settings.

Parameter	**Setting**
GC-System	Agilent 6890
Injection	Headspace
Injection mode	Split (5:1)
Syringe volume	2.5 mL
Syringe temperature	80 °C
Incubation temperature	100 °C
Incubation time	30 min
Injection volume	2 mL
Column	DB-1, Length: 15 m, Inner diameter: 0.25 mm, Film thickness: 0.25 µm (or similar)
Carrier gas	Helium
Temperature programme	Start: 40 °C (1 min) 8 °C/min to 90 °C (0 min) 40°C/min to 280 °C (8 min)
MS – System	Agilent 5973
Transfer line temperatur	280 °C
Detector temperatur	230 °C
Measurement mode	Single Ion Monitoring (SIM)

Analyte	**Quantification (Quantifierion/Target ion) (m/z)**	**Qualification (Qualifier ion) (m/z)**	**Retention time [min]**
Benzyl chloride	91	126	3.50
Benzyl chloride-d7	98	133	3.45



App. Fig. 3 Chromatographs for benzyl chloride and benzyl chloride-d7 of a 5 µg/half filter standard.

Sample analysis

The samples are measured on a calibrated HS-GC-MS system. Before analysing the sample, a calibration check is performed by analysing at least one control standard. To check the validity of the measurement data, at least one (QC) standard of known concentration is additionally recorded at the end of the sample sequence. In the case of long sample sequences, it makes sense to run (QC) standards not only at the beginning and end, but also periodically within a sample sequence.

Evaluation of the measurement results

As an example, the retention times of the analytes and ISTD are taken from the sample chromatogram in App. Fig. 3. The baseline, peak identification and peak separation performed by the analysis software must be checked and, if necessary, corrected manually.

The corresponding absolute mass of the deuterated standard (ISTD; benzyldimethyldecylammonium chloride-d7) in µg/half filter must be entered into the analysis software.

The analysis software calculates the result for the analytes on the basis of the calibration. It is displayed as µg/half filter.

Acceptance criteria

During the validation, the limitations of the method became clear. Therefore, the internal requirements for analytical methods (based on the EMA Guideline) applicable at Fraunhofer ITEM were adapted. For the determination of benzalkonium chloride via the thermal decomposition product benzyl chloride by GC-MS, the following acceptance criteria were defined:

- The investigated concentration range should be covered by 5 calibration standards. Linearity is given, if a regression coefficient (R^2) of at least 0.98 is achieved.

- The precision of the overall method (with respect to reprocessing and analysis of technical replicates) should be ≤ 20 %. An exception is the smallest calibration standard, for which the precision should not exceed 25 %.

- The accuracy (average of 6 technical replicates) should be ± 20 % of the nominal value. An exception is the smallest calibration standard, for which the accuracy should be 75–125 % of the nominal value.

Documentation

Raw data are the printouts of the quantification results generated by the analysis software. For further processing, the data are transferred to an Excel spreadsheet. Besides the analysis results this table should contain information on:

- Sample type
- Sample ID
- Sample materia
- GC-MSD file name
- Date of analyis

Characteristic data of the procedure

Limit of quantification
The theoretical limit of quantification is calculated as follows:

Limit of quantification = noise + 10x STDV of noise.

The limit of quantification for benzyl chloride[24] calculated according to this principle was 2 ng/half filter. Here, the smallest standard 0.5 µg/half filter was used as the practical limit of quantification. Quantification below the 0.5 µg/half filter requires the establishment of a second calibration range. Since at present the required working range for the workplace samples to be obtained later in the project is not known, the validation is limited to the BAC amounts of 0.5 to 6 µg/half filter.

Accuracy and precision (in-series)
The data on accuracy collected during validation showed large scattering around the theoretical nominal value on some days, which was also seen in the precision values. This variation did not appear to be concentration related since it was observed for all

[24] Benzyl chloride as a thermal decomposition product was used for quantification of benzalkonium chloride.

three QC levels. The deviation from the nominal value was sometimes so high (e.g. recovery of 704 %) that an analytical error could be excluded. During the spiking of the PTFE filters with the analyte and ISTD standard solution, it was observed that the solvent was not immediately absorbed by the filter material. This, as well as the consistent results obtained in aerosol release experiments (see interim report March 2018), suggest that the cause of the deviations lies in the spiking step of the PTFE filters.

It is postulated that the observed large variation will not be observable for real samples. In the case of real samples, the analyte is collected as an aerosol and is not dosed by spiking with a liquid. It is therefore suggested to generate control standards by aerosol application of PTFE filters (e.g. spray application of a benzalkonium chloride product of known BAC and marker substance concentration, such as caesium chloride), to subsequently spike these with ISTD and, after appropriate sample preparation, to determine the benzyl chloride content by HS-GC-MS. The marker substance can be used to verify the HS-GC-MS result by determining the content in the case of caesium chloride after the HS-GC-MS analysis from the same samples after aqueous extraction using ICP-MS (Inductively Coupled Plasma – Mass Spectrometry).

Storage stability – filter matrix
As part of the validation, the storage stability for benzalkonium chloride on PTFE filters was investigated at A: 7–12 °C and B: at room temperature and was confirmed over a period of at least 2 weeks.

Quality assurance measures

Calibration check
The calibration of the HS-GC-MS system should be checked at regular intervals. Calibration standards should be included in the measurement series at the beginning and at the end of a sample sequence. In the case of large sample sequences, the calibration should also be checked within the measurement series using control standards (please see suggestion above) (e.g. after every 10th chromatography run). The acceptance criteria listed above apply here (accuracy: ± 20 % of the nominal concentration; exception smallest calibration standard: ± 25 % of the nominal concentration)

Appendix 5 Standard operating procedure: Measurement method for the determination of potential dermal exposure by the application of QAC-containing biocidal products

Usage of polyethylene coveralls and cotton gloves for the collection of dermal exposure data of workers

General

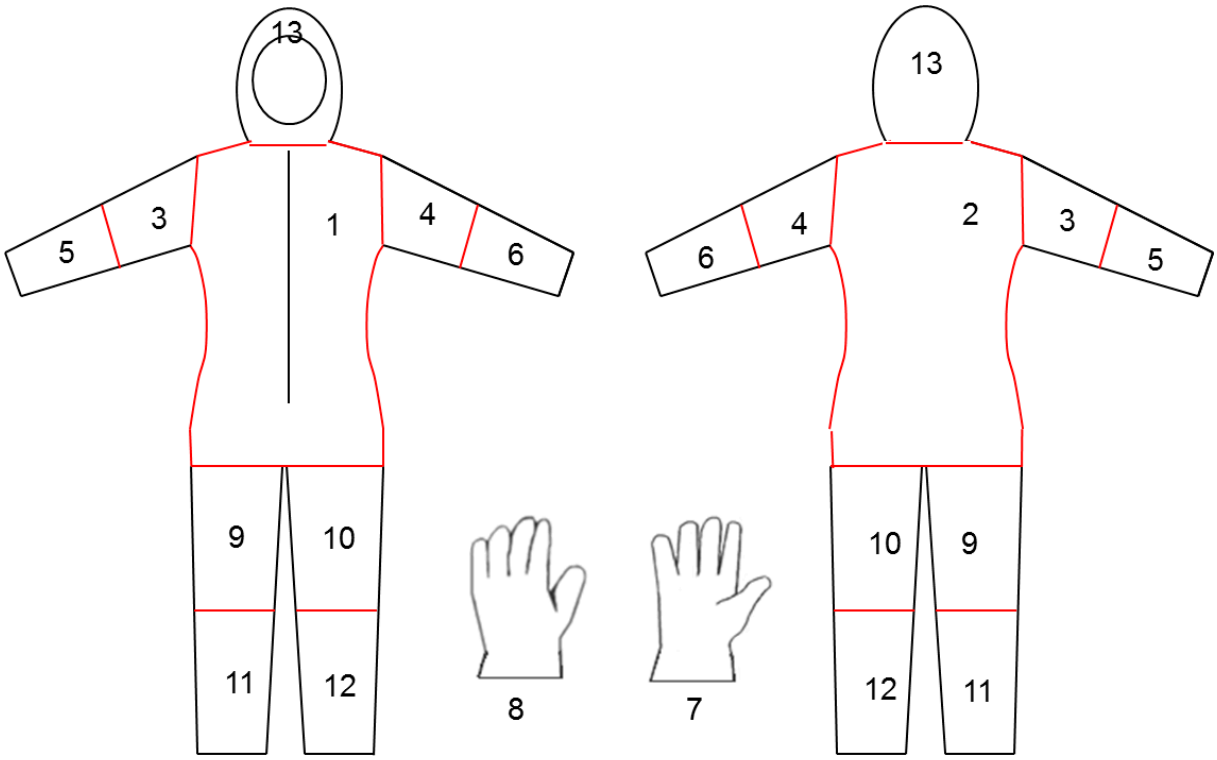
Polyethylene coveralls and cotton gloves are used as whole-body dosimeters for the collection of potential dermal exposure data during spraying or foaming of active substance containing biocidal products.

Samplers

- Coveralls made of polyethylene material (DuPont® Tyvek® Classic Expert Model CHF5, Chemical Protection Coverall Category III, Type 5B and 6B); Arbeitsschutz-Express GmbH, Leipheim, Germany
- Cotton gloves (Carex® cotton-jersey gloves, medium-heavy, lined, white, per STANDARD 100 by OEKO-TEX® (Size: 12 or 14) Trebes+Henning Handschuhe und Arbeitskleidung GmbH & Co. KG, Brieselang, Germany

Collection of dermal exposure data using polyethylene coveralls and cotton gloves

- Tyvek® whole-body coveralls, Tyvek® booties, and cotton gloves are made available by study personnel.
- With the assistance of study personnel, workers first put on Tyvek® booties followed by the coveralls, after which the booties are removed. This course of action prevents the contamination of the coveralls' interior by soiled work shoes.
- The gloves are put on.
- During sample collection, the type and duration of each activity, as well as any observed contamination events, are recorded in the surveillance sheet.
- Study personnel assist workers in the removal of their gloves.
- With the assistance of study personnel, workers first put on Tyvek® booties and remove the coveralls, after which the booties are removed. This course of action prevents the contamination of the coveralls' interior by soiled work shoes.
- The coveralls are disassembled into eleven segments according to the given cutting pattern (App. Fig. 4).
- The Tyvek® coverall segments and the non-segmented gloves are folded with the contaminated sides facing inward, wrapped in aluminium foil, placed in labelled polyethylene storage pouches, and stored during the field study at 6 °C.
- Following transport into the laboratory, the samplers are stored at −20 °C until processing.



App. Fig. 4 Cutting pattern for the disassembly of the coveralls into eleven segments. Cutting guidance is indicated in red.

Determination of the benzyldimethylalkyl(C_{8-18})ammonium chloride content in QAC-charged polyethylene or cotton materials by headspace-GC-MS

The benzyldimethylalkyl(C_{8-18})ammonium chlorides are extracted from the sampling material using acetone, whereby the samples are intensively shaken for five minutes on a shaking table (200 min^{-1}). Following thermolysis at 170 °C, the analytes are quantified by headspace-GC-MS using a deuterated internal standard.

Equipment, chemicals and sampler materials

For the determination of benzyl chloride, a 7890A gas chromatograph (Agilent Technologies) with an autosampler and a 5975C mass spectrometer (Agilent Technologies) are used. The column utilised is an HP-1-5 µm column (30 m × 0.320 mm, Agilent Technologies).

Headspace

Headspace sampler	Perkin Elmer, Turbo Matrix 40 Trap
Settings:	Carrier: 18.0 psi Needle: 180 °C Transfer line: 190 °C Oven: 170 °C Pressurisation: 1 min Injection time: 0.04 min Dwell time (needle in vial): 0.4 min Cycle time: 48.0 min Thermostat time: 60.0 min Time between injections (PII): 50.0 min

Gas chromatography

Capillary column:	Designation: HP-1 Stationary phase: 100 % dimethylpolysiloxane Length: 30 m Inner diameter: 0.320 mm Film thickness: 5 µm
Temperatures:	Column: Initial temperature of 40 °C for 0.1 min; increase at a rate of 8 °C/min to 90 °C for 1 min; increase at a rate of 15 °C/min to 250 °C for 20 min
Carrier gas:	Helium 5.0 Flow rate: 1 mL/min

Mass spectrometry

Ionisation type:	EI
Source temperature:	230 °C
Quadrupole temperature:	150 °C
Detection mode:	Selected Ion Monitoring (SIM)
Dwell time:	50 ms
Solvent delay:	2 min

Laboratory equipment and materials

- Horizontal shaker
- Nitrogen evaporator
- Laboratory bottles with screw thread (Eppendorf 100, 500- or 1000-mL)
- 100- or 500-mL graduated cylinder
- Variable pipettes (10–100 µL; 100–1000 µL) (Fa. Eppendorf, Germany)
- 1 µm syringe filters
- Headspace-GC vials with high-temperature septa and crimp caps

Chemicals

- BAC-C_8; BAC-C_{10}; BAC-C_{12}; BAC-C_{14}; BAC-C_{16}; BAC-C_{18} (e.g. HPC-Standards GmbH, Cunnersdorf, Germany)
- Acetone for analysis (e.g. Fa. Merck)
- Toluol for analysis (e.g. Fa. Merck)

Extraction of benzalkonium chlorides from polyethylene or cotton materials

- The sampler material is, if necessary, further disassembled and the volume of the extracting agent is adjusted to match the amount of material. During this process, up to 6 g of Tyvek® material is extracted with 50 mL of acetone and up to 20 g of Tyvek® material is extracted with 100 mL of acetone. The gloves are extracted with 100 mL of acetone.
- The materials are placed in glass bottles and the corresponding volumes of acetone are added.
- The well-sealed glass bottles are intensely shaken for five minutes on a horizontal shaker.
- From the extraction containers, 1 mL of the acetone extract is withdrawn as a sample as well as 20 mL as a retention sample.
- The withdrawn 1 mL extracts are mixed with the deuterated internal standard (1 µg/vial) and blown down under a stream of nitrogen. The usage of a keeper is not necessary when handling the relatively low-volatility benzalkonium chlorides.
- If it is necessary to concentrate the extracts in order to quantify the analytes, extracts can be concentrated by a factor of 10 or 20.
- A sampler blank and a reagent blank are included in each analytical run.

Selected ion monitoring (SIM technique)

Benzyl chloride, which is used for quantitation, displays a retention time of 14.584 min (App. Tab. 10).

App. Tab. 10 Single-mass registration.

Retention time	**Q [*m/z*]**	**Decomposition products**
14.584 min	91	Benzyl chloride, Quantifier
	126	Benzyl chloride, Qualifier
14.528 min	98	D7-Benzyl chloride, Quantifier
	133	D7-Benzyl chloride, Qualifier

For evaluation, the peak area of benzyl chloride is normalised to that of the deuterated internal standard in order to correct for variation in the GC-MSD system. The deuterated benzyl chloride, which arises as a decomposition product of the internal standard (D7-Benzyldimethyldodecylammonium chloride), eluates directly prior to the corresponding non-deuterated benzyl chloride.

Appendix 6 Standard operation procedure: Measurement of the amount of biocidal aerosol released during spraying and foaming

Introduction and objective

This SOP serves to determine the amount of aerosol released during spray and foam application of biocidal products with commercially available devices. This document is used as a guideline for a research and development project. Deviations (e.g. biocidal product used, application technique, etc.) may occur in the test implementation, which do not influence the process of aerosol sampling.

Procedure

Principle of the method:

To record the amount of aerosol released during spray or foam application, either caesium chloride (CsCl) is added to the aqueous biocidal product solution as a labelling substance or, in the case of formulations containing pyrethroids, the active substance is determined directly. In both cases the aerosol is collected with two total dust sampling systems (GSP) on mixed cellulose membrane filters (MCE filters). [25]

In some trials the released aerosol is additionally sampled in three particle size regimes using two Respicons, each equipped with MCE filters. The vacuum required for the Respicon and GSP samplers is supplied by a rotary vane vacuum pump. The specific flow rate through the sampling devices is stabilised using critical orifices. It is measured with a volumetric flow meter and documented before the foam or spray is applied.

In order to evaluate dermal exposure in the large model room, six deposition pads equipped with Tyvek material are used in some experiments (three with vertical and three with horizontal orientation). In addition, closed-face filter cassettes (CFC) equipped with appropriate critical nozzles can be positioned near them. The CFCs are only used for BAC (benzalkonium chloride) analysis in the large and small model rooms and serve as reserve samples for BAC analysis (determination of the benzalkonium chlorides).

Finally, real-time measurements are carried out using an aerosol laser spectrometer (31 channels, particle diameter from 265 nm to 34 µm).

Instruments and materials

The foam and spray equipment is used in the different model rooms depending on the mass flow of the device. The volumes of the model rooms are 158 m³ (large), 41 m³ (medium) and 1.5 m³ (small)

- Data logger for temperature and relative humidity (z. B. EL-USB-2-LCD)
- Two Respicon samplers, temporary
- Two inhalable dust samplers (GSP)
- Six closed faced filter cassettes (CFC), temporary

[25] If, in addition to CsCl, the BAC or pyrethroids are also to be measured, the MCE filter is replaced by a PTFE filter or glass fibre filter.

