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Biocides in spray products - exposure and health

(Biocider i sprayprodukter - eksponering og sundhed)

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Content

1. Preface

This project on exposure and health to biocides in spray products was carried out between May 2014 and December 2017 and was funded by the Danish EPA's Pesticide Research Programme (J. no. MST-667-00211).

The project was conducted as a collaboration between the National Research Centre for Working Environment (Project Manager Ismo K. Koponen) and DHI (Senior Toxicologist Ann Detmer).

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2. Abbreviations

ART: Advanced REACH Tool

BAuA: German Federal Institute for Occupational Safety and Health

BEAT: Bayesian Exposure Assessment Tool

BPR: Biocidal Product Regulation

CPC: Condensing Particle Counter

Dode: benzyl dimethyl dodecyl ammonium chloride

ECHA: European Chemicals Agency

ELPI: Electric Low Pressure Impactor

FMPS: Fast Mobility Particle Sizer

GC-MS: Gas chromatography – mass spectrometry

MST: Miljøstyrelsen (Danish Environmental Protection Agency)

OPS: Optical Particle Sizer

PID: Photo Ionization Detector

QAC: Quaternary Ammonium Compounds

RIVM: Dutch National Institute of Public Health and Environment

SMPS: Scanning Mobility Particle Sizer

Tetra: benzyl dimethyl tetradecyl ammonium chloride

3. Summary

A biocide is defined in the biocidal product regulation (BPR) as a chemical substance or mixture intended to destroy, deter, render harmless, or exert a controlling effect on any harmful organism by chemical or biological means (EU, 2012). Biocidal products are classified into 22 biocidal product types according to their intended use and can be divided into four major groups: “disinfectants”, “preservatives”, “pest control”, and “other biocidal products”. Currently, all biocidal active substances within the EU are being re-evaluated within their respective product types. The active substance(s) in a biocidal product must be approved in order to obtain authorisation for marketing the product. In order to have a biocidal product authorised, the applicant must provide documentation of safe use of the product for humans and environment. The documentation of safe use should be based on a thorough exposure and risk assessment of all relevant uses of the product. Human exposure assessments can be done by carrying out studies and generate new data or, if no actual measurement of the exposure is available, by using exposure-modelling software programs, e.g. ConsExpo, to evaluate consumer products or BEAT (Bayesian Exposure Assessment Tool) to evaluate products for professional use. These computer software models are recommended by the EU and are included in the guidance documents of the BPR.

The main objective of this project was to evaluate existing models in ConsExpo and BEAT by comparing computed exposure calculations with experimental exposure data for three selected biocide spray products. The aim was to compare standard scenarios in ConsExpo and BEAT as well as scenarios similar to the experimental conditions with experimental exposure data obtained in the project.

In order to address this objective, we performed spray scenarios in a controlled exposure chamber (20.3 m^3) and compared measured data with exposure modelling results from ConsExpo and BEAT. This was done firstly to evaluate the models for exposure assessment of the biocide spray products and thus further validate the software tools. Secondly, the aim was to produce data that may be used to improve ConsExpo and BEAT’s calculation of exposure to biocide spray products.

Three products were chosen: **Tanaco Fluestop** (used for rapid control of flying insects, propellant drive spray can with active substances: Pyrethrum extract, permethrin, piperonyl butoxide), **Demand CS** (indoor insecticide professional use, pumped spray, active substance: λ- Cyhalothrin), and **Ecolab Mikro-Quat Extra** (for disinfection and cleaning, pumped spray, active biocide substance: Benzalkonium chloride)

Particle measurements were performed to characterize number size distribution spectra and total concentration in the exposure chamber after spraying while chemical analyses of air samples were carried out to characterize the chemical composition of the particle and gas phases.

The exposure to the selected products were calculated in ConsExpo and BEAT using default scenarios, as well as scenarios where model parameters were adjusted to fit the experimental chamber conditions. Both the exposure by inhalation and the dermal exposure were measured. Further, the secondary exposure to two of the products (Tanaco Fluestop and Demand CS), was calculated in ConsExpo and compared with surface wiping measurements from the exposure chamber. For the secondary exposure, a worst-case scenario was considered, where a child is crawling on and around the exposed area with exposure of skin and with hand-to-mouth contact.

The particle measurements in the exposure chamber showed low particle number concentrations in the breathing zone area that we chose only to analyse for Tanaco Fluestop. This does

not exclude inhalable exposure from other products. Thus, the inhalational exposure (Potential dose inhalation + oral via air) estimated based on the modelling and the measurement was compared only for Fluestop.

The results show that the modelling data provide lower or similar levels of exposure in comparison with the chemical measurements and lower estimates compared to the estimate using particle concentration. The particle exposure estimates based on the measurement data and the chemical measurements in air are therefore not directly comparable to the exposure estimated in the models. For piperonyl butoxide, both the exposure estimates based on the chemical and the particle measurements (0.34 and 0.43 mg/kg/day) are higher compared to the level calculated by ConsExpo (0.014 mg/kg/day). For permethrin and pyrethrum extract the estimates from ConsExpo are similar to the estimates based on the chemical measurements; however, the estimates based on the particles are higher than both of these estimates.

Selection of parameters in ConsExpo not completely in line with the experimental setup could contribute to these discrepancies. However, as the modelling was also setup using values from the experiments, this may only slightly impact the results. Thus, the primary factor causing the differences in exposure estimates between the modelled and the measured values, appears to be the initial size distribution default applied in ConsExpo, as this is higher compared to out actual size measurements. The inhalation cut off default in ConsExpo is 15 µm, thus only particles below 15 µm is included in the inhalation exposure model. Thus, a comparison is hampered, because our measurements are all below 10 µm. Data on particle size and distribution is essential in the estimation of exposure. A new web-based version of ConsExpo (ConsExpo Web) has recently been released, where it is now possible to insert data on this in the model. We did not use this version for our modelling, but a preliminary estimate of piperonyl butoxide exposure was performed. A better estimate of the inhalational exposure was achieved in comparison with the experimental data. Default values in ConsExpo are likely to be chosen in case of no information about the particle size distribution of the product; thus resulting in considerable underestimation of exposure.

Particle and chemical measurements are not always consistent when comparing the individual active compounds. There may be several reasons for this, e.g. only particles up to 10 µm were measured with the particle instruments, whereas the air sampling for chemical analysis there was not limit on particle size. Furthermore, the accuracy of the given chemical composition is not known. However, the estimates based on particle and chemical measurement resulted in fair agreement with total concentration for the active compounds in the air.

The dermal exposure after secondary exposure was also compared. After spraying with the products in the exposure chamber, wipe samples were taken on the floor and lower walls (child height). The amount detected on the wipe samples was compared to the default values in ConsExpo for *dislodgeable amount*. The amount measured on the samples was comparable to the default values in ConsExpo. Based on this comparison the default levels for dislodgeable amounts in ConsExpo appear realistic for this specific product. The amount of dislodgeable product may be different with other products or types of products.

Based on our comparison of experimental data with the models, we conclude that the applied version of ConsExpo (4.1 and 5.0b) showed unsatisfactorily results in comparison with the airborne exposure measurements. However, our studies only include one product which had a potential for inhalable exposure; thus, it is not possible to generalize from these results. For the secondary exposure we found better agreement between the measurements and modelling, which indicates that the models may predict the secondary exposure for this specific product type, but additional experimental data are required before an assessment and conclusion can be drawn.

4. Sammenfatning

Ifølge biocidproduktforordningen (BPR, Biocidal Products Regulation) defineres et biocidprodukt som et kemisk stof eller blanding, der har til formål at ødelægge, afskrække, uskadeliggøre, eller kontrollere en potentiel skadelig organisme ved hjælp af kemiske eller biologiske virkemidler (EU, 2012). Biocidprodukter klassificeres i 22 biocidprodukttyper alt efter deres formål. De inddeles i fire hovedgrupper: ”desinfektionsmidler”, ”konserveringsmidler”, ”skadedyrsbekæmpelse” og ”andre biocidprodukter”. Samtlige biocid aktivstoffer inden for EU er pt ved at blive revalueret inden for deres respektive produkttyper. Det aktive stof eller de aktive stoffer i et biocidprodukt skal godkendes inden produktet kan opnå bemyndigelse til markedsføring. For at kunne opnå bemyndigelse til markedsføring af et biocidholdigt produkt, skal ansøgeren dokumentere, at produktet kan anvendes sikkert for mennesker og miljø. Dokumentationen for sikker anvendelse af produktet skal baseres på udførlige eksponerings- og risikovurderinger i forbindelse med brugen af det pågældende produkt. Eksponeringsvurderinger for mennesker kan udføres ved generering af nye data fra eksperimentelle undersøgelser. Såfremt ingen eksponeringsmål er tilgængelige, kan computersoftwareprogrammer med eksponeringsmodeller benyttes, som fx ConsExpo til evaluering af forbrugsprodukter eller BEAT (Bayesian Exposure Assessment Tool) til evaluering af produkter til professionel anvendelse. Computersoftwareprogrammerne anbefales af EU og indgår i BPR’s dokumenter om retningslinjer.

Projektets hovedformål var at evaluere eksisterende modeller i ConsExpo og BEAT ved at sammenligne computereksponeringsberegninger med forsøgsdata for tre udvalgte biocidholdige sprayprodukter. Vores mål var at udføre dette ved at sammenligne standardscenarier i ConsExpo og BEAT samt scenarier svarende til de eksperimentelle forhold med eksperimentelle eksponeringsdata fra projektet.

For at kunne undersøge dette, udførte vi sprayscenarier i et kontrolleret eksponeringskammer (20 m3) og sammenlignede måledata med resultater fra modellering ved brug af ConsExpo og BEAT. Dette blev først og fremmest udført for at evaluere eksponeringsmodeller af de biocidholdige sprayprodukter og dermed yderligere ved at validere softwareredskaberne. Derudover var målet at fremskaffe data til forbedring af ConsExpo og BEAT-estimeringer af eksponeringen for biocidholdige sprayprodukter.

Der blev udvalgt tre produkter: Tanaco Fluestop (benyttes til hurtig bekæmpelse af flyvende insekter, benytter gas som drivmiddel, aktive stoffer: Pyrethrumekstrakt, permethrin, piperonylbutoxid), Demand CS (insektmiddel til professionel brug indendørs, pumpespray, aktive stoffer: λ- Cyhalothrin) og Ecolab Mikro-Quat Extra (til desinficering og rengøring, pumpespray, aktive biocidholdige stoffer: Benzalkoniumchlorid).

Der blev udført partikelmålinger med henblik på karakterisering af antalstørrelsesfordelingsspektre samt den totale partikelkoncentration i kammeret efter at produktet var blevet tilført, og de kemiske målinger blev udført med henblik på karakterisering af den totale kemiske sammensætning (gas- og partikelfase).

Eksponeringen af de udvalgte produkter blev beregnet i ConsExpo og BEAT ved hjælp af default scenarier samt scenarier, hvor modelparametrene efterfølgende blev justeret og tilpasset de eksperimentelle forhold. Både indhalation- og hudeksponering blev målt. Derudover blev den sekundære eksponering for to af produkterne (Tanaco Fluestop og Demand CS) beregnet i ConsExpo og sammenlignet med overflademålingerne fra eksponeringskammeret. Den sekundære eksponering, blev vurderet ud fra et ’worst-case’ scenarie af et barn der kravler på et behandlet/kontamineret område. Både hudeksponering og hånd-til-mund kontakt blev medtaget.

De udførte aerosolmålinger i eksponeringskammeret viste, at partikelantallet i indåndingszonen var så lavt for flere af produkterne, at vi valgte kun at analysere Tanaco Fluestop i forbindelse med inhalerbar eksponering. Det betyder dog ikke, at inhalerbar eksponering i forbindelse med andre produkter ikke kan finde sted. Den estimerede inhaleringseksponering (potentielle dosis-inhalation + oralt via luften) blev ligeledes beregnet i ConsExpo, og målingerne blev sammenlignet for alle aktivstoffer i Fluestop.

Resultaterne af sammenligningen viser, at ConsExpo enten beregner lavere eller lignende eksponeringsniveauer sammenlignet med kemiske målinger udført i eksponeringskammeret, og lavere estimater sammenlignet med koncentrationer beregnet på baggrund af aerosolmålingerne. Eksponeringsestimaterne baseret på måledata fra partikelmålinger og de direkte kemiske målinger er derfor ikke direkte sammenlignelige med eksponeringsestimaterne i modellerne. For piperonylbutoxid fandt vi således, at eksponeringsestimaterne baseret både på de kemiske og aerosolmålingerne (hhv. 0,34 og 0,43 mg/kg/dag) var højere sammenlignet med det modellerede niveau fra ConsExpo (0,014 mg/kg/dag). For permethrin og pyrethrumekstrakt svarede estimaterne fra ConsExpo bedre til estimaterne baseret på den kemiske luftkoncentration, partikelestimaterne er imidlertid højere end begge disse.

Valg af parametre i ConsExpo afveg i forhold til de eksperimentelle forhold og kan muligvis være en medvirkende årsag til ovennævnte uoverensstemmelser. Da vi har tilrettet modelscenarierne efter de eksperimentelle forhold, har disse faktorer dog formentlig begrænset betydning for resultaterne. Det ser ud til, at den primære årsag til forskellene i eksponeringsestimater mellem modellen og de målte værdier, er den standard partikelstørrelsesfordeling, som benyttes i ConsExpo i det valgte sprayscenarie, da denne ligger væsentlig højere sammenlignet med de målte størrelsesfordelinger i dette projekt. Desuden er standardgrænsen for inhalation i ConsExpo 15 µm, og partiklerne under denne værdi medtages i beregningen af eksponering via inhalation i modellen. Det er derfor svært at sammenligne resultatet af modelleringsestimaterne med de eksperimentelle målinger, som kun har målinger under 10 µm, da man ikke kan ændre partikelstørrelsesfordelingen i pågældende version af ConsExpo. Data vedrørende partikelstørrelse og fordeling er meget vigtig i forbindelse med eksponeringsestimatet. En ny web-baseret version af ConsExpo (ConsExpo Web) er for nylig blevet lanceret, hvor det nu er muligt at indsætte data vedr. dette i modellen. Vi benyttede ikke denne version i forbindelse med vores beregninger, men en foreløbig beregning af eksponeringen for piperonylbutoxid gav et estimat af inhalationseksponeringen der stemte bedre overens med de eksperimentelle data. Da man vil være tilbøjelig til at vælge standard-værdierne i ConsExpo, når der mangles viden om et produkts partikelstørrelsesfordeling; vil dette dermed resultere i en betragtelig underestimering i eksponeringen.

Eksponeringsestimaterne baseret på aerosolmålinger og kemiske målinger er ikke altid konsistente for alle aktivstoffer, hvilket der kan være forskellige grunde til; fx måler vi kun partikler på 10 µm og derunder med aerosolmåleudstyr, mens luftprøverne til kemisk analyse ikke begrænses af partikelstørrelsen. Endelig, kendes nøjagtigheden for produktets angivne sammensætning ikke. Estimaterne fra partikel- og kemiske målinger var imidlertid i rimelig overensstemmelse for den totale koncentration af aktive stoffer i luften.

Hudeksponering efter sekundær eksponering blev ligeledes sammenlignet. Efter at produktet var blevet sprayet i eksponeringskammeret, blev der taget wipe prøver på gulv og vægge (i børnehøjde). Den målte mængde blev sammenlignet med standardværdierne i ConsExpo for overførbar mængde. De målte mængder fra eksponeringskammeret viste sig at være sammenlignelige med standardværdierne i ConsExpo. Ud fra denne sammenligning må standardværdierne for overførbar mængde i ConsExpo siges at være realistiske for de undersøgte produkter. Mængden af overførtbart produkt kan være anderledes for andre produkter eller produkttyper.

Baseret på vores sammenligning af eksperimentielle data med modellerne, kan vi derfor konkludere, at den anvendte ConsExpo version (4.1 og 5.0b) gav et utilfredsstillende resultat sammenlignet med det målte luftbårne eksponeringsestimat. Vores undersøgelser inkluderede imidlertid kun ét produkt, som havde potentiale for inhalerbar eksponering, det er derfor ikke muligt at generalisere ud fra disse resultater. For den sekundære eksponering, fandt vi en bedre overensstemmelse mellem målingerne og modellerne, hvilket indikerer, at modellerne kan forudsige eksponeringer med hensyn til den sekundære eksponering for den pågældende produkttype, men yderligere forsøg vil være påkrævet før en endelig vurdering og konklusion.

5. Background

In the Biocidal Product Regulation (BPR), a biocide is defined as a chemical substance or microorganism intended to destroy, deter, render harmless, or exert a controlling effect on any harmful organism by chemical or biological means (EU 528/2012). Biocidal products are classified into 22 biocidal product types, grouped in four major groups: “disinfectants”, “preservatives”, “pest control”, and “other biocidal products”.

5.1 Authorisation of biocidal products

The active substance(s) in a biocidal product must be approved according to the BPR in order to obtain authorisation for marketing the product. Under this regulation, all biocidal active substances and products are being evaluated and regularly re-evaluated to remain on the market in the EU. If an active substance is approved, it triggers a deadline for the authorisation of the biocidal products containing the approved active substance. In order to have a biocidal product authorised the applicant must provide documentation of specific chemical and physical properties of the product. The applicant must also provide documentation of the efficacy of the product related to the claims made. Finally, safe use of the product about human health and the environment must be documented and demonstrated. This part is an essential condition for obtaining an authorisation and is based on a thorough exposure and health risk assessment of all relevant uses of the product.

Until the active substances are approved under the EU review program, the products are covered by the local Danish authorization system for biocides. Approximately 1500 different biocidal products are on the market in Denmark. Of these, 650 products are disinfectants and 180 are insecticides and repellents.

