Fraunhofer ITEM

Report

Experimental assessment of inhalation and dermal exposure to industrial spraying products during industrial and professional spraying activities (PROC 7 and PROC 11)

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Abbreviation

C. V.	Coefficient of variation
DP	Deposition plate
FID	Flame Ionisation Detector
GC-FID	Gas chromatography coupled to flame ionisation detector
GSP	Inhalable dust sampler (Gesamtstaubprobenahme an der Person)
IPA	Isopropyl alcohol
MW	Molecular weight
MV	Mean value
PROC	Process category
PTEO	Propyltriethoxysilane
STDEV	Standard deviation
Vp	Vapour pressure

Content

1 Introduction and Objective

The ECETOC TRA tool is a tier 1 model applied to give dermal and inhalation exposure estimates for professional and industrial processes as well as consumers and the environment. For several process categories (PROCs) it has been demonstrated to provide conservative estimates for work exposure [BAuA F2303[1], Kupczewska-Dobecka et al. 2011[2], Hofstetter et al. 2013[3]]. Industrial spraying (PROC 7) and professional spraying (PROC 11) are two process categories where model and field data differ according to BAuA F2303. BAuA analysis of measurement data for such tasks compared to exposure estimates provided by ECETOC TRA for PROC 7 and PROC 11 activities suggests the model values may not be sufficiently conservative for these process categories.

The special aspect of solvent release in spray processes in contrast to wiping, brushing and rolling is the creation of a high liquid surface area due to the liquid dispersion into fine droplets. In most cases, this spray related airborne evaporative surface area is much higher than the treated surface area from which the solvent evaporates. This can result in a much higher exposure concentration as estimated from Tier1 models based on simple fugacity considerations. In addition to the gas phase of the volatiles in the spray cloud, exposure to solvents in the aerosol phase may contribute to the overall inhalation exposure.

Based on physical properties as well as on the activity duration, inhalation exposure estimates are calculated which neither consider the amount of the applied compound nor the surface area. Formation of aerosols and the accompanying substantial increase of surface area from which the compound can evaporate are an integral part of PROC 7 and PROC 11 activities. ECETOC TRA does not consider the aerosol contribution in the estimation of inhalation exposure of workers during spraying applications [TRA 114, 2012[4]], suggesting this shortcoming as a possible reason behind the mismatch between model and field data.

Currently the lack of field/experimental data does not allow an evaluation of the ECETOC TRA performance in regards to dermal exposure during industrial and professional spraying.
ESIG proposed to generate data regarding inhalation (vapour and aerosol) and dermal exposure during PROC 7 and PROC 11 activities. These experimental data are necessary to shed more light on the performance of the ECETOC TRA tool when it comes to these two process categories. The aim of this project was to generate inhalation and dermal exposure data to assess aerosol and vapour phase contributions to inhalation and dermal exposure during PROC 7 and PROC 11 spray activities.

2 Line of thought

Industrial and professional process categories, PROC 7 and 11, do not differ in their general description of the process. The made distinction of two work environments suggests the extent

[1] BAuA F2303: Evaluation of Tier 1 Exposure Assessment Models under REACH (eteam) Project - Final Overall Project Summary Report. Endbericht zur Evaluierung von Tier 1-Modellen (2015).

[2] Kupczewska-Dobecka, M., Czerczak, S., Jakubowski, M. (2011) Evaluation ofthe TRA ECETOC model for inhalation workplace exposure to different organic solvents for selected process categories. *Int J Occup Med Environ Health*. 24(2):208-217.

[3] Hofstetter, E., Spencer, J.W., Hiteshew, K. Coutu, M., Neally, M. (2013) Evaluation of recommended REACH exposure modeling tools and near-field, far-field model in assessing occupational exposure to toluene from spray paint. *Ann Occup Hyg*, 57(2):210-220.

[4] TR114: ECETOC AISBL, (2012), ECETOC TRA version 3: Background and Rationale for the Improvements. *Technical Report No. 114*.

and effectiveness of applied control measures as a conceivable distinctive feature; insinuating more sophisticated standards in industrial environments. The underlying mechanisms of the spray processes determining exposure during application, however, are considered the same for PROC 7 and 11 scenarios. In general, sprays can be applied either by a locally fixed device (e.g. spraying booth) or by transportable spraying equipment (e.g. spray guns). Having the technical feasibility in mind, the conduction of spray simulation with manual spray guns are favoured in this study. The vapour pressure band of a sprayed product dictates the set default value for the initial inhalation exposure estimate (no control measures in place) for PROC 7 and PROC 11 applications in ECETOC TRA. Unambiguous definition of the term "spraying activity"[5] is crucial/desirable for the correct and uniform use of an exposure estimation tool such as ECETOC TRA. The following theoretical derivation for inhalation exposure during spraying processes considers the spraying activity only and does not take into account any peripheral activities related to the spraying process.