- Tyvek material (large model room)
- MCE-filter (SKC, 5 µm pores, 37 mm diameter)
- PTFE-Filter (PALL, Zefluor™, 2 µm pores, 37 mm diameter)
- Critical orifices
- Two vacuum pumps,Type Schmalz EVE-TR 4 AC F
- Volume flow meter (MesaLabs Bios Defender 520)
- Laser aerosol spectrometer (Type Grimm 1.09)
- Measuring cylinder (1 l)
- Tweezers
- Funnel
- Beaker
- Centrifuge tubes, 50 ml (z. B. TPP, Art.Nr.: 91051)
- Platform scale (Kern, EOB 150K100)
- Precision balance (Sartorius, Talent TE1502S)
- Room ventilators (e.g. Rowenta Turbo Silence Extreme, 40 cm rotor diameter) – Four in the large model room; one in the medium model
- Axial fan (Papst 4850 Z, 100 m³/h, 11 cm blade diameter) – use in the small model room, only (hood)

Examples of application devices:

- Pressure foamer G (large model room)
- Pressure foamer B (large model room)
- Pressure foamer P (large model room)
- Low pressure foam gun (large model room, use with Grundfos pump, type JP6-8-8-CVBP water pressure 3bar)
- High pressure foam and spray gun (large model room, use with Grundfos pump, type JP6-8-8-CVBP; pump pressure 3 bar, high pressure device: nominal operating pressure)
- Hand foamer/sprayer (small model room)
  - Hand pump foamer, hand pump sprayer
  - Hand compression sprayer 2 (spray nozzle 0.5 mm, 0.8 mm, 1.2 mm)
  - Hand compression foamer and sprayer (foam nozzle, regulating nozzle, fan nozzle TPU 8002 PP and XR 8002 VS)
- Insect foam can (B.1, B.2) and insect spray B (medium model room)
- Insect foam can F (medium model room)

Chemicals and solvents

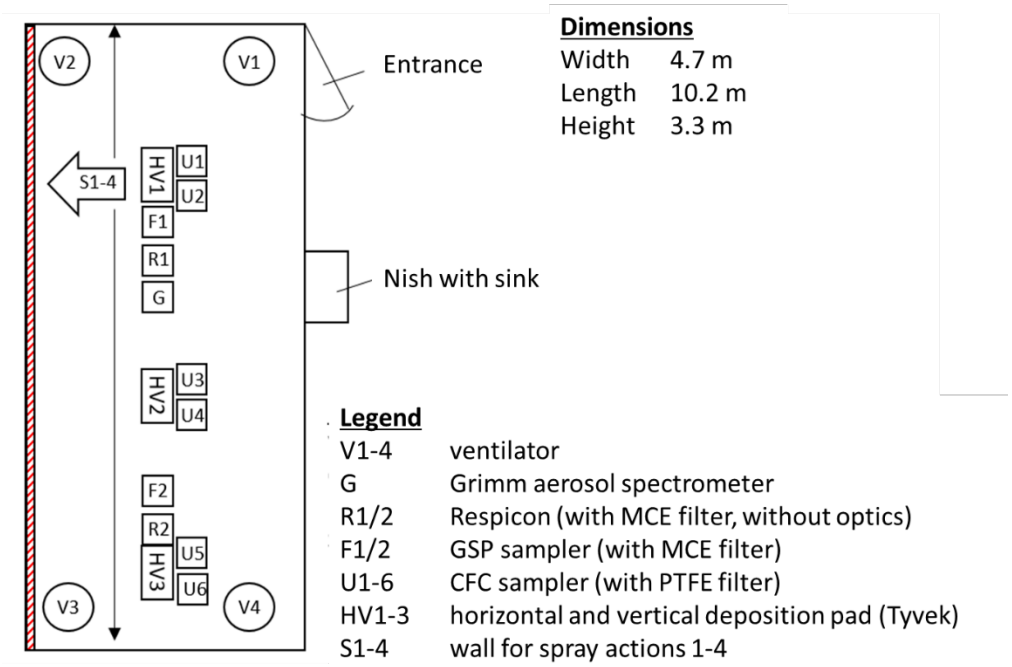
For example:

- QAC E
- QAC F
- Insect foam B.1 and B.2
- Insect foam B
- Insect foam F
- PER F
- QAC M
- Test foam-N 1 % (Dr. Sthamer, Hamburg) used in conjunction with PER F
- Caesium chloride (CsCl, z. B. Roth, ≥ 99,9 %, pure)

Caesium chloride is added to the water for dilution of the concentrated formulations QAC E, QAC F, QAC M and PER F. The aerosol release fraction is determined by measuring the CsCl in the air instead of the active substances. In the case of pressurised cans with propellant gas, the aerosol release is determined by analysing the active substance, as it is not possible to add the tracer into the cans.

Implementation in the large model room

The positions of the equipment and tools are shown in the figure below (App. Fig. 5). The wall surface to be treated is marked in red.

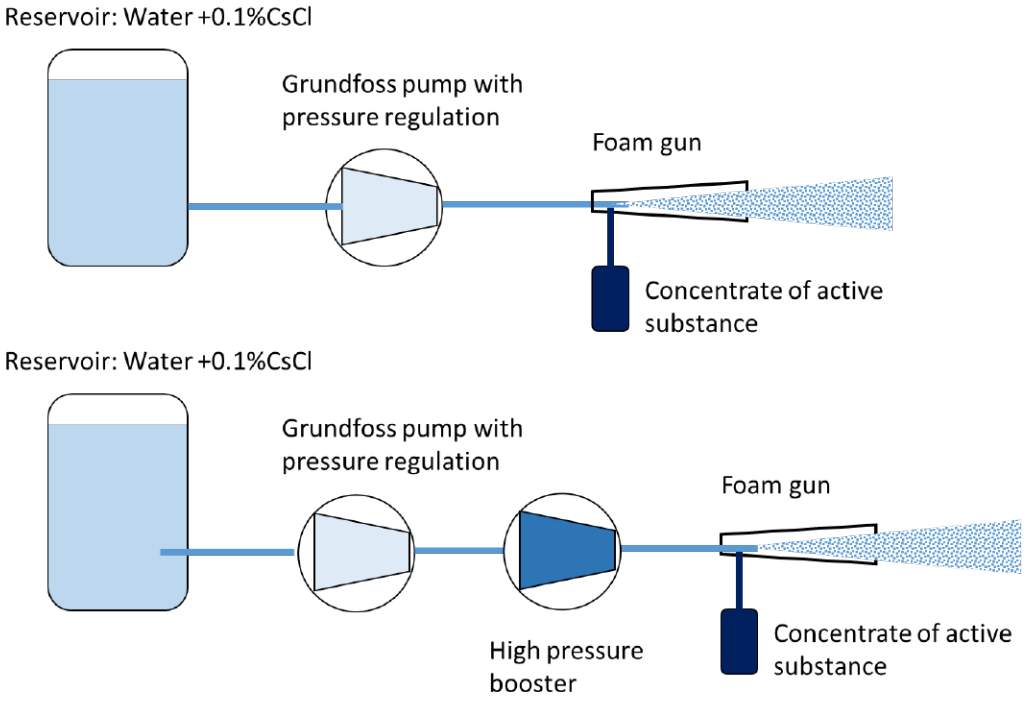


App. Fig. 5 Schematic representation of the experimental setup in the large model room.

CFCs are used as a back-up for chemical analysis. Respicons are implemented in the experimental setup, if information on inhalable, thoracic and respirable aerosol size fractions is required. Dermal surrogates are used when the deposition of aerosols on horizontal and vertical surfaces is of interest. CFC, Respicon and dermal surrogates are therefore not mandatory components for all experiments.

1.) The four weaving fans are started at the lowest level of the rotational speed of the blades.
2.) The data logger recording the temperature and humidity is started.*
3.) GSPs and, if applicable, Respicons or CFCs are equipped with MCE filters (PTFE[26], if applicable) and connected to the corresponding critical nozzles. The volume flow rates through the devices are determined and recorded.
4.) GSPs (3.5 L/min) and, if applicable, Respicons (3.11 L/min) are connected to vacuum pump A.; if applicable, CFCs (2.0 L/min) are connected to vacuum pump B.
5.) In some experiments, horizontal and vertical deposition pads are loaded with Tyvek material and positioned.

6.) The empty foamer/sprayer is weighed on the platform scale, tared and filled with the appropriate amount of water. The biocidal product is added using a measuring cylinder and the solution is mixed. Finally, a defined amount of CsCl (if necessary) is weighed on the precision balance and is added to the solution. The solution is mixed again by manual stirring.
7.) The unit is closed and connected to compressed air. The foam and pump pressure (pressure foamer or pressure sprayer G) or the system pressure (pressure foamer B) is adjusted and documented. The tank pressure of the pressure foamer or pressure sprayer P is kept constant by supplying compressed air during application. For application with the low-pressure foam gun and the high-pressure system, in both cases CsCl-spiked water is fed from a storage vessel to the device by means of a pump (3 bar) (see App. Fig. 6):



App. Fig. 6 Mode of operation of the foam guns with low-pressure and high-pressure connection. Grundfoss pump adjusted to 3 bar. High pressure booster operated under nominal conditions (no pressure adjustment possible).

8.) Start of the aerosol laser spectrometer.*
9.) Activation of the room ventilation.*
10.) Start of vacuum pump B.* (if applicable)
11.) Start of vacuum pump A.*
12.) Start of foam/spray application.*

Foam application
The application begins in the lower right area of the wall and is carried out from right to left. When the left end of the wall is reached, the next free area above it is foamed from left to right. This is repeated until the wall is completely covered with foam. Make sure that areas that have already been foamed are not covered with

foam again. The covered area is then approx. 10 × 2 m². The distance between the nozzle and the wall is approx. 50 cm for all foam applications.

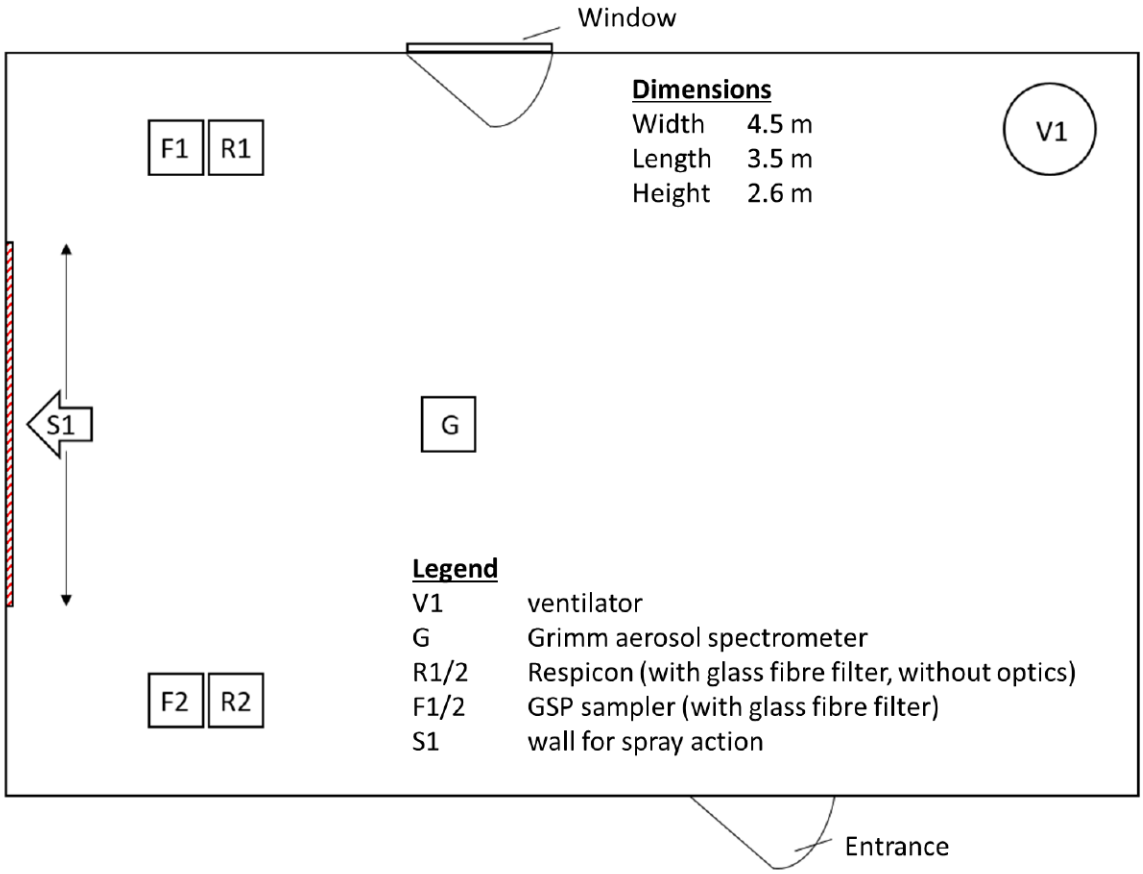
Spray application

The spray application is carried out vertically from top to bottom, spraying the entire length of the wall in this way. The covered area is then approx. 10x2 m². The nozzle distance to the wall is approx. 50 cm.

13.) The application is terminated.*
14.) Ten minutes after the end of spraying, vacuum pump A is switched off.*
15.) Turn on room ventilation for air exchange (approx. 8 air changes per hour)*.
The treated wall and affected floor surfaces of the model room are thoroughly rinsed with cold tap water.
16.) 30 minutes after activating the room ventilation, it is deactivated again.*
17.) If necessary, steps 11–16 are repeated twice, steps 11–13 are then repeated for the last application.
18.) Ten minutes after the end of the last application, vacuum pumps A and B (if applicable) and the aerosol laser spectrometer are turned off and the room ventilation is turned on.*
19.) If there is still biocidal product solution in the device, the residual amount is determined using the platform scale.
20.) Both the sampling filters and, if applicable, the Tyvek material on the deposition plates are transferred individually into the centrifuge tubes with the aid of tweezers, making sure that the loaded surfaces of the filters or plates face inwards.
21.) After completion of the experiment, the treated wall and affected floor surfaces of the model room are thoroughly rinsed with cold tap water.
*) The time to the second is noted.

Implementation in the medium model room

The positions of the equipment and tools are shown in the figure below (App. Fig.7). The wall surface to be treated is marked in red.



App. Fig.7 Schematic representation of the experimental setup in the medium model room. Respicons can be implemented in the experimental setup, if information on the respirable, thoracic and alveolar aerosol size fractions is required. Respicons are therefore not mandatory components for all experiments.

In this model room, which is preferably used for the release tests with the insect foams and sprays, only one fan is required for aerosol homogenisation. The exposed area (upper third of a 1.25 × 2 m² plasterboard) is located at the front of the room. The duration of the surface treatment and the size of the treated area depend on the device and its use in practice. Pressurised cans can be completely emptied after less than 1 minute. Suitable conditions must be determined in preliminary tests. For insect foam/spray B and insect foam F, the active substance is determined directly. The measurements are carried out according to the steps listed below:

1.) A new plasterboard (1.25 × 2 m²) is placed against the front wall (see illustration) of the room.
2.) The mixing fan is set to the lowest speed and started.
3.) The recording of temperature and humidity data logger is started.
4.) GSPs and, if applicable, Respicons are equipped with glass fibre filters and connected to the corresponding critical orifices. Their volume flow rates are determined and recorded.

5.) GSPs (3.5 L/min) and, if applicable, Respicons (3.11 L/min) are connected to vacuum pump A.
6.) The weight of the full can of insect spray or foam is determined on the precision balance.
7.) The aerosol laser spectrometer is started.*
8.) The window of the room is closed.
10.) Vacuum pump A is started.*
11.) The can is well shaken and the application is started.*

Foam application – Insect foam B.1
The foam is applied to the upper third of the plasterboard of 1.25 × 2 m² size. Application is started in the lower right area (of the upper third of the wall) and is carried out from right to left. When the left end of the wall is reached, the next free area above is covered with foam from left to right. This is repeated until the upper third is covered with foam and the can is empty. The covered area is then approx. 0.8 m². The distance between the plasterboard and the nozzle opening (end of the foam applicator) is approx. 1 m.

Foam application – Insect foam F
The foam is applied directly to the wall in two applications. An area of 2.7 m² is treated in each case. Application is started in the lower right area and proceeds from right to left. When the left end of the area is reached, the next free area above covered with foam from left to right. Between the two applications, the pumps are switched off, the foam is removed from the wall and the room is ventilated for 0.5 h by opening the windows, until the particle concentration in the room has reached the threshold level. The inhalable particle fraction is collected for both applications on the same filters for a period of 60 min each.

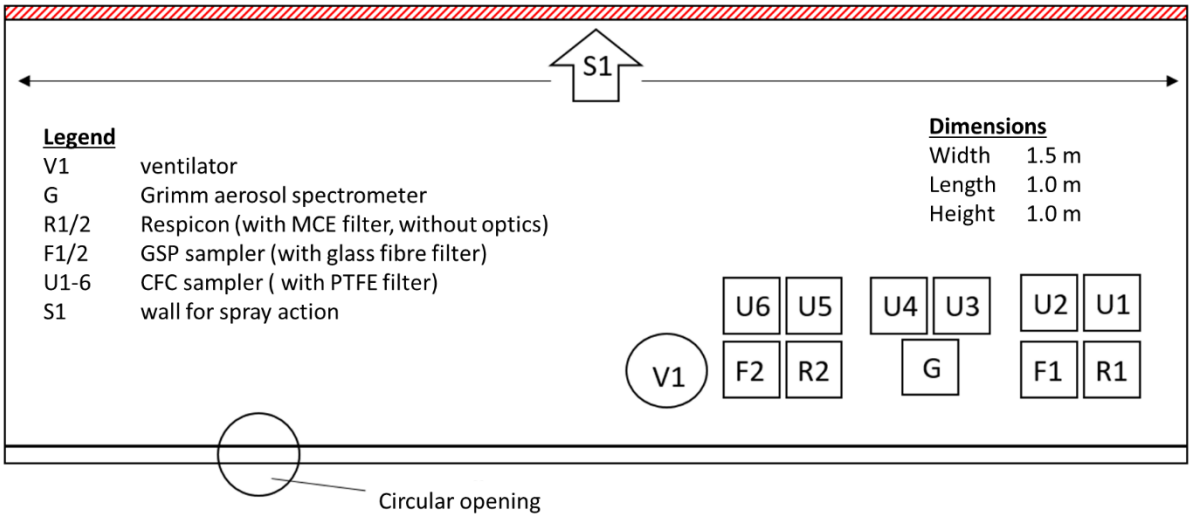
Spray application – insect spray B
The spray application is performed vertically from top to bottom in the upper third of the plasterboard. This is repeated until the upper third is sprayed and the can is empty. The sprayed area is then approx. 0.8 m². The distance between the plasterboard and the nozzle is approx. 2–3 m.

12.) The application is terminated.*
13.) Vacuum pump A is switched off 60 minutes after the end of spraying.*.
14.) The window is opened for ventilation (the room has no active room ventilation).*
15.) The sampling filters are transferred one at a time into the centrifuge tubes using tweezers, making sure that the loaded surfaces of the filters face inwards. The centrifuge tubes are wrapped in aluminium foil to ensure light protection (pyrethroids are light-sensitive substances).
16.) The filter samples are stored in a cool place (7–12°C) immediately after transfer to the centrifuge tubes.
17.) After the applications, the foam/spray can is weighed again to determine the average biocidal product consumption.
18.) As soon as the particle count in the room has dropped to the initial level before application, the aerosol spectrometer is deactivated*.
19.) The plasterboard is removed from the room.
*) The time to the second is noted.

A single application is carried out per test, unless otherwise described.