The group of active substances used in disinfectants and insecticides is still under review in a rolling plan until 2018 as can be seen in the Biocidal Products Committee (BPC) work programme from 07 July 2017. When an active substance is approved, there is a window of two years where applications for authorisation of biocidal products with the active substance may be submitted and where the products may still be on the market during the evaluation. If a product application has not been submitted within these two years, the product authorisation is automatically withdrawn and the product must be taken off the market. Most companies therefore choose to apply for product authorisation within the time period. However, if a product contains more than one active substance, the latest deadline is applicable, and authorisation is still expected within the next years for the disinfectants and insecticides.

The consequence of the new approval system for active substances in biocidal products is that the industry now has a deadline for submission of applications for authorisation of their individual biocidal products. In order to obtain authorisation of a biocidal product, the applicant must show safe use of the product for both humans and the environment. A significant part of the application is therefore to generate information about human exposure during correct use of the biocidal product in order to demonstrate its safety. Human exposure assessments can be obtained from experimentally determined exposure studies and generate new data or, if no actual measurement of the exposure is available, by use of exposure modelling software programs e.g. ConsExpo to evaluate consumer products or BEAT (Bayesian Exposure Assessment Tool) to evaluate products for professional use. Several guidelines exist on assessment of exposure to biocides and these computer software models are recommended by the EU and are included in the guidance documents of the BPR.

5.2 Exposure from biocidal spray products

Biocidal spray products such as insecticides, repellents and disinfectants have been used by professional users for decades and have in recent years been marketed for private use. However, limited knowledge and data are available about the exposure of the users to the biocidal active substances and thus the associated health risks. Many biocidal spray products are used indoors, representing an additional risk, as the substances are more likely to be present in the air around the user for longer periods due to generally lower ventilation rates (1/h) indoors. Furthermore, there is a risk of secondary exposure of particularly children present in areas where spray products have been used. Children can thus be exposed both by inhalation, by skin contact with treated areas and by ingestion primarily if hands are contaminated. Very few of the biocidal active substances used for disinfection have occupational or indoor limit values (guidelines); thus, it is difficult for authorities and consumers to compare the health risks associated with these products.

One of the major challenges for risk assessment of airborne chemical substances is to assess the exposure by inhalation. Thus, it is important to describe both the spread of these chemicals in the air, the concentration, and the duration of their presence in the air. This depends on several factors, including the physical chemical parameters (e.g., vapour pressure), droplet size, velocity of the spray, nozzle shape, ventilation rate, relative humidity, etc. Furthermore, it is important to assess the secondary exposure from the active substances being deposited on surfaces.

From the use of professional insecticidal biocides in private homes, Jensen and co-workers reported high accumulation of active substances on treated surfaces, when apartments were repeatedly treated with synthetic pyrethroids. It was concluded that when premises were treated more often than every 3-4 weeks, accumulation of active substances must be expected, however, this will depend on the cleaning activity (Jensen et al., 2015).

5.3 Software for modelling exposure to spray products

Data and measurements of the exposure during use of biocidal spray products are often difficult to obtain, and no specific guideline exists as to how the measurements should be carried out. Due to lack of data from experimentally determined exposure measurements to support applications for approval of biocidal products, exposure modelling software programmes are often used to predict the exposure. Authorities therefore often rely on results from computed exposure assessments when evaluating product applications. The European Chemicals Agency (ECHA) recommends using ConsExpo for assessments of consumer products and BEAT for assessments of products for professional use (ECHA 2016).

ConsExpo was developed by the Dutch National Institute of Public Health and Environment (RIVM) to estimate and assess exposure to substances from consumer products, e.g. paint, cleaning agents and personal care products. For spray products, a specific model was incorporated to describe the exposure to formed non-volatile aerosols (particles). This was developed based on experimental measurements using both spray cans and pump sprays (trigger sprays) at different spray rates and droplet diameters (controlled by the spray equipment). ConsExpo includes measurements from spraying on people, into rooms and on surfaces. The particle size distribution and their concentration in the air were measured as a function of time after spraying at different distances from the spray position (Delmaar & Bremmer, 2010). ConsExpo is based on a number of general rational equations, which enables calculations and exposure assessment of chemical substances from consumer products used indoors. ConsExpo can calculate both external and internal (systemic) human exposure via inhalation, skin contact and ingestion at both acute and chronic exposures to a defined substance in the biocidal spray product.

BEAT is a Bayesian task-based exposure model, developed by HSE/HSL and TNO under the auspices of ECHA. It covers dermal exposure but can also be used for aerosols, however, for volatile substances the Advanced REACH Tool (ART) described in ECHA Guidance R.14 should be followed. BEAT is based on a large database of experimental data from the use of professional biocidal products. It provides exposure estimates based upon the strength of analogy between an assessment scenario and multiple exposure scenarios contained within an internal exposure database. The database contains measured work-related exposures relevant for biocide products and includes about 70 datasets. The internal database contains full records of every data point (including multiple exposure measurements and contextual information) and can be updated as new exposure measurements become available. BEAT predicts median exposure rates to in-use biocidal formulations and also provides estimates of both exposure variability and uncertainty. This allows a variety of exposure percentiles to be derived dependent upon the circumstances of the assessment. BEAT is useful for estimating exposures when there are insufficient experimental exposure data or the choice of a single unambiguous generic data model is unclear. Furthermore, an activity based search function is included in BEAT enabling searches for the most relevant exposure scenarios based on the input information. This software is therefore relevant for calculations of professional exposure. When entering data for the scenario in question, default values from the most suitable experiments will be shown. The user can find the most representable data in the database. BEAT does not take the composition of the product into account, but focuses solely on the exposure to one substance at the time. The user should also be aware that physical and chemical parameters of the substances are not included in the calculation, which means that the results are only based on the concentration of the substance in question. The primary parameters used in the assessment are air concentration and body and hand deposit. Oral exposure is not included.

Other public domain software models for human exposure worth mentioning are SprayExpo and ART (Advanced REACH Tool). SprayExpo was developed by the Federal Institute for Occupational Safety and Health (BAuA) in Germany. It calculates the airborne concentration of respiratory, thoracic and inhalable fractions of aerosols, as well as other fractions of aerosols generated during work processes. Biocide-containing aerosols released from biocidal spray products are of special concern in the indoor environment. Based on the calculated concentration, inhalation and skin exposures are determined. However, secondary emission of volatile substances from walls and other surfaces is not included. SprayExpo has been validated using measurements from spray application of antifouling products on ships and of spray disinfection in grain silos (Koch et al., 2012). However, it is not validated whether the SprayExpo with equal precision can predict exposure to other types of products in indoor environments.

ART was developed in a collaboration between BAuA, HSE, IOM, Research Centre for Health and TNO, and it is described in detail by Tielemans et al. (2011). ART is a mechanistic model for the calculation of inhalation exposure with the opportunity of statistically updating the estimates with measurements selected from a built-in exposure database or on the user's own data.

5.4 Statement of problem

Deterministic or probabilistic exposure assessment requires solid knowledge of the model and experience from validation since uncertainty and errors will have a big impact on predictability. Common to all software tools is that it is necessary to specify a number of parameters specific to the product, and to the substances in the product, as well as on the user scenario.

In this project, we have chosen to focus on ConsExpo and BEAT since they are the recommended software tools in the BPR guidelines and the preferred tools for most authorities.

RIVM has developed various guidelines to ConsExpo for standard parameters for different types of products, including biocidal products in spray form. However, ConsExpo do not consider the evaporation of substances from aerosols. Furthermore, the default data in ConsExpo is insufficient to assess the accuracy of the exposure due to the high uncertainty of the values (Arnold 2014).

The software tools have not yet been validated for all possible exposure scenarios and product types. In fact, only a few scenarios are validated. Nonetheless, the tools are still likely to be used to calculate the exposure in the many product applications that are expected to be submitted to MST and other authorities in the EU in the coming years. Since predicted exposure is used in the calculation of the risk characterisation ratio (RCR), and the resulting RCR value is the basis for the decision on a product's approval, it is essential that the exposure estimates from the calculation models do not differ significantly from the experimentally determined exposure in a given set-up.

We therefore sought to compare actual measurements of specific products with calculated values from both ConsExpo and BEAT for further validation of these tools and to assess their compatibility. Both ConsExpo and BEAT have a wide array of parameters that need to be set in each exposure assessment and it often proves difficult to set them at the appropriate levels even for risk assessment experts. Therefore, we also set out to examine which parameters would have a large impact on the exposure calculations by comparing scenarios using default parameter settings with scenarios where parameters were changed to fit the controlled experimental set-up.

5.5 Hypotheses

The overall hypothesis of this project was that the software tools ConsExpo and BEAT need further validation and improvement for calculation of exposure from spray products. Thus, it is hypothesised that there is a discrepancy between modelled exposure estimates and experimentally determined exposures for certain products, which may influence the approval procedure.

5.6 Objectives

The main objective of this project was to evaluate existing models in ConsExpo and BEAT by comparing exposure calculations with experimentally determined exposure data for selected biocide spray products. It was our aim to do this by comparing computed exposure data from ConsExpo and BEAT using standard scenarios as well as scenarios similar to the experimental conditions with experimental exposure data obtained in the project.

In addition, the project aimed at identifying weak spots, key parameters and potential optimizations of the models to achieve better estimations of exposure levels for disinfectants, insecticides and repellents.

6. Methods

6.1 Selection of biocidal spray products

Biocidal spray products are available in two forms: aerosol spray cans and trigger sprays. Aerosol spray cans are pressure resistant containers from which a liquid is discharged under the pressure of a propellant; these cans are ready-to-use spray products. Trigger sprays are dispensers turning a liquid into a (fine) spray. Biocidal trigger sprays exist both as ready-for-use products and as formulations, which should be mixed and loaded in a plant sprayer. By turning the nozzle of the plant sprayer the spray distribution can be adjusted, which results in a spray with fine or coarse droplets (RIVM report 320005002/2006 Pest Control Products Fact Sheet).

A number of biocidal spray products were under consideration for testing in this project. In consultation with MST, the following three products were chosen:

- *Tanaco Fluestop* (used for rapid control of flying insects, propellant driven spray can)
    - Active biocide substances: Pyrethrum extract, Permethrin, Piperonyl butoxide
- *Demand CS* (indoor insecticide professional use, pumped spay)
    - Active biocide substance: λ- Cyhalothrin
- *Ecolab Mikro-Quat Extra* (for disinfection and cleaning, pumped spray)
    - Active biocide substance: Benzalkonium chloride

These products were chosen to have a broad representation of biocidal spray product types. Tanaco Fluestop is thus a spray can intended for use by private consumers, which normally would be evaluated with ConsExpo. Demand CS is a product for professional use where the product is diluted and loaded into a handheld trigger spray and Mikro-Quat Extra is a disinfection/cleaning product automatically diluted and loaded into a handheld trigger spray. Both Demand CS and Mikro-Quat Extra would normally be evaluated with BEAT.

6.2 Experimental methods (NFA)

6.2.1 Chemicals (used in the analyses)

1,2-benzisothiazol-3(2h)-one (97%), Lambda-cyhalothrin (Pestanal, 1,2-propanediol (ACS Reagent), piperonyl butoxide (Pestanal), permethrin (mixture of cis and trans isomers Pestanal), pyrethrum extract (Pyrethrin I & II) (Pestanal) were obtained from Sigma-Aldrich. The quaternary ammonium compounds (QAC) benzyl dimethyl dodecyl ammonium chloride (≥99.0%) and benzyl dimethyl tetradecyl ammonium chloride (≥99.0%) were also obtained from Sigma-Aldrich. Methanol (MS-grade) and decane (99.8%) were from Fluka. Toluene (99.8%) was from Merck.

LC solvents: Methanol (MS grade, Fluka) and Millipore water with 2 mM ammonium acetate (LC-MS ultra, Aldrich-Sigma) and 1% formic acid (98%, Merck).

6.2.2 Air sampling tubes, surface sampling wipes and filters for skin deposition

Tenax TA, 200 mg/tube (mesh 60-80, Perkin Elmer) and ORBO™ 43 Supelpak™-20 specially treated Amberlite® XAD®-2 (20/40), Sigma-Aldrich were used to sample airborne organic compounds. Tenax TA is a medium polar porous polymer, based on 2,6-diphenyl-p-phenylene oxide, which is suitable for medium volatile polar and non-polar organic compounds. Its high temperature stability makes it suitable for release of adsorbed compounds by thermal desorption which makes the analysis very sensitive for low air concentrations.

XAD-2 is a hydrophobic adsorbent of copolymer of styrene-divinylbenzene which is able to adsorb and release both ionic species and non-polar high boiling organic compounds, e.g. PAH.
Alkoholswabs (Mediq, Denmark A/S): Single packed wipes (30 x 60 mm) of 60% viscose, 20% polyester and 20% other synthetic fibres soaked in 70 % isopropyl alcohol solution were used to sample compounds on the surfaces of the climate test chamber. Glass microfibre filters (GF/C 47mm Ø circles, cat no 1822 047) from Whatman placed at the face and on the arm of the spray performing operator in the exposure scenarios were used to sample compounds as proxy for skin deposition exposure.

6.2.3 Climate test chamber and execution of exposure scenarios

The products were emission tested in simulated exposure scenarios in a controlled climate chamber with an ante-chamber at 22± 1°C, 50 ± 2% RH and air exchange of 0.5 h-1. The dimensions of the chamber are 2.56 M x 3.46 M x 2.29 M (W x L x H), i.e. 20.3 m³. For further specifications, see Fig. 6-1 and Nørgaard et al. (2014). The chamber was cleaned twice before and between each emission spray test, first with 50/50% ethanol/water and subsequently with water. Background samples were taken before the emission tests were started. Background levels for the specific chemicals were generally between limit of detection (LOD) and 5 µg/m^3.

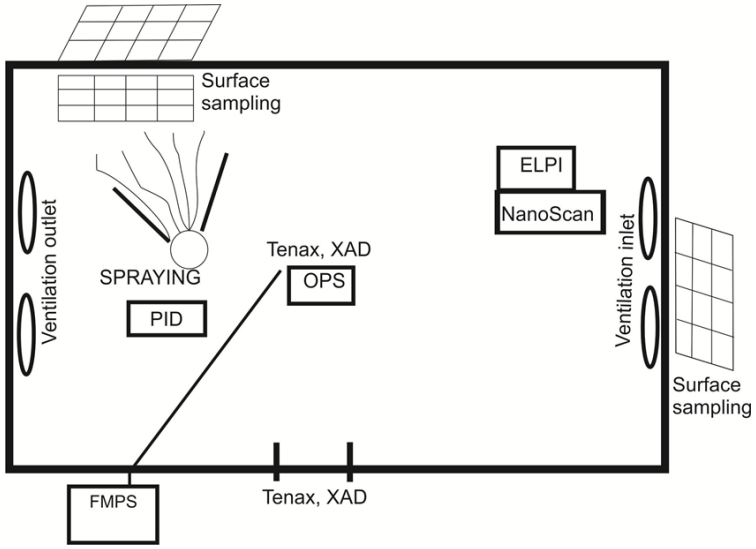


Figure 6-1 Climate chamber schematic. Sampling position for chemical samples is marked as Tenax,XAD. Aero-sols were measured in the middle (FMPS, OPS) and right side (ELPI, NanoScan (SMPS)) of the chamber.

6.2.4 Spray products, their composition and application in the exposure scenarios

The spray products were selected on the basis of diversity and content of both volatile and non-volatile biocides. Table 6-1 lists both declared chemicals according to data sheets and compounds identified by qualitative analysis of the content using GC-MS and LC-MS and sampling methods used in the chamber experiments.

The application of the products was performed in accordance with the manufacturer's guidelines. Tanaco Fluestop was sprayed in different directions and Demand CS and Mikro-Quat

extra were sprayed using the Gloria 505 pumped spray (orifice = 2 mm, spraying angle 80º) in one corner of the chamber on a 2-m² steel plate. For Mikro-Quat the floor was washed 20 min after the spraying according to the instruction on the product, presumably to remove excess active compound which after that time has reached full effect. The test conditions, amount, and time of spraying are shown in Table 6-2. Sampling is described in paragraph 6.2.5.

Table 6-1 List of declared chemicals in 3 biocide spray products according to datasheets (active biocides marked with *), identified by chemical analysis of the biocide products and sampling method(s) used in the chamber experiments.

Product	Compound	Formula	CAS	Sampling method
Fluestop	Alkanes			Tenax, XAD
	Dimethoxy methane	$C_3H_8O_2$	109-87-5	Tenax, XAD
	Phenylethyl alcohol	$C_8H_{10}O$	60-12-8	Tenax, XAD
	Lilial	$C_{14}H_{20}O$	80-54-6	Tenax, XAD
	Nopyl acetate	$C_{13}H_{20}O_2$	105-133-148	Tenax, XAD
	Piperonyl butoxide*	$C_{19}H_{30}O_5$	51-03-6	Tenax, XAD, Wipes
	Pyrethrum extract*	$C_{21}H_{20}Cl_2O_3$	80003-34-7	Tenax, XAD, Wipes
	Permethrin*	$C_{21}H_{20}Cl_2O_3$	52645-53-1	Tenax, XAD, Wipes
	Other fragrances			Tenax, XAD
Demand	1,2,4-Trimethylbenzene	C_9H_{12}	96-63-6	Tenax, XAD
	Propylbenzene	C_9H_{12}	103-65-1	Tenax, XAD
	Indane	C_9H_{10}	496-11-7	Tenax, XAD
	Lambda-Cyhalothrin *	$C_{23}H_{19}ClF_3NO_3$	91465-08-6	Tenax, XAD, Wipes
	1,2-Benzisothiazol-3(2H)-one	C_7H_5NOS	2634-33-5	Tenax, XAD, Wipes
Mikro-Quat Extra	Benzalkonium chlorides*	$C_6H_5CH_2N(CH_3)_2RCl$ (R=C_8H_{17} to $C_{18}H_{37}$)	63449-41-2	Tenax, XAD, Wipes

Table 6-2 The amount of product sprayed into the chamber.