The main source for inhalation exposure of workers during spraying processes is the overspray, f_o, defined as the solvent fraction not being deposited on the surface. The overspray consists of an aerosol/droplet phase and a gas phase. Their individual contribution to the near field inhalation exposure is influenced by mainly two parameters: the droplet size distribution (influenced by application pressure, nozzle parameter, flow rate etc.) and the vapour pressure of the substance of interest (non-volatile, co-formulant, propellant) in the spraying product. Figure 1 shows a schematic of an exposure scenario. The spray cone is moving up and down. For sufficiently high vapour pressures of the solvent there will be vapour saturation; C_s inside the spray cone at any time during spraying; the mass flux, Q_v, of vapour released into the atmosphere is given by the translational motion of the spray cone characterized by the volume velocity dV/dt and C_s:

$$Q_{vap} = \frac{dV}{dt} \cdot C_s \qquad \text{Eq. 1}$$

This contribution to the vapour mass flux is independent of the material throughput through the spray nozzle. A second contribution of vapour mass flux originates from the evaporating droplets of the overspray i.e. the fraction of the liquid not deposited on the surface. These two determine the near field vapour concentration of the sprayer. Far field contributions result from the dispersion of the near field cloud as well as vapour emissions from treated surfaces. Aerosol contribution to airborne solvent mass flux, Q_{aer}, can only originate from the overspray formation. The spray droplet size distribution of the overspray is a key quantity controlling the inhalable aerosol fraction, η_i. The inhalable aerosol source term is characterized by

$$Q_{aer} = \dot{M} \cdot f_o \cdot \eta_i \qquad \text{Eq. 2}$$

where $\dot{M}$ is the mass flux of spray liquid.

Previous studies at Fraunhofer ITEM with one-component spraying products (organolsilane, fugacity band: low) showed a strong vapour pressure dependence of the aerosol-vapour partitioning in the overspray. The lower the vapour pressure the higher the aerosol contribution.

[5] Considering the activity of spraying only *vs* considering spraying and any peripheral work associated with it.

In this context, substances with vapour pressures above 100 Pa turned out to be “highly volatile” because the aerosol fraction in the overspray was negligibly small compared to the vapour concentration. The outcome of this study suggests the following hypothesis:

- the vapour release weakly depends on the spray droplet size distribution and the product mass flow,
- the aerosol contribution to exposure strongly depends on the droplet distribution and the product mass flow.

Based on this experience, the focus in this study was on liquids in a vapour pressure band Vp: 0.01 – 500 Pa to simulate the transition from aerosol to vapour dominated exposure.

Variation of the vapour pressure can be achieved by using one-component spraying products (e.g. organosilanes, higher alcohols), with the additional advantage of having a simple composition of the exposure atmosphere. Different one-component liquids with varying vapour pressure are commercially available. The primary droplet size distribution of the spray relevant for aerosol-dominated exposure can be controlled by the spray nozzle type and the operating pressure of the spray nozzle.

Table 1 Initial exposure estimates (no control measures in place) for PROC 7 and PROC 11 applications in ECETOC TRA.

Fugacity	**Vapour pressure [Pa]**	**Industrial exposure prediction (PROC 7) [ppm]**	**Professional exposure prediction (PROC 11) [ppm]**
High	≥ 10,000	500	1000
moderate	500 – 10,000	250	500
low	0.01 – 500	100	100
very low	< 0.01	100	100

The specific study aims to carry out experiments to measure the vapour and aerosol mass flux relevant for inhalation exposure under realistic worst-case conditions and using these data to model baseline concentrations for various other spray application scenarios. Furthermore, the selected configuration for the measurement of the vapour release should also represent a realistic (worst-case) workplace example.

This was chosen to be the case for a room of 41.5 m^3 with a floor area of 16 m^2 and no air exchange, in which a short spray action is carried out. Spraying was performed by directing the spray cone against a vertical wall.

A pre-study was carried out to develop a measuring strategy and to define the spraying parameters, in particular to explore the influence on primary droplet on inhalable aerosol and vapour release.

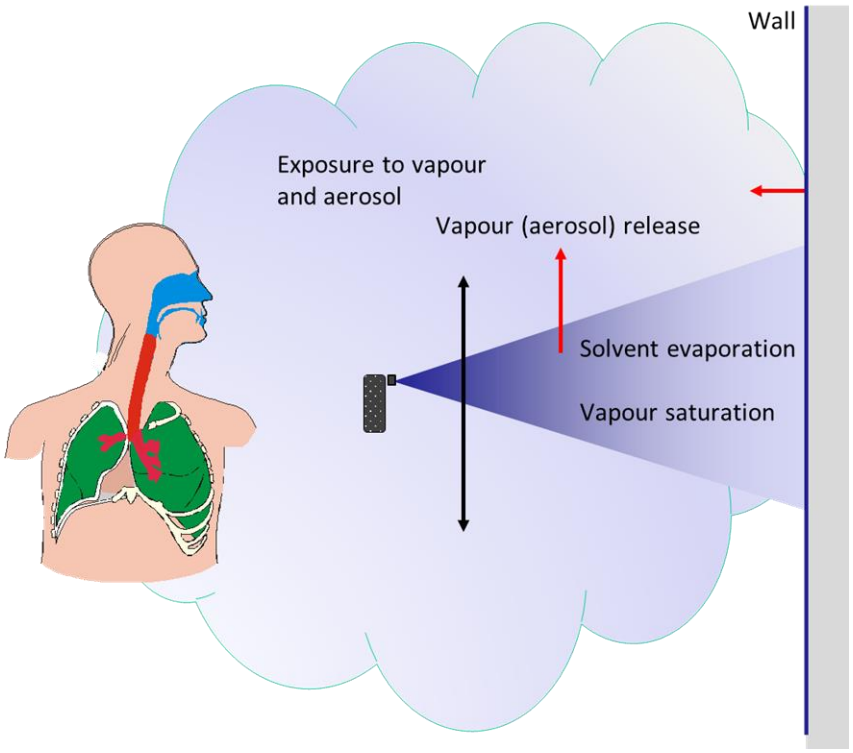

Figure 1 Schematic of inhalation exposure scenario during spraying processes. Black arrows indicate the upward and downward movement of the spraying device during application; Red arrows show the vapour (aerosol) emission sources; namely and spraying cone (primary source) and sprayed surface (secondary source).