Implementation in the small model room

This room is a modified fume hood. The positions of the equipment and tools are shown in App. Fig. 8 below. The wall surface to be treated is marked in red. The fume hood is used for the release tests with the manual trigger systems. The duration of the surface exposure and the size of the treated area depend on the type of equipment used and its application in practice. The suitable conditions are to be determined in preliminary tests.



App. Fig. 8 Schematic representation of the experimental setup in the small model room. Respicons can be implemented in the experimental setup, if information on respirable, thoracic and inhalable aerosol size fractions is required. Respicons are therefore not mandatory components for all experiments.

In this model room, only one axial fan is required for aerosol homogenisation. The disinfectant is applied against the rear wall of the fume hood (W × H = 1.5 m × 1 m). The user's arm passes through an opening (Ø 21 cm) so that the distance from the spray nozzle to the rear wall is approx. 50 cm. After finishing the application, the opening is immediately closed again. Otherwise, the procedure is the same as in the large test room. Due to the large volume flow rate of the fume hood, a ventilation phase of 5 min is sufficient. The measurements are carried out according to the steps listed below:

1.) The ventilator is set to the lowest speed to mix the air inside the hood and started.
2.) The recording of temperature and humidity data logger is started.
3.) GSPs and, if applicable, Respicons and CFCs are equipped with MCE filters (PTFE[26], if applicable) and connected to the corresponding critical orifices. The respective volume flow rates are determined and recorded.
4.) GSPs (3.5 L/min) and, if applicable, Respicons (3.11 L/min) are connected to vacuum pump A; if applicable, CFCs (2.0 L/min) are connected to vacuum pump B.
5.) The handheld device is weighed in the empty state on the precision balance, tared and filled with the appropriate amount of water. The biocidal product is added using a measuring cylinder and the solution is mixed. Finally, a defined amount of

CsCl is weighed on the precision balance and added to the solution. The solution is mixed again by manual shaking.
6.) The unit is closed. In the case of the hand compression foamer or sprayer, pumping is continued until the safety valve is triggered.
7.) The aerosol laser spectrometer is started.*
8.) The fume hood ventilation is deactivated.*
9.) Vacuum pump B is started.*
10.) Vacuum pump A is started.*
11.) Application is started.*

Foam application
The application starts in the lower right area of the fume hood wall and is carried out from right to left. When the left end of the wall is reached, the next free area above is covered with foam from left to right. This is repeated until the wall is completely covered with foam. Make sure that areas that have already been covered are not covered with foam again. The covered area is approx. 1.5 × 1 m. The distance between the wall and the foam nozzle is approx. 0.5 m.

Spray application
The spray application is carried out vertically from top to bottom, spraying the entire length of the wall in this way. The distance between the wall and the nozzle is approx. 0.5 m.

12.) Application is terminated.*
13.) Ten minutes after the end of application, vacuum pump A is switched off.*
14.) The fume hood ventilation (min. 400/h) is activated.* The treated wall and affected floor surfaces of the fume hood are thoroughly rinsed with cold tap water.
15.) The fume hood ventilation is switched off 5 minutes after activation.*
16.) Steps 9–15 are performed up to two more times. Steps 9–12 are repeated for the final application. Ten minutes after the end of the application, the vacuum pumps A&B and the aerosol laser spectrometer are switched off.* The fume hood ventilation is activated.*
17.) After the applications, the handheld device is re-weighed to determine the average consumption of the solution.
18.) Using tweezers, transfer the sampling filters one at a time into the centrifuge tubes, making sure that the loaded surfaces of the filters face inwards.
19.) After completion of the experiment, the treated wall and affected bottom surfaces of the fume hood are rinsed thoroughly with cold tap water.
*) The time to the second is noted.)

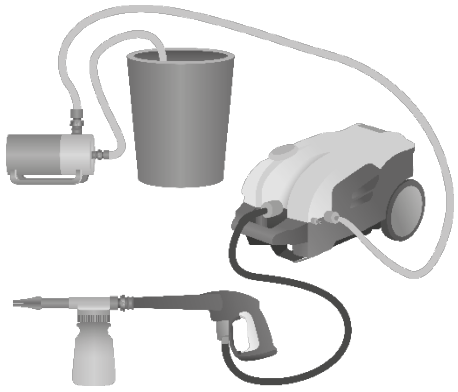
Appendix 7 Survey – Application technologies in the model room investigations

The equipment in this project included devices representative for large-scale as well as small-scale surface treatments.

Stationary/quasi-stationary devices for pressure- and volume-controlled application of biocidal products (low pressure <6 bar as well as high pressure range >10 bar) in industrial environments (large-area application)

There are a variety of wall-mounted, mobile and portable devices that can be equipped with different foam and spray nozzles and operate continuously or discontinuously. For the model room tests for large-scale application carried out in the project, the pressure foamer and sprayer G, the compressed air-driven pressure foamer B (1–6 bar), pressure foamer P and a low-pressure foam gun (active supply of water with water pump at 3 bar) in the medium-pressure range (operating pressure: 3–6 bar) and the high-pressure foam gun were used. With the exception of the low pressure foam gun, all units were used for both spray and foam application (see App. Fig. 9). App. Fig. 10 shows an example of the test set-up for the applications using the high-pressure foam gun and the high-pressure unit.

App. Fig. 9 Devices used, from left to right: Pressure foamer G, B, P, low pressure foam gun, high pressure device.



App. Fig. 10 Test set-up- High pressure foaming using the high pressure foam gun and booster.

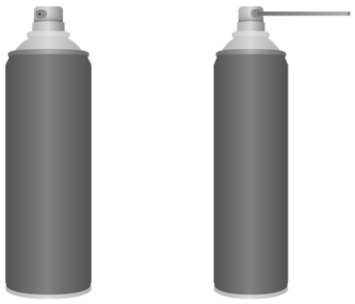
Devices for small-scale surface treatment – Handheld compression foamer/sprayer and trigger systems (hand pump foamer or sprayer (bottle))

Here, too, a variety of device types are available. Regardless of the special type, nozzle parameters determine the aerosol formation during application in both foam and spray mode. The hand compression device (max. pressure 3 bar) can be used for spray as well as foam application, depending on the nozzle selection. Another hand compression sprayer (No. 2, max. pressure 12 bar) was tested with different nozzles that enabled fine (fog nozzle 0.5 mm) or coarse (fog nozzle 1.2 mm) atomisation. For the trigger system category, the hand pump bottle was tested in model rooms for both spray and foam application, depending on the nozzle attachment (see App. Fig. 11).

App. Fig. 11 Top: Hand compression sprayer and foamer (up to 3 bar); Bottom: Hand pump sprayer and foamer.

Propellant-based pressurised cans for insecticide applications

Since only fixed combinations of application technique (propellant-based) and active substance formulation are available here, three commercially available insecticides were used. These are the products insect foam B.1 and B.2, insect spray B and insect spray F (see App. Fig.12).



App. Fig.12 Propellant cans used.

Appendix 8 Parameters and results of the release experiments in the model rooms

App. Tab. 11 Data set for release studies in the three model rooms[26]

	Concentrations [µg/m³]							
	R1			R2			GSP	
	iR1	tR1	rR1	iR2	tR2	rR2	iGSP1	iGSP2
V1	23.7	15.3	4.2	18.0	12.5	4.5	24.3	23.5
V2	61.1	43.1	13.7	51.9	35.8	14.9	66.5	66.6
V3	4.9	3.3	0.6	4.2	2.6	0.7	4.6	4.5
V4	17.1	8.6	7.3	22.4	14.2	8.4	32.9	32.8
V5	9.8	9.3	3.5	6.2	5.3	3.9	6.5	6.8
V6	25.6	19.1	12.4	28.5	22.8	14.6	32.0	31.8
V7	5.3	4.1	3.5	6.9	5.7	4.4	9.3	8.2
V8	7.7	5.6	4.5	9.8	7.9	5.2	10.5	11.2
V9	4.5	3.4	2.8	4.5	3.7	3.0	5.8	5.4
V10	6.2	4.8	3.4	6.2	5.0	3.8	7.5	7.4
V11	12.3	9.3	5.4	12.0	9.6	6.0	13.3	13.4
V12	57.3	21.1	10.5	70.1	39.9	14.2	92.1	88.8
V13	51.1	32.3	5.0	36.0	19.2	6.4	47.3	46.9
V15	100.1	66.4	41.5	127.7	101.1	50.6	150.1	142.9
V16	7.8	3.4	2.2	10.0	5.5	1.9	14.0	13.1
V17	3.6	2.7	0.9	3.6	2.3	0.8	4.1	3.8
V18	6.4	5.4	3.0	6.3	5.1	2.6	6.4	6.2
V19	14.5	10.2	6.6	14.3	9.9	6.0	19.1	19.6
V20	4.6	3.2	2.7	7.1	5.7	2.5	6.1	6.2
V21	4.0	3.2	2.5	5.3	4.5	2.4	5.4	5.1
V22	87.5	57.3	13.8	92.4	57.4	12.4	95.0	92.9
V23	50.4	33.1	6.7	46.6	26.4	5.9	52.3	50.8
V24							8.4	8.7
V25							11.4	11.0
V26							15.6	15.8
V27							20.4	21.0
V28							22.1	21.1
V29							2.3	2.2
V30							6.2	6.2
V31							8.6	8.3
V32							43.0	43.3
V36							5.8	6.0
V37							5.2	4.9
V38							5,5	5,5

[26] V14 was not listed because analytical data were not available due to a sampling error. V33-V35 were not release fraction measurements, but workplace simulations with fans turned off. KSK22 and P1 had no data for either GSP1 or GSP2. Therefore, they were not listed here.

	Concentrations [µg/m³]							
	R1			R2			GSP	
	iR1	tR1	rR1	iR2	tR2	rR2	iGSP1	iGSP2
V39							7.8	7.6
V40							376.2	364.7
V41							260.3	269.8
V42							163.3	166.5
V43							52.7	52.2
V44							22.7	22.7
V45							1.9	1.8
V46							108.0	117.1
V47							116.1	114.1
V48							6.4	6.4
V49							6.2	6.5
V49A							5.9	6.4
V50							1.8	1.9
V51							7.4	7.4
V52							17.7	19.5
V53							10.6	11.0
V54							10.1	10.5
V55							110.8	121.9
V56							13.0	14.2
V57							10.9	12.2
V58							11.0	12.0
V59.2							49.5	44.9
V60							0.05	0.05
V61							0.10	0.08
V62							0.08	0.07
V63							324.4	338.0
KSK1	353.6	275.5	134.7	371.0	271.2	129.4	462.3	454.9
KSK2	61.7	31.5	4.0	54.2	25.5	3.8	61.4	59.6
KSK3	14.3	6.8	0.4	12.6	5.8	0.4	12.5	12.5
KSK4	73.4	39.1	4.7	60.5	29.0	4.9	84.0	78.0
KSK5	121.8	77.8	14.4	109.7	52.4	13.5	134.3	124.6
KSK6	3.6	2.4	0.4	3.9	2.5	0.4	4.4	4.4
KSK7	96.3	51.1	14.0	75.3	40.1	12.4	108.6	106.4
KSK8	107.6	69.3	17.8	104.0	59.0	15.9	133.4	132.8
KSK9	146.8	91.7	12.2	139.3	86.3	12.8	168.3	164.4
KSK10							1.3	1.5
KSK11							1.2	1.3
KSK12							1.1	1.4
KSK13							96.1	94.6
KSK14							93.6	96.9
KSK15							87.0	95.5
KSK16							10.1	10.0

	Concentrations [µg/m³]							
	R1			R2			GSP	
	iR1	tR1	rR1	iR2	tR2	rR2	iGSP1	iGSP2
KSK17							11.7	11.6
KSK18							8.4	8.3
KSK19							14.4	15.5
KSK20							15.6	16.5
KSK21							16.7	17.3
KSK22								
KSK23							728.8	771.3
KSK24							539.3	557.6
KSK25							186.8	196.7
KSK26							141.1	144.9
KSK27							166.8	170.7
KSK28							2.3	2.5
KSK29							2.6	2.6
KSK30							2.8	3.0
P1								
P2	0.10	0.05	0.02	0.10	0.05	0.02	0.1	0.1
P3	122.8	84.4	43.5	121.6	86.8	49.3	141.6	151.0
P4	208.5	152.4	90.2	208.7	144.9	85.6	236.0	252.0
P5							1.9	1.7

App. Tab. 12 Parameters of the release tests carried out in the large (158 m³) model room.

Test	Device	Nozzle	Mode	Biodical Product (BP)	Pressure	Flow rate		E
					bar	l/min		
						Air	Formul.	
V1	Pressure foamer G	50/200	Foam	2 % QAC F	3.5	–	9.0	
V2	Pressure sprayer G	BSBT Washjet ¼ MEG 4030	Spray	2 % QAC F	–	–	9.0	
V3	Pressure foamer G	50/200	Foam	2 % QAC F	2	–	12.1	
V4	Pressure foamer G	50/200	Foam	2 % QAC F	4.5	–	8.8	
V5	Pressure foamer G	50/200	Foam	2 % QAC F	6	–	4.8	
V6	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	5.5	78.0	2.9	6.9
V7	Pressure foamer G	50/200	Foam	2 % QAC F	6	112.0	5.2	21.8
V8	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	3.5	40.0	1.4	9.6
V9	Pressure foamer G	50/200	Foam	2 % QAC F	6	115	3.1	21.8
V10	Pressure foamer G	50/200	Foam	2 % QAC F	6	113.0	6.0	21.8
V11	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	50.0	1.8	9.3
V12	Pressure sprayer G	BSBT Washjet ¼ MEG 4030	Spray	2 % QAC F	–	–	10.7	
V13	Pressure sprayer G	BSBT Washjet ¼ MEG 4030	Spray	2 % QAC F	–	–	7.9	
V14	Pressure sprayer P	TeeJet 110 06 VP	Spray	2 % QAC F	3	–	–	
V15	Pressure sprayer P	TeeJet 110 06 VP	Spray	2 % QAC F	3	–	0.8	
V16	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	2 % QAC F	3	5.0	0.8	7.3
V17	Pressure foamer P	Teejet 11006 VP, black cartridge	Foam	2 % QAC F	3	3.0	0.3	9.4
V18	Pressure foamer G	50/200	Foam	2 % QAC E	6	113.0	5.4	21.8
V19	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC E	5.5	56.0	3.4	4.1
V20	Pressure foamer G	50/200	Foam	2 % QAC E	6	115.0	5.0	21.8
V21	Pressure foamer G	50/200	Foam	2 % QAC E	6	116.0	4.7	21.8

Test	Device	Nozzle	Mode	Biodical Product (BP)	Pressure	Flow rate		E
					bar	l/min		
						Air	Formul.	
V22	Pressure sprayer G	BSBT Washjet ¼ MEG 4030	Spray	2 % QAC E	–	–	11.2	
V23	Pressure sprayer G	BSBT Washjet ¼ MEG 4030	Spray	2 % QAC E	–	–	7.9	
V24	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	52.0	1.8	9.7
V25	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	52.0	1.8	9.7
V26	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	52.0	1.8	9.7
V27	Pressure foamer P	Teejet 11006 VP, blue cartridge,	Foam	2 % QAC F	2.9	5.0	0.9	7.3
V28	Pressure foamer P	Teejet 11006 VP, black cartridge	Foam	2 % QAC F	2.9	4.0	0.7	8.5
V29	Pressure foamer P	Teejet 11006 VP, red cartridge,	Foam	2 % QAC F	2.9	2.4	0.4	10.3
V30	Pressure foamer G	50/200	Foam	2 % QAC F	6	120.0	3.7	21.8
V31	Pressure foamer G	65/150	Foam	2 % QAC F	6	124.0	3.9	12.8
V32	Pressure foamer G	50/100	Foam	2 % QAC F	6	122.0	3.9	4.2
V33	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	48.0	1.8	8.3
V34	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	48.0	1.8	8.3
V35	Pressure foamer B	H1/4U Veejet 4050	Foam	2 % QAC F	4.5	48.0	1.8	8.3
V36	Pressure foamer B	Fan nozzle A	Foam	2 % QAC F	4.5	48.0	1.8	21
V37	Pressure foamer B	Fan nozzle B	Foam	2 % QAC F	4.5	47.0	1.8	20
V38	Pressure foamer B	Fan nozzle C	Foam	2 % QAC F	4.5	47.0	1.8	20
V39	Pressure foamer B	Fan nozzle D	Foam	2 % QAC F	4.5	47.0	1.8	17
V40	Pressure foamer B	Fan nozzle E	Foam	2 % QAC F	4.5	45.0	1.7	2
V41	Pressure foamer B	Fan nozzle F	Foam	2 % QAC F	4.5	45.0	1.7	2
V42	Pressure foamer B	Fan nozzle H	Foam	2 % QAC F	4.5	46.0	1.8	3
V43	Pressure foamer B	Fan nozzle J	Foam	2 % QAC F	4.5	46.0	1.8	7
V44	Pressure foamer B	Fan nozzle K	Foam	2 % QAC F	4.5	47.0	1.8	10

Test	Device	Nozzle	Mode	Biodical Product (BP)	Pressure	Flow rate		E
					bar	l/min		
						Air	Formul.	
V45	Pressure foamer B	Fan nozzle L	Foam	2 % QAC F	4.5	47.0	1.8	25
V46	Pressure sprayer P	TeeJet 110 06 VP	Spray	2 % QAC F	3	7.0	0.8	
V47	Pressure sprayer P	TeeJet 110 06 VP	Spray	2 % QAC F	3	8.0	0.8	
V48	High pressure device	PA LS-10 foam gun	Foam	1.8 % QAC F	–	–	6.5	4
V49	High pressure device	PA LS-10 foam gun	Foam	1.9 % QAC F	–	–	6.5	4
V49a	High pressure device	PA LS-10 foam gun	Foam	2 % QAC F	–	–	6.5	4
V50	Low pressure foam gun	Foam gun V8	Foam	0.78 % QAC E	–	–	5.6	6.5
V51	Low pressure foam gun	Foam gun V8	Foam	3.12 % QAC E	–	–	5.6	11
V52	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	0.5 % PER F+foaming agent	3	5.4	0.2	9
V53	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	0.5 % PER F+foaming agent	3	4.5	0.2	9
V54	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	0.5 % PER F+foaming agentl	3	5.2	0.2	9
V55	Pressure sprayer P	TeeJet 110 06 VP	Spray	0.5 % PER F	3	9.2	1.0	
V56	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	20 % QAC M	3	8.1	0.4	9
V57	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	20 % QAC M	3	9.4	0.4	9
V58	Pressure foamer P	Teejet 11006 VP, blue cartridge	Foam	20 % QAC M	3	8.4	0.4	9
V59_2	Pressure sprayer P	TeeJet 110 06 VP	Spray	20 % QAC M	3		0.9	
V60	Pressure foamer P	Universal foam nozzle	Foam	20 % QAC M	3	8.7	1.8	3
V61	Pressure foamer P	Universal foam nozzle	Foam	20 % QAC M	3	9.0	0.9	7
V62	Pressure foamer P	Universal foam nozzle	Foam	20 % QAC M	3	10.0	0.7	8
V63	High pressure device	VP 145 Vario Power Jet Full Contr.	Spray	2 % QAC F			5.8	

App. Tab. 13 Parameters of the release tests carried out in the small (1.5 m³) model room.