Product	Amount	Spray time (sec) / pressure (bar)	Number of tests
Fluestop	32 g	10	3
Demand	2% solution in water	2.5-4.5 / 5.5	5
Mikro-Quat Extra	2% solution in water	5.5-6 / 5.5	4

6.2.5 Sampling protocols

Airborne organic compounds on Tenax TA and XAD:

• Tenax TA tubes were cleaned before sampling in a stream of pure nitrogen at 300 °C for 180 min and 340 °C for 30 min using a sample tube conditioning apparatus (TC-20, Markes International, UK). Background concentration for single VOCs < 0.1 ng/tube. XAD-2 tubes were used as bought without any cleaning.

• Chamber background samples on Tenax TA tubes and XAD-2 tubes were collected in duplicate by sampling for 10 min with 200 mL/min and 2000 mL/min, respectively. Sampling positions were a-s indicated in Figure 6-1 at a height of 1 m. Sampling pumps were placed outside the chamber.

• Sampling in duplicate of airborne organic compounds on Tenax TA and XAD-2 inside the chamber, was started immediately (1-2 min) after the spraying event by sampling for 10 min with 200 mL/min and 2000 mL/min, respectively.

• 10-min samples in duplicate were taken for every 15^{th} min within the first hour, than every 30^{th} min for the next hour, and once/hour for the following 6-7 hours, all together between 9 and 13 samples for each test depending on the concentrations.

• For Mikro-Quat the floor was washed 20 min after spraying (according to the instruction on the product, presumably to remove excess active chemical which after that time has reached full effect).

• Total organic concentration in the gas phase was followed by PID (Photo ionization detector) (MiniRAE3000, RAE Systems Inc.).

Surface contamination by wipe sampling:
The floor and walls was wiped with alcohol swabs. The wiped area was 20 cm x 10 cm (200 cm^2) and taken at five positions, on a clean floor steel plate in the spraying area (left and right position) and on the walls in front of ,and behind the spray position in child and adult height (left and right positions), respectively. Child height was 30-50 cm and adult height 120-140 cm. The sample was taken by wiping back and forth with both sides of the swab in the entire test area using gloves. The test area was wiped before (background) and 6-8 hours and 24 hours (in a new wipe test area next to the first) after spaying. After wiping the swab was placed in a 10 mL glass vial with screw cap. The extraction of the wipes was performed as soon as possible by adding 6 ml of methanol and placing the vial in an ultra-sonic bath for 30 min. Samples were stored in freezer until analysis.

Skin deposition exposure measured by personal worn glass microfibre filters:
Glass microfibre filters (GF/C 47mm Ø circles, cat no 1822 047) from Whatman placed at the face and on the arm of the spray performing operator in the exposure scenarios were used to sample compounds as proxy for skin deposition exposure.

Analysis of airborne organic compounds, sampled on Tenax TA, with thermal desorption GC-MS:
The Tenax TA tubes were analysed by thermal desorption gas chromatography and mass spectrometry (TD-GC-MS) using a Perkin Elmer Turbo Matrix 350 thermal desorber coupled to Bruker SCION TQ GC-MS system (Bruker Daltonics, Bremen, DE). Desorption was carried out in a He flow of 1 ml/min at 275° for 20 min and desorbed organic compounds collected in a cold trap with at -20°, followed by flash desorption of the cold trap at 275°C for 1.5 min transferring the organic compounds to the GC column. The column was a 5% phenyl polydimethylsiloxane of 30 m x 0.25 mm with 0.25µm film thickness (VF-5MS, Agilent Technologies, US). The GC oven program was 40°C for 2 min, ramp 1: 20°C/min to 150°C for 10 min, ramp 2: 5°C/min to 275° hold for 6 min and ramp 3: 3°C/min to 300°C hold for 1 min. The transfer line and the source were kept at 280°C. The MS was operated in electron ionization (EI) mode, in scan mode (mass range m/z 40-500), and SIM mode for the relevant ions of the compounds, respectively.

Analysis of XAD-2 tubes, wipes, and glass fibre filters with split less injection GC-MS/MS:
XAD-2 tubes were carefully broken and the contents of XAD-2 and cotton pulled into a 10 ml vial, covered with 5 ml methanol, and extracted in ultra-sonic bath for 30 min. Extracts were kept in freezer until analysis.

Wipes and glass microfibre filters were covered with 6 ml of methanol in a 10ml glass vial and extracted 30 min in an ultra-sonic bath. Extracts were kept in freezer until analysis.

The extracts were analysed by injecting 1 µl using a Bruker CP-8400 auto sampler and a programmable temperature vaporizing (PTV) injector at 220°C at a column He flow of 1 ml/min coupled to Bruker SCION TQ GC-MS system (Bruker Daltonics, Bremen, DE). The column was a 5% phenyl polydimethylsiloxane of 30 m x 0.25 mm with 0.25 µm film thickness (VF-5MS, Agilent Technologies, US). The GC oven program was 40°C for 1 min, ramp 1: 20°C/min to 150°C, ramp 2: 5°C/min to 230° hold for 6 and ramp 3: 3°C/min to 300° for 1 min. Transfer line and MS source were kept at 275°C. The MS was operated in electron ionization (EI) mode, in scan mode (mass range m/z 40-500), and in selected ion MS/MS mode for specific ions relevant for each biocide. The concentration of permethrin was reported as the sum of cis- and trans- isomers.

Analysis of XAD-2 tubes, wipes and glass fibre filters with LC-MS:
XAD-2 tubes were carefully broken and the contents of XAD-2 and cotton pulled into a 10 ml vial, covered with 5 ml methanol, and extracted in ultra-sonic bath for 30 min. Extracts were kept in freezer until analysis.

Wipes and glass microfibre filters were covered with 6 ml of methanol in a 10ml glass vial and extracted 30 min in an ultra-sonic bath. Extracts were kept in freezer until analysis.

LC-ESI-MS (electrospray ionization LC-MS) analysis was performed using an Agilent 1200 LC system (Agilent Technologies, Palo Alto, CA, USA) coupled to a Bruker Daltonics micro-Q-TOF MS with electrospray ionization interface (Bruker Daltonics). An Agilent, Zorbax Eclipse plus C18 column (2.1 x 50 mm and 1.8 µm particle size) was used for separation.

For 1,2-benzisothiazol-3(2H)-one the flow rate was 0.5 ml/min and the injection volume 20 µl. Chromatographic separation was achieved using solvent A: water with 2 mM ammonium acetate and 0.1% formic acid and solvent B: methanol with 2 mM ammonium acetate and 0.1% formic acid. Gradient conditions were started at 50 % A and 50 % B and changed to 10 % A and 90 % B over 10 min. Finally, gradient composition was changed to initial condition (50 % A and 50 % B) over 1 min and then held at this condition for 1 min before next injection. The column oven temperature was held at 30°C.

Benzalkonium chlorides were analysed using a flow rate of 0.3 ml/min and an injection volume of 5 µl. A gradient of water and methanol with 2 mM ammonium acetate and 0.1% formic acid were used for the mobile phase. The column oven temperature was held at 50°. Chromatographic separation was achieved using solvent A: Water with 2 mM ammonium acetate and 0.1% formic acid and solvent B: Methanol with 2 mM ammonium acetate and 0.1% formic acid. Gradient conditions were started at 50 % A and 50 % B and changed to 10 % A and 90 % B over 25 min. Finally, gradient composition was changed to initial condition (50 % A and 50 % B) in 1 min and then held at this condition for 1 min before next injection.

For both methods the source temperature was 200° and N_2 dry gas 6 l/min and nebulizer pressure 1.0 bar. Scan was from 50-3000 m/z. Extracted ion chromatograms were used for quantitation and peak identification.

TGA analysis (thermogravimetric analysis)

The analysis was carried out on a Netsch STA 449 F3 Jupiter by measuring the mass changes in weight between 25-1000°C. Approximately 0.3 to 1 ml of a product was weighed into an Al_3O_2 crucible and analysed in air at 20 ml/min. The sample was heated from 25°C with a rate of 10°/min to 1000°C.

Calibration curves and analytical performance

Three stock solutions in methanol containing biocide compounds, toluene and decane were produced. Except for the biocide compounds calibration curves of toluene and decane were used to calculate concentrations of all other compounds in toluene or decane equivalents, see Table 6-3. More volatile organic compounds were calibrated with toluene and less volatile with decane. The stock solutions were diluted with methanol for 6-9 different concentration levels in the range of 100 ng/µl to 0.001 ng/µl, see Table 6-3. The standards were kept at -18°C, when not in use. For Tenax TA tubes 5 µl of the standard solution was spiked on the tubes in a He flow of 60 ml/min for 3 min to evaporate the methanol. Limit of detection (LOD) values were estimated as three times the standard deviation of 20 measurements of the lowest standard and divided with the slope of the calibration curve, see Table 6-4. The LODs were in the order of 0.1 to 1 µg/m^3 at a sampling volume of 2 l. Recovery from wipes was estimated by spiking 20 wipes with 100 µl of a mixture containing all compounds resulting in an amount for each compound of 2 - 6 µg/wipe and then followed by extraction in a static ultra-sonic bath for 30 min with methanol (6 ml), see Table 6-5. Analytical data were corrected for the recovery and represent the mean of a left and right sample.

Table 6-3 Calibration of compounds

Compounds	Calibration curve		Conc. Range ng/µl	
	Six-point	Nine-point	Low	High
1.2 Benzisothiazol-3(2H)-one	+		0.4	81
1.2-Propandiol	+		1.2	104
Lambda-Cyhalothrin	+		0.2	19
Permethrin	+		0.3	27
Pyrethrum extract	+		0.5	59
Piperonyl butoxide	+		0.6	15
Decane	+		0.7	71
Toluene	+		0.8	84
Benzyl dimethyl dodecyl ammonium chloride		+	0.003	4.2
Benzyl dimethyl tetradecyl ammonium chloride		+	0.001	2.1

Table 6-4 Limit of detection (LOD) of compounds sampled on XAD sampling tubes and by wiping of surfaces

Compound	Conc. of standard used to estimate LOD ng/µl	Analytical LOD ng/µl	LOD air samples µg/m^3	LOD surfaces µg/m^2
1.2 Benzisothiazol-3(2H)-one	0.4	0.06	~ 14	~17
Benzyl dimethyl dodecyl ammonium chloride	0.003	0.005	~1	~ 2
Benzyl dimethyl tetradecyl ammonium chloride	0.001	0.003	~1	~ 1
Piperonyl butoxide	0.001	0.23	~57	~ 68
Pyrethrum extract	0.3	0.30	~74	~ 89
Permethrin	0.5	0.07	~17	~ 20
Lambda-Cyhalothrin	0.2	0.09	~22	~ 26
Toluene (TIC ion 91)	1	3.3	~833	~ 999
Decane (TIC ion 57)	1	0.6	~154	~ 185

Table 6-5 Recovery of compounds spiked on wipes

Compound	Number samples	Recovery %	SD
1.2 Benzisothiazol-3(2H)-one	20	77	3
Lambda-Cyhalothrin	20	115	16
Permethrin	20	110	11
Pyrethrum extract	20	121	20
Piperonyl butoxide	20	63	10
Benzyl dimethyl dodecyl ammonium chloride	19	88	9
Benzyl dimethyl tetradecyl ammonium chloride	19	104	17

6.2.6 FLEC measurements on Tanaco Fluestop

To investigate whether the biocides in Tanaco Fluestop enter the gas phase or stays on the surface, an emission test in a FLEC (Field and Laboratory Emission Cell) was performed.

Sampling procedure for the FLEC experiments

The FLEC is a circular small emission cell/chamber with an internal volume of 35 mL and an internal diameter of 150 mm (~ 0.0177 m² material areas) and made of stainless steel. An air supply is connected to the emission cell inlet. The air is then distributed by a channel following the perimeter and providing an evenly distributed flow over the test material surface. The air leaves the emission cell at the top center. Active sampling of the outlet air is performed by connecting adsorbent tubes to the outlet couplings and using calibrated low-flow sampling pumps.

An experiment with Tanaco Fluestop in duplicate was performed and the test conditions were: Inlet air flow rate at 450 mL/min, 50% RH and 22°C.

Two clean glass plates were softly sprayed with Tanaco Fluestop (0.7g and 1g) for 2 sec. and the test materials were immediately placed under the FLECs. A third FLEC with a clean glass plate was used as blank.

Samples of the outlet air were collected in duplicate using the adsorbent tubes Tenax TA and XAD-2 with a sampling flow rate of 100 ml/min on Tenax TA and 200 ml/min on XAD. The sampling time was 10 min for Tenax TA and 30 min for XAD-2.

The sampling strategies were as followed in duplicate:

- For Tenax TA: a background sample on the clean glass plate and a sample 5 min after the Tanaco Fluestop was applied on the glass plate and placed under the FLEC, then every hour for the next 4-5 hours and after 24 hours.
- For XAD-2: a background sample on the clean glass plate and 4 hours after the Tanaco Fluestop was applied on the glass plate and placed under the FLEC, then 24 hours and 48 hours.

Samples on Tenax tubes were taken to measure the volatile organic components and on XAD2 tubes to measure the biocides in the gas phase.

After the experiments were finished the surfaces of the glass plates and the surfaces in the FLECs were wiped in order to measure the surface concentration of biocides. For details of the sampling tubes/wipes, extraction methods and analysis, see paragraph 6.2.5.

6.2.7 Aerosol particle measurements

Number size distribution measurements were conducted to measure size distribution spectra from 6 nm to 10 µm from different locations in the chamber. We used three different instruments; 1) Fast Mobility Particle Sizer (FMPS, TSI Model 3091, Shoreview, NM), at one second time resolution in the measurement range: 0.056-0.56 µm; the sampling flow was 10 L/min and with exhaust outside the chamber, 2) SMPS nanoparticle sizer (NanoScan, TSI Model 3910, Shoreview, NM), measurement range is from 10 to 420 nm with one minute resolution and OPS (Optical Particle Sizer) was used to measure particles from 320 nm to 10 µm with one minute resolution. In the data analysis all online data is averaged to 1 minute.

In addition we used also ELPI (Electric Low Pressure Impactor, Dekati Ltd.) and SMPS (Scanning Mobility Particle Sizer) to measure in the same location as NanoScan. We found that the mixing inside the chamber was so fast that one measurement position is representative for the exposure concentration. Measured data was similar from between the instruments in the different locations and therefore focused to use FMPS, NanoScan and OPS to cover the size range of particles (droplets) that can reach alveolar region of the lung. Particles larger than 10 µm are still inhalable, and are deposited in the head airways, however terminal settling velocity for 10 µm particle in standard conditions is 18 cm/min (See Figure 6-2). Therefore, lifetime of the bigger particles is short compared to the exposure time (240 min).

Total number concentration was integrated from the number size distribution measurements. Number size distributions and total number concentrations were converted to the mass. A mean density of 1.2 for spherical (SOA) particles was assumed for the mass calculations.

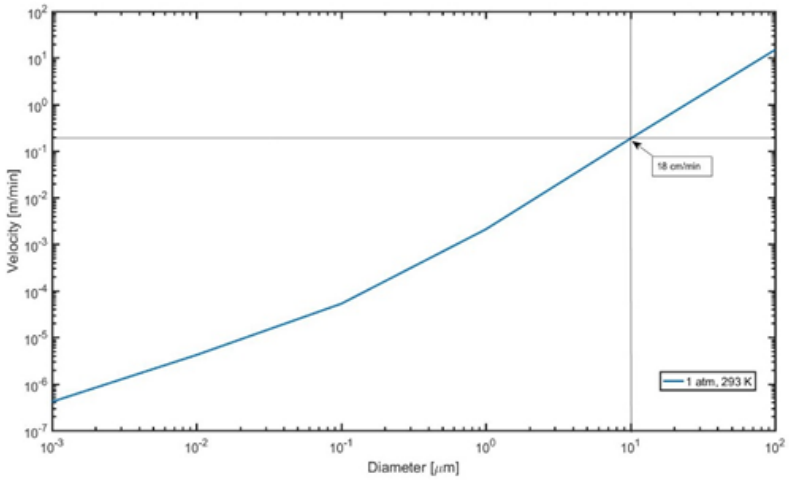


Figure 6-2 Terminal settling velocity for spherical particles as function of aerodynamic diameter (Standard density at 293 K).

6.3 Model evaluations

Exposure to biocidal spray products for both professional and private users is related to the use phase. The total exposure can thus be divided into three distinct phases; 1) mixing/diluting and loading of the product to the final application concentration, 2) application (spraying) and 3) post-application phase. Primary exposure is directly related to the first two phases; whereas secondary exposure is related to the third phase e.g. from evaporation from or contact with the treated surface. Secondary exposure is also a concern for bystanders during spraying and for persons (especially children) in the sprayed area who might have skin contact to treated or contaminated surfaces.

6.4 Exposure calculations in ConsExpo and BEAT

The exposure to the selected products, Tanaco Fluestop, Demand CS and Ecolab Mikro-Quat Extra, was calculated in ConsExpo and BEAT using default scenarios, as well as scenarios where model parameters were adjusted to experimental conditions. In order to compare with the experimental measurements described in 6.2, calculations were performed on the application phase. Both the exposure by inhalation and the dermal exposure were included. Further, the secondary exposure to two of the products (Tanaco Fluestop and Demand CS) was calculated in ConsExpo and compared with results from the surface wiping obtained from the experimental measurements.