3 Experimental

3.1 Equipment and Chemicals

Equipment

- Flame Ionisation Detector (FID, Bernath atomic – model 9900)
- Glass fibre filter
- Gas chromatography couple to a flame ionisation detector (GC-FID, HP 5890 II)
- GSP
- Respicon
- Aerosol spectrometer (1.109, Grimm)
- Petri dishes
- Erlenmeyer flasks (100 mL)
- Compressed air spray gun (Walther, Pilot)

Chemicals

- Dynasylan® PTEO (Vp = 80 Pa)
- Ethylene glycol (Vp = 7 Pa)
- Diethylene glycol (Vp = 0.7 Pa)
- Hydrogen (g)
- Isopropyl alcohol (IPA)
- n-hexane

3.2 Laboratory based simulations - Spray applications

3.2.1 Test substances

Based on previous studies, the switch from aerosol dominated to gas (vapour) phase dominated inhalation exposure was expected for the ECETOC TRA fugacity “low” band. Diethylene glycol, ethylene glycol and Propyltriethoxysilane (PTEO) were chosen as model substances. All three liquids are categorised as substances with a low vapour pressure, according to the ECETOC TRA tool. Table 2 details the substance specific information of the test substances.

Table 2 Test substances – Substance specific information

Substance	MW [g/mol]	Vp [Pa]	Sat. Conc. (gas) [mg/m³]	Sat. Conc. (gas) [ppm]
PTEO	206	80	6700	800
Ethylene glycol	62	7	177	70
Diethylene glycol	106	0.7	30	7

3.2.2 Outcome of pilot study

As part of a pilot study exemplary simulations investigating the impact of droplet size on the aerosol and gas phase exposure during spraying activities were run using PTEO as model compound. Primary droplet size distribution was adjusted by using different spraying nozzle and/or varying application pressure. In total three different mean ($\bar{x}_{50}$) droplet size were considered in the experiments:

- $\bar{x}_{50}$ = > 300 µm (GLORIA 142 TC, fan nozzle, application pressure: 3 bar)
- $\bar{x}_{50}$ = approx. 375 µm (compressed air spray gun Walther-Pilot, application pressure: 0.8 bar)
- $\bar{x}_{50}$ = approx. 45 µm (compressed air spray gun Walther, application pressure: 2 bar)

These values were determined in separate measurements prior to the spray tests using laser diffraction spectrometry.

Aerosol data was collected using a Respicon® device. The data showed a strong correlation between the primary spray droplet size and the aerosol counts. The smaller the droplet size the higher the aerosol concentration during spraying (Figure 2). The aerosol concentration increased by a factor of 15 when the primary droplet size was reduced from 400 µm to 45 µm.

A much less pronounced effect was observed for the gas phase (Figure 3). The gas phase concentrations increased only by 30 % when spraying with the 45 µm droplets compared to the outcome when using the 400 µm spray droplets.

Note: During the pilot study, uniform distribution of the aerosol and gas phase was achieved by a fan.

ECETOC TRA aims at providing conservative exposure estimates. Hence, all laboratory-based simulations were run using the compressed air spray gun at an application pressure of 2 bar, resulting in a mean primary droplet size of the spray of approx. 45 µm. This would represent a realistic worst case scenario, when there is a significant aerosol contribution to exposure, whereas this choice is irrelevant for high vapour pressure substances where inhalation exposure is dominated by the vapour phase of the solvent.