Test	Device	Nozzle	Mode	Biocidal Product (BP)	Pressure	Flow rate		E
					bar	l/min		
						Air	Formul.	
KS1	Hand pump sprayer	Spray nozzel (fan unspecified)	Spray	2 % QAC F	–	–	0.2	
KS2	Hand compression sprayer 2	Spray nozzle 08	Spray	2 % QAC F	–	–	0.2	
KS3	Hand compression foamer	Foam nozzle	Foam	2 % QAC F	–	–	0.3	5
KS4	Hand compression sprayer	TPU 8002 PP	Spray	2 % QAC F	–	–	0.4	
KS5	Hand compression sprayer	Regulating nozzle, max GUZ	Spray	2 % QAC F	–	–	0.4	
KS6	Hand compression foamer	Foam nozzle G 3/8“	Foam	2 % QAC F	–	–	1.3	6.8
KS7	Hand compression sprayer 2	Spray nozzle 0.5 mm	Spray	2 % QAC F	–	–	0.1	
KS8	Hand compression sprayer 2	Spray nozzle 1.2 mm	Spray	2 % QAC F	–	–	0.2	
KS9	Hand compression sprayer	XR 8002 VS	Spray	2 % QAC F	–	–	0.6	
KS10	Hand compression foamer	Foam nozzle G 3/8“	Foam	20 % QAC M	–	–	1.4	9
KS11	Hand compression foamer	Foam nozzle G 3/8“	Foam	20 % QAC M	–	–	1.3	9
KS12	Hand compression foamer	Foam nozzle G 3/8“	Foam	20 % QAC M	–	–	1.4	9
KS13	Hand compression sprayer	TPU 8002 PP	Spray	20 % QAC M	–	–	0.4	
KS14	Hand compression sprayer	TPU 8002 PP	Spray	20 % QAC M	–	–	0.5	
KS15	Hand compression sprayer	TPU 8002 PP	Spray	20 % QAC M	–	–	0.5	
KS16	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	5

Test	Device	Nozzle	Mode	Biocidal Product (BP)	Pressure	Flow rate		E
					bar	l/min		
						Air	Formul.	
KS17	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	5
KS18	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	5
KS19	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	7
KS20	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	7
KS21	Hand pump foamer	Foam nozzle	Foam	2 % QAC E	–	–	0.2	7
KS22	Hand pump sprayer	Spray nozzle (wide fan)	Spray	2 % QAC E	–	–	0.1	
KS23	Hand pump sprayer	Spray nozzle (wide fan)	Spray	2 % QAC E	–	–	0.1	
KS24	Hand pump sprayer	Spray nozzle (wide fan)	Spray	2 % QAC E	–	–	0.1	
KS25	Hand pump sprayer	Spray nozzle (narrow fan)	Spray	2 % QAC E	–	–	0.1	
KS26	Hand pump sprayer	Spray nozzle (narrow fan)	Spray	2 % QAC E	–	–	0.1	
KS27	Hand pump sprayer	Spray nozzle (narrow fan)	Spray	2 % QAC E	–	–	0.1	
KS28	Hand compression foamer	Foam nozzleG 3/8“	Foam	2 % QAC F	–	–	1.4	6.8
KS29	Hand compression foamer	Foam nozzle G 3/8“	Foam	2 % QAC F	–	–	1.3	6.8
KS30	Hand compression foamer	Foam nozzle G 3/8“	Foam	2 % QAC F	–	–	1.4	6.8

App. Tab. 14 Results of the release tests carried out in the medium (41 m³) model room.

Test	Device	Nozzle	Mode	Biocidal Product (BP)	Pressure	Flow rate		E
					bar	g/s		
						Air	Formul.	
P1	Propellant can	–	Foam	Insect foam B.1	–	–	6.7	46
P2	Propellant can	–	Foam	Insect foam B.1	–	–	5.8	46
P3	Propellant can	–	Spray	Insect spray B	–	–	22.3	
P4	Propellant can	–	Spray	Insect spray B	–	–	21.0	
P5	Propellant can	–	Foam	Insect foam F	–	–	1.4	46

App. Tab. 15 Results of the release tests carried out in the large (158 m³) model room.

	R^s						Measured CsCl-concentration µg/m³			Pad coverage µg/m²	
	Mean value			Standard deviation							
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Hor.	Vert.
V1	3.0E-04	1.7E-04	4.9E-05	3.2E-05	1.7E-05	2.0E-06	22.0	12.5	4.5		
V2	8.6E-04	5.0E-04	1.6E-04	2.2E-05	1.3E-05	4.2E-06	61.7	35.8	14.9		
V3	5.7E-05	3.4E-05	7.7E-06	3.3E-06	1.9E-06	4.4E-07	4.4	2.6	0.7		
V4	3.6E-04	1.7E-04	9.2E-05	2.7E-05	1.3E-05	3.2E-06	29.4	14.2	8.4		
V5	8.3E-05	6.7E-05	5.0E-05	9.3E-06	7.6E-06	5.6E-06	6.5	5.3	3.9		
V6	5.1E-04	3.9E-04	2.5E-04	8.1E-05	6.3E-05	8.3E-05	30.8	22.8	14.6		
V7	1.2E-04	8.6E-05	6.7E-05	2.0E-05	1.4E-05	1.1E-05	8.1	5.7	4.4		
V8	3.8E-04	2.9E-04	1.9E-04	2.9E-05	2.2E-05	1.4E-05	10.5	7.9	5.2		
V9	9.2E-05	6.5E-05	5.0E-05	2.5E-06	1.8E-06	1.4E-06	5.2	3.7	3.0		
V10	9.7E-05	7.0E-05	5.2E-05	7.7E-06	5.5E-06	4.1E-06	7.0	5.0	3.8	80.6	39.1

	R^s						Measured CsCl-concentration µg/m³			Pad coverage µg/m²	
	Mean value			Standard deviation							
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Hor.	Vert.
V11	4.5E-04	3.3E-04	2.0E-04	1.8E-05	1.3E-05	7.8E-06	12.9	9.6	6.0	136.4	78.2
V12	1.7E-03	8.2E-04	2.6E-04	1.7E-04	8.2E-05	2.6E-05	83.7	39.9	14.2	2101	383
V13	1.2E-03	5.3E-04	1.6E-04	6.0E-05	2.6E-05	8.0E-06	43.4	19.2	6.4	892	103.4
V14**	–	–	–								
V15	1.7E-02	1.3E-02	6.0E-03	1.6E-03	1.2E-03	5.6E-04	140.2	101.1	50.6	1470	197
V16	9.7E-04	4.3E-04	1.3E-04	1.5E-03	6.5E-04	1.9E-04	12.4	5.5	1.9	231.9	75.8
V17	8.2E-04	4.9E-04	1.5E-04	8.2E-05	4.9E-05	1.5E-05	3.8	2.3	0.8	55.9	16.4
V18	1.7E-04	1.4E-04	6.1E-05	1.7E-05	1.4E-05	6.1E-06	6.3	5.1	2.6	63.0	18.3
V19	4.4E-04	2.5E-04	1.4E-04	4.4E-05	2.5E-05	1.4E-05	17.7	9.9	6.0	132.4	26.4
V20	1.4E-04	1.2E-04	5.4E-05	1.4E-05	1.2E-05	5.4E-06	6.4	5.7	2.5	45.8	13.6
V21	1.8E-04	1.6E-04	8.4E-05	1.8E-05	1.6E-05	8.4E-06	5.3	4.5	2.4	32.5	9.2
V22	1.8E-03	1.1E-03	2.1E-04	1.8E-04	1.1E-04	2.1E-05	93.4	57.4	12.4	1662	449
V23	1.4E-03	7.3E-04	1.5E-04	1.4E-04	7.3E-05	1.5E-05	49.9	26.4	5.9	872	162
V24	4.2E-04			4.2E-05			8.5				
V25	5.4E-04			2.9E-05			11.2				
V26	3.9E-04			7.9E-05			15.7				
V27	5.6E-04			5.6E-05			20.7				
V28	4.3E-04			4.3E-05			21.6				
V29	2.4E-04			2.4E-05			2.3				
V30	1.6E-04			3.8E-05			6.2				
V31	2.0E-04			2.0E-05			8.4				
V32	1.1E-03			3.2E-04			43.1				

	R^s						Measured CsCl-concentration µg/m³			Pad coverage µg/m²	
	Mean value			Standard deviation							
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Hor.	Vert.
V33*							5.8				
V34							10.4				
V35							13.1				
V36	2.1E-04			1.5E-06			5.9	*5.5****			
V37	1.2E-04			1.2E-05			5.0	*4.8*			
V38	1.5E-04			3.1E-06			5.5	*5.4*			
V39	2.1E-04			2.6E-05			7.7	*7.4*			
V40	2.1E-02			6.1E-04			370.4	*279.0*			
V41	1.5E-02			1.0E-03			265.1	*188.0*			
V42	9.1E-03			1.9E-04			164.9	*134.0*			
V43	1.5E-03			2.4E-04			52.5	*46.4*			
V44	6.9E-04			6.9E-05			22.7	*21.3*			
V45	5.0E-05			1.6E-05			1.9	2.4			
V46	1.4E-02			2.4E-03			112.5				
V47	1.6E-02			6.9E-04			115.1				
V48	1.9E-04			2.3E-05			6.4				
V49	1.7E-04			3.5E-05			6.4				
V49a	1.9E-04			1.5E-05			6.1				
V50	2.8E-05			4.4E-06			1.9				
V51	1.4E-04			2.2E-05			7.4				
V52	7.7E-03			1.6E-03			18.6				
V53	3.7E-03			3.5E-04			10.8				

	R^s						Measured CsCl-concentration µg/m³			Pad coverage µg/m²	
	Mean value			Standard deviation							
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Hor.	Vert.
V54	5.8E-03			1.0E-03			10.3				
V55	1.2E-02			1.5E-03			116.3				
V56	2.2E-03			1.1E-03			13.6				
V57	2.3E-03			1.0E-03			11.6				
V58	1.8E-03			1.2E-03			11.5				
V59_2	8.8E-03			2.2E-03			47.2				
V60	1.3E-06			2.3E-07			0.05				
V61	4.0E-06			6.6E-07			0.09				
V62	4.9E-06			6.9E-07			0.07				
V63	1.1E-02			2.2E-03			331.2				

*simulated workplace measurements (no values for the release fraction): These tests were conducted in the model room as artificial workplaces. The experiments were conducted according to the standard operating procedure for model room investigations. The only deviations were 1. the implementation of a third GSP sampler, operated as a personal sampler during the application, 2. the fans were switched off all the time and 3. the room ventilation was active continuously (during and after application).
** Sampling pumps for GSP and Respicon accidentally not switched on, therefore no analytical evaluations available.
*** Concentration values of the inhalable fraction obtained with personal sampling device. The tests were carried out according to the standard operating procedure for the model room tests. The only deviation was the use of a third personal GSP sampler attached to the operator.

App. Tab. 16 Results of the release tests carried out in the small (1.5 m³) model room.

	R^s						Measured CsCl-concentration µg/m³ Mean value		
	Mean value			Standard deviation					
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.
KS1	8.7E-02	5.8E-02	2.9E-02	9.0E-03	6.0E-03	3.0E-03	416.9	279.0	140.7
KS2	8.3E-03	3.9E-03	4.8E-04	2.2E-03	8.3E-04	1.3E-04	55.7	26.2	4.4
KS3	1.7E-03	8.4E-04	2.9E-05	4.0E-04	1.7E-04	6.6E-06	12.7	6.2	0.5
KS4	3.8E-03	2.0E-03	2.1E-04	4.5E-04	2.7E-04	3.6E-05	76.2	40.0	5.6
KS5	4.7E-03	2.5E-03	5.8E-04	4.1E-04	2.2E-04	5.1E-05	122.1	66.4	15.3
KS6	3.4E-05	2.3E-05	2.7E-06	9.7E-06	6.7E-06	7.7E-07	4.4	3.1	0.4
KS7	1.1E-02	6.3E-03	1.8E-03	1.3E-03	6.9E-04	1.9E-04	95.8	52.4	14.7
KS8	9.8E-03	4.4E-03	1.4E-03	1.0E-03	4.6E-04	1.5E-04	113.3	50.9	18.3
KS9	4.7E-03	2.9E-03	4.1E-04	5.8E-04	2.8E-04	5.8E-05	155.9	95.7	14.7
KS10	8.5E-06			2.2E-06			1.4		
KS11	9.2E-06			1.5E-06			1.3		
KS12	1.0E-05			1.1E-06			1.2		
KS13	6.1E-03			6.5E-04			95.3		
KS14	4.2E-03			3.6E-04			95.2		
KS15	3.9E-03			6.8E-04			91.2		
KS16	7.8E-04			1.6E-04			10.1		
KS17	8.9E-04			1.1E-04			11.7		
KS18	7.2E-04			9.5E-05			8.3		
KS19	1.2E-03			6.7E-05			14.9		
KS20	1.5E-03			1.3E-04			16.0		
KS21	1.6E-03			7.6E-05			17.0		

	R^s						Measured CsCl-concentration µg/m³ Mean value		
	Mean value			Standard deviation					
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.
KS22	1.3E-01			1.4E-02			728.0		
KS23	1.3E-01			2.4E-02			750.0		
KS24	1.3E-01			2.5E-02			548.4		
KS25	2.7E-02			1.7E-03			191.8		
KS26	1.8E-02			9.4E-04			143.0		
KS27	2.3E-02			3.9E-03			168.7		
KS28	1.4E-05			1.6E-06			2.4		
KS29	1.7E-05			7.9E-07			2.6		
KS30	2.0E-05			3.0E-06			2.9		

App. Tab. 17 Results of the release tests carried out in the medium (41 m³) model room.

	R^s						Measured CsCl-concentration µg/m³ Mean value		
	Mean value			Standard deviation					
	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.	Inh.	Thorac.	Resp.
P1	2.9E-05	1.4E-05	2.8E-06				0.09	0.04	0.02
P2	3.6E-05	1.9E-05	4.7E-06				0.09	0.05	0.02
P3	7.1E-02	4.5E-02	1.4E-02				138.1	87.0	49.3
P4	1.2E-01	7.4E-02	2.1E-02				232.3	145.0	85.6
P5	6.4E-05						1.81 (Permethrin)		

Appendix 9 Mathematical details of exposure modelling

In the formulation of the 2-box model, a constant mass flow rate of active substance, $\dot{M}^S$, is assumed during the entire application period, T. Thereafter, the concentration decreases exponentially during the additional residence time, T_r, starting from the value at timepoint T. The concentration curve results from the aerosol release fraction, R_i^S, according to Eq. 3.5:

(App. 9. 1)

$$c(t \le T) = R_i^S \cdot \dot{M}^S \cdot \int_0^t \chi(t - t')dt' = R_i^S \cdot \dot{M}^S \cdot \int_0^t \chi(t')dt', \quad t \le T$$

$$c(t > T) = c(T) \cdot e^{-\Gamma(t-T)} \qquad T < t < T + T_r$$

with

(App. 9. 2)

$$\chi(t) = \frac{1}{V_P} \ f\ddot{u}r\ t < T_M; \ \ \chi(t) = \frac{e^{-\Gamma t}}{V_R} \ f\ddot{u}r\ T_M \le t < T$$

It was assumed here that the mixing time in the personal volume, T_M, is small compared to the duration of application, T. The loss rate, Γ, has no influence on the near field concentration.