For all three selected products calculations were made of the primary exposure of the user, including the period immediately after use of the product. The secondary exposure was calculated for Tanaco Fluestop and Demand CS. For the secondary exposure, a worst case exposure was considered where a child is crawling on the exposed area with exposure of skin as well as hand-to-mouth contact. The parameters used for each of the products in the exposure calculations is described below.

For primary exposure, the exposure in at least two scenarios for each product was calculated. This includes calculations of exposure in a “default scenario” where the calculations were based completely on the default values in ConsExpo or BEAT. Further scenarios in the ConsExpo calculations, where the experimental setup was taken into consideration, was calculated in

order to compare with the experimental measurements. In these calculations, parameters as the room size, spray duration etc. was set to match with the experimental setup. All used parameters can be seen in tables below. The data from the air measurements could not be entered in the ConsExpo, and therefore default values for size distribution of the particles were used also in the second set of calculations. For Demand CS and Mikro-Quat Extra, which are intended for professional users, the exposure was estimated both in BEAT and ConsExpo to compare the two software estimations. For Mikro-Quat Extra two scenarios in ConsExpo was compared.

Calculations were made for all active substances in the products. Substances of concern and other non-active compounds present in the biocide products were not evaluated in this project, as the objective was to evaluate the quality of ConsExpo and BEAT as assessment tools and not on specific risk assessments of the selected products.

6.4.1 Tanaco Fluestop

Tanaco Fluestop is a biocide used for rapid control of flying insects. It contains the following active substances: Piperonyl butoxide, Permethrin (cis/trans), and Pyrethrum extract (Pyrethrin I & II). The physical parameters of the active substances used in the exposure assessment is given in Table 6-6.

Table 6-6 Physical parameters for active substances in Tanaco Fluestop

Active substance name (conc.)	Piperonyl butoxide (1.22 %)	Permethrin (cis/trans) (0.216 %)	Pyrethrum extract (0.5%)
CAS	CAS 51-03-6	52645-53-1	8003-34-7
Mol weight	338.44 g/mol	391.29 g/mol	700.91 g/mol
Log Kow	4.75	6.1	6.15
Vapour pressure	$5.2*10^{-6}$ mm Hg at 25 °C	$2.155*10^{-6}$ mm Hg at 20°C	$3.0*10^{-6}$ mm Hg at 25°C

Tanaco Fluestop is a product for private users. Therefore, the exposure was assessed using the ConsExpo software. Based on the instructions for use, the air space application scenario for Pest control spray products was selected as the most representable scenario in ConsExpo. Three different scenarios were calculated for exposure to each active substance in the product. Two for primary exposure and one for secondary exposure. These are listed in the Table 6-7.

Table 6-7 List of scenarios for calculation of exposure to the active substances in Tanaco Fluestop

Scenarios	**Description**
Primary exposure	
Scenario 1, ConsExpo default	Default scenario using the ConsExpo scenario: Pest control, spray product, air space application. All values are defaults.
Scenario 2, ConsExpo mix	Mix scenario using the ConsExpo scenario: Pest control, spray product, air space application where parameters on surroundings are based on the experimental setup
Secondary exposure	
Scenario 3, ConsExpo child	Default scenario using the ConsExpo scenario: Pest control, spray product, air space, post application (child). All values are defaults

Primary exposure, Scenario 1 and 2:

To assess the primary exposure to Tanaco Fluestop, the most relevant scenario in ConsExpo was identified as: Pest control, spray product, air space application. Default values for this scenario were used in the calculation of exposure to the spray. All parameters can be seen in Table 6-8. In Scenario 1, all values are defaults (column 1). In scenario 2, the relevant experimental parameters were used instead of default values (column 2). In all cases, when no value from the experimental setup was available, the default value from Pest control, spray product, air space application was applied. Although the particle size distribution was measured in the present study, it was not possible to insert the data in the used version of ConsExpo, and therefore the defaults for particle size distribution were used in both scenarios.

Table 6-8 Parameters used in scenarios for Tanaco Fluestop

Parameter	**Default ConsExpo; Pest control, spray, air space application**	**From experimental setup**
Room volume	58 m^3	20.3 m^3
Ventilate rate	0.5 /h	0.5 /h
Exposure duration	240 minutes	-
Spray duration	0.33 minutes	10 sec
Room height	2.5 m	2.5 m
Mass generation rate	0.75 g/sec	3.1 g/sec
Airborne fraction	1	-
Weight fraction propellant	0.6	-
Density non-volatile	1.8 g/cm^3	-
Particle distribution median	20 µm	-
Weight fraction non-volatile	Same as AS conc.	-
Particle distribution C.V.	0.4 fraction	-
Inhalation cut off	15 µm	10 µm
Evaporation:	fast	-
Spray direction:	from person upwards	-
Exposure frequency	90 times/year	1/day
Contact rate	269 mg/min	-
Exposure duration for dermal exposure	0.33 min	10 sec
Exposed area	1.124 $m^{2(*)}$	-

(*) Calculated from defaults in ConsExpo general fact sheet

Secondary exposure, scenario 3:

For calculation of the secondary exposure to Tanaco Fluestop, the same scenario in ConsExpo, Pest control, spray, air space application, was used for the calculation of the exposure to a child crawling on exposed area. Parameters are shown in Table 6-9.

Table 6-9 Parameter values used for assessment of dermal exposure to Tanaco Fluestop in scenario 3 (secondary exposure)

Parameter	Value	Source of value
Dermal parameters		
Child weight:	8.69 kg	Default ConsExpo
Surface area exposed	2800 cm^2	Calculated from defaults in ConsExpo general fact sheet (ref)*
Dislodgeable amount	0.8 g/m^2	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Exposure duration: 60 min	60 min	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Rubbed surface:	22 m^2	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Transfer coefficient:	0.6 m^2/h	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Actual rubbed off area:	22*0.6= **13.2 m^2**	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Dermal uptake fraction	100%	Default dermal uptake, worst case
Oral parameters		
Exposure duration:	60 min	Default ConsExpo; Pest control, spray, air space application, child crawling on exposed area
Ingested amount:	10% of external dermal exposure	Default fraction, ConsExpo
Uptake fraction:	100%	Default oral uptake, worst case

*Uncovered skin (hands, feet, arms, legs, head) = 65% of total. Skin of child 10.5 month, total body: 0.437 m^2 (Default)

6.4.2 Demand CS

Demand CS is an indoor insecticide for professional use. The active substance in Demand is lambda-cyhalothrin. Table 6-10 shows the physical characteristics of lambda-cyhalothrin used in the assessment of the exposure.

Table 6-10 Physical parameters for active substance in Demand

Active substance name (conc.)	lambda-cyhalothrin (9.7 %, in use: 0.2%)
CAS	91465-08-6
Mol weight	449.85 g/mol
Log Kow	7
Vapour pressure	$3.6*10^{-10}$ mm Hg at 25 °C

Four scenarios were addressed for the calculation of exposure to Demand CS. In order to compare the chosen assessment tools, calculations were performed in both BEAT and ConsExpo. The scenario Low pressure spraying (Dutch pest control spraying), was chosen as the most representable scenario for the product in BEAT. BEAT is normally the preferred software tool for calculation of exposure for products for professional use. However, the crack and crevice application for pest control spray products in ConsExpo was also identified as a suitable scenario and thus evaluated here. The four scenarios are listed in Table 6-11.

Table 6-11 Exposure scenarios for calculation of exposure to Demand

Scenarios	**Description**
Primary exposure	
Scenario 1, BEAT	Low pressure spraying (Dutch pest control spraying) in BEAT (professional user). Default values in BEAT combined with time used in experimental setup.
Scenario 2, ConsExpo default	Default scenario using the ConsExpo scenario: Pest control, spray, crack and crevice. All values are defaults.
Scenario 3, ConsExpo mix	Mix scenario using the ConsExpo scenario Pest control, spray, crack and crevice application where parameters on surroundings are based on the experimental setup
Secondary exposure	
Scenario 4, ConsExpo child	Default scenario using the ConsExpo scenario: Pest control, spray, crack and crevice, post application (child). All values are defaults

Primary exposure - BEAT

BEAT is considered the most relevant tool for assessing the exposure for professional users. The scenario Low pressure spraying (Dutch pest control spraying), was chosen as the most representative scenario for the product. The used parameters are shown in Table 6-12.

Table 6-12 Parameter values used for assessment of exposure to Demand CS in scenario 1 in BEAT (primary exposure)

Parameter	Default value in Low pressure spraying (Dutch pest control spraying), BEAT	Based on experimental set-up
Inhalational parameters		
Indicative value	27.01 µl/m^3	-
Duration		4.5 sec
Inhalation rate	1.25 m^3/h	-
Mitigation by RPE (PF):	None (1)	-
Dermal parameters		
Total body exposure, indicative value	86 µl/min	-
Duration:		4.5 sec
Clothing type	50% penetration (minimal clothing)	-
Hand exposure, indicative value (potential)	126 µl/min	-
Mitigation by gloves	0.1 (10% penetration)	-
Dermal absorption	100 %*	

*Default dermal exposure, worst case

Primary exposure – ConsExpo

The primary exposure assessment to Demand CS in BEAT was compared with the most relevant scenario in ConsExpo, i.e. Pest control, spray product, crack and crevice application. Default values for this scenario were used in the calculation of exposure to the spray. All parameters can be seen in the Table 6-13. In Scenario 1, all values are defaults (column 1). In scenario 2, the relevant experimental parameters were used instead of default values (column 2). In all cases, where no value from the experimental setup was available, default from Pest control, spray product, crack and crevice application were applied.

Table 6-13 Default values and values from the experimental setup used for the parameters in the calculation of exposure to Demand CS in ConsExpo for scenario 1 and 2

Parameter	Default ConsExpo; Pest control, spray, crack and crevice	From experimental setup
Room volume	58 m^3	20.3 m^3
Ventilate rate	0.5 /h	0.5 /h
Exposure duration	240 minutes	-
Spray duration	0.33 minutes	4.5 sec
Room height	2.5 m	2.5 m
Mass generation rate	0.38 g/sec	-
Airborne fraction	1	-
Weight fraction propellant	0.5	-
Density non-volatile	1.8 g/cm^3	-
Particle distribution median	25 µm	-
Weight fraction non-volatile	Same as AS conc.	-
Particle distribution C.V.	0.4 fraction	-
Inhalation cut off	15 µm	10 µm
Evaporation:	fast	-
Spray direction:	from person upwards	-
Exposure frequency	90 times/year	1/day
Contact rate	269 mg/min	
Exposure duration for dermal exposure	0.33 min	4.5 sec
Exposed area	1.124 m^2	-

(*) Calculated from defaults in ConsExpo general fact sheet

Secondary exposure – ConsExpo

Crack and crevice scenario in ConsExpo, child crawling on exposed area. Default parameters for this scenario was used and shown in Table 6-14.

Table 6-14 Parameter values used for assessment of dermal exposure to Demand in scenario 4 (secondary exposure)

Parameter	Value	Source of value
Inhalational parameters		
Child weight:	8.69 kg	Default ConsExpo
Surface area exposed	2800 cm^2	Calculated from defaults in ConsExpo general fact sheet* (ref)
Dislodgable amount	11.6 g/m^2	Default ConsExpo; Pest control, spray crack and crevice, child crawling on exposed area
Exposure duration: 60 min	60 min	Default ConsExpo; Pest control, spray crack and crevice, child crawling on exposed area
Rubbed surface:	2 m^2	Default ConsExpo; Pest control, spray, crack and crevice, child crawling on exposed area
Transfer coefficient:	0.6 m^2/h	Default ConsExpo; Pest control, spray, crack and crevice, child crawling on exposed area
Actual rubbed off area:	2*0.6= **1.2 m^2**	Default ConsExpo; Pest control, spray, crack and crevice, child crawling on exposed area
Dermal uptake fraction	100%	Default dermal uptake, worst case
Dermal parameters		
Exposure duration:	60 min	Default ConsExpo; Pest control, spray, crack and crevice, child crawling on exposed area
Ingested amount:	10% of external dermal exposure	Default fraction, ConsExpo
Uptake fraction:	100%	Default oral uptake, worst case

*Uncovered skin (hands, feet, arms, legs, head) = 65% of total. Skin of child 10.5 month, total body: 0.437 m^2 (Default)

6.4.3 Mikro-Quat Extra

Ecolab Mikro-Quat Extra is a product for disinfection and cleaning for professional users. The active biocide substances in Mikro-Quat Extra is benzalkonium chloride and didecyl dimethyl ammonium chloride. Table 6-15 shows the physical parameters for the active substance(s) used in the assessment. The concentration of the active substances was measured in a recently finished project by Kjeldgaard et al. (2017) to be 7.6% benzalkonium chloride and 1,1% didecyl dimethyl ammonium chloride. The product is used in a 2% solution giving the use concentrations of 0.15 % and 0.02 % for benzalkonium chloride and didecyl dimethyl ammonium chloride, respectively.

Table 6-15 Physical parameters for active substances in Mikro-Quat extra

Active substance name (conc.)	Benzalkonium chloride (7.6%, in use 0.16%)	Didecyl dimethyl ammonium chloride (1.1%, in use 0.02%)
CAS	68424-85-1	7173-51-5
Mol weight	368 g/mol	362 g/mol
Log Kow	3.91	2.59
Vapour pressure	$3.6*10^{-10}$ mm Hg at 25°C	$<4.3*10^{-5}$ mm Hg at 25°C

2% dilution (106 g product in 5 L = 2.12% solution = 0.16 % Benzalconium chloride)

Five scenarios were addressed for the calculation of exposure to the Mikro-Quat Extra. In order to compare the chosen assessment tools, calculations were performed in both BEAT and ConsExpo. The 5 scenarios are listed in Table 6-16.

Table 6-16 Exposure scenarios for calculation of exposure to Demand

Scenarios	**Description**
Primary exposure	
Scenario 1, BEAT	*Spraying for disinfection* in BEAT (professional user). Default values in BEAT combined with time used in experimental setup.
Scenario 2, ConsExpo default, disinfection	Default scenario using the ConsExpo scenario *disinfectants for indoor use, spraying*. All values are defaults.
Scenario 3, ConsExpo mix, disinfection	Mix scenario using the ConsExpo scenario *disinfectants for indoor use, spraying* where parameters on surroundings are based on the experimental setup
Scenario 4, ConsExpo default, cleaning	Default scenario using the ConsExpo scenario *cleaning and washing, all purpose cleaners, spraying*. All values are defaults.
Scenario 5, ConsExpo mix, cleaning	Mix scenario using the ConsExpo scenario *cleaning and washing, all purpose cleaners, spraying* where parameters on surroundings are based on the experimental setup

Primary exposure BEAT

As Mikro-Quat Extra is a product for professional use, BEAT is considered the most relevant tool for assessing the exposure. The scenario *spraying for disinfection* was chosen as the most representable scenario for the product (parameters for Scenario 1 are shown in Table 6-17).

Table 6-17 Parameter values used for assessment of inhalational exposure to Mikro-Quat Extra in BEAT (primary exposure)

Parameter	Default value in spraying for disinfection, BEAT	Based on experimental setup
Inhalational parameters		
Indicative value	97.47 µl/m^3	-
Duration		0.1 min
Inhalation rate	1.25 m^3/h	-
Mitigation by RPE (PF):	None (1)*	-
Dermal parameters		
Total body exposure, indicative value	2400 µl/min	-
Duration:		0.1 min
Clothing type	50% penetration (minimal clothing)	-
Hand exposure, indicative value (actual)	9.395 µl/min	-
Mitigation by gloves	None Not applicable as hand value is actual (measured with gloves)	-
Dermal absorption	100 %**	-

*None required according to SDS
** Default dermal exposure, worst case

Primary exposure – ConsExpo

2 scenarios in ConsExpo were calculated (see table 6-16). First the exposure was calculated using the scenario of Disinfectants for indoor use, spraying. Default values for this scenario were used in the calculation of exposure to the spray. All parameters can be seen in the table 6.18 below. In Scenario 2, all values are defaults (column 1). In scenario 3, the relevant experimental parameters were used instead of default values (column 2). In all cases, where no value from the experimental setup was available, default from Disinfectants for indoor use, spraying were applied.

Table 6-18 Default values and values from the experimental setup used for the parameters in the calculation of primary exposure to Mikro-Quat Extra for scenario 2 and 3 based on the default scenario for disinfection in ConsExpo

Parameter	Default ConsExpo; Disinfectants for in-door use, spraying	From experimental setup
Room volume	15 m^3	20.3 m^3
Ventilate rate	2.5 /h	0.5 /h
Exposure duration	60 minutes	60 minutes
Spray duration	0.51 minutes	5 sec
Room height	2.5 m	2.5 m
Mass generation rate	0.75 g/sec	-
Airborne fraction	0.2	-
Density non-volatile	1.8 g/cm^3	-
Particle distribution median	50 µm	-
Weight fraction non-volatile	Same as AS conc.	-
Particle distribution C.V.	0.6 fraction	-
Inhalation cut off	15 µm	10 µm -
Spray direction:	from person	-
Exposure frequency	365 times/year	1 time/day
Contact rate	46 mg/min	-
Release duration for dermal exposure	0.51 min	0.1 min
Exposed area	1.124 $m^{2(*)}$	-

(*) Calculated from defaults in ConsExpo general fact sheet

ConsExpo scenario: Cleaning and washing, all-purpose cleaners, spraying

Next, the exposure to Mikro-Quat Extra was calculated using the scenario of Cleaning and washing, all-purpose cleaners, spraying. Default values for this scenario were used in the calculation of exposure to the spray. All parameters can be seen in the table 6.19 below. In Scenario 4, all values are defaults (column 1). In scenario 5, the relevant experimental parameters were used instead of default values (column 2). In all cases, where no value from the experimental setup was available, default from Cleaning and washing, all-purpose cleaners, spraying were applied.