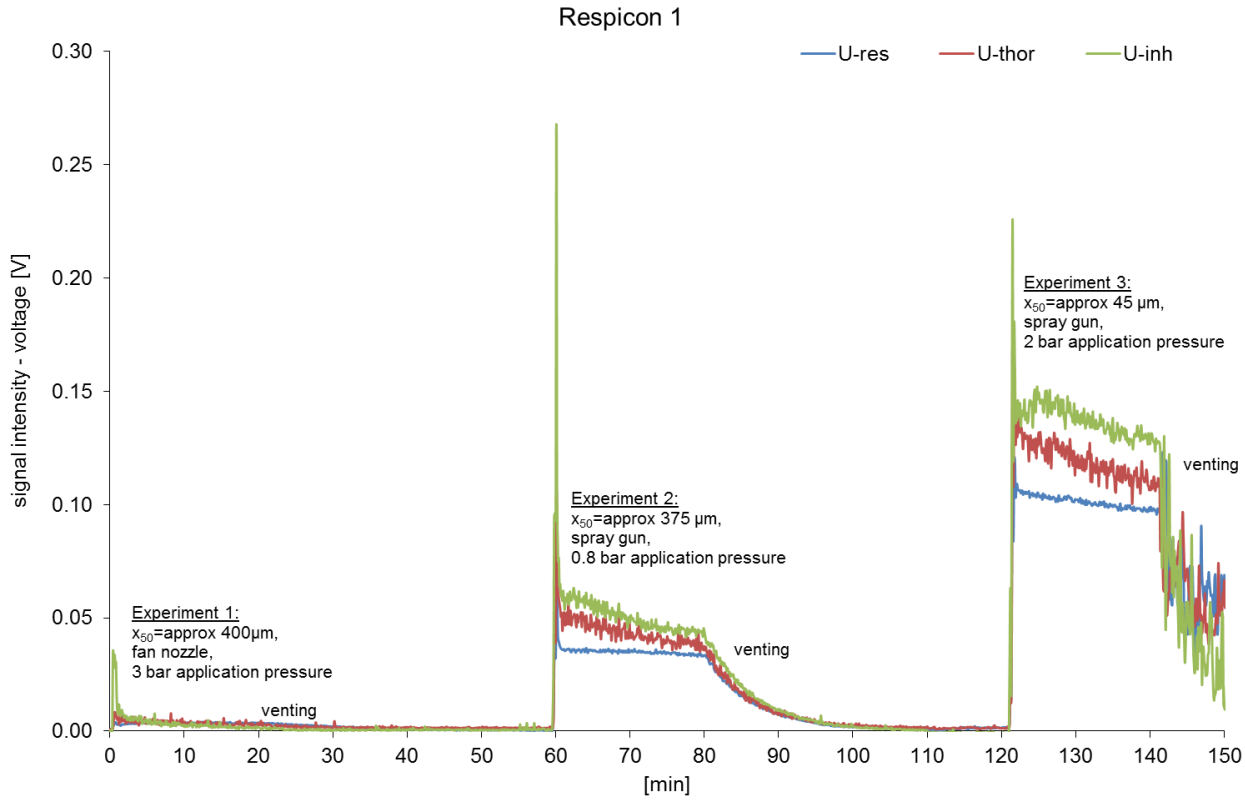

Figure 2 Pilot study – Investigation of nozzle type and application pressure on aerosol concentration. The duration of the spraying activity for all three events was 0.5 min.

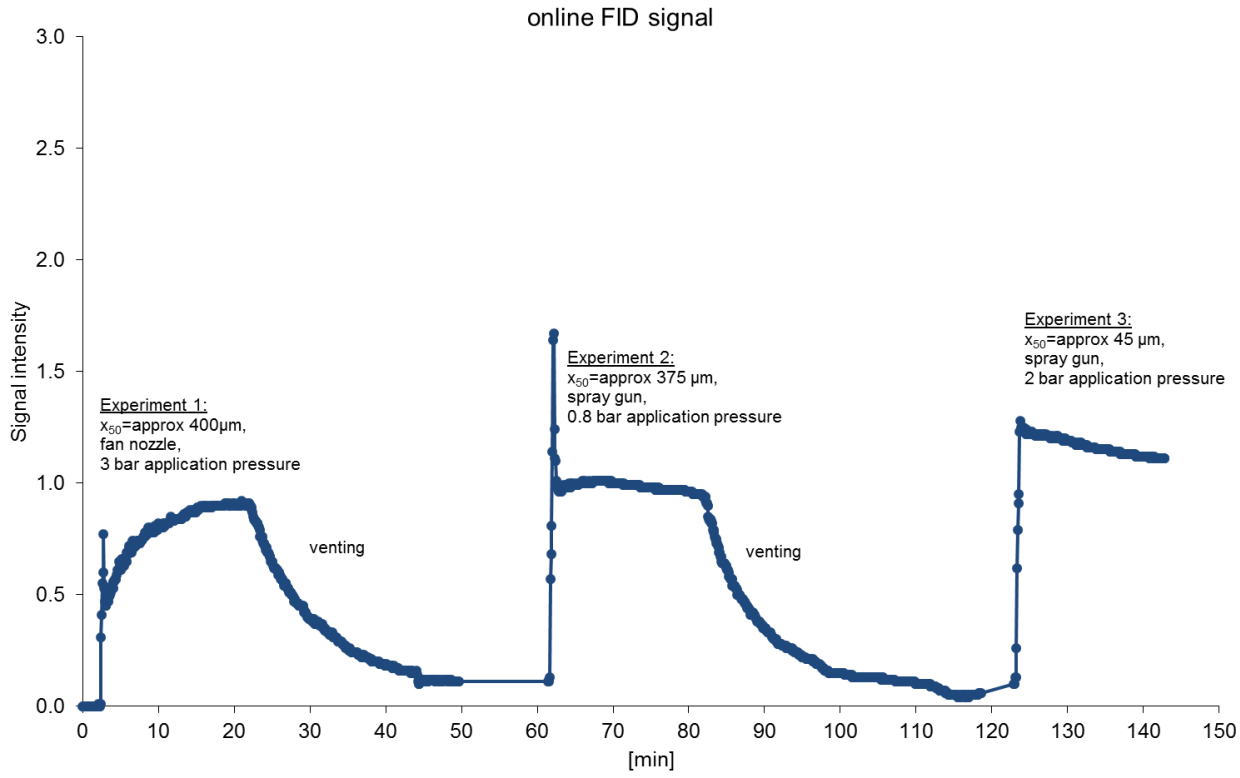

Figure 3 Pilot study – Investigation of nozzle type and application pressure on gas phase concentration. The duration of the spraying activity for all three events was 0.5 min.

3.2.3 Experimental simulations (baseline scenario)

PROC 7 and PROC 11 spraying activities were simulated in a model room (41.5 m³, no ventilation or any other RMMs in place) by spraying the respective liquid at a plasterboard (2 m x 1.2 m) three times during the time span of 1 min. The distance of the spraying nozzle (Walther-Pilot) to the plasterboard was 0.5 m. The compressed air pressure for operating the spraying gun was set to 2 bar resulting in a mean droplet size of 45 µm. The operator remained in the room for an additional 2 min after completion of the spraying process. This non-spraying period was meant to represent other work activities, such as tidying away of equipment or refilling of the spraying equipment, are considered as part of the job. Inhalation and dermal exposure samples were collected.