For $t < T_M$ one obtains from Eq. (App. 9. 1) a concentration pattern that increases linearly in time inside the control volume, V_P:

(App. 9. 3)

$$c(t) = \frac{R_i^S \cdot \dot{M}^S}{V_P} \cdot t$$

For $t > T_M$:

(App. 9. 4)

$$c(t) = R_i^S \cdot \dot{M}^S \left\{ \frac{T_M}{V_P} + \frac{1}{V_R \cdot \Gamma} (e^{-\Gamma T_M} - e^{-\Gamma t}) \right\} \qquad t \le T$$

$$c(t) = R_i^S \cdot \dot{M}^S \left\{ \frac{T_M}{V_P} + \frac{1}{V_R \cdot \Gamma} (e^{-\Gamma T_M} - e^{-\Gamma T}) \right\} \cdot e^{-\Gamma(t-T)} \qquad T < t \le T + T_r$$

The first term in the curly brackets is the near-source contribution, the second the contribution from the mixing of the introduced active substance aerosol in the entire room. The time average concentration is obtained by time integration of Eq. (App. 9. 3) and Eq. (App. 9. 4):

(App. 9. 5)

$$\bar{c} = \frac{1}{T+T_r}\int_0^{T+T_r} c(t)dt$$

$$= \frac{R_i^s \cdot \dot{M}^s}{T+T_r}\cdot\left[\frac{1}{V_P}\int_0^{T_M} t dt + \int_{T_M}^{T}\left\{\frac{T_M}{V_P}+\frac{1}{V_R\cdot\Gamma}(e^{-\Gamma T_M}-e^{-\Gamma t})\right\}dt + \left\{\frac{T_M}{V_P}+\frac{1}{V_R\cdot\Gamma}(e^{-\Gamma T_M}-e^{-\Gamma T})\right\}\int_{t=T}^{T+T_r} e^{-\Gamma(t-T)}\,dt\right]$$

Carrying out the integration and using the fact that the near field mixing time is small compared to the averageing ($T_M \ll T$), and assuming a constant mass flow rate of active substance during the application time period ($M^s = T\cdot\dot{M}^s$) one obtains:

(App. 9. 6)

$$\bar{c} = \frac{R_i^s \cdot M^s}{V_R}\frac{T}{T+T_r}\cdot\left[\frac{V_R}{V_P}\frac{T_M}{T}\left(1-\frac{1}{2}\cdot\frac{T_M}{T}\right)+\frac{1}{\Gamma T}\left\{1-\frac{1}{\Gamma T}(1-e^{-\Gamma T})\right\} + \frac{1-e^{-\Gamma T_r}}{\Gamma T}\left\{\frac{V_R}{V_P}\cdot\frac{T_M}{T}+\frac{1}{\Gamma T}(1-e^{-\Gamma T})\right\}\right]$$

The mean exposure concentration is again the sum of a near-field and a far-fied contribution. The third term in parentheses describes the contribution from the residence time in the room after application. The dispersion factor is given by:

(App. 9. 7)

$$\bar{\kappa} = \frac{T}{T+T_r}\left[\frac{V_R}{V_P}\cdot\frac{T_M}{T}\left(1-\frac{1}{2}\cdot\frac{T_M}{T}\right)+\frac{1}{\Gamma T}\left\{1-\frac{1}{\Gamma T}(1-e^{-\Gamma T})\right\} + \frac{1-e^{-\Gamma T_r}}{\Gamma T}\left\{\frac{V_R}{V_P}\cdot\frac{T_M}{T}+\frac{1}{\Gamma T}(1-e^{-\Gamma T})\right\}\right].$$

For the 1-box approximation ($T_M = 0$) this reduces to:

(App. 9. 8)

$$\bar{\kappa} = \frac{1}{\Gamma\cdot(T+T_r)}\left\{1-\frac{1}{\Gamma T}(1-e^{-\Gamma T})+\frac{1}{\Gamma T}(1-e^{-\Gamma T})(1-e^{-\Gamma T_r})\right\}$$

with

(App. 9. 9)

$$\bar{\kappa} \to \frac{1}{(T+T_r)}\left(\frac{1}{2}T + T_r\right) \quad \text{für } \Gamma T \to 0 \text{ und } \Gamma T_r \to 0.$$

To further illustrate the 2-box model, Eq. (App. 9. 6) is transformed for $T_r = 0$ as follows:

(App. 9. 10)

$$\bar{c}^s = \frac{R_i^s \cdot M^s}{V_R} \cdot \left[\frac{V_R}{V_P} \cdot \frac{T_M}{T}\left(1 - \frac{1}{2} \cdot \frac{T_M}{T}\right) + \frac{1}{\Gamma T}\left\{1 - \frac{1}{\Gamma T}(1 - e^{-\Gamma T})\right\}\right]$$

$$\approx \frac{R_i^s \cdot M^s}{V_R} \cdot \frac{T_M}{T} + \frac{R_i^s \cdot M^s}{V_R} \cdot \frac{1}{\Gamma T}\left\{1 - \frac{1}{\Gamma T}(1 - e^{-\Gamma T})\right\}, \quad \text{da} \quad \frac{T_M (= 0.1 \text{ min})}{T} \ll 1$$

$$= \frac{R_i^s \cdot \dot{M}^s \cdot T_M}{V_P} + \frac{R_i^s \cdot M^s}{V_R} \cdot \frac{1}{\Gamma T}\left\{1 - \frac{1}{\Gamma T}(1 - e^{-\Gamma T})\right\}$$

$$= R_i^s \cdot \dot{M}^s \left[\frac{T_M}{V_P} + \frac{T}{V_R} \cdot \frac{1}{\Gamma T}\left\{1 - \frac{1}{\Gamma T}(1 - e^{-\Gamma T})\right\}\right]$$

The first term in the third line is the contribution of the personal spray cloud characterised by its volume and the residence time of the released aerosol. This contribution is proportional to the aerosol mass flow rate introduced and is independent of the room volume. Its contribution is dominant for large rooms. The second term describes the contribution from the uniform distribution in the room volume. The weighting of the two contributions can be derived from the last line by comparing the quantities $T_M/V_P = 0.01$ [min/m³] with the ratio T/V_R calculated for the respective scenario.

Appendix 10 Measurement at workplaces – survey

App. Tab. 18 Measurement at workplaces – hand compression foamer and sprayer (< 3 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
1	Foaming of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 60 s • Duration of exposure: 360 s • Material consumption: 325 g • Foam expansion ratio: n.s. • Room volume: 13.3 m³ • Treated area: 3.56 m² • Ventilation: on (8/h)	2 % QAC F (0.16 % BAC); Tracer: 0.1 % CsCl	• Hand compression foamer • Foam nozzle G 3/8“ • Pressure: < 3 bar 	CsCl: 0.10 BAC*: 0.16	BAC: 2019	BAC: 52816 (Foaming + wiping)
3	Spraying of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 60 s • Duration of exposure: 270 s • Material consumption: 95.6 g • Foam expansion ratio: NA • Room volume: 13.3 m³ • Treated area: 3.56 m² • Ventilation: on (8/h)	2 % QAC F (0.16 % BAC); Tracer: 0.1 % CsCl	• Hand compression sprayer • Spray nozzle XR 8002 VS • Pressure: < 3 bar 	CsCl: 5.66 BAC*: 9.06	BAC: 826	BAC: 12756 (Spraying + wiping)

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation

App. Tab. 19 Measurement at workplaces – hand pump foamer and sprayer (< 3 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
2	Foaming of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 33 s • Duration of exposure: 220 s • Material consumption: 63 g • Foam expansion ratio: n.s. • Room volume: 13.3 m³ • Treated area: 3.56 m² • Ventilation: on (8/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Hand pump foamer • Foam nozzle • Pressure: NA 	CsCl: 1.16 BAC*: 1.86	BAC: 322	BAC: 7905 (Foaming + wiping)
4	Spraying of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 77 s • Duration of exposure: 267 s • Material consumption: 67.8 g • Foam expansion ratio: NA • Room volume: 13.3 m³ • Treated area: 3.56 m² • Ventilation: on (8/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Hand pump sprayer • Spray nozzle • Pressure: NA 	CsCl: 38.6 BAC*: 61.7	BAC: 327	BAC: 5547 (Spraying + wiping)

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation;

App. Tab. 20 Measurement at workplaces – propellant devices.

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
11 & 12	Artificial indoor wasp nest (treatment of 2 nests) • Duration of application: 218 s (1 m distance) and 206 s (1.5 m distance) • Duration of exposure: 218 and 206 s • Material consumption: 549 and 371 g • Foam expansion ratio: n.s. • Room volume: 41 m³ • Treated area: – • Ventilation: off	Insect foam B.2 (1.5 g/kg Phenothrin)	Insect foam B.2 Propellant can 	Phenothrin: AP 11: 1.20 AP 12: 0.23	Phenothrin: AP 11: 1.78 AP 12: 81.4	Phenothrin: AP 11: 213 AP 12: 0.295
13	Artificial indoor wasp nest (treatment of 1 nest) • Duration of application: 23 s • Duration of exposure: 23 s • Material consumption: 334 g • Foam expansion ratio: n.s. • Room volume: 41 m³ • Treated area: – • Ventilation: off	Insect spray B (Phenothrin) (1 g/kg Phenothrin)	Insect spray B Propellant can 	Phenothrin: 220	Phenothrin: 356	Phenothrin: 71.8

n.s. – not specifed; NA – not applicable

App. Tab. 20 Measurement at workplaces – propellant devices (cont.).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
27	Artificial indoor wasp nest and formation of barriers • Duration of application: 1200 s • Duration of exposure: 1200 s • Material consumption: 679 g • Foam expansion ratio: 28 • Room volume: 16 m³ • Treated area: – • Ventilation: off	Insect foam B.1 (1.05 g/kg Phenothrin)	Insect foam B.1 Propellant can 	Phenothrin: 1.43	Phenothrin: 600	Phenothrin: 82.3
28	Formation of barriers (indoor) • Duration of application: 1200 s • Duration of exposure: 1200 s • Material consumption: 246 g • Foam expansion ratio: 41 • Room volume: 34 m³ • Treated line: 57 m • Ventilation: off	Insect foam F (28 g/l Permethrin)	Insect foam F Propellant can 	Permethrin: 0.60	Permethrin: 147	Permethrin: 427

n.s. – not specifed; NA – not applicable

App. Tab. 21 Measurement at workplaces – high pressure devices (70–200 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
14	Foaming of walls, separation walls, floors and ceiling in a small pig stable • Duration of application: 720 s • Duration of exposure: 720 s • Material consumption: 225 L • Foam expansion ratio: 3.5 • Room volume: 310 m³ • Treated area: 215 m • Ventilation: off, open doors	QAC E (Application solution: 1.32 g BAC/L; consumption 3.8 L) 10 % foaming stabilizing agent	• High pressure pump with foam lance and mixing section for concentrate • Foam nozzle with grid: fan nozzle (LS-10 nozzle 1.5 mm), nominal flow rate 25 L/min; nominal pressure: 200 bar • Application pressure: n.s. • Pump pressure: 95–100 bar  Ex.	BAC: <12	BAC:1002	BAC:1180
17	Spraying of walls, separation walls, floors and ceiling in a small pig stable • Duration of application: 420 s • Duration of exposure: 420 s • Material consumption: 100 L • Foam expansion ratio: NA • Room volume: 310 m³ • Treated area: 215 m • Ventilation: off, open doors	QAC E (Application solution: 1.32 g BAC/L) Tracer: 0.09 % CsCl	• High pressure pump with spray lance • Fan nozzle 15/10 • Application pressure: n.s.: • Pump pressure: 200 bar  Ex.	CsCl: 256 BAC: 348	BAC:10764	BAC:1438

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation

App. Tab. 21 Measurement at workplaces – high pressure devices (70–200 bar) (cont.).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
15	Foaming of walls, floors, troughs and ceilings in a large chicken stable ⊙ Duration of application: 720 s ⊙ Duration of exposure: 720 s ⊙ Material consumption: 230 L ⊙ Foam expansion ratio: 7 ⊙ Room volume: 6000 m³ ⊙ Floor space: 1100 m² ⊙ Ventilation: off, open doors	QAC A (formulation: 0.5 g BAC/L)	• High pressure pump with foam lance and mixing section for concentrate • Foam nozzle with grid: fan nozzle (LS-10 nozzle 1.5 mm), nominal flow rate 25 L/min; nominal pressure: 200 bar • Application pressure: n.s. • Pump pressure: 70–80 bar  Ex.	BAC: <12	BAC:1367	BAC: 297
16	Spraying of walls, floors, troughs and ceilings in a large chicken stable • Duration of application: 360 s • Duration of exposure: 360 s • Material consumption: 270 L • Foam expansion ratio: NA • Room volume: 6000 m³ • Floor space: 1100 m² • Ventilation: off, open doors	QAC A (0.5 g BAC/L)	• High pressure pump with spray lance • Fan nozzle: no information • Nozzle capacity:120 L/min • Flow rate: 50 l/min • Application pressure: n.s.: • Pump pressure: 120 bar  Ex.	BAC: 141	BAC:1814	BAC: 95,9

n.s. – not specifed; NA – not applicable; Ex. – example

App. Tab. 21 Measurement at workplaces – high pressure devices (70–200 bar) (cont.).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
21	Foaming of walls, floor, boxes and separation walls in a pig stable • Duration of application: 720 s • Duration of exposure: 720 s • Material consumption: 2 L BAC concentrate • Foam expansion ratio: 3 (probably too low) • Room volume: 616 m³ • Floor space 154 m² • Treated area: 504 m² • Ventilation: off, open doors	QAC AF (0.4 g BAC/L)	• High pressure foam gun • Fan nozzle PA LS-10 or similar • Application pressure: NA: • Pump pressure 150 bar  Ex.	BAC: 9.33	BAC:7190	BAC: 1456

n.s. – not specifed; NA – not applicable; Ex. – example

App. Tab. 22 Measurement at workplaces – foam gun (3–5 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
18	Foaming of walls and floor in sauna area • Duration of application: 351 s • Duration of exposure: 378 s • Material consumption: 150 mL concentrate (76 mgBAC/g) • Foam expansion ratio: 3 • Room volume: 1000 m³ • Floor space: 140 m² • Ventilation: off	QAC N (0.4 g BAC/L formulation)	• Foam gun with dosing head connected to water supply • Foam adapterV8 (Art.-Nr. 50013-08) • Aplication pressure: 3–5 bar (system pressure) Ex. 	BAC: <24	BAC: 752	BAC: 1013
20	Foaming of walls and floor in sauna area • Duration of application: 312 s • Duration of exposure: 440 s • Material consumption: 150 mL concentrate (76 mgBAC/g) • Foam expansion ratio: 4 • Room volume: 1000 m³ • Floor space: 167 m² • Ventilation: off	QAC N (0.6 g BAC/L formulation)	• Foam gun with dosing head connected to water supply • Foam adapterV8 (Art.-Nr. 50013-08) • Aplication pressure: 3–5 bar (system pressure) Ex. 	BAC: <27	BAC: 325	BAC: 305

NA – not applicable; Ex. – example

App. Tab. 23 Measurement at workplaces – mobile pressure sprayer (3 bar, battery operated).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
19	Disinfection of pool side with battery operated pressure sprayer • Duration of application: 960 s • Duration of exposure: 1260 s • Material consumption: 38 L • Foam expansion ratio: NA • Room volume: 10700 m³ • Floor space (treated: 415 m² • Ventilation: max. 35000 m³/h; 50 % reduction possible depending on temperature and humidity	QAC N (1.9 g BAC/L formulation)	• battery operated pressure sprayer • Fan nozzle, M40040 (angle: 40°; capacity: 3.5 L/min) • Application pressure: 2 bar • 2.4 L/min	BAC: 30.0	BAC: 637	BAC: 12.4

Anh. Tab. 24 Measurment at workplaces – pressure foamer/sprayer (2 to 3 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
24	Foaming on wall surface • Duration of application: 1200 s • Duration of exposure: 1200 s • Material consumption: 9.5 kg • Foam expansion ratio: 5 • Room volume: 54 m³ • Treated area: 57 m² • Ventilation: off	20 % QAC M (1.5 % BAC in formulation) Tracer: 0.1 % CsCl	• Pressure foamer P2 (manually) • Universal foam nozzle • Application pressure: unknown (appr. 2–3 bar) • Tank pressure: unknown Ex. 	CsCl: 0.69 BAC*: 13.7	BAC: 15722	BAC: 68665
25	Foaming on wall surface • Duration of application: 1860 s • Duration of exposure: 1860 s • Material consumption: 8 kg • Foam expansion ratio: 10 • Room volume: 54 m³ • Treated area: 57 m² • Ventilation: off	20 % QAC M (1.5 % BAC in formulation) Tracer: 0.1 % CsCl	• Pressure foamer P • Fan nozzle TeeJet 110 06VP (with cartridge, black) • Application pressure: 2.4 bar • Tank pressure: 3 bar Ex. 	CsCl: 27.0 BAC*: 539	BAC: 2832	BAC: 1885
26	Spraying on wall surface • Duration of application: 720 s • Duration of exposure: 720 s • Material consumption: 5 kg • Foam expansion ratio: NA • Room volume: 54 m³ • Treated area: 59 m² • Ventilation: off	20 % QAC M (1.5 % BAC in formulation) Tracer: 0.1 % CsCl	• Pressure sprayer P2 • Standard hollow cone nozzle, adjustable • Application pressure: unknown (appr. 2–3 bar) • Tank pressure: unknown Ex. 	CsCl: 49.9 BAC*: 997	BAC: 14835	BAC: 4747

App. Tab. 25 Measurement at artificial workplaces – hand pump foamer/sprayer (< 3 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
9	Foaming of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 1140 s • Duration of exposure: 1140 s • Material consumption: 559 g • Foam expansion ratio: NA • Room volume: 696 m³ • Treated area: 21 m² • Ventilation: on (2.3 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Hand pump foamer • Foam nozzle • Pressure: NA Ex. 	CsCl: 0.15 BAC*: 0.25	BAC: 57.5	BAC: 24397 (foaming+ wiping)
10	Spraying of surfaces followed by removal/distribution of the formulation by wiping • Duration of application: 1020 s • Duration of exposure: 1020 s • Material consumption: 519 g • Foam expansion ratio: NA • Room volume: 696 m³ • Treated area: 21 m² • Ventilation: on (2.3 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Hand pump sprayer • Spray nozzle • Pressure: NA Ex. 	CsCl: 38.3 BAC*: 61.3	BAC: 327	BAC: 12494 (foaming+ wiping)

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation; Ex. – example

App. Tab. 26 Measurement at artificial workplaces – pressure foamer/sprayer (2–3 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
6	Foaming of wall surfaces • Duration of application: 192 s • Duration of exposure: 192 s • Material consumption: 2.9 kg • Foam expansion ratio: NA • Room volume: 158 m³ • Treated area: 22.5 m² • Ventilation: on (8 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Pressure foamer P • Fan nozzle TeeJet 110 06VP (with foam adapter: black cartridge) • Pressure: 2–2.5 bar • Tank pressure: 3 bar Ex. 	CsCl: 9.81 BAC*: 15.7	BAC: 127	BAC: 49.3
8	Spraying of wall surfaces • Duration of application: 60 s • Duration of exposure: 60 s • Material consumption: 0.8 kg • Foam expansion ratio: NA • Room volume: 158 m³ • Treated area: 22.5 m² • Ventilation: on (8 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Pressure sprayer P • Fan nozzle TeeJet 110 06VP • Pressure: 1.5 bar • Tank pressure: 3 bar Ex. 	CsCl: 26.1 BAC*: 41.8	BAC: 34.2	BAC: 22.3

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation; Ex. – example

App. Tab. 27 Measurement at artificial workplaces – pressure foamer/sprayer (5–6 bar).

WP #	WP – Parameter	Substance analysed active substance/ tracer)	Device	Inhalation [µg/m³]	Dermal overall [µg]	Dermal-Gloves [µg]
5	Foaming of wall surfaces • Duration of application: 110 s • Duration of exposure: 110 s • Material consumption: 10.4 kg • Foam expansion ratio: NA • Room volume: 158 m³ • Treated area: 22.5 m² • Ventilation: on (8 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Pressure foamer G • Fan nozzle(50/200) • Pressure: • Tank pressure: 6 bar Ex. 	CsCl: 10.3 BAC*: 16.5	BAC: 55.6	BAC: 207
7	Spraying of wall surfaces • Duration of application: 55 s • Duration of exposure: 55 s • Material consumption: 12 kg • Foam expansion ratio: NA • Room volume: 158 m³ • Treated area: 22.5 m² • Ventilation: on (8 1/h)	2 % QAC F (0.16 % BAC) Tracer: 0.1 % CsCl	• Pressure sprayer G • Fan nozzle (30/40) • Pressure: • Tank pressure: 5.5 bar Ex. 	CsCl: 48.5 BAC*: 77.5	BAC: 383	BAC: 330

n.s. – not specifed; NA – not applicable; * calculated concentration based on CsCl results and composition of the formulation; Ex. – example

Appendix 11 Potential dermal exposure by the foaming and spraying of QAC- or pyrethroid-containing biocidal products – Supplemental information on the workplace measurements

Evaluation of the questionnaires

During the field study, interviews were conducted with the biocide users in order to obtain information on personal protective measures and hygiene behaviour. In total, ten subjects participated in the investigations for the measurement of potential dermal exposure, including eight men and two women. On average, these biocide users were 43 ± 13 years old, 177 ± 12 cm in height, and weighed 82 ± 15 kg (App. Tab. 28). Two test subjects who worked with QAC reported skin complaints, which, according to the subjects themselves, had nothing to do with their work.