Table 6-19 Default values and values from the experimental setup used for the parameters in the calculation of primary exposure to Mikro-Quat Extra for scenario 4 and 5 based on the default scenario for cleaning in ConsExpo

Parameter	Default ConsExpo; Cleaning and washing, all purpose cleaners, spraying	From experimental setup
Room volume	15 m^3	20.3 m^3
Ventilate rate	2.5 /h	0.5 /h
Exposure duration	60 minutes	60 minutes
Spray duration	0.41 minutes	0.1 minutes
Room height	2.5 m	2.5 m
Mass generation rate	0.78 g/sec	-
Airborne fraction	0.2	-
Weight fraction propellant	0	-
Weight fraction non-volatile	0.05	-
Weight fraction solvent	1	-
Density non-volatile	1.8 g/cm^3	-
Particle distribution median	100 µm	-
Weight fraction non-volatile	Same as AS conc.	-
Particle distribution C.V.	0.6 fraction	-
Inhalation cut off	15 µm	10 µm
Evaporation	slow	-
Spray direction:	from person	-
Exposure frequency	365 times/year	-
Contact rate	46 mg/min	-
Release duration for dermal exposure	0.41 min	0.1 min
Exposed area	1.124 $m^{2(*)}$	-

$^{(*)}$ Calculated from defaults in ConsExpo general fact sheet

6.5 Comparison of model derived exposure assessments with specific exposure measurements

Measured primary and secondary exposure for the three products were compared with the assessments made in ConsExpo and BEAT. Margin of Exposure (MoE) or RCR was not calculated for the different exposure scenarios as the scope of the present project was not to evaluate the risk of the exposure. Emphasis were put on the comparison of actual measurement data with model calculations for the same scenarios performed in ConsExpo and BEAT. The comparisons of the assessments made in ConsExpo and BEAT with actual measurements were used to identify knowledge gaps, including concrete parameters missing in the models. This formed the basis of an analysis of concrete improvements to be proposed for exposure calculations using these models.

7. Results

7.1 Results of the measurements

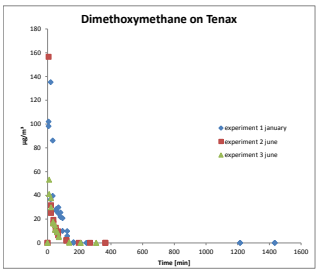
7.1.1 Tanaco Fluestop

Figure 6-1 shows the experimental setup for studying the dispersion of the biocide sprays inside the chamber. The aim was to follow to follow the development of the aerosol, gaseous and surface deposited substance from the initial spray event to the time point when airbourne concentrations reached the background level. The inorganic fraction in Tanaco Fluestop was less than 0.2% estimated by TGA. The emission test experiment was repeated 3 times (for conditions, see Table 6-2). All airborne identified chemicals were quantified by sampling on Tenax TA and XAD-2 tubes, see Table 6-1.

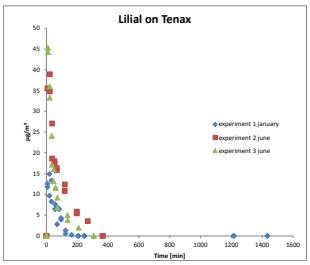
Samples collected on Tenax TA and XAD-2 tubes

The main substances, the biocides and n-alkanes, were present on both Tenax and the XAD-2 tubes. It is assumed that both the gas and particle phases of the substances are collected during the air sampling. This is reflected in relative ratios between the sampling methods of 0.75, 2, 5-7, and 1.2 for alkanes, permethrin, piperonyl butoxide and pyrethrum extract, respectively. This is in part, caused by the large difference in the sampling flows and volumes, Tenax (2 l) versus XAD (20 l); which may have influenced the sampled fraction of particles and their size distribution. Note, it was not possible to spray exactly the same amount in each exposure scenario due to the short spraying time, which is reflected by variations in the concentrations of VOCs and SVOCs.

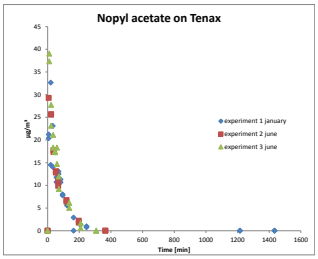
a)



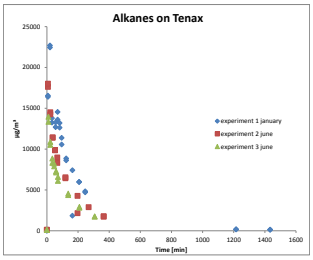
b)



c)



d)



e)

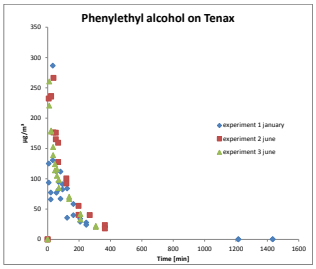
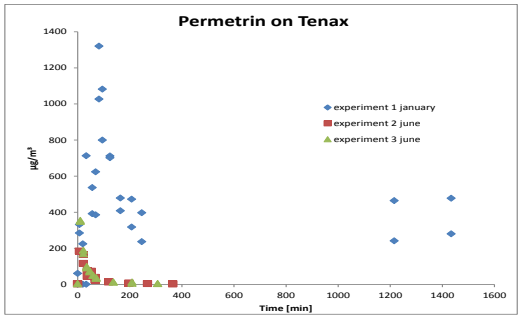


Figure 7-1 Concentration of the Tenax TA measurements

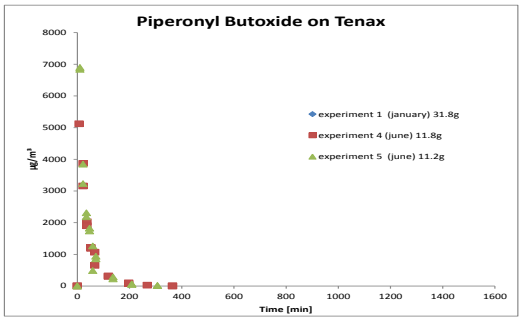
Figure 7-1 and 7-2 are presenting concentration of substances measured by Tenax TA tubes during the spray experiments. Data point at time 0 is the pre-spraying background concentration. This was measured to ensure that the chamber was clean. The background measurements were done after chamber was flushed and the aerosol concentration was at background level.

The biocides, and the additives lilial and dimethoxy methane, where no longer detected in the chamber air about 3 hours after spraying; generally, much faster than a first-order decay following the air exchange rate (see Fig.7-1a, b and Fig.7-2). This behavior was also observed for the aerosol particles. This implies that the above mentioned compounds mainly were associated with the aerosols and may have deposited fast along with the aerosols on the chamber walls. The decay of the alkanes, phenylethyl alcohol and nopyl acetate followed a first-order decay reaching baseline after 4 to 6 hours (Fig. 7-1c, d, e).

a)



b)



c)

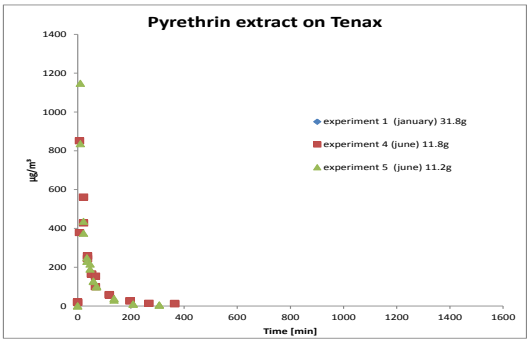


Figure 7-2 Concentration of the biocides measured on Tenax TA tubes

FLEC measurements on Fluestop

On the Tenax TA tubes the volatile substances e.g. dimethoxy methane and lilial were detected. No biocides were detected in any of the XAD-2 tubes from the FLEC-experiment. Table 7-1 shows the percentage of biocides in the total mass sprayed on the surfaces of the glass plate and FLEC compared to the contents in the product.

Table 7-1 Percentage of biocides on the surfaces of the glass plate and the FLEC (after 48h) of the total mass spray compared to the content in the original product. (n.d.: not detected)

Chamber	Surface	Permetherin (0.2% in product)	Pyrethrum extract (0.5% in product)	Piperonyl butoxide (1.2% in product)
A	Glass	0.2	0.9	0.5
B	Glass	0.1	0.5	0.5
C (blank)	Glass	n.d.	n.d.	n.d.
A	FLEC	0.0008	0.0007	0.003
B	FLEC	n.d.	n.d.	0.0007
C (blank)	FLEC	n.d.	n.d.	n.d.

The biocides were recovered on the glass surface and while nothing were detected on the FLEC surface. Given the uncertainty of the product application to the glass plate and the wiping method into account, the percentage content of each biocides from the product (Fluestop) were largely found on the wipes.

These FLEC experiments show that the biocides in Fluestop remain on the surface, where it is applied, for at least 48 hours under the applied test conditions.

Conclusions from the FLEC experiment

- The organic additives (lilial, dimethoxy methane, nopyl acetate, alkanes, and phenylethyl alcohol) from Fluestop were all detected on the Tenax TA tubes.
- No biocides were detected on the XAD tubes, thus the emission of biocides from Fluestop was limited in the FLEC.
- The biocides in Fluestop remained largely on the surface where it was applied for at least 48 hours (under the conditions: 22°C, 50% RH and a flow rate of 450mL/min).

Aerosol measurements

Figure 7-3 shows the development of the number size distribution during the experiment integrated from OPS and NanoScan measurements (from 0.01 µm to 10 µm), the upper panel shows the size distribution and lower panel the total number concentration data. The total number concentration prior to spraying was 300 cm^{-3} which increased rapidly after spraying of Fluestop. The maximum number concentration was 8000 cm^{-3} and the calculated total mass concentration was 310 mg/m^3 (assuming spherical particles and density 1.2). As it was previously described for the development in substance concentration, aerosol total number concentration was decreasing with time mainly due to the ventilation. The initial number concentration distribution peaked between 0.07 and 1 µm. We did online measurements overnight to observe if there were any changes in the aerosol size distribution, but it was unchanged, and after 13 hours aerosol total number concentration had reached background levels.

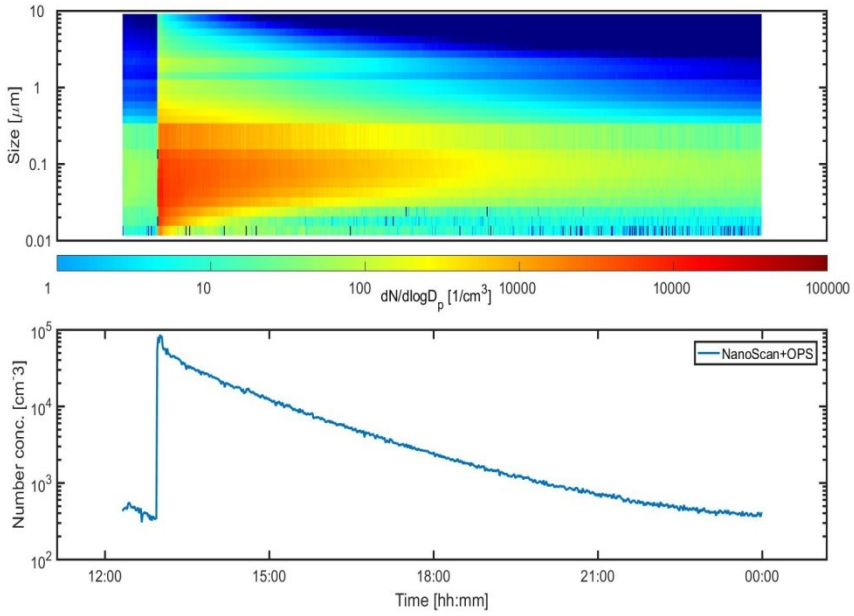


Figure 7-3 Upper panel: Aerosol number size distribution, lower panel: corresponding total aerosol number concentration during the Fluestop experiments.

Figure 7-4 presents concentration changes as function of time and initial size distribution spectra in number and mass. In Figure 7-4a number concentration for particles smaller than 0.3 µm (NanoScan, red line) and particles larger than 0.3 nm (OPS, black line) is illustrating removal of the particles from the chamber. Figure 7-4b shows that the mass concentration of particles above 0.3 µm is decreasing faster due to the deposition, for particles smaller than 0.3 µm dominating removal is ventilation. Figure 7-4a and d are presenting number (dotted line is pre experiment size distribution) and mass size distributions, respectively. Number size distribution is peaking in around 0.08 µm and mass distribution has one peak around 1.5 µm.

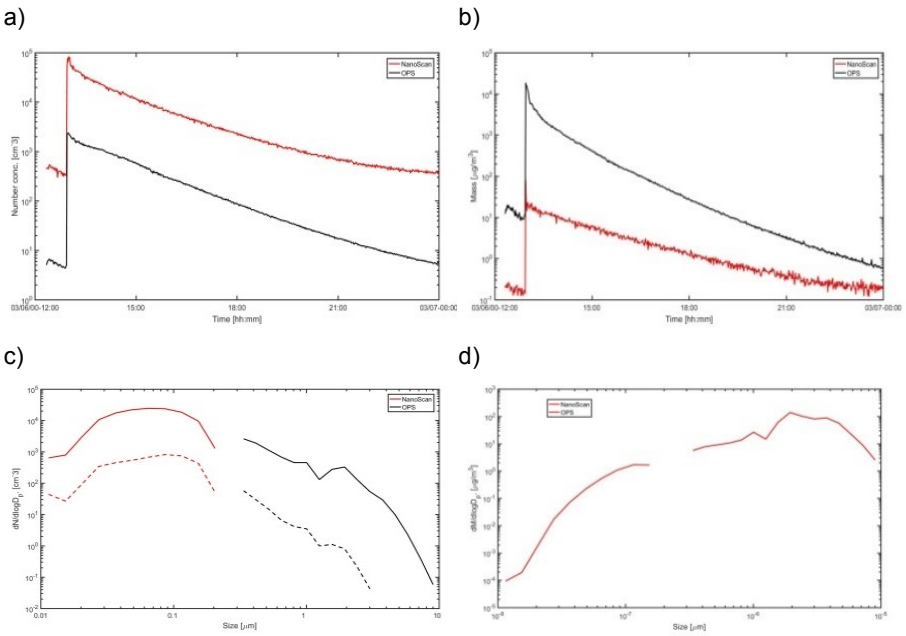


Figure 7-4 a) development of the total number concentration during the experiment. Data from OPS (black) and NanoScan (red) is presented separately. b) mass concentration calculated from the online data during experiments. c) and d) number and mass aerosol size distribution after spraying, respectively.

Figure 7-5 presents the development in number and mass concentration during the experiment. Both concentrations measures rapidly reached their maximum and then decayed over time following the air exchange rate. Mass concentration was decreasing faster, which can be explained by higher deposition rate of the larger (above 1 µm) particles, see Figure 1 for the settling velocities and Figure 7-4 for the differences between mass and number distribution.

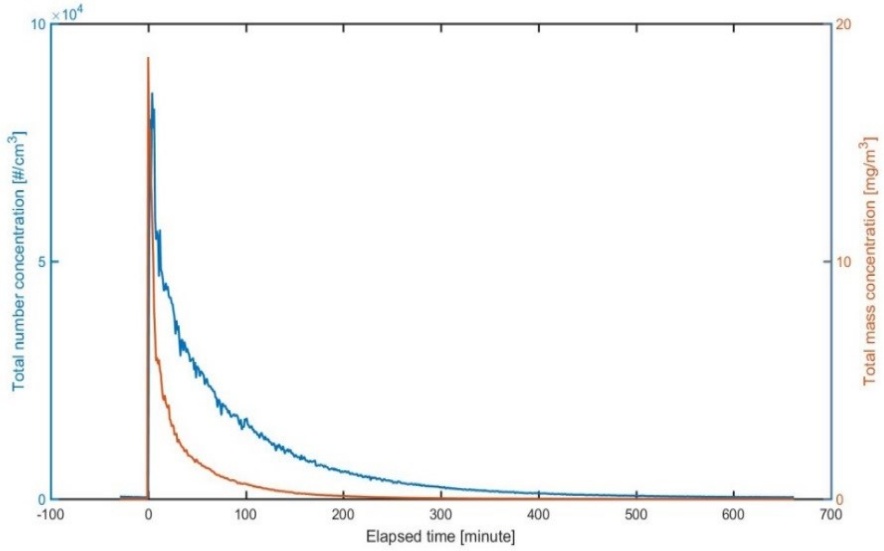


Figure 7-5 Development of total mass concentrations calculated from the NanoScan and OPS measurements

The calculated concentration of substances based on aerosol measurements can be compared with the results of the chemical analyses when assuming that the amount of active substance given by the manufacturer is correct. Table 7-2 presents concentrations calculated from the measured aerosol size distributions and concentrations from the chemical analysis. Aerosol

measurement number size distribution data is transformed to volume assuming spherical particles, volume is multiplied with the assumed density 1.05. These concentrations are then multiplied mass fraction of each substance. In addition, exposure was calculated following the values from ConsExpo (65 kg, inhaled volume 5.8 l).

Table 7-2 Exposure based on chemical and aerosol measurements.