The outcome of these experimental simulations was two-fold. First, the short-term measurements provided information on the near field concentration, $C_{activity}$, averaged over the duration, $T_{activity}$ of the spray activity and a short period thereafter. Non-spraying times when the worker is moving away from the spray zone were not included, here. In our surrogate setup the worker would leave the room during the non-spraying periods. Assuming the near zone exposure during spraying activities dominates the overall exposure to the substance of interest during a shift, the shift average value, C_{shift}, can be extrapolated from $C_{activity}$, obtained in this study, when shift-duration (T_{shift}) and total spraying (activity) duration ($T_{activity}$) are known.

$$C_{shift} = C_{activity} \frac{T_{activity}}{T_{shift}} \qquad \text{Eq. 3}^{6;7}$$

Secondly, vapour and aerosol release rates, two quantities characteristic for spraying, processes were determined for substances with different vapour pressures. These data were used as input parameters to model baseline concentrations for scenarios different from the one selected here.

The sampling equipment used for the assessment of inhalation exposure consisted of aerosol samplers/monitors (3 GSP samplers, 2 Respicon®, aerosol spectrometer) and gas phase samplers/monitors (1 set of wash bottles holding an appropriate solvent, FID). One GSP sampler was connected to the inlet of the wash bottles, preventing particles from entering and allowing for offline quantification of the sprayed liquid in the gas phase. The FID inlet was also equipped with a filter, thereby allowing online monitoring of the evaporated liquid. All samplers were stationary and positioned close to the operator (Figure 4 and Figure 5).
Horizontal and vertical deposition plates assessed potential dermal exposure. Two glass petri dishes were used as horizontal deposition plates with surface areas of a. 87 cm² and b. 165 cm² respectively. These plates were positioned in immediate proximity of the operator at a height of 0.65 m and distance of 0.75 m from the plasterboard. Six circular filter papers were used as vertical deposition plates (=patches; 95 cm² each) attached to the operator (Figure 4 and Figure 7).

All samplers were switched off after 3 min (1 min spraying activity + 2 min additional residence) and the deposition plates as well as the personal dermal samplers (patches) were removed from the room/operator. The filters of the GSP samplers were removed, transferred into Erlenmeyer flasks and covered with the respective extraction solvent (5 mL) after each run. The Respicon® samplers were used to accumulate the particles released over all three runs of each simulation scenario. The collection of the gas phase in wash bottles was also accumulated over three runs.

The patches (personal dermal sampler) were removed, transferred in Erlenmeyer flasks and covered with extraction solvent (50 mL). The deposition plate (petri dish) was rinsed twice with extraction solvent (IPA: ethylene glycol and diethylene glycol; n-hexane: PTEO) and the extracts were combined to one sample.

[6] Please note, that several spraying activities can be conducted by one person over the duration of a work-shift.
[7] Please note, that the term activity can comprise either: 1. Spraying process only or 2. Spraying process and peripheral work associated with it.

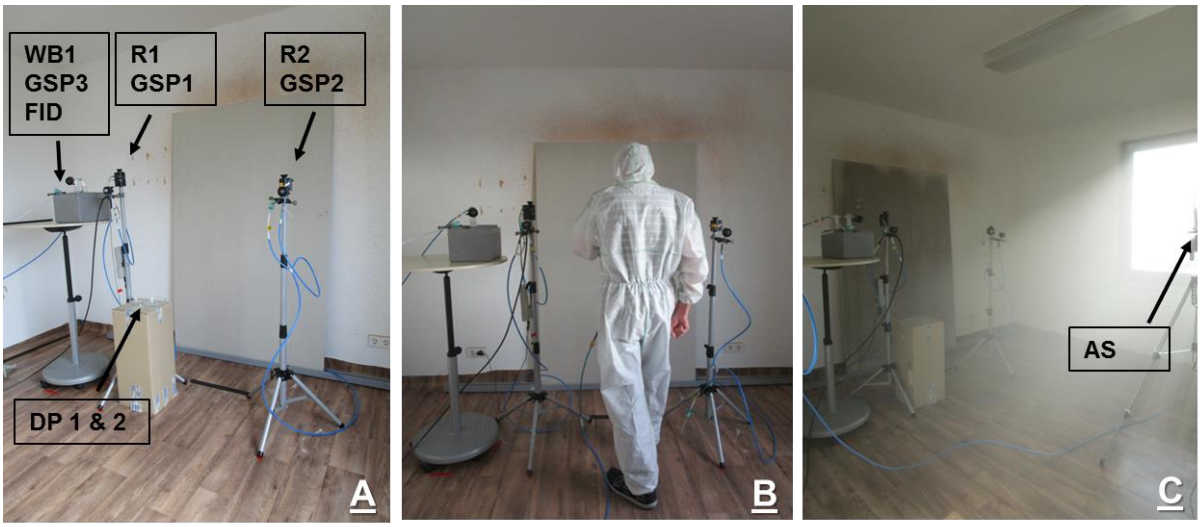

Figure 4 Simulation of baseline workplace scenario. A and B: General set-up before spray application; C: General set-up 3 min after spray application of ethylene glycol where a visible aerosol mist is generated. WB – wash bottle, R – Respicon®, DP – horizontal deposition plate, AS – Aerosol spectrometer.