App. Tab. 28 Descriptive statistics for the participant group (n = 10).

	Mean	SD	Median
Age [y]	43	13	44
Height [cm]	177	12	181
Weight [kg]	82	15	84

When asked about their frequency of biocidal product usage, professional biocide users (n = 8) reported daily usage (n = 5), usage every two weeks (n = 1), usage every four weeks (n = 1), or even more rarely (n = 1) regarding the application of QAC- or pyrethroid-containing biocidal products.

The subjects who participated in this study were also surveyed as to their personal protective measures during the foaming and spraying of biocidal products. In order to create a realistic picture, only information from professional biocide users (n = 8) is considered here.

When applying biocidal products, four of the professional biocide users usually wear protective coveralls (disposable coveralls or oilskin suits), while four others do not wear protective coveralls. Seven of the eight biocide users usually wear protective gloves made of nitrile or rubber, and six wear protective footwear (rubber boots or work shoes). In addition, seven of the eight professionals wear protective eyewear when applying biocidal products (protective goggles, visors, or full face masks), while respiratory protection (half or full masks) is worn regularly by three professional biocide users, sometimes by two users, and never by three users. Skin-protective cream is used regularly or as needed by four biocide users, and not at all by the remaining four subjects.

Further interview questions concerned the cleaning of soiled body parts (e.g. hands, face) during work hours, namely personal hygiene behaviour. The professional biocide users reported primarily washing their hands during work hours (n = 8). Hands are mainly washed at the end of the workday (n = 7), before breaks (n = 7), and at the end of a task (n = 6). In workplaces that provide shower facilities, these are used either

daily (n = 3), rarely (n = 1), or never (n = 2). Data on personal protective measures and personal hygiene behaviour is summarised in App. Tab. 29.

Six biocide users reported changing their workwear in the workplace, whereas two users change their workwear at home. Three of the biocide users wear new workgear at least daily (e.g. disposable coveralls) and four of the users wear new workgear as needed. We were unable to collect data for this question from one biocide user.

App. Tab. 29 Data on personal protective measures and personal hygiene behaviour by the foaming and spraying of biocidal products (n = 8, multiple answers possible).

Pers. protective measures	**Answered affirmatively in interview (n = 8)**	**Pers. hygiene behaviour: cleaning of soiled body parts**	**Answered affirmatively in interview(n = 8)**
Spec. protective wear: disposable coveralls or oilskin suits	4	…at the end of the workday	7
Protective gloves: made of nitrile or rubber	7	…before breaks (eating, smoking, WC)	7
Work shoes	6	…at the end of a work procedure	6
Protective eyewear: protective goggles, visors, or full face masks	7	…after heavy soiling	4
Respiratory protection: half or full face masks	3 regularly; 2 sometimes	…occasionally during a shift	3
Skin-protection cream	4	…as needed	2

Evaluation of surveillance sheets

During sampling, participants' performed activities were recorded. In addition to a description of working routines and individual tasks, attention was primarily given to direct contact with biocidal products (foam flakes, splashes, mists), treated surfaces, and, where applicable, contaminated equipment. Activities and working routines were also documented photographically.

The corresponding participant protocols provide detailed descriptions of the measurements performed to quantify potential dermal exposure with additional information as to the procedural methods of the biocide users as well as any irregularities observed during sampling. A tabular summary of the most important parameters can be found in App. Tab.30.

App. Tab. 30 Overview of measurements performed to quantify potential dermal exposure by the foaming and spraying of QAC- or pyrethroid-containing biocidal products.

Measure-ment/Appli-cation	Date	Application duration [min]	Application type	Device	Product applied	Dilution used	Amount of application solution used	Amount of active sub-stance used [g]
1	24.04.2018	6.00*	Foam	Hand compression foamer	QAC F	2 % sol. (0.16 % BAC)	0.325 kg	0.520
2	24.04.2018	3.67*	Foam	Hand pump foamer	QAC F	2 % sol. (0.16 % BAC)	0.063 kg	0.101
3	24.04.2018	4.50*	Spray	Hand compression sprayer	QAC F	2 % sol. (0.16 % BAC)	0.0956 kg	0.153
4	24.04.2018	4.45*	Spray	Hand pump sprayer	QAC F	2 % sol. (0.16 % BAC)	0.0678 kg	0.108
5	25.04.2018	1.83	Foam	Pressure foamer G	QAC F	2 % sol. (0.16 % BAC)	10.4 kg	16.6
6	25.04.2018	3.20	Foam	Pressure foamer P	QAC F	2 % sol. (0.16 % BAC)	2.9 kg	4.64
7	25.04.2018	0.92	Spray	Pressure sprayer G	QAC F	2 % sol. (0.16 % BAC)	12.0 kg	19.2
8	25.04.2018	1.00	Spray	Pressure sprayer P	QAC F	2 % sol. (0.16 % BAC)	0.8 kg	1.28
9	24.04.2018	19.0*	Foam	Hand pump foamer	QAC F	2 % sol. (0.16 % BAC)	0.559 kg	0.895
10	24.04.2018	17.0*	Spray	Hand pump sprayer	QAC F	2 % sol. (0.16 % BAC)	0.519 kg	0.830
11	26.04.2018	3.63	Foam	Wasp-foam can B.2	Wasp foam B.2	ready-to-use product	0.549 kg	0.824
12	26.04.2018	3.43	Foam	Wasp-foam can B.2	Wasp foam B.2	ready-to-use product	0.372 kg	0.557
13	26.04.2018	0.38	Spray	Wasp-spray can B	Wasp spray B	ready-to-use product	0.334 kg	0.334
14	29.05.2018	12.0	Foam	Foam gun, operated with a water pump, product and foaming agent in storage tank	QAC E; 10 % foaming agent	0.033 % sol.	3.8 L 2 % sol. (+ water, total 225 L)	5.02

* Given application duration includes application as well as wiping of surfaces – and thereby corresponds to duration of usage.

App. Tab. 30 (continued) Overview of measurements performed to quantify potential dermal exposure by the foaming and spraying of QAC- or pyrethroid-containing biocidal products.

Measure-ment/Appli-cation	Date	Application duration [min]	Application type	Device	Product applied	Dilution used	Amount of application solution used	Amount of active sub-stance used [g]
15	29.05.2018	12.0	Foam	Foam gun, application solution supplied via pump, foaming agent in storage tank	QAC A; 10 % foaming agent	2 % sol. (0.5 g/L)	230 L	115
16	29.05.2018	6.00	Spray	Spray gun, application solution supplied via pump (self-construction)	QAC A	2 % sol. (0.5 g/L)	270 L	135
17	30.05.2018	7.00	Spray	Spray gun, application solution supplied via pump (self-construction)	QAC E	2 % sol.	100L	132
18	27.11.2018	5.85	Foam	Foam gun	QAC N	0.78 % sol.	150 mL concentrate + water	11.4
19	27.11.2018	16.0	Spray	Battery pressure sprayer	QAC N	0.78 % sol.	38 L	64.8
20	28.11.2018	5.20	Foam	Foam gun	QAC N	0.78 % sol.	150 mL concentrate + water	11.4
21	25.02.2019	12.0	Foam	Foam gun with high-pressure washer	QAC AF	1 % sol.	2 L concen-trate + water	148
24	22.05.2019	20.0	Foam	Pressure foamer P2	QAC M	1:5 diluted (1.985 kg concentrate in 10 L)	9.5 L	189
25	22.05.2019	31.0	Foam	Pressure foamer P	QAC M	1:5 diluted (1.992 kg concentrate in 10 L)	8 L	159
26	22.05.2019	12.0	Spray	Pressure sprayer P2	QAC M	1:5 diluted (1.987 kg concentrate in 10 L)	5 L	99.4
27	23.05.2019	20.0	Foam	Wasp-foam can B.1	Wasp foam B.1	ready-to-use product	0.679 kg	0.713
28	23.05.2019	20.0	Foam	Insect-foam can F	Insect foam F	ready-to-use product	0.246 kg	6.89

Data analysis – Supplemental information on Chapters 5.2.1.1 and 5.2.1.2

App. Tab. 31 Absolute exposure quantified on the coverall segments [µg] (n = 26).

Coverall No.	Active substance	Exposure of body areas [µg]											
		Breast/ Stomach	Back/ Buttocks	Upper arm, right	Upper arm, left	Forearm, right	Forearm, left	Thigh, right	Thigh, left	Lower leg, right	Lower leg, left	Hood	Sum
1	BAC*	131	2.35	48.2	0.379	1810	7.24	2.38	11.7	0.391	0.455	0.561	**2020**
2	BAC*	24.6	0.762	2.32	0.457	289	3.20	0.305	0.409	0.308	0.482	0.343	**322**
3	BAC*	33.0	1.41	19.1	0.261	760	6.73	0.475	0.451	0.943	2.41	1.03	**826**
4	BAC*	22.7	3.09	37.2	0.498	253	4.70	1.37	0.786	1.00	1.04	1.27	**327**
5	BAC*	9.67	9.78	2.26	3.19	0.759	1.84	4.96	3.99	8.50	9.89	0.768	**55,6**
6	BAC*	11.5	12.7	5.10	8.39	1.64	1.82	8.15	5.64	35.5	34.3	2.31	**127**
7	BAC*	17.6	15.7	16.4	10.3	47.2	3.94	24.6	33.3	112	60.7	42.1	**383**
8	BAC*	5.16	1.81	1.86	1.64	1.26	0.660	3.34	2.10	8.08	7.39	0.936	**34,2**
9	BAC*	17.8	5.90	2.48	2.85	3.53	10.2	5.54	2.91	2.20	2.28	1.79	**57,5**
10	BAC*	24.4	19.3	3.90	4.06	4.82	205	12.6	10.7	20.2	16.1	6.33	**327**
11	Phenothrin	0.377	0.078	0.089	0.112	0.787	0.100	0.034	0.076	0.029	0.057	0.040	**1,78**
12	Phenothrin	0.258	0.060	0.120	0.061	80.3	0.201	0.021	0.199	0.011	0.106	0.010	**81,4**
13	Phenothrin	36.3	49.3	33.1	30.7	48.5	68.5	6.37	7.60	11.3	7.24	57.1	**356**
14	BAC*	266	50.5	21.5	62.5	58.5	47.7	139	176	53.3	84.4	42.4	**1000**
15	BAC*	453	69.5	31.6	32.3	58.7	56.9	95.7	115	159	224	71.5	**1370**
16	BAC*	278	210	89.7	119	94.4	64.6	151	189	215	255	148	**1810**
17	BAC*	1440	1420	806	307	1030	400	714	784	1770	1150	936	**10800**
18	BAC*	46.9	15.0	5.86	12.9	8.55	77.1	60.9	76.8	237	210	1.02	**752**
19	BAC*	60.2	35.8	5.51	3.65	15.8	7.47	49.7	54.3	243	156	4.64	**637**
20	BAC*	20.6	13.1	5.44	3.14	5.26	5.16	9.72	39.5	66.0	155	2.48	**325**
21	BAC*	2100	58.8	7.94	5.35	7.02	206	900	818	1160	1900	20.3	**7190**
24	BAC*	4400	68.3	32.9	5.08	309	23.6	1400	8060	679	713	43.2	**15700**
25	BAC*	414	344	374	90.8	498	111	144	215	190	234	218	**2830**
26	BAC*	8370	371	130	94.1	140	124	204	4360	421	389	231	**14800**
27	Phenothrin	8.14	2.98	0.426	364	6.04	205	0.492	10.9	0.885	1.40	0.907	**600**
28	Permethrin	21.2	3.20	5.74	1.40	79.6	8.67	11.9	2.25	1.15	9.19	2.31	**147**

* BAC = Benzalkonium chlorides

App. Tab. 32 Absolute exposure quantified on the coverall segments, normalised to the relevant amount of active substance applied [mg/kg] (n = 26).

Coverall No.	Active substance	Exposure of body areas [mg/kg]											
		Breast/ Stomach	Back/ Buttocks	Upper arm, right	Upper arm, left	Forearm, right	Forearm, left	Thigh, right	Thigh, left	Lower leg, right	Lower leg, left	Hood	Sum
1	BAC*	252	4.53	92.7	0.729	3490	13.9	4.58	22.6	0.752	0.875	1.08	**3880**
2	BAC*	244	7.55	23.0	4.53	2860	31.7	3.03	4.06	3.05	4.78	3.40	**3190**
3	BAC*	216	9.22	125	1.71	4970	44.0	3.10	2.95	6.17	15.8	6.73	**5400**
4	BAC*	210	28.5	343	4.59	2330	43.3	12.7	7.24	9.25	9.55	11.7	**3010**
5	BAC*	0.581	0.588	0.136	0.191	0.046	0.110	0.298	0.240	0.511	0.594	0.046	**3.34**
6	BAC*	2.47	2.73	1.10	1.81	0.354	0.392	1.76	1.22	7.66	7.40	0.498	**27.4**
7	BAC*	0.918	0.816	0.854	0.535	2.46	0.205	1.28	1.74	5.81	3.16	2.19	**20.0**
8	BAC*	4.03	1.41	1.45	1.28	0.981	0.516	2.61	1.64	6.31	5.78	0.732	**26.7**
9	BAC*	19.9	6.60	2.78	3.18	3.94	11.4	6.19	3.25	2.46	2.55	2.00	**64.2**
10	BAC*	29.4	23.2	4.70	4.89	5.81	247	15.2	12.9	24.4	19.4	7.63	**394**
11	Phenothrin	0.457	0.095	0.108	0.136	0.955	0.121	0.042	0.092	0.035	0.069	0.048	**2.16**
12	Phenothrin	0.463	0.107	0.215	0.110	144	0.360	0.037	0.357	0.019	0.191	0.018	**146**
13	Phenothrin	109	148	99.1	91.9	145	205	19.1	22.8	34.0	21.7	171	**1070**
14	BAC*	53.0	10.1	4.29	12.5	11.7	9.50	27.8	35.2	10.6	16.8	8.45	**200**
15	BAC*	3.94	0.604	0.275	0.281	0.510	0.495	0.832	1.00	1.38	1.95	0.622	**11.9**
16	BAC*	2.06	1.55	0.665	0.878	0.699	0.478	1.12	1.40	1.59	1.89	1.10	**13.4**
17	BAC*	10.9	10.8	6.11	2.33	7.78	3.03	5.41	5.94	13.4	8.74	7.09	**81.5**
18	BAC*	4.11	1.32	0.514	1.14	0.750	6.76	5.34	6.74	20.8	18.4	0.090	**66.0**
19	BAC*	0.930	0.552	0.085	0.056	0.245	0.115	0.767	0.838	3.76	2.42	0.072	**9.83**
20	BAC*	1.81	1.15	0.477	0.276	0.461	0.453	0.853	3.46	5.79	13.6	0.217	**28.5**
21	BAC*	14.2	0.397	0.054	0.036	0.047	1.39	6.08	5.53	7.82	12.9	0.137	**48.6**
24	BAC*	23.3	0.362	0.174	0.027	1.64	0.125	7.40	42.7	3.60	3.78	0.229	**83.4**
25	BAC*	2.60	2.16	2.34	0.570	3.12	0.697	0.903	1.35	1.19	1.47	1.37	**17.8**
26	BAC*	84.2	3.73	1.30	0.947	1.41	1.25	2.05	43.9	4.24	3.91	2.33	**149**
27	Phenothrin	11.4	4.18	0.597	510	8.47	287	0.691	15.2	1.24	1.97	1.27	**842**
28	Permethrin	3.08	0.465	0.834	0.203	11.6	1.26	1.73	0.327	0.167	1.33	0.336	**21.3**

* BAC = Benzalkonium chlorides

App. Tab. 33 Absolute exposure quantified on the coverall segments, normalised to the relevant amount of active substance applied and the segment area [µg/(kg × cm²)] (n = 26).