	Piperonyl butoxide (mg/m^3)	Permethrin (mg/m^3)	Pyrethrum extract (mg/m^3)	Total (mg/m^3)
Aerosol measurement	3.8	0.69	1.6	6.1
Chemical measurement	4.8	0.020	0.068	4.9
	mg/kg bw/d	**mg/kg bw/d**	**mg/kg bw/d**	**mg/kg bw/d**
Aerosol measurement	0.34	0.06	0.14	0.54
Chemical analysis	0.43	0.0018	0.0060	0.44

The wipe samples showed that the biocides were deposited on the surfaces near the spray position, mostly on the floor and considerably less at child/adult height (Figure 7-6). Mean concentrations from 3 wipe tests at floor level were 2.3, 0.9, and 10.4 mg/m^2, respectively, for pyrethrum extract, permethrin, and piperonyl butoxide on day 1. Their concentrations were not statistically different the day after 24 hours. The personal exposure sampled on glass fibre filters did not detect any organic compounds including the biocides.

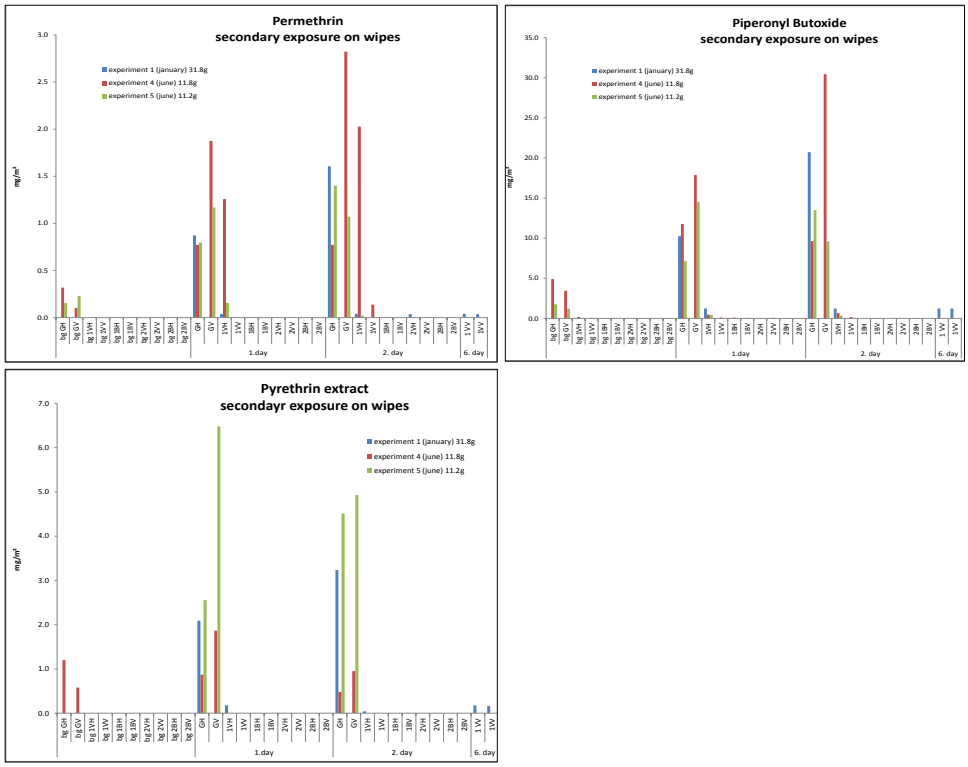


Figure 7-6 Surface deposition concentrations analysed from the wipe samples. bg: background, G:floor, V:adult, B:child, H/V: replicates at the same position

7.1.2 Demand CS

The inorganic fraction was less than 4 % estimated by TGA. The additive organic compounds were found on Tenax TA tubes only. They followed a first order decay reaching background level after approximately 7 hours. The decay of propylene glycol appeared erratic, see Figure 7-7.

The two biocides lambda-cyhalothrin and 1,2-benzisothiazol-3(2H)-one were neither detected on Tenax TA nor on the XAD tubes. The biocides were only detected on the sampled wipes, mostly on the floor and at children's height (position 1) near the spray area, while the amount at adult height was limited.

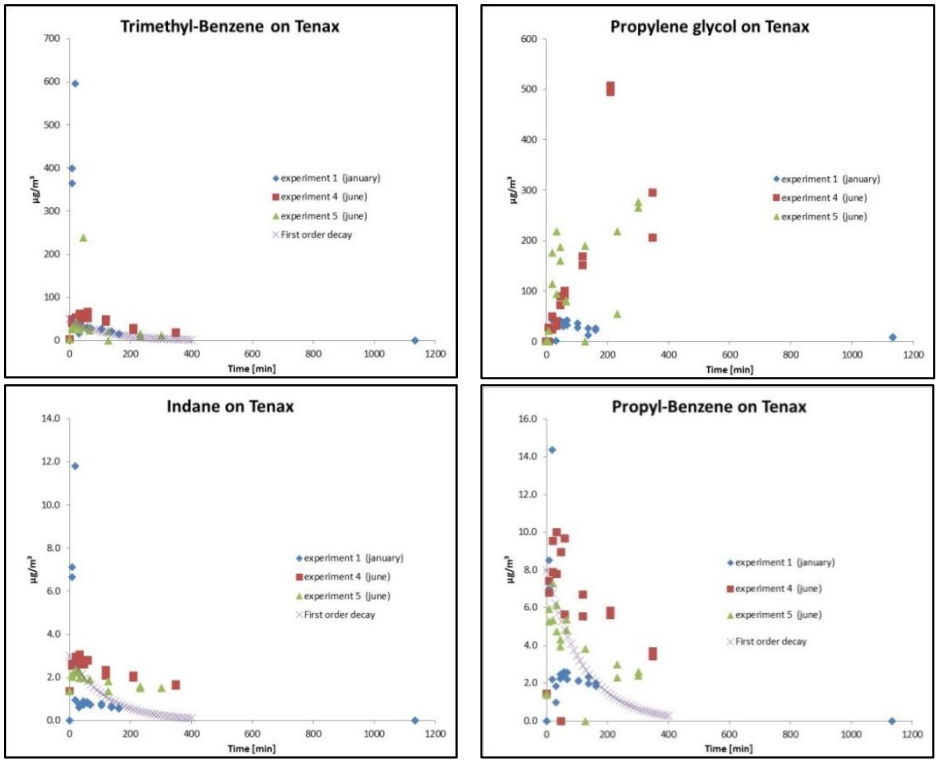


Figure 7-7 Concentrations of substances on the Tenax tubes after spraying Demand CS in the chamber.

Figure 7-8 presents aerosol size distribution and number concentration data during the Demand CS experiment. After the application a plume of particles above 0.5 µm was observed, however, the concentration was very low, less than 20 cm^{-3}.

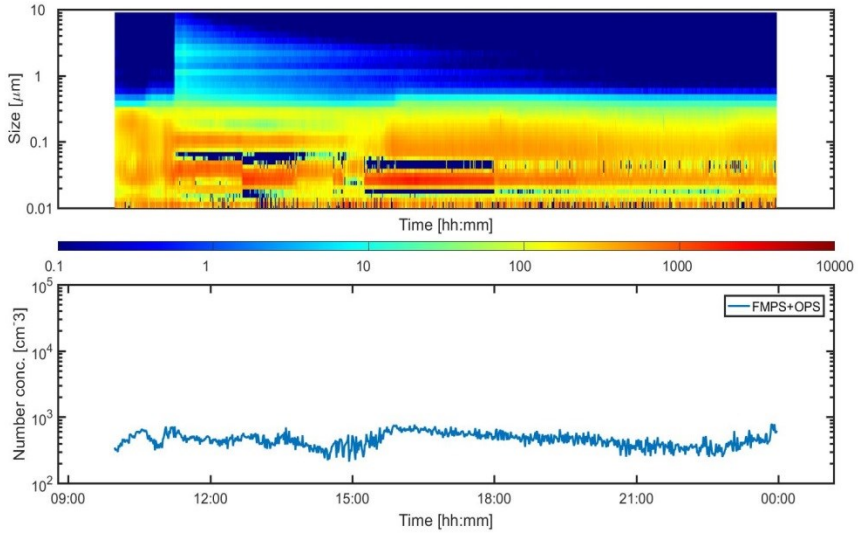


Figure 7-8 Upper panel: Aerosol number size distribution, lower panel: corresponding total aerosol number concentration during the Demand CS experiment.

Figure 7-9 presents concentration changes as a function of time and initial size distribution spectra in number and mass. In Figure 7-9a number concentration for particles smaller than 0.3 µm (NanoScan, red line) and particles larger than 0.3 nm (OPS, black line) are illustrating removal of the particles from the chamber. Figure 7-9a reveals clearly that concentration for particles under 0.3 µm we could not see any change compared to initial concentration in the chamber. This agrees with the chemical measurements from air where active compounds were under the limits of detection and total mass was 0.1 mg/m^3.

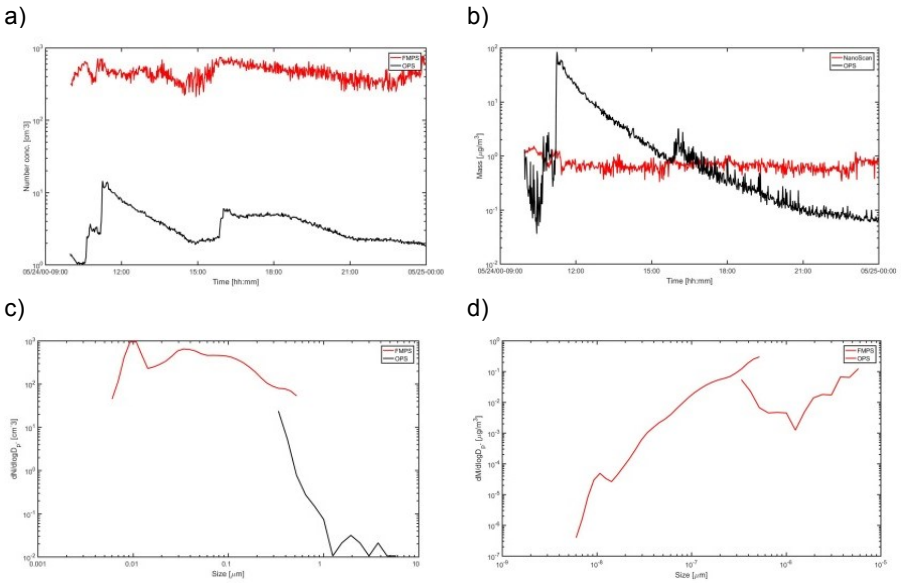


Figure 7-9 a) development of the total number concentration during the experiment. Data from OPS (black) and NanoScan (red) are presented separately. b) mass concentration calculated from the online aerosol data. c) and d) number and mass aerosol size distribution after spraying, respectively.

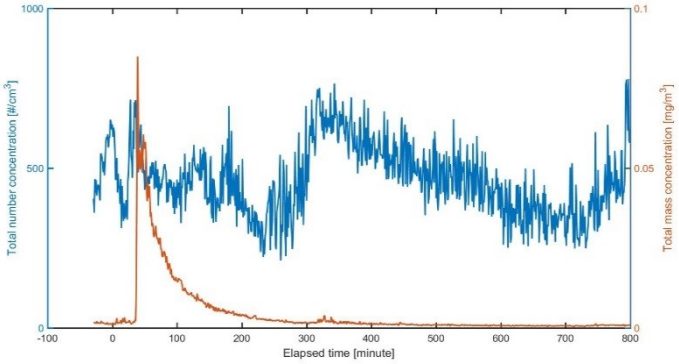


Figure 7-10 Development of total mass concentrations calculated from the FMPS and OPS measurements.

Results of secondary exposure (skin contact with surfaces) of biocides on wipes

The maximum level on the floor after spraying 4-5 sec were observed on the first day, where 5 and 11 mg/m^2 lambda-cyhalothrin and 1,2-benzisothiazol-3(2H)-one was measured, respectively. The level at children height was a factor of 5 and 2 lower, respectively, on the first day. The floor concentration was unaltered on day 2, while it was below limit of detaction at children height. The personal exposure on glass fibre filters was also below limit of detection for all organic compounds including the biocides.

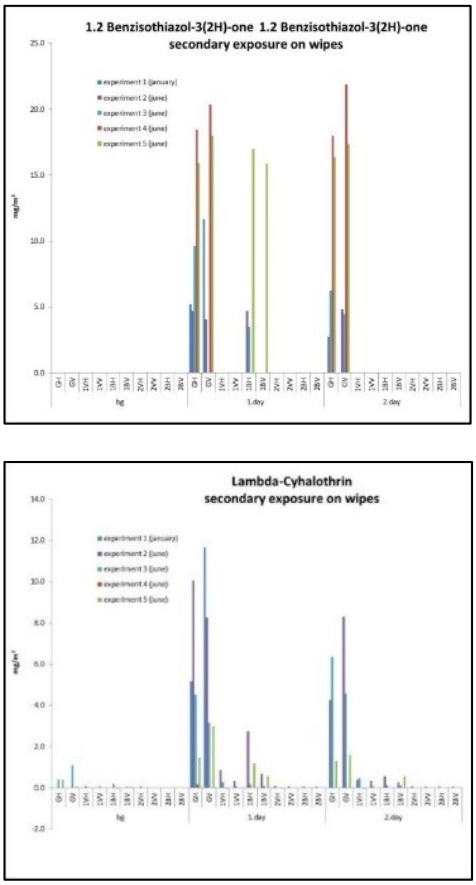


Figure 7-11 Concentrations of the secondary exposure of biocides on wipes.

7.1.3 Micro-Quat Extra

The inorganic fraction was less than 2% estimated by TGA. The main substances were identified on the XAD-2 tubes, not Tenax TA tubes, were benzalkonium chloride (benzyl dimethyl dodecyl ammonium chloride (in the following referred to as “dode”) and benzyl dimethyl tetradecyl ammonium chloride (in the following referred to as “tetra”)), see Figure 7-12. They were observed between 5 and 25 min after the spraying, peaking after about 9 min. The concentrations of the benzalkonium chlorides in the air from start to 40 min after spraying were higher or at same level as the limit of detection. The decay of the QAC in the chamber did not follow a first order decay; the QAC were below LOD after 40 min. This reflects that they have no vapour pressure and are completely associated with the aerosols.

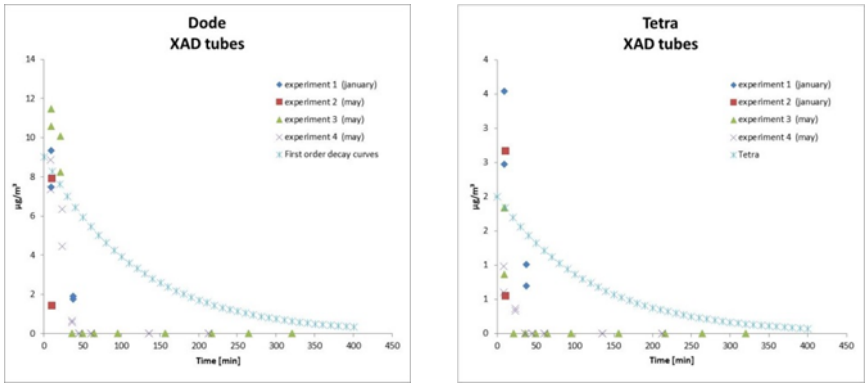


Figure 7-12 Concentrations of organic substances on the XAD tubes after spraying Micro-Quat in the chamber and first order decay curve simulating ventilation losses.

Figure 7-13 presents aerosol size distribution and number concentration data during the Mikro-Quat Extra experiment. After the application we could measure a plume of particles above 0.5 µm; however concentration was below 20 cm^{-3}, which is very low. For particles under 0.3 µm we could not see any effect compared to initial concentration in the chamber, thus this is the background concentration. This agrees with the chemical measurements from air where the active compounds were below the limits of detection and total mass concentration was 0.2 mg/m^3.

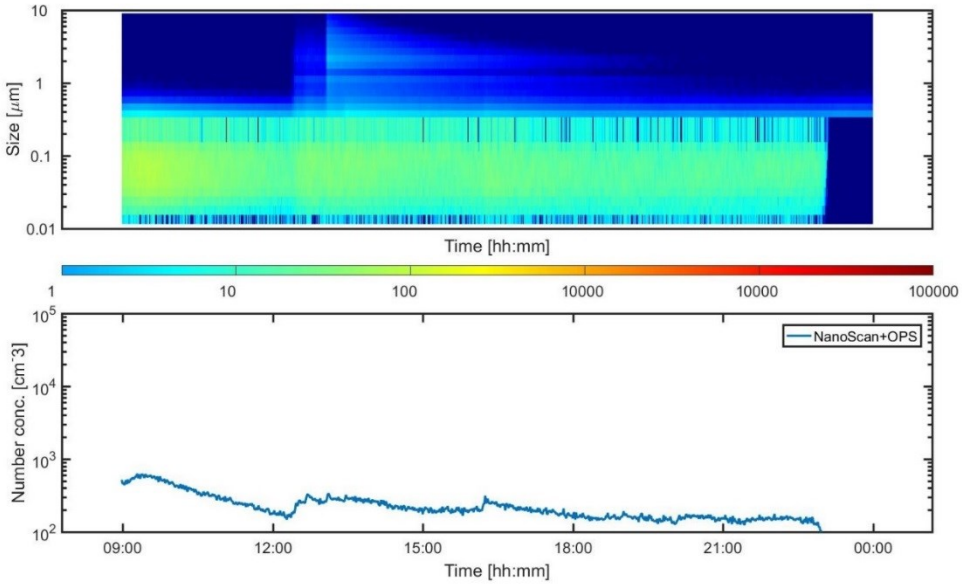


Figure 7-13 Development of the number size distribution during the experiments. Upper panel: aerosol number size distribution, and lower panel: corresponding total aerosol number concentration.