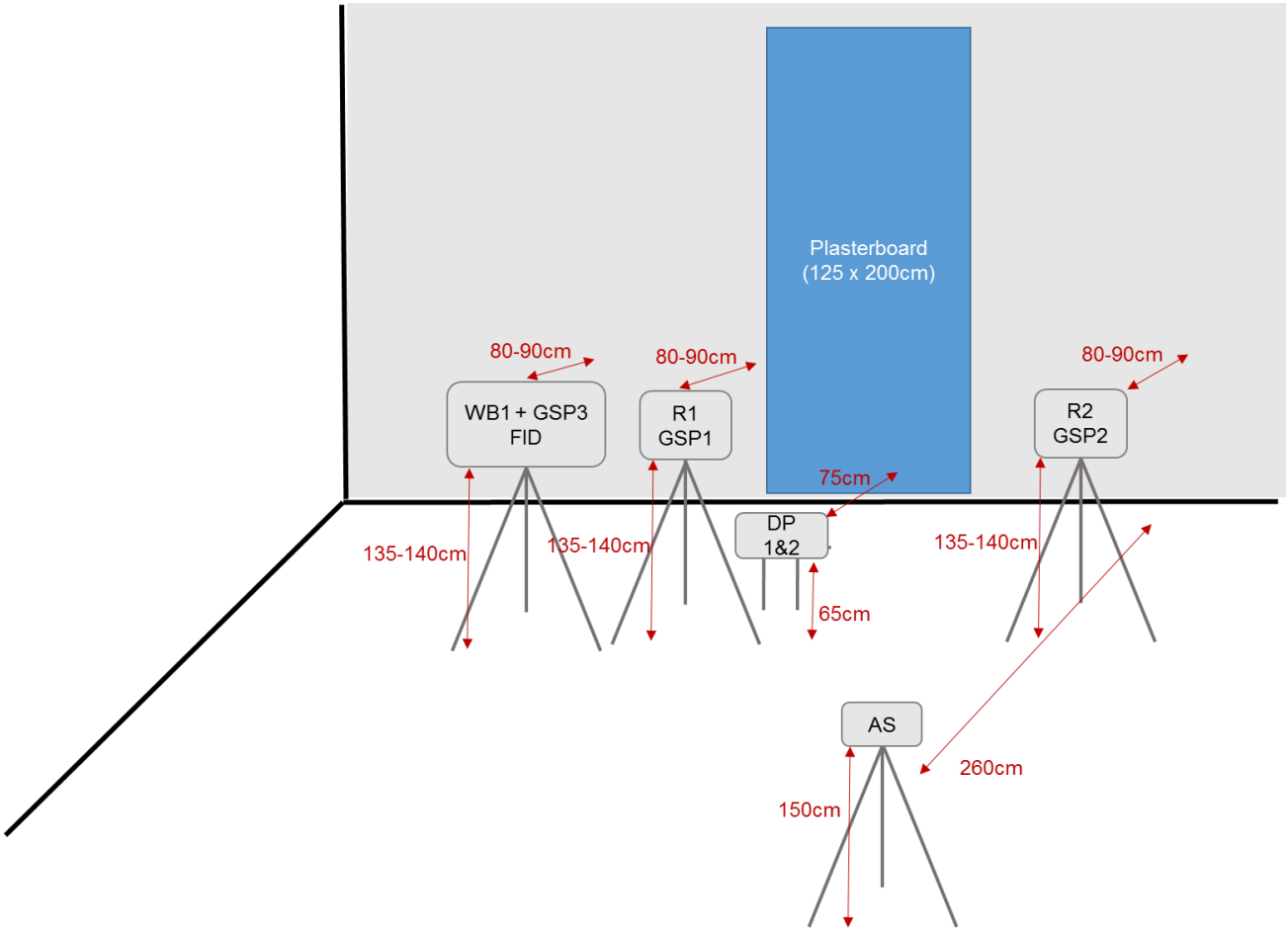

Figure 5 Positioning of the sample equipment in the room. WB –Wash bottle; R – Respicon, GSP – Inhalable dust sampler; DP – horizontal deposition plates; AS – Aerosol spectrometer

Table 3 Three consecutive spray test were carried out with each substances. The total amount of spray liquid applied during one minute of spraying are listed as well as the release rate (for the spray liquid) calculated from this value

#	**Applied amount of spray liquid [g]**	**Spray liquid release rate [g/sec]**
Diethylene glycol (Vp 0.7Pa)		
E1	267	4.5
E2	257	4.3
E3	260	4.3
MV	**261**	**4.4**
Ethylene glycol (Vp 7Pa)		
E1	270	4.5
E2	256	4.3
E3	283	4.7
MV	**270**	**4.5**
PTEO (Vp 80 Pa)		
E1	253	4.2
E2	246	4.1
E3	253	4.2
MV	**251**	**4.2**

3.3 Determination of aerosol and gas phase concentration

3.3.1 Aerosol

The aerosols released during the spraying activities were monitored using

a. An aerosol spectrometer (1.109; Grimm) providing time-resolved records of air-borne particles (0.3 to 30 µm)
b. Two Respicon samplers with one containing an optical unit allowing time-resolved monitoring of the particles classes (< 40 µm; < 10 µm; < 5 µm)
c. GSP samplers – for off-line quantification of inhalable particles (< 100 µm).

The filters of the Respicon and GSP samplers were subsequently extracted with a suitable solvent (IPA: ethylene glycol and diethylene glycol; n-hexane: PTEO) and subjected to GC-FID analysis (chapter 3.3.2, Table 4).