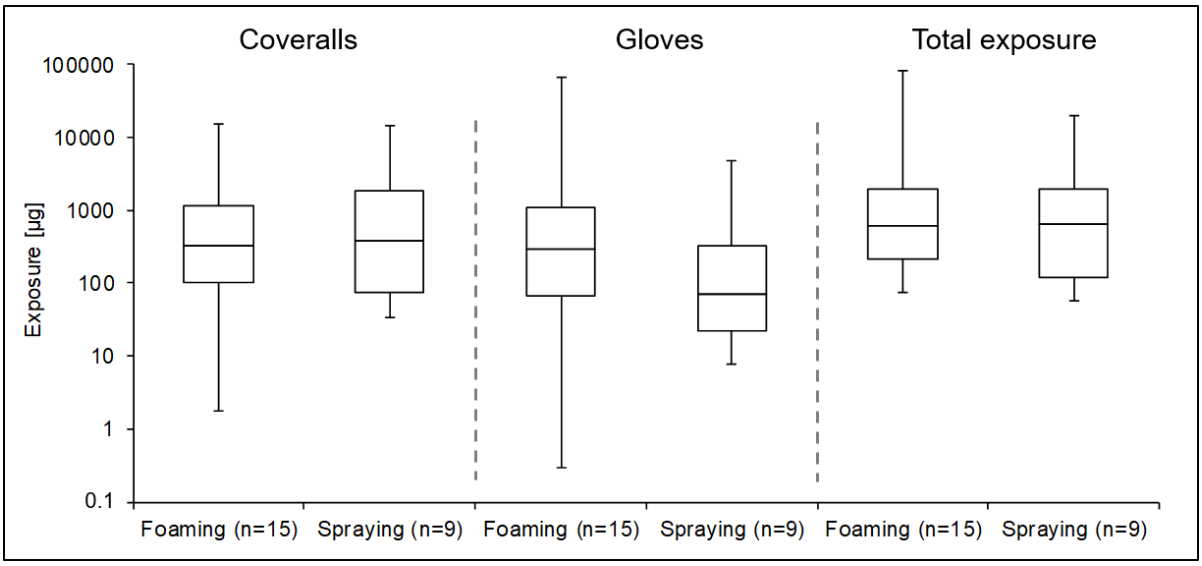
Coverall No.	Active substance	Exposure of body areas [µg/(kg × cm²)]											
		Breast/ Stomach	Back/ Buttocks	Upper arm, right	Upper arm, left	Forearm, right	Forearm, left	Thigh, right	Thigh, left	Lower leg, right	Lower leg, left	Hood	Mean
1	BAC*	37.0	0.685	57.5	0.452	2960	11.8	1.82	8.97	0.357	0.415	0.527	**128**
2	BAC*	35.9	1.14	14.3	2.81	2430	26.9	1.20	1.61	1.45	2.27	1.66	**105**
3	BAC*	31.8	1.39	77.5	1.06	4220	37.4	1.23	1.17	2.93	7.48	3.28	**178**
4	BAC*	30.8	4.31	213	2.85	1980	36.8	5.03	2.88	4.39	4.53	5.72	**99.5**
5	BAC*	0.085	0.089	0.084	0.119	0.039	0.094	0.119	0.095	0.242	0.282	0.023	**0.110**
6	BAC*	0.363	0.413	0.682	1.12	0.301	0.333	0.698	0.483	3.64	3.51	0.243	**0.904**
7	BAC*	0.135	0.123	0.530	0.332	2.09	0.175	0.509	0.690	2.76	1.50	1.07	**0.659**
8	BAC*	0.592	0.213	0.900	0.793	0.833	0.438	1.04	0.653	2.99	2.74	0.357	**0.883**
9	BAC*	2.93	1.00	1.72	1.97	3.35	9.67	2.46	1.29	1.17	1.21	0.976	**2.12**
10	BAC*	4.32	3.51	2.92	3.03	4.94	210	6.05	5.14	11.6	9.23	3.72	**13.0**
11	Phenothrin	0.067	0.014	0.067	0.084	0.811	0.103	0.017	0.037	0.017	0.033	0.023	**0.071**
12	Phenothrin	0.068	0.016	0.133	0.068	122	0.306	0.015	0.142	0.009	0.091	0.009	**4.82**
13	Phenothrin	16.0	22.3	61.5	57.0	123	174	7.58	9.05	16.1	10.3	83.4	**35.2**
14	BAC*	7.79	1.52	2.66	7.73	9.90	8.07	11.0	14.0	5.05	7.99	4.12	**6.60**
15	BAC*	0.579	0.091	0.171	0.174	0.433	0.420	0.331	0.398	0.656	0.925	0.303	**0.393**
16	BAC*	0.303	0.235	0.412	0.545	0.594	0.406	0.445	0.557	0.756	0.898	0.535	**0.444**
17	BAC*	1.61	1.63	3.79	1.44	6.61	2.57	2.15	2.36	6.38	4.15	3.46	**2.69**
18	BAC*	0.604	0.200	0.319	0.704	0.637	5.74	2.12	2.68	9.89	8.73	0.044	**2.18**
19	BAC*	0.137	0.084	0.053	0.035	0.208	0.098	0.305	0.333	1.78	1.15	0.035	**0.325**
20	BAC*	0.266	0.174	0.296	0.171	0.392	0.385	0.339	1.38	2.75	6.43	0.106	**0.941**
21	BAC*	2.09	0.060	0.033	0.022	0.040	1.18	2.42	2.20	3.71	6.11	0.067	**1.60**
24	BAC*	3.43	0.055	0.108	0.017	1.39	0.106	2.94	17.0	1.71	1.80	0.112	**2.75**
25	BAC*	0.382	0.327	1.45	0.353	2.65	0.592	0.359	0.536	0.567	0.698	0.666	**0.587**
26	BAC*	12.4	0.565	0.809	0.588	1.20	1.06	0.816	17.4	2.01	1.86	1.14	**4.93**
27	Phenothrin	1.68	0.632	0.370	316	7.20	244	0.275	6.05	0.589	0.935	0.620	**27.8**
28	Permethrin	0.453	0.070	0.517	0.126	9.82	1.07	0.687	0.130	0.079	0.633	0.164	**0.703**

* BAC = Benzalkonium chlorides

App. Tab. 34 Potential dermal exposure on the gloves (n = 26).

	Absolute exposure [µg]			Exposure normalised to the amount of active substance applied [mg/kg]			Exposure normalised to the amount of active substance applied and to the relevant segment area of 410 cm^2 per hand [µg/(kg × cm^2)]		
Glove No.	**Right**	**Left**	**Total**	**Right**	**Left**	**Total**	**Right**	**Left**	**Mean**
1-1 (application)	<LOQ	9.35	10.3	<LOQ	18.0	19.9	<LOQ	43.9	24.3
1-2 (wiping)	52800	<LOQ	52800	102000	<LOQ	102000	247800	<LOQ	124000
1 (application + wiping)	52800	10.5	52800	102000	20.1	102000	247800	49.1	124000
2-1 (application)	7.62	32.1	39.7	75.6	318	394	184	777	480
2-2 (wiping)	7860	6.32	7870	78000	62.7	78000	190000	153	95200
2 (application + wiping)	7870	38.4	7900	78000	381	78400	190000	930	95600
3-1 (application)	6.42	<LOQ	7.62	42.0	<LOQ	49.8	102	<LOQ	60.7
3-2 (wiping)	12600	113	12700	82600	740	83300	201000	1800	102000
3 (application + wiping)	12600	114	12800	82600	748	83400	202000	1820	102000
4-1 (application)	48.1	<LOQ	48.7	443	<LOQ	449	1080	<LOQ	548
4-2 (wiping)	5440	60.2	5500	50100	555	50700	122000	1350	61800
4 (application + wiping)	5490	60.9	5500	50600	561	51100	123000	1370	62400
5	169	38.5	207	10.1	2.31	12.5	24.7	5.65	15.2
6	14.4	34.9	49.3	3.10	7.52	10.6	7.56	18.3	13.0
7	256	73.7	330	13.3	3.84	17.2	32.5	9.36	20.9
8	12.4	9.91	22.3	9.66	7.74	17.4	23.6	18.9	21.2
9 (application+ wiping)	14700	9660	24400	16500	10800	27300	40200	26300	33300
10 (application + wiping)	4960	7530	12500	5980	9080	15100	14600	22100	18400
11	180	32.9	213	218	39.9	258	533	97.4	315
12	0.154	0.141	0.295	0.276	0.253	0.529	0.674	0.618	0.646
13	21.0	50.9	71.8	62.8	152	215	153	372	262
14	297	883	1180	59.2	176	235	144	429	287
15	49.2	248	297	0.428	2.16	2.59	1.04	5.27	3.15

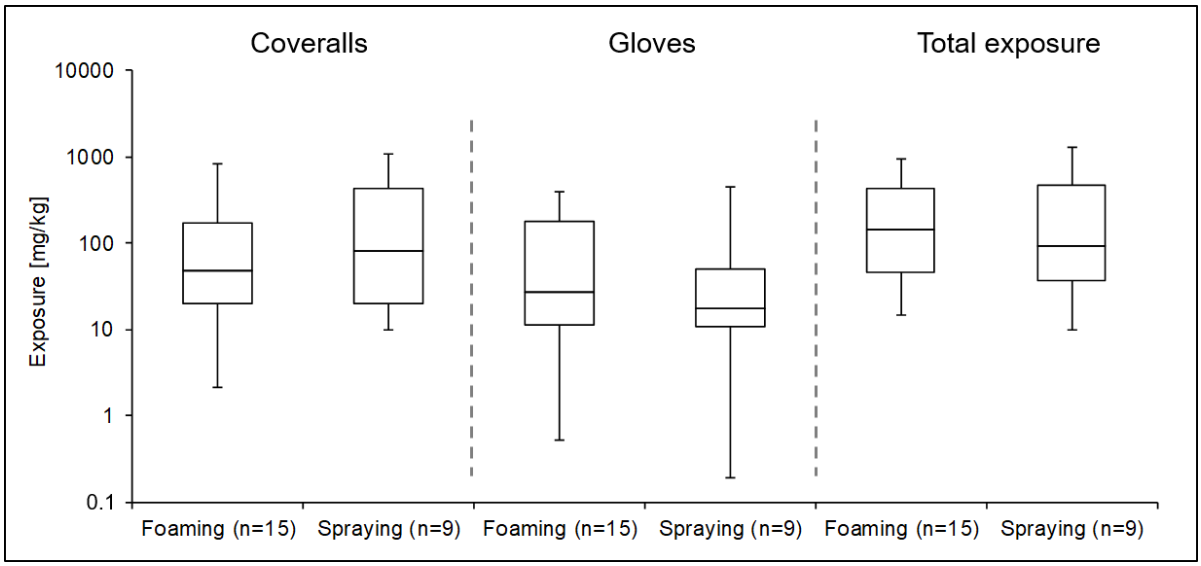
	Absolute exposure [µg]			Exposure normalised to the amount of active substance applied [mg/kg]			Exposure normalised to the amount of active substance applied and to the relevant segment area of 410 cm^2 per hand [µg/(kg × cm^2)]		
Glove No.	**Right**	**Left**	**Total**	**Right**	**Left**	**Total**	**Right**	**Left**	**Mean**
16	60.6	35.4	95.9	0.449	0.262	0.711	1.09	0.639	0.867
17	762	676	1440	5.77	5.12	10.9	14.1	12.5	13.3
18	72.1	941	1010	6.32	82.6	88.9	15.4	201	108
19	8.44	3.99	12.4	0.130	0.062	0.192	0.318	0.150	0.234
20	30.0	275	305	2.63	24.1	26.7	6.41	58.8	32.6
21	391	1070	1460	2.64	7.20	9.84	6.44	17.6	12.0
24	67100	1530	68700	356	8.13	364	868	19.8	444
25	508	1380	1890	3.19	8.64	11.8	7.77	21.1	14.4
26	3760	992	4750	37.8	9.98	47.8	92.2	24.3	58.3
27	26.9	55.4	82.3	37.8	77.6	115	92.1	189	141
28	182	245	427	26.4	35.6	62.0	64.3	86.9	75.6



App. Fig. 13 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application only, without wiping). The figure shows the samplers' absolute exposure [µg].

App. Tab. 35 Absolute exposure on samplers after foaming or spraying of biocidal products [µg] (application only, without wiping). Evaluation per application type.

	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Absolute exposure on the coveralls [µg]					
Foam (n = 15)	**1.78**	**325**	**1180**	**9750**	**15700**
Spray (n = 9)	**34.2**	**383**	**1810**	**13200**	**14800**
Absolute exposure on the gloves [µg]					
Foam (n = 15)	**0.295**	**297**	**1100**	**21900**	**68700**
Spray (n = 9)	**7.62**	**71.8**	**330**	**3420**	**4750**
Total absolute exposure [µg]					
Foam (n = 15)	**72.9**	**630**	**1970**	**31400**	**84400**
Spray (n = 9)	**56.5**	**649**	**1910**	**16600**	**19600**



App. Fig. 14 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application only). The figure shows samplers' exposure normalised to the amount of active substance applied [mg/kg].

App. Tab. 36 Samplers' exposure normalised to the applied amount of active substance after foaming or spraying of biocidal products [mg/kg] (application only). Evaluation per application type.

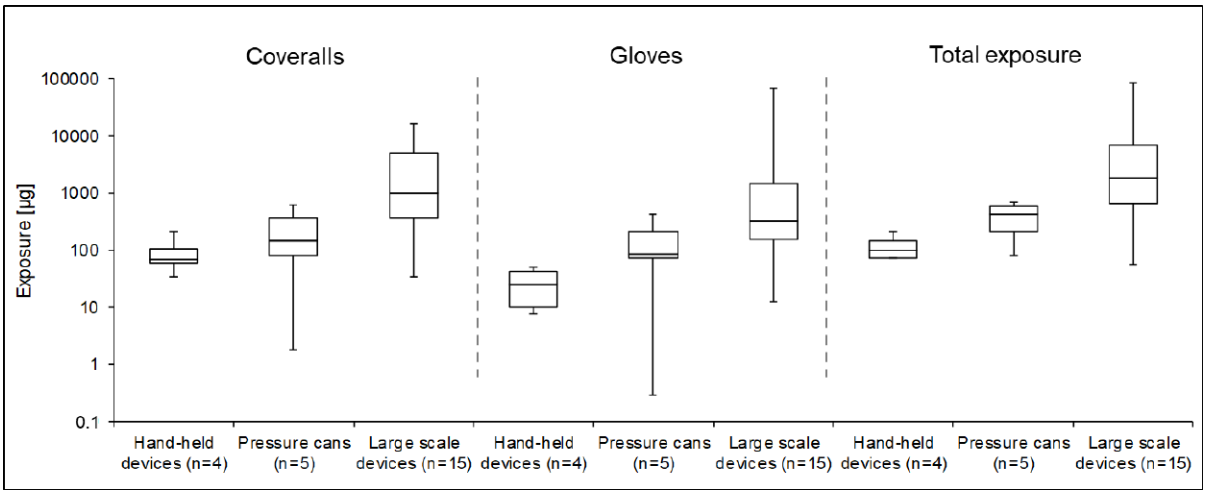
	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Exposure on the coveralls normalised to the amount of active substance applied [mg/kg]					
Foam (n = 15)	**2.16**	**48.6**	**173**	**528**	**842**
Spray (n = 9)	**9.83**	**81.5**	**431**	**912**	**1070**
Exposure on the gloves normalised to the amount of active substance applied [mg/kg]					
Foam (n = 15)	**0.529**	**26.7**	**175**	**373**	**394**
Spray (n = 9)	**0.192**	**17.4**	**49.8**	**356**	**449**
Total exposure normalised to the amount of active substance applied [mg/kg]					
Foam (n = 15)	**14.5**	**147**	**424**	**793**	**957**
Spray (n = 9)	**10.0**	**92.4**	**480**	**1220**	**1280**

App. Tab. 37 Samplers' exposure normalised to the amount of active substance applied and to the relevant area of the sampling media after foaming or spraying of biocidal products [µg/(kg × cm²)] (application only). Evaluation per application type.

	Minimum	Median	75th perc.	95th perc.	Maximum
Exposure on the coveralls normalised to the amount of active substance applied and to the area of the coveralls [µg/(kg × cm²)]					
Foam (n = 15)	**0.071**	**1.60**	**5.71**	**17.8**	**27.8**
Spray (n = 9)	**0.325**	**2.69**	**14.8**	**30.5**	**35.2**
Exposure on the gloves normalised to the amount of active substance applied and to the area of the gloves [µg/(kg × cm²)]					
Foam (n = 15)	**0.646**	**32.6**	**214**	**455**	**480**
Spray (n = 9)	**0.234**	**21.2**	**60.7**	**434**	**548**

App. Tab. 38 Exposure on the five least exposed coverall segments normalised to the amount of active substance applied and to the relevant segment area [µg/(kg × cm²)]. Evaluation per application type.

Exposure normalised to the amount of active substance applied and to the relevant segment area [µg/(kg × cm²)]	Minimum	Median	75th perc.	95th perc.	Maxi-mum
Foam (n = 16)	**0.019**	**0.286**	**0.539**	**1.82**	**3.28**
Spray (n = 10)	**0.067**	**1.10**	**3.24**	**8.85**	**12.9**



App. Fig. 15 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application only). The figure shows the samplers' absolute exposure [µg] due to application with various application devices.

App. Tab. 39 Samplers' absolute exposure after foaming or spraying of biocidal products [µg] (application only). Evaluation per application device.

Legend: Handheld devices – Hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer, operating pressure 1–3 bar with a volumetric capacity less than 2 L; pressurised cans – propellant-based cans for foam or spray applications and stationary devices – devices for large-scale application, operating pressure 1–6 bar as well as high pressure with a volumetric capacity greater than 2 L.

	Minimum	Median	75th perc.	95th perc.	Maximum
Absolute exposure on the coveralls [µg]					
Handheld devices (n = 4)[a]	**33.2**	**69.8**	**106**	**185**	**205**
Pressurised cans (n = 5)	**1.78**	**147**	**356**	**551**	**600**
Stationary devices (n = 15)	**34.2**	**1000**	**5010**	**15100**	**15700**
Absolute exposure on the gloves [µg]					
Handheld devices (n = 4)[a]	**7.62**	**25.0**	**42.0**	**47.4**	**48.7**
Pressurised cans (n = 5)	**0.295**	**82.3**	**213**	**384**	**427**
Stationary devices (n = 15)	**12.4**	**330**	**1450**	**23900**	**68700**
Total absolute exposure [µg]					
Handheld devices (n = 4)[a]	**72.9**	**98.0**	**146**	**201**	**215**
Pressurised cans (n = 5)	**81.6**	**428**	**574**	**661**	**683**
Stationary devices (n = 15)	**56.5**	**1770**	**6680**	**39000**	**84400**

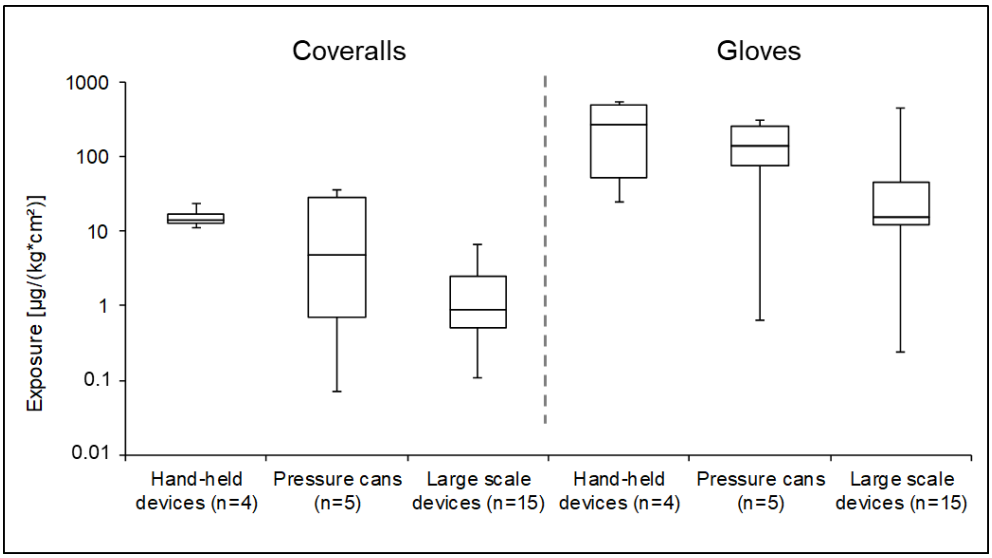
[a] Exposure on the coveralls according to Tab. 5.5

App. Tab. 40 Samplers' exposure normalised to the applied amount of active substance after foaming or spraying of biocidal products [mg/kg] (application only). Evaluation per application device.