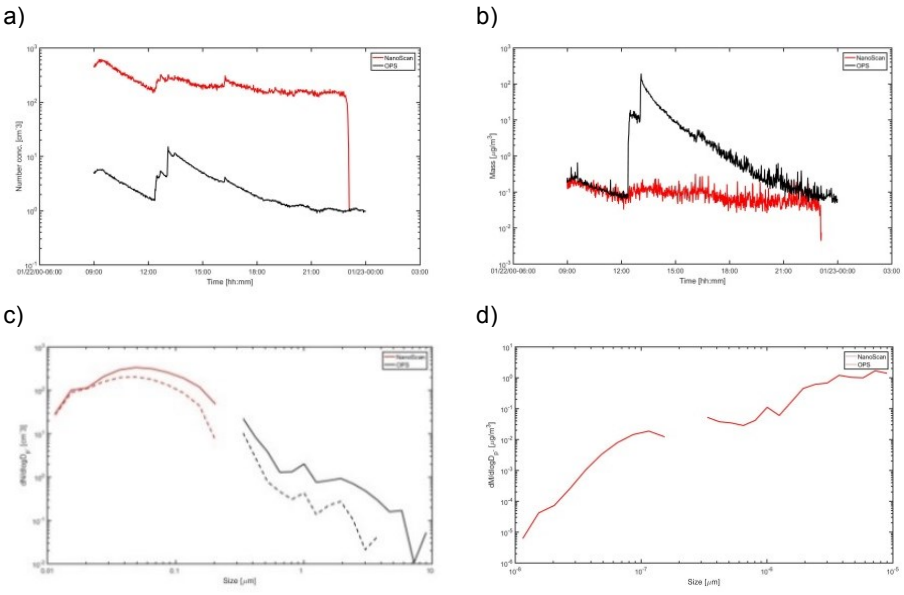


Figure 7-14 a) development of the total number concentration during the experiment. Data from OPS (black) and NanoScan (red) ARE presented separately. B) mass concentration calculated from the online data. c) and d) number and mass aerosol size distribution after spraying, respectively.

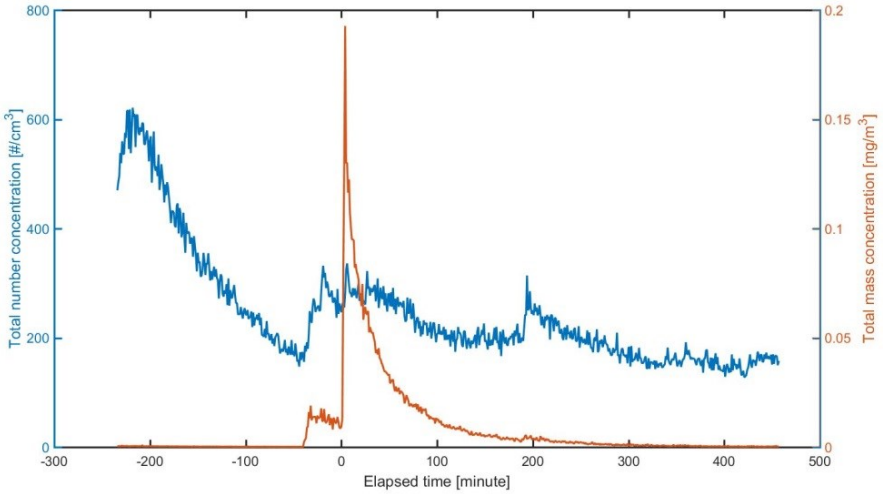


Figure 7-15 Development of total mass concentrations calculated from the NanoScan and OPS measurements.

The wipe samples showed that the QACs are concentrated around the spray area (position 1), mainly at the floor and with minor concentrations at adult and children heights (Table 7-3). The wipes showed approximately the same concentration, considering the uncertainty of the wiping.

Table 7-3: Measured chemical concentrations.

Product	Compound	Max air conc. (mg/m^3)	Mean. Surf. dep (mg/m^2) Floor/Children height
Tanaco Fluestop	Alkanes	13	
	Dimethoxy methane	0.05	
	Phenylethyl alcohol	0.24	
	Lilial	<0.05	
	Nopyl acetate	<0.05	
	Piperonyl butoxide*	7	10.4±5.2/ <LOD
	Pyrethrum extract*	1	2.3±2.2 / <LOD
	Permethrin*	<0.4	0.9±0.6 / < LOD
	Other fragrances	0.008	
Demand CS	1,2,4-Trimethylbenzene	<0.4	
	Propylbenzene	0.008	
	Indane	0.007	
	Lambda-Cyhalothrin *	< LOD	5.0±3.4 / 1.0±1.1
	1,2-Benzisothiazol-3(2H)-one	<LOD	11.4±7.7 / 5.2±7.2
Ecolab Mikro-Quat Extra	Benzyldimethyldodecyl-ammonium chloride *	0.01	10.5±1.7 / 0.2±0.03 (adult height 0.5±0.3)
	Benzyldimethyl-tetradecyl-ammonium chloride *	0.001	4.0±2.5 / 0.4±0.2 (adult height 0.1±0.003)

7.2 Exposure assessments in ConsExpo

As described in section 6.4, the exposure was calculated for each product in ConExpo and/or BEAT. In ConsExpo, one scenario was calculated based solely on the default values and one scenario was calculated using the relevant parameters from the experimental setup. The results from the calculations are described below and in section 7.3 the calculated results are compared to the experimental results.

7.2.1 Tanaco Fluestop

The exposure to Tanaco Fluestop was calculated for all active substances in the product; Piperonyl butoxide, permethrin (cis/trans) and pyrethrum extract (Pyrethrin I & II) in both a default scenario and a mix scenario (including parameters from the experimental setup). The calculation was made based on the *air space application* scenario available in ConsExpo. All used parameter can be seen in section 6.4.1. The results of the model calculations are shown in the following tables (7-4 to 7-6). Results are given for inhalational, oral and dermal potential dose (internal exposure) as well as total potential dose. The sum of the potential dose trough oral and inhalation route was also calculated as this will be compared to the exposure estimated based on the experimental measurements. The oral exposure calculated here, is the results of the product aerosol entering the mouth through breathing.

Table 7-4 Piperonyl butoxide, 1.22 %, primary exposure

Exposure route	Default scenario mg/kg bw/day	Mix scenario mg/kg bw/day
Inhalation chronic potential dose	0.00031	0.00082
Oral chronic potential dose	0.00031	0.013
Potential dose inhalation + oral	*0.00062*	*0.014*
Dermal chronic potential dose	0.0041	0.0083
Total chronic potential dose	**0.0047**	**0.022**

Table 7-5 Permethrin (cis/trans); 0.216 %, primary exposure

Exposure route	Default scenario mg/kg bw/day	Mix scenario mg/kg bw/day
Inhalation chronic potential dose	$5.7*10^{-5}$	0.00015
Oral chronic potential dose	$5.7*10^{-5}$	0.0023
Potential dose inhalation + oral	*0.000114*	*0.0024*
Dermal chronic potential dose	0.00074	0.0015
Total chronic potential dose	**0.00085**	**0.004**

Table 7-6 Pyrethrum extract (Pyrethrin I & II); 0.5 %, primary exposure

Exposure route	Default scenario mg/kg bw/day	Mix scenario mg/kg bw/day
Inhalation chronic potential dose	0.00013	0.00034
Oral chronic potential dose	0.00013	0.0053
Potential dose inhalation + oral	*0.00026*	*0.0056*
Dermal chronic potential dose	0.0017	0.0035
Total chronic potential dose	**0.002**	**0.0091**

As can be seen from above, the estimated exposure based on the parameters from the experimental setup are higher compared to the default scenarios. This difference is primarily caused by differences in the amount of product released per second (mass generation rate). The default value in ConsExpo in the air space application is 0.75 g/sec while the measured maximum mass generation rate from Tanaco Fluestop was 3.1 g/sec.

Secondary exposure results:

The secondary exposure to Tanaco Fluestop was calculated in ConsExpo based on the available default values in the *air space application* scenario for rubbing off. The secondary exposure is an estimate of the exposure of a child crawling on the treated floor area after the application. The results for the three active substances can be seen in the following tables 7-7, 7-8 and 7-9.

Table 7-7 Piperonyl butoxide; 1.22 %, secondary exposure

Exposure route	**mg/kg bw/day**
Inhalation chronic potential dose	-
Oral chronic potential dose	0.017
Dermal chronic potential dose	0.17
Total chronic potential dose	0.187

Table 7-8 Permethrin (cis/trans); 0.216 %, secondary exposure

Exposure route	**mg/kg bw/day**
Inhalation chronic potential dose	-
Oral chronic potential dose	0.003
Dermal chronic potential dose	0.03
Total chronic potential dose	**0.033**

Table 7-9 Pyrethrum extract (Pyrethrin I & II); 0.5 %, secondary exposure

Exposure route	**mg/kg bw/day**
Inhalation chronic potential dose	-
Oral chronic potential dose	0.007
Dermal chronic potential dose	0.07
Total chronic potential dose	**0.077**

7.2.2 Demand CS

The exposure to Demand CS was calculated for the active substance in the product, lambda-cyhalothrin, in both BEAT and in ConsExpo in a default scenario and a mix scenario (including parameters from the experimental setup). The calculation in BEAT was made based on the *pest control spray* scenario and the calculations in ConsExpo were made based on the *crack and crevice application* scenario available in ConsExpo. All used parameter can be seen in tables section 6.4.2. The results of the calculations can be seen in the following table 7-10:

Table 7-10 lambda-cyhalothrin; 0.2 %, primary exposure (spray = 4.5 sec)

Exposure	BEAT	Default scenario mg/kg bw/day	Mix scenario mg/kg bw/day
Inhalation chronic potential dose (mg/kg/day):	$1.3*10^{-6}$	$3.1*10^{-5}$	$1.4*10^{-6}$
Oral chronic potential dose (mg/kg/day):		$8.8*10^{-5}$	0.0001
Dermal chronic potential dose (mg/kg/day):	0.000128	0.0003	0.00023
Total chronic potential dose (mg/kg/day):	**0.00013**	**0.00042**	**0.00034**

As can be seen from the tables, the results from all calculations are quite similar and all estimate very low exposure.

Secondary exposure:

The secondary exposure to Demand SC was calculated in ConsExpo based on the available default values in the *crack and crevice application* scenario for rubbing off. The secondary exposure is an estimate of the exposure of a child crawling on the treated floor area after the application. The results for the active substance lambda-cyhalothrin can be seen in the following table:

Table 7-11 lambda-cyhalothrin; 0.2 %, secondary exposure

Exposure route	mg/kg bw/day
Inhalation chronic potential dose	-
Oral chronic potential dose	1.7
Dermal chronic potential dose	17
Total chronic potential dose	**18.7**

7.2.3 Mikro-Quat Extra

The exposure to Mikro-Quat Extra was calculated for the active substance in the product, Benzalconium chloride in both BEAT and in ConsExpo in a default scenario and a mix scenario (including parameters from the experimental setup) in the available scenarios: one for cleaning and one for disinfection. The calculation in BEAT was made based on the *disinfection spray* scenario and the calculations in ConsExpo was made based on the *spraying for disinfection* and *cleaning* scenario available in ConsExpo (see Table 6-16 Exposure scenarios for calculation of exposure to Demand) All used parameters can be seen in tables in section 6.4.3. The results of the calculations can be seen in the following tables 7-12 and 7-13:

Table 7-12 Benzalconium chloride 0.15%, primary exposure, disinfection scenario

Exposure	BEAT	ConsExpo, disinfection default	ConsExpo, disinfection mix
Inhalation chronic potential dose (mg/kg/day):	0.0005	$9.4*10^{-6}$	$1.8*10^{-7}$
Oral chronic potential dose (mg/kg/day):		$5.9*10^{-5}$	$1.5*10^{-7}$
Dermal chronic potential dose (mg/kg/day):	0.003	0.00058	0.00011
Total chronic potential dose (mg/kg/day):	**0.0033**	**0.00064**	**0.00012**

Table 7-13 Benzalconium chloride 0.15%, primary exposure, cleaning scenario

Exposure	BEAT	ConsExpo, cleaning default	ConsExpo, cleaning mix
Inhalation chronic potential dose (mg/kg/day):	0.0005	$1.3*10^{-7}$	$9*10^{-10}$
Oral chronic potential dose (mg/kg/day):		$5.9\text{-}10^{-6}$	$1.2*10^{-6}$
Dermal chronic potential dose (mg/kg/day):	0.003	0.00047	0.00011
Total chronic potential dose (mg/kg/day):	**0.0033**	**0.00047**	**0.00011**

As can be seen from the tables, the results from BEAT are higher compared to the calculations in ConsExpo. The calculations in ConsExpo are quite similar and all estimate very low exposure, regardless of the used scenario.

No secondary exposure scenario exists in these exposure scenarios.

7.3 Model derived exposure assessments compared with data from specific measurements

Comparison of our experimental data with model calculations for the same scenarios performed with ConsExpo for inhalation.

The estimated exposure based on the actual measurements was calculated after the following equation:

Total mass * % active compound * 5.8 m^3 (1.45 m^3/hour (35 m^3/day)*4 hours (240 min))/body weight of adult (ConsExpo general fact sheet default: 65 kg)

To compare the results with the actual measurements, the ConsExpo estimates of oral non-respirable material exposure is added to the inhalational exposure.

Fluestop calculations:

- Piperonyl butoxide: 313 mg/m^3 * 0.0122 piperonyl butoxide * 5.8 m^3 / 65 kg = 0.34 mg/kg bw/day
- Permethrin: 313 mg/m3 * 0.0022 permethrin * 5.8 m3 / 65 kg = 0.061 mg/kg bw/day
- Pyrethrum extract (Pyrethrin I & II): 313 mg/m^3 * 0.005 pyrethrum * 5.8 m^3 / 65 kg = 0.14 mg/kg bw/day

Table 7-13 Comparison of calculated and measured inhalational exposure for Fluestop.

Exposure route	**Mix**	**Aerosol**	**Chemical**
Potential dose inhalation + oral	**mg/kg bw/day**	**mg/kg bw/day**	**mg/kg bw/day**
Piperonyl butoxide, 1.22 %	0.014	0.34	0.43
Permethrin (cis/trans); 0.22%	0.0024	0.06	0.002
Pyrethrum extract (Pyrethrin I & II);0.5 %	0.0056	0.14	0.006

8. Discussion

The main objective of this project was to evaluate existing models in ConsExpo and BEAT by comparing exposure calculations using default scenarios of specific biocide spray products with experimentally determined exposure data.

Three products were chosen for the project in consultation with MST, *Tanaco Fluestop* (for control of flying insects), *Demand CS* (indoor insecticide for professional use) and *Ecolab Mikro-Quat Extra* (for disinfection and cleaning).

The general approach for our evaluations was to compare computed exposure data from ConsExpo or BEAT using standard scenarios as well as scenarios similar to the experimental conditions with experimental exposure data obtained in the project.

The comparisons of computed data from ConsExpo or BEAT with our experimental data also included evaluations of the importance of the available parameters. Furthermore, the comparisons were used to identify knowledge gaps within the software tools and to evaluate whether the inclusion of other parameters or parameters that could be changed could improve the models.

8.1 Evaluations of ConsExpo and BEAT

During use, spray products produce an aerosol cloud. The speed with which the droplets deposit depends on the size of the droplet. Smaller droplets stay in the air for longer time. The aerosol generation also means that few volatile substances remain in the air for an extended period of time. It has been shown, that a much higher exposure occurs where spraying is carried out above the head than when it is applied at floor level (Llewellyn et al. 1996). This can be attributed to the contact with the aerosol cloud. There are three main aspects when characterizing the exposure of spray applications:

- The type of spraying device (spray can or trigger spray).
- Whether the formulation still needs to be processed before application (mixing and loading).
- Target of the application.

When using ConsExpo and BEAT to calculate the exposure to a given product, it is important to understand the use of the product in order to choose the most suitable scenario from the exposure library. For each scenario the initial parameters must be chosen to the present use in order to create the most realistic scenario.

The tools are more sensitive for some initial parameters and choices made can therefore greatly influence the results and should thus should be selected carefully. In the following we discuss some of the default values identified in this study, which may need further attention and consideration when using ConsExpo or BEAT. In case the parameters are not correctly understood, the tools may possibly calculate the exposure inaccurately, which may lead to an inadequate conclusion.

Spray duration and mass generation rate

When assessing exposure from spray products that produce aerosols, e.g. Tanaco Fluestop, in ConsExpo, the exposure time and spray duration may vary depending on the chosen scenario. Default values for spray duration vary from 20 seconds in the scenario for *air space* application to 90 seconds in the scenario for *targeted spot* application. These values directly influence the calculation of the total mass sprayed in the application space area and therefore may greatly

impact the exposure assessment. If the recommended spray duration is given in the instructions for use of the product, this value should be used, as this will result in a more realistic exposure estimation. If a range is given, the highest value should be applied.

For example the spray duration in the *air space* scenario (e.g. used in Tanaco Fluestop) a default value of 10 seconds is recommended (spraying takes place over 20 sec.). However, the user instructions for Tanaco Fluestop recommends to spray for a minimum of 4 sec in a room of 30 m^3. This could potentially give 120 % error for the initial values which would considerably influence the final result. It is therefore important to emphasize that realistic values for exposure time is used, as this parameter has great influence on the results. This is specifically important if the margin to unacceptable exposure is small.