3.3.2 Gas phase

A Flame Ionisation Detector (FID) monitored the gas phase concentration of the respective one-component spraying products. For diethylene glycol and ethylene glycol, calibration of the FID signal was achieved by measuring the gas phase above the spraying product in a closed container, where the equilibrium concentration between liquid and gas phase exists. Based on the vapour pressure the saturated gas phase concentration can be calculated. The two values, experimental FID reading and calculated value, permit the calibration of the FID for the respective spraying product. An example is given in Figure 6, where the FID reading of the gas phase concentration for ethylene glycol above ethylene glycol (l) in a closed container is depicted. A conversion factor of 2.3 was determined between the experimental reading of

30 ppm and the calculated 70 ppm. The gas phase concentration in the test room during the spraying of ethylene glycol was determined by multiplying the FID reading by factor 2.3.

The volatility of PTEO did result in analyte concentration in the sorbent of the wash bottles well above the limit of quantification of the GC-FID method, allowing the calibration of the on-line FID signal using those data.

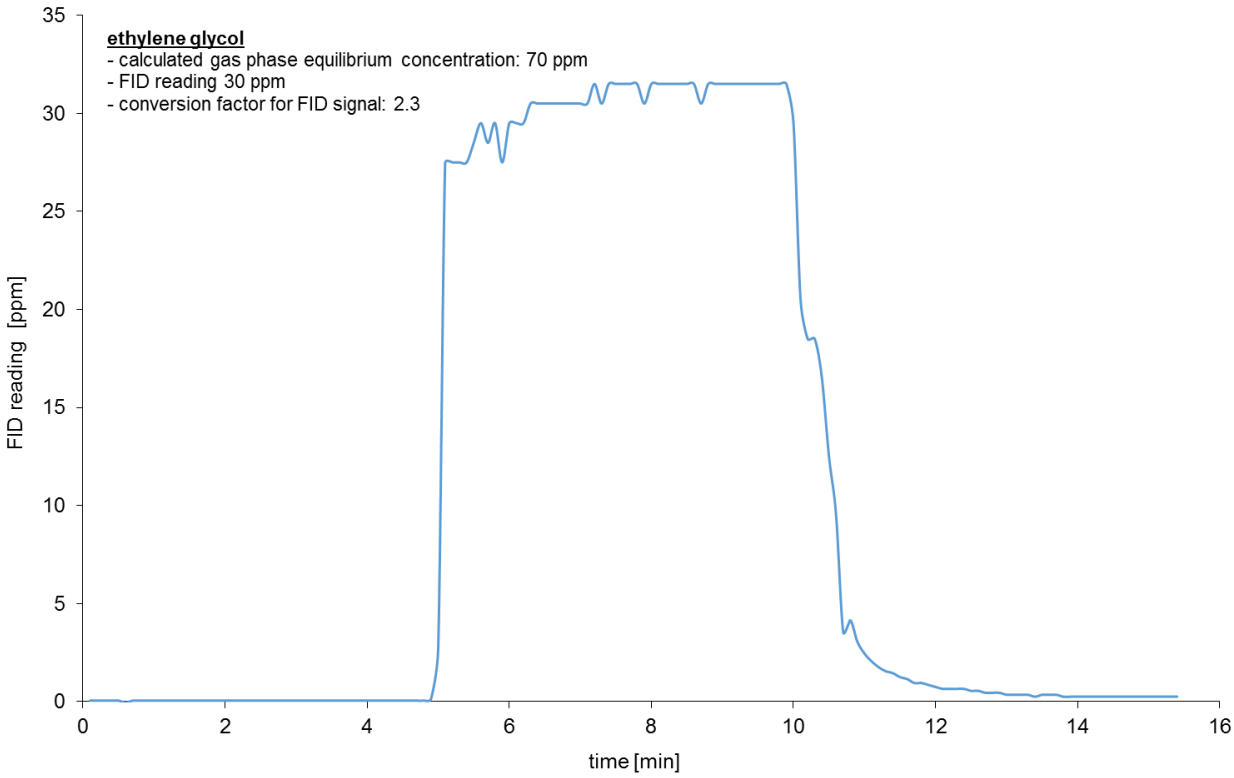

Figure 6 Determination of FID conversion factor – Example: ethylene glycol

In addition, the spraying product in the gas phase was also collected in wash bottles containing an appropriate solvent (IPA: ethylene glycol and diethylene glycol; n-hexane: PTEO). Subsequently, the concentration of the spraying product in the sorbent was determined by GC-FID analysis (Table 4).

Table 4 GC-FID Parameters and settings

Column	DB5-MS; 30 m x 0.32 mm; 0.25 µm
Injection volume	1 µL
Injection mode	Splitless
Temperature program	Initial temperature: 60 °C for 2 min; 20 °C/min to 120 °C (1 min) 70 °C/min to 230 °C (2 min)

3.4 Determination of potential dermal exposure

Potential dermal exposure was captured by horizontal (glass petri dishes) and vertical (filter paper) deposition plates. The horizontal deposition plates (n=2; ∅ = 10.0 and 14.5 cm) were positioned next to the operator at a height of 0.65 m from the floor and distance of 0.75 m from the plasterboard. The vertical deposition plates (n=6; ∅ = 11.0 cm) were personal samplers, attached to the operator according the schematic shown in Figure 7.