Legend: Handheld devices – hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer, operating pressure 1–3 bar with a volumetric capacity less than 2 L; pressurised cans – propellant-based cans for foam or spray applications and stationary devices – devices for large-scale application, operating pressure 1–6 bar as well as high pressure with a volumetric capacity greater than 2 L.

	Minimum	Median	75th perc.	95th perc.	Maximum
Exposure on the coveralls normalised to the amount of active substance applied [mg/kg]					
Handheld devices (n = 4)[a]	**329**	**412**	**493**	**642**	**679**
Pressurised cans (n = 5)	**2.16**	**146**	**842**	**1020**	**1070**
Stationary devices (n = 15)	**3.34**	**27.4**	**73.8**	**164**	**200**
Exposure on the gloves normalised to the amount of active substance applied [mg/kg]					
Handheld devices (n = 4)[a]	**19.9**	**222**	**408**	**441**	**449**
Pressurised cans (n = 5)	**0.529**	**115**	**215**	**250**	**258**
Stationary devices (n = 15)	**0.192**	**12.5**	**37.3**	**274**	**364**
Total exposure normalised to the amount of active substance applied [mg/kg]					
Handheld devices (n = 4)[a]	**414**	**602**	**825**	**1070**	**1130**
Pressurised cans (n = 5)	**83.3**	**261**	**957**	**1220**	**1280**
Stationary devices (n = 15)	**10.0**	**44.1**	**124**	**439**	**448**

[a] Exposure on the coveralls according to Tab. 5.5



App. Fig. 16 Box-plot diagram of potential dermal exposure after foaming or spraying of biocidal products (application only, without #9, #10). The figure shows samplers' exposure normalised to the amount of active substance applied and to the relevant area of the sampling media [µg/(kg × cm²)] after application with various application devices.

App. Tab. 41 Samplers' exposure normalised to the amount of active substance applied and to the relevant area of the sampling media after foaming or spraying of biocidal products [µg/(kg × cm²)] (application type). Evaluation per application device.

Legend: Handheld devices – Hand pump foamer and sprayer (bottles) as well as hand compression foamer and sprayer, operating pressure 1–3 bar with a volumetric capacity less than 2 L; pressurised cans – propellant-based cans for foam or spray applications and stationary devices – devices for large-scale application, operating pressure 1–6 bar as well as high pressure with a volumetric capacity greater than 2 L).

	Minimum	**Median**	**75th perc.**	**95th perc.**	**Maximum**
Exposure on the coveralls normalised to the amount of active substance applied and to the relevant segment area [µg/(kg × cm²)]					
Handheld devices (n = 4)[a]	**2.12**	**102**	**123**	**166**	**178**
Pressurised cans (n = 5)	**0.071**	**4.82**	**27.8**	**33.7**	**35.2**
Stationary devices (n = 15)	**0.110**	**0.904**	**2.44**	**5.43**	**6.60**
Exposure on the gloves normalised to the amount of active substance applied and to the relevant segment area [µg/(kg × cm²)]					
Handheld devices (n = 4)[a]	**12500**	**54000**	**68500**	**80900**	**84700**
Pressurised cans (n = 5)	**0.441**	**96.2**	**179**	**208**	**215**
Stationary devices (n = 15)	**0.160**	**10.4**	**31.0**	**228**	**303**

[a] Exposure on the coveralls according to Tab. 5.5

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Exposure patterns on the coveralls

In order to recognise exposure patterns on the coveralls, the amounts of active substance on each individual coverall segment were normalised to the total exposure on the corresponding coveralls. The percentage distribution of the individual coverall segments thus calculated is presented in App. Tab. 42. To highlight patterns more clearly, the measurements were grouped according to device and application type. For the individual device types, fluid colour changes indicate the lowest exposures in green, medium exposures in yellow, and the highest exposures in red.

From App. Tab. 42, a dependence emerges between application devices and the exposure focal points on the coveralls. For handheld devices in both foam and spray applications, exposure on the forearms and breast/stomach area could be attributed to the wiping of treated surfaces. Exposure on the breast/stomach is understandable given the fact that the disinfected work surfaces were at about the height of the stomach (Coveralls #1 to #4) or the thighs (Coveralls #9 and #10), and because the users stood in front of the surfaces to be treated. There was no difference between the application types (foaming or spraying).

The relatively homogenous exposure on Coveralls #9 and #10 was notable in a measurement in which cafeteria tables were disinfected. During these applications, considerably more of the active substance was applied than with Coveralls #1 to #4, leading to a formation of aerosol that was noticeable even by smell, and in turn, to a more homogenous exposure on the coveralls.

During biocidal product applications with pressurised cans for foaming and spraying, which at least partially required overhead application, exposure on the forearms is evident. Additional high exposure levels were seen on individual coverall segments as a result of foam flakes Coverall #27: a large foam flake on the left upper arm as well as a small foam flake on the left forearm). During biocidal product application with a pressurised can for spraying, the hood, breast/stomach, back, and upper arms were heavily exposed due to falling spray mists.

After large-scale foaming and spraying of biocidal producs, the lower legs, thighs, and breast/stomach area were more heavily exposed than the remaining segments, while the head and arms were only minimally exposed, even though the measurements at least partially required application on overhead surfaces. It is clear from these device types that floors and floor-adjacent wall areas were treated, whereby the individual spatial conditions varied widely. Even with these device types, no difference between the foaming and spraying of biocidal products could be observed.

Regarding App. Tab. 42, it is important to note the different sizes of the coverall segments, such that even with homogenous exposure, large segments like the breast/stomach and back produce more prominent data. For this reason, in App. Tab. 43, the quantified active substance amounts on the individual segments was divided by the area of the segment in question as well as by the amount of active substance applied, in order to obtain standardised and thereby more comparable values in units of µg/(kg × cm²). These values were grouped analogously to the data in App. Tab. 42 and colour-coded.

The colour-coded diagram in App. Tab. 43 shows that, for handheld devices in both foam and spray applications, the exposure levels on the forearms of Coveralls #9 and #10 were not nearly as high as those on the right forearms of Coveralls #1 to #4, with regard to the data normalised to the amount of active substance applied and to the segment area. This can be explained by the fact that the disinfected surfaces in measurements #1 to #4 were 90 cm high, whereas in measurements #9 and #10, the surfaces were only 75–80 cm high; moreover, the height of biocide users was 1.64 m for Coveralls #1 to #4 and 1.84 m for Coveralls #9 and #10. As a consequence, the worker who wiped cafeteria tables (Coveralls #9 and #10) had to hold his arm at a significantly steeper angle, causing his forearms to have little contact with the treated surfaces.

For the pressurised cans for foaming and spraying, the data representation in App. Tab. 42 and App. Tab. 43 clearly shows that the spraying of pyrethroids (#13) led to a significantly higher and more homogenously distributed exposure on the coveralls compared to foaming (#11–#12, #27–#28). The high mean exposure on Coverall #27 is due primarily to two foam flakes found on the left arm.

The predominant exposure on the legs is confirmed by the data regarding the large-scale application of biocidal products, while the exposure on the breast/stomach area is considerably modified when normalised to segment area. During biocidal product application with this device type, Coveralls #14 and #17, which show considerably high exposure levels on all segments, are especially conspicuous. The cause of these deviating exposure patterns, as explained above, can be ascribed to the fact that a small pigsty, which was separated into smaller sections by gridded fencing, was disinfected in measurements #14 and #17. The biocide user had to move the separatory grids and therefore had a lot of contact with already-treated surfaces. Due to the numerous structures and limited space, the measurement coveralls were also subject to potential additional exposure by backsplash of the application solution or small foam flakes.

The high exposure levels on the left thigh as well as the breat/stomach area of Coveralls #24 and #26 can be explained by the fact that the biocide user picked up the nearly empty storage tank of pressure sprayer P and positioned it diagonally across his thigh in order to apply the remaining application solution from the container.

App. Tab. 42 Proportional exposure on individual coverall segments [%]. For the individual types of devices, the fluid colour changes indicate the lowest exposures in green, medium exposures in yellow, and the highest exposures in red.

Measure-ment	Applica-tion type	Breast/ Stom-ach	Back/ But-tocks	Upper arm, right	Upper arm, left	Forearm, right	Forearm, left	Thigh, right	Thigh, left	Lower leg, right	Lower leg, left	Hood	Sum
Handheld foam and spray devices													
1	**Foam**	6.49	0.117	2.39	0.019	89.9	0.359	0.118	0.581	0.019	0.023	0.028	100
2		7.64	0.237	0.722	0.142	89.7	0.994	0.095	0.127	0.096	0.150	0.106	100
9		31.0	10.3	4.32	4.95	6.13	17.7	9.64	5.06	3.83	3.97	3.11	100
3	**Spray**	4.00	0.171	2.31	0.032	92.0	0.814	0.057	0.055	0.114	0.292	0.125	100
4		6.95	0.946	11.4	0.152	77.5	1.44	0.420	0.240	0.307	0.317	0.389	100
10		7.46	5.89	1.19	1.24	1.47	62.6	3.86	3.28	6.18	4.93	1.93	100
Pressurised cans for foaming and spraying													
11	**Foam**	21.2	4.41	5.03	6.28	44.2	5.62	1.92	4.26	1.62	3.21	2.23	100
12		0.317	0.073	0.147	0.075	98.7	0.247	0.025	0.245	0.013	0.131	0.012	100
27		1.36	0.496	0.071	60.6	1.01	34.1	0.082	1.81	0.147	0.234	0.151	100
28		14.5	2.18	3.91	0.953	54.3	5.91	8.11	1.54	0.785	6.26	1.58	100
13	**Spray**	10.2	13.8	9.29	8.62	13.6	19.2	1.79	2.13	3.18	2.03	16.0	100
Devices for large-scale application													
5	**Foam**	17.4	17.6	4.06	5.73	1.36	3.31	8.93	7.17	15.3	17.8	1.38	100
6		9.02	9.98	4.02	6.60	1.29	1.43	6.42	4.44	28.0	27.0	1.82	100
14		26.5	5.04	2.15	6.24	5.84	4.76	13.9	17.6	5.32	8.42	4.23	100
15		33.1	5.08	2.31	2.36	4.29	4.16	7.00	8.42	11.6	16.4	5.23	100
18		6.23	2.00	0.779	1.72	1.14	10.2	8.10	10.2	31.6	27.9	0.136	100
20		6.34	4.05	1.67	0.968	1.62	1.59	2.99	12.2	20.3	47.5	0.763	100
21		29.3	0.817	0.110	0.074	0.098	2.86	12.5	11.4	16.1	26.5	0.282	100
24		28.0	0.434	0.209	0.032	1.97	0.150	8.88	51.2	4.32	4.54	0.275	100
25		14.6	12.1	13.2	3.20	17.6	3.92	5.08	7.58	6.72	8.27	7.68	100
7	**Spray**	4.60	4.09	4.28	2.68	12.3	1.03	6.42	8.70	29.1	15.8	11.0	100
8		15.1	5.27	5.43	4.78	3.67	1.93	9.76	6.15	23.6	21.6	2.74	100
16		15.3	11.6	4.95	6.53	5.21	3.56	8.34	10.4	11.9	14.1	8.16	100
17		13.4	13.2	7.49	2.85	9.54	3.71	6.63	7.29	16.5	10.7	8.70	100
19		9.46	5.62	0.866	0.574	2.49	1.17	7.80	8.52	38.2	24.6	0.728	100
26		56.4	2.50	0.874	0.634	0.946	0.838	1.37	29.4	2.84	2.62	1.56	100

App. Tab. 43 Exposure on individual coverall segments normalised to the segment area and the applied amount of active substance [µg/(kg × cm²)]. For the individual types of devices, the fluid colour changes indicate the lowest exposures in green, medium exposures in yellow, and the highest exposures in red.

Measure-ment	Applica-tion type	Breast/ Stom-ach	Back/ Buttocks	Upper arm, right	Upper arm, left	Forearm, right	Forearm, left	Thigh, right	Thigh, left	Lower leg, right	Lower leg, left	Hood	Mean
Exposure on coverall segments [µg/(kg × cm²)]: handheld foam and spray devices													
1	**Foam**	37.0	0.685	57.5	0.452	2970	11.8	1.82	8.97	0.357	0.415	0.527	**128**
2		35.9	1.14	14.3	2.81	2430	26.9	1.20	1.61	1.45	2.27	1.66	**105**
9		2.93	1.00	1.72	1.97	3.35	9.67	2.46	1.29	1.17	1.21	0.976	**2.12**
3	**Spray**	31.8	1.39	77.5	1.06	4220	37.4	1.23	1.17	2.93	7.48	3.28	**178**
4		30.8	4.31	213	2.85	1980	36.8	5.03	2.88	4.39	4.53	5.72	**99.5**
10		4.32	3.51	2.92	3.03	4.94	210	6.05	5.14	11.6	9.23	3.72	**13.0**
Exposure on coverall segments [µg/(kg × cm²)]: pressurised cans for foaming and spraying													
11	**Foam**	0.067	0.014	0.067	0.084	0.811	0.103	0.017	0.037	0.017	0.033	0.023	**0.071**
12		0.068	0.016	0.133	0.068	122	0.306	0.015	0.142	0.009	0.091	0.009	**4.82**
27		1.68	0.632	0.370	316	7.20	244	0.275	6.05	0.589	0.935	0.620	**27.8**
28		0.453	0.070	0.517	0.126	9.82	1.07	0.687	0.130	0.079	0.633	0.164	**0.703**
13	**Spray**	16.0	22.3	61.5	57.0	123	174	7.58	9.05	16.1	10.3	83.4	**35.2**
Exposure on coverall segments [µg/(kg × cm²)]: Devices for large-scale applications													
5	**Foam**	0.085	0.089	0.084	0.119	0.039	0.094	0.119	0.095	0.242	0.282	0.023	**0.110**
6		0.363	0.413	0.682	1.12	0.301	0.333	0.698	0.483	3.64	3.51	0.243	**0.904**
14		7.79	1.52	2.66	7.73	9.90	8.07	11.0	14.0	5.05	7.99	4.12	**6.60**
15		0.579	0.091	0.171	0.174	0.433	0.420	0.331	0.398	0.656	0.925	0.303	**0.393**
18		0.604	0.200	0.319	0.704	0.637	5.74	2.12	2.68	9.89	8.73	0.044	**2.18**
20		0.266	0.174	0.296	0.171	0.392	0.385	0.339	1.38	2.75	6.43	0.106	**0.941**
21		2.09	0.060	0.033	0.022	0.040	1.18	2.42	2.20	3.71	6.11	0.067	**1.60**
24		3.43	0.055	0.108	0.017	1.39	0.106	2.94	17.0	1.71	1.80	0.112	**2.75**
25		0.382	0.327	1.45	0.353	2.65	0.592	0.359	0.536	0.567	0.698	0.666	**0.587**
7	**Spray**	0.135	0.123	0.530	0.332	2.09	0.175	0.509	0.690	2.76	1.50	1.07	**0.659**
8		0.592	0.213	0.900	0.793	0.833	0.438	1.04	0.653	2.99	2.74	0.357	**0.883**
16		0.303	0.235	0.412	0.545	0.594	0.406	0.445	0.557	0.756	0.898	0.535	**0.444**
17		1.61	1.63	3.79	1.44	6.61	2.57	2.15	2.36	6.38	4.15	3.46	**2.69**
19		0.137	0.084	0.053	0.035	0.208	0.098	0.305	0.333	1.78	1.15	0.035	**0.325**
26		12.4	0.565	0.809	0.588	1.20	1.06	0.816	17.4	2.01	1.86	1.14	**4.93**

Anh. Tab. 44 Ratio between inhalation and dermal dose based on the data gathered during the workplace monitoring campaigns and equation 5.3.

AP #	Active sub-stance concen-tration [µg/m³]	Exposure duration T [min]	Calculated inhalation dose D_{inhal} [µg]	Total coverall		hood	
				Measured dermal dose D_{dermal} [µg]	D_{inhal}/ D_{dermal}	Measured dermal dose D_{dermal} [µg]	D_{inhal}/ D_{dermal}
1	0.2	6.0	0.02	2019	0.001 %	0.561	4 %
2	1.9	3.7	0.14	322	0.04 %	0.343	41 %
3	9.1	4.5	0.84	826	0.10 %	1.03	81 %
4	62	4.5	5.71	327	1.75 %	1.27	450 %
5	16.50	1.8	0.63	55.6	1.13 %	0.768	82 %
6	16	3.2	1.04	127	0.82 %	2.31	45 %
7	78	0.9	1.48	383	0.39 %	42.1	4 %
8	42	1.0	0.87	34.2	2.54 %	0.936	93 %
9	0.3	19.0	0.10	57.5	0.2 %	1.79	6 %
10	61	17.0	21.7	327	6.63 %	6.33	342 %
11	1.2	3.6	0.09	1.8	5.09 %	0.04	227 %
12	0.2	3.4	0.02	81.4	0.02 %	0.01	164 %
13	220	0.4	1.75	356	0.49 %	57.1	3 %
14	<12	12.0	3.00	1002	0.30 %	42.4	7 %
15	<12	12.0	3.00	1367	0.22 %	71.5	4 %
16	141	6.0	17.6	1814	0.97 %	148	12 %
17	348	7.0	50.7	10764	0.47 %	936	5 %
18	<24	5.9	3.0	752	0.39 %	1.02	291 %
19	30	16.0	9.98	637	1.6 %	4.64	215 %
20	<27	5.2	2.96	325	0.9 %	2.48	119 %
21	9.3	12.0	2.33	7190	0.03 %	20.3	11 %
24	13.7	20.0	5.70	15722	0.04 %	43.2	13 %
25	539	31.0	347.5	2832	12.3 %	218	159 %
26	997	12.0	248.9	14835	1.68 %	231	108 %
27	1.4	20.0	0.59	600	0.10 %	0.907	66 %
28	0.6	20.0	0.25	147	0.17 %	2.31	11 %