The mass generation rate of the product was also shown to have great impact on the estimated exposure. The default value for mass generation rate in the air space application is 0.71 g/sec. This is based on the experiments embedded in the ConsExpo database. For comparison, the mass generation rate measured in this study ranges from 3.0 to 3.1 g/sec. When using the worst case of the measured values (3.1 g/sec) the estimated exposure increases by 10-fold. Although these measurements are only based on one product, the results shows that there might be great variation in the mass generation rate, both from product to product, but also in between the individual cans of the same product. Actual measurements of the mass generation rate, may therefore be an important parameter to investigate further in the assessment of a biocidal spray-can product.

Ventilation rate and exposure time

The default value for most scenarios for ventilation rate is 0.5/hour. This is representative for a living room without mechanical ventilation. Ventilation rate is directly changing the exposure due to the dilution and will influence the exposure, especially if the exposure time in the room is long. The default of exposure time is usually set to 240 minutes and therefore ventilation has important role for total exposure/dose calculations.

If the product is intended for use in private homes, one must expect the worst case scenario that the user stays in the treated area afterwards, unless otherwise is stated on the product.

In BEAT, one must be aware that only the exposure during application of the product is taken into consideration. The application time can be changed according to the intended use of the product.

It is therefore important to evaluate whether realistic values are chosen. The results from the measurements show that the particle (aerosol) and chemical substance concentrations in the room decrease almost linearly with the ventilation rate.

Application mode and application area

The exposure to the product and its active substance(s) may differ substantially according to the application mode of the product. Therefore, it is important to consider the use of product and perform the exposure assessment according to the instructions and in an appropriate scenario relevant for the product. If the product is intended for spot targeting, e.g. a specific defined area, emissions will be limited to the treated area, compared to for example air space application, as with Tanaco Fluestop, where the product is sprayed in different directions in the air. In the latter case, the product will be distributed in a much larger area in the air and to more surfaces in the room.

In BEAT, the indicative values are based on studies of professionals in user situations. It is important that the scenarios are carefully studied, as the choice of scenario, may greatly influence the resulting indicative values. Thus, it is important, that realistic indicative values are selected on the basis of the intended use of the product. For example, the indicative value for body exposure vary from 75.3 µl/min to 2400 µl/min within studies of different spray biocides categorised as "spraying for disinfection". It is therefore important to go through the different studies and select the best suited value, otherwise results may be under- or overestimated.

Application area is an important factor for the secondary exposure calculation. The default areas in ConsExpo vary considerably between different pest control scenarios. Defaults areas for crack and crevice (scenario used for Demand calculations) is 8 m^2 and for the air space scenario it is 22 m^2.These values are relevant when calculating secondary exposure for a child crawling where *exposed area* is the initial parameter. Using a small area in the calculation may underestimate the exposure in case the product is actually used for larger areas, and it is therefore important to evaluate whether realistic values are used in relation to the expected use of the products.

It is also important to take into consideration the composition of the product. If the active substances are volatile (vapour pressure: Pa > 0.1), then the evaporation model in ConsExpo must be applied.

Frequency

Frequency of the product application is one of the input parameters in ConsExpo. The default value for the frequency of use also varies according to the chosen scenario. However, when performing the risk assessment afterwards, the exposure dose concentration must be compared to a limit value (e.g., OEL). These values are typically based on occupational exposure limits per (working) day. In order not to underestimate the exposure, by dividing it into exposure over days/year, the frequency should always be set to 1/day.

BEAT vs ConsExpo

For the two products intended for professional exposure, the exposure assessment was performed in both BEAT and ConsExpo. The reason that this is relevant is that the Human Exposure Expert Group (HEEG) has evaluated that ConsExpo also can be used for products intended for professional use to estimate exposure as long as the values are adapted for professional users (HEEG opinion 3).

For Demand, the estimations performed in BEAT and ConsExpo were similar. For Mikro-Quat Extra, however, the exposure estimates in BEAT, were higher compared to the estimates made in two scenarios in ConsExpo. It is worth noticing that in BEAT only the exact time of exposure during the use is included in the calculation. This is based on the usual use of professionals, where they usually do no stay in the room after use of the product. In ConsExpo, both the time using the product and the expected total time of exposure, including time spend in the room afterwards, is included in the assessment calculation. However, this does not explain why the estimate in BEAT is higher compared to estimates in ConsExpo.

Furthermore, there is also a difference in the approach to assess dermal exposure. In BEAT, the total amount of product on the body and hands is estimated and hereafter the amount mitigated by clothes or protective equipment (gloves etc.) is subtracted. In ConsExpo, no protective equipment is expected as it is for private use, and instead the worst case exposed area of bare skin is calculated and used in the assessment. These parameters are all important factors that can influence the calculation of exposure. Thus, it is essential to set these parameters correctly.

8.2 Comparison of modelled and measured results

8.2.1 Inhalation parameters

Tanaco Fluestop

As can be seen in Table 7-13 the exposure estimates based on the experimental data (aerosol measurements and direct chemical measurements) are not completely similar to the exposure estimated in the models. For piperonyl butoxide, the exposure estimates based on both the chemical and the aerosol measurements (0.34 and 0.43 mg/kg/day) are considerably higher compared to the level calculated by ConsExpo (0.014 mg/kg/day). For permethrin and pyrethrum extract, the estimates from ConsExpo are quite similar to the estimates based on the chemical measurements. However, the estimates based on aerosol measurements are higher than the other estimates.

As discussed in section 8.1, there are several sources of error for exposure estimates in ConsExpo, which could contribute to these discrepancies. However, as we have taken all these potential errors into consideration in the current estimates, these factors may only have a minor impact on the results. It seems that the greatest factor, that causes the differences in exposure estimates between the modelled and the measured values, is the initial size distribution used by ConsExpo in the spray scenario. Figure 8.1 presents the initial size distribution used in the scenario (air space application) for the Tanaco Fluestop. It shows a probability density distribution peaking around 18 µm. For comparison, the measurements peak around 2 µm. The current ConsExpo defaults for particle size distribution within aerosol sprays, therefore it appears too high on the basis of the chamber exposure measurements.

In the ConsExpo version, it is not possible to enter data with lower size distribution, or to enter data to move the distribution to the left (towards lower particle size). When the inhalation cut off is set to 10 or 15 µm, only the part of the particles (aerosols) below these values will be accounted for in the exposure model. As a result of this, the estimates of inhalational exposure in ConsExpo will therefore turn out lower in comparison with the chamber exposure measurements.

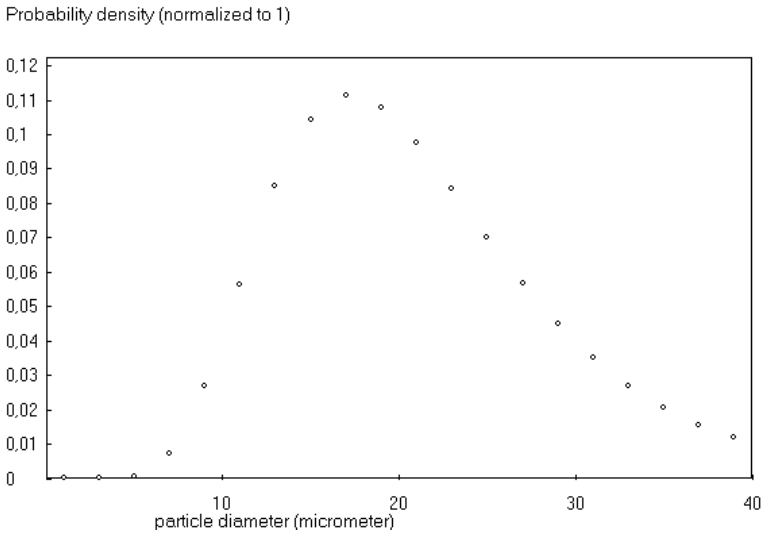


Figure 8-1 The particle distribution used in ConsExpo

Recently, a new web version of ConsExpo was released. In this version, the particle size distribution can be set according to the product´s use. However, since this version was not available at the onset of this study, we only used it for a preliminary calculation of piperonyl butoxide exposure to compare the effect of changing the particle size distribution. We found that when using a mean of 2 µm for the particle distribution and a maximum of 15 µm, the estimated inhalational exposure was calculated to be 0.5 mg/kg/day, without taking the oral intake into consideration. The possibility of entering the correct particle size distribution thus seems to give a better estimate of the inhalational exposure to this type of spray products. However, in order to use this function correctly and thus take this important parameter into consideration, knowledge of the particle size distribution of the product in question is a prerequisite.

Table 7-13 also shows that aerosol measurements and chemical measurements are not consistent either, when comparing the individual active substances. For example, the exposure to permethrin estimated on the basis of the particle measurements is 0.14 mg/kg/day, whereas the exposure to permethrin based on chemical measurements is 0.006 mg/kg/day. There are several reasons for this; for example, we only measured until 10 µm with the aerosol instruments and with sampling of substances, we do not know the limit and accuracy of the composition of the product. However, these two methods result in fair agreement with the total concentration of the active substances in the air (See Table 7-1).

Demand and Mikro-Quat Extra

The measurements of the professional product Demand, showed that there were no particles present in the air below 10 µm after use and the air concentration of the active substance, lambda-cyhalothrin, was below the detection limit of 22 µg/m^3.

In BEAT the estimated air concentration of the product is 2.03 µl/m^3 based on the indicative value for inhalational exposure of 27 µl/m^3 product per minute times the spray-time of 4.5 sec. With 0.2% lambda-cyhalothrin in Demand, this results in 0.004 µl/m^3. If a density of 1.2 is assumed, this will approximate 0.0049 mg/ m^3 (4.9 µg/$m^{3)}$, thus below the detection limit of the analysis.

The inhalational exposure in BEAT is calculated to be 1.3 ng/kg/day. Since it was not possible to measure Demand in the air due to the concentration being below the detection limit, the results cannot be compared. However, it can be assumed that the inhalational exposure to this product is minimal. The same is concluded for Mikro-Quat Extra. It should however be mentioned, that the time used for application during the chamber exposure measurements, is low compared to the time assumed for professional use of the product. This was done for practical reasons in the chamber. However, based on the application mode and the size of the droplets, the particle size, and formation of potential aerosol is not expected to be affected by this. If the calculations were to be used for risk assessment, the spray time would need to be changed to a more realistic estimate for a professional user (e.g. 120 minutes or similar).

The risk of inhalational exposure to this type of application is therefore not assumed to be significant. With regards to Demand, it should also be mentioned that the active substance exists in the product in small capsules, from which it gradually leaks out. It would therefore be expected to pose a greater risk of dermal/secondary exposure.

8.2.2 Dermal exposure

Dislodgeable amount

The secondary exposure was calculated for Tanaco Fluestop and Demand CS. In the estimation of the secondary exposure for a child crawling on the floor after the application of a biocidal product, one of the critical parameter for the results is the dislodgeable amount of the product. The dislodgeable amount, is the amount of product which is anticipated to be brushed off by contact with the treated area. In order to compare the potential secondary exposure estimates with the experimental measurements, the comparison of the dislodgeable amount with the measured wipe concentrations, was considered to be the best measure for comparison.

The ConsExpo default for the dislodgeable amount is set at 30% based on experimental data. Depending on the scenario, the dislodgeable amount differs, as different amounts of product are assumed to be used, as well as the assumed treated area is different according to the type of application. If for example the application is *air space application*, the amount present on the floor is expected to be lower compared to *crack and crevice application*, where a smaller surface area is expected to be treated. As can be seen in section 6.4 (Table 6.9 and 6.14, respectively), the dislodgeable amount for air space application is set to 0.82 mg/m^2 in ConsExpo, where in crack and crevice the value is set to 11.6 mg/m^2. Thus, selection of a realistic value is important for calculation of the secondary exposure.

We have compared the default values in ConsExpo with the concentrations measured on wipes taken on the treated areas in our experimental set-up. For each active substance the dislodgeable amount was calculated based on the ConsExpo default value and the concentration in the product. These values were compared to the chamber exposure measurements (see Table 8-1).

Table 8--1 Comparison of calculated and measured dislodgeable amount of the active substances in Tanaco Fluestop and Demand CS

Product	Substance,	ConsExpo default	Measured
Fluestop air space	Piperonyl butoxide	9.8 mg/m^2	10.4 mg/m^2
	Permethrin	1.8 mg/m^2	0.9 mg/m^2
	Pyrethrum extract	4 mg/m^2	2.3 mg/m^2
Demand Crack and crevice	Lambda-cyhalothrin	23.2 mg/m^2	5 mg/m^2

As can be seen in Table 8-1, the measured concentrations from the wipe measurements are of the same order as the default values from ConsExpo taken from the relevant scenarios. For permethrin, pyrethrum extract and lambda-cyhalothrin the default values overestimate the amount by two to four times. Based on this comparison, the default levels in ConsExpo appear realistic. It must however be mentioned that this is only based on one experiment. The amount of dislodgeable product may be different with other products/types of products.

9. Conclusions

The present report presents a pilot study with the aim to evaluate the existing software models ConsExpo and BEAT, by comparison of exposure assessments of spray products performed in the software models to experimental measurements carried out in an exposure chamber in controlled climatic conditions and ventilation rate.

Three different biocidal products were selected and sprayed according to user instructions in the exposure chamber. Particle size distribution spectra, particle number concentration and chemical composition was measured to characterize the inhalable exposure. In addition, wipe samples were taken from surfaces in the exposure chamber to estimate secondary exposure.

Model evaluations were performed in ConsExpo and BEAT using two different methods: 1) by applying model default values for the spray application and 2) by substituting some of the default values with values from the measurements obtained in the exposure chamber. These results were then compared to calculations of exposure based on the experimental data from the exposure chamber.

The experimental data revealed that measurable aerosols only were found after testing the Tanaco Fluestop and not after testing Demand or Mikro-Quat Extra. This indicates that products where the application is performed with low pressure equipment, creating foam or similar, is not likely to be as critical regarding exposure to inhalable aerosols.

It was seen that the estimated inhalational exposure from Tanaco Fluestop, based solely on default values in ConsExpo, was considerably lower in comparison to the estimates from the experimental data obtained in the exposure chamber. This indicates that measured data on the spray function, particularly on mass generation rate, should be used in the models when estimating the exposure. Other parameters, such as exposure time and area, should also be considered carefully as these parameters were shown to substantially influence the results. Furthermore, the results show that the default particle size distribution in ConsExpo is not representative for all spray products, and certainly not for Tanaco Fluestop. Data on the particle size and distribution is therefore also essential for the estimation of exposure. A new web-based version of ConsExpo (ConsExpo Web) has recently been released where it is now possible to insert data on this point in the model. A preliminary calculation with this version of piperonyl butoxide exposure was performed, which resulted in a better estimate of the inhalational exposure in comparison with the experimental data. Default values in ConsExpo are likely to be chosen without knowledge of the particle size distribution of the product in question; this may considerably underestimate the exposure.

It is concluded on the basis of the comparison of experimental data with the models that the old version of ConsExpo did not perform adequately for the airborne exposure estimation. However, the pilot study only includes one product which had a potential for inhalable exposure. It is therefore not possible to generalize from these preliminary results. For the secondary exposure, a better agreement was seen between the measurements and modelling. Thus, based on these results, it is possible that the new models may predict the secondary exposure more accurately for this type of product, however, additional experiments and comparisons are required for a validation.

10. Perspectives

The findings of the present study emphasize the importance of a thorough and detailed knowledge of the intended use of the products in order to create the best fitted exposure scenario.

In the present study, the estimates of exposure to the consumer product Tanaco Fluestop assessed by the software program ConsExpo were found to be lower compared to aerosol measurements. This was assumed to be primarily due to a lower particle size distribution compared to the default in ConsExpo. As this was performed on one product only, more studies on the particle size distribution in spray from new spray products is necessary in order to identify the most realistic and relevant default values for this parameter.

Furthermore, it would be relevant to compare more spray products in the new web version of ConsExpo, where it is actually possible to set the particle size distribution of the products. This way it would be possible to evaluate further, whether the models in ConsExpo are covering the full risk of inhalational exposure of both private and professional users of biocidal spray products. According to the HEEG, ConsExpo can also be used for exposure estimates for professionals, as long as the parameters are adjusted to fit a professional scenario. However, it would be relevant to investigate exposure assessments for professionals made in ConsExpo, especially in the new web version, in more detail by comparing with actual measurements. Here it would be of special interest to examine the importance of the particle size distribution.

The secondary exposure measured as dislodgeable amount and wipes from applied areas was very comparable in the present study. However, the models also indicated that there may be a significant secondary exposure after the use of especially the professional products. As these products may be used in private homes, more knowledge of the secondary exposure to the private consumer in the home after use of professional products may also be of great importance. Likewise, it would be of importance to obtain more knowledge on the accuracy of especially the web version of ConsExpo with regards to secondary exposure assessment of products for professional use.

11. References

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Biocides in spray products - exposure and health

In this we present a pilot study, where it was sought to evaluate the existing software models ConsExpo and BEAT, by comparing exposure assessments of spray products performed in the software models to actual measurements performed in a human exposure chamber.

Three different biocidal products were chosen and sprayed according to use instructions in the human exposure chamber. Aerosol size distribution spectra, number concentration and chemical composition were monitored to measure inhalation exposure. In addition, wipe samples were taken from surfaces in the chamber to estimate secondary exposure.

Model evaluations were performed in ConsExpo and BEAT using two different methods: 1) by applying model default values for the spray application and 2) by substituting some of the default values with values from the actual measurements in the human exposure chamber. These results were compared to calculations of exposure based purely on data measured in the human exposure chamber.

Our comparison of experimental data with the models, showed that the version of ConsExpo we used did not perform ideally for the airborne exposure estimation. However, our studies only include one product which has a potential for inhalable exposure. It is therefore difficult to draw conclusions from these results. For the secondary exposure, we found better agreement between the measurements and modelling, which indicates that the models may predict the secondary exposure for this product type.

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