After the spraying event the horizontal deposition plates were removed from the test room and each rinsed twice with defined amounts of extraction solvent (IPA: ethylene glycol and diethylene glycol; n-hexane: PTEO). The two extracts were combined to one sample and subjected to GC-FID analysis. The vertical deposition plates were individually extracted using a suitable extraction solvent (50 mL) and the analyte of interest quantified by GC-FID analysis.

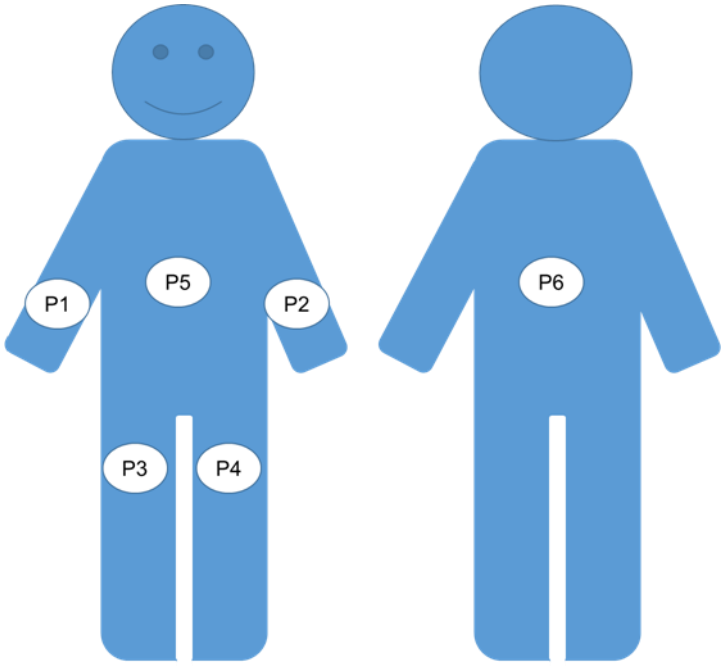

Figure 7 Vertical deposition plates (P) – Schematic of their location on operator during spraying activity.

4 Results

4.1 Literature evaluation

During the project, the available evaluations of PROC 7 and 11 estimations by ECETOC TRA have been scanned for indicators which might be responsible for the underestimation of estimated exposure values.

In the Evaluation of Tier 1 Exposure Assessment Models under REACH (ETEAM) Project report (Lamb et al. 2015; van Tongeren et al 2017) it is presented in Table 3.22 that for industrial spraying (PROC 7) 74% (n=195) of the measured concentrations of volatile liquids (> 10 Pa) are above the tool estimate using ECETOC TRA v3. As in this exercise the substances of concern were substances with mostly relatively high vapour pressures (high and moderate fugacity), it is likely that not the aerosol phase is responsible for the underestimation. Moreover, it is expected that during the ETEAM evaluation the underestimation of the tool estimate is influenced by the used modifiers, i.e. coding of the measured situations into ECETOC TRA,. For example, if the LEV is not well defined in the contextual information of the

measured situation the highest possible modifier (“Indoors with LEV and enhanced general ventilation”) has been used resulting in the lowest estimate, which is the worst-case for this exercise. Therefore, the ascertained underestimation is not solely based on the initial exposure estimate (baseline). For PROC 11 the dataset was very limited (n=23) and 0% of the estimate are below measured concentrations. Therefore, the results are of limited use and not presented in the peer-reviewed publication (van Tongeren et al 2017). The coding was revised during re-evaluation by ECETOC and presented at Poster at ISES 2016 (Bachler et al. 2016), which results still in some situations where an underestimation of the workplace situation exist.

4.2 Laboratory based simulations - Spray applications

The results of the concentration measurements are summarized in Table 5. The average concentration, $\bar{c}$, is calculated based on 3 minutes residence time in the room, of which 1 min was dedicated to the spraying process and the remaining 2 min were spent as additional residence time in the room. The temporal concentration pattern is determined by a linear increase during the spraying time and an almost constant pattern during the extra residence time as shown in Figure 13 for diethylene glycol (mainly aerosol) and Figure 15 for the example of PTEO (mainly vapour phase). Based on this pattern, the total airborne mass (vapour + aerosol), M_a, released as well as the release rate, R_a, can be calculated from the average concentration. For 1-minute spray time (T_1) and 2 minutes additional residence time (T_2), the following relations are obtained (see Appendix):

$$R_a = \bar{c}\,\frac{T_1 + T_2}{T_1 \cdot (0.5 \cdot T_1 + T_2)} \cdot V \qquad \text{Eq. 4}$$

and

$$M_a = R_a \cdot T_1 \qquad \text{Eq. 5}$$

where, V, is the room volume.

The three different compounds showed a vapour pressure dependent partitioning between aerosol and vapour phase during spraying. For the substance with a vapour pressure of 0.7 Pa the exposure was dominated by the aerosol phase, whereas aerosol exposure for the substance with a vapour pressure of 80 Pa (and above) was negligible and exposure to the vapour phase only.

The release rate is the quantity characterizing the spray process; it represents the source strength for human exposure and can be used for generalization of the exposure scenario. The release rates measured with the Walther-Pilot spray gun at 2 bar (producing a very fine droplet spray, MMD=45 µm) varied from approx. 0.27 g/s (Diethylene glycol) to 1.25 g/s (PTEO). When the exposure is aerosol dominated the fraction of liquid becoming available to exposure is about 6% and for the (volatile) PTEO, releasing only vapour, it is 28%.

In the following paragraph the data obtained with the spray gun are compared with data from previous investigations at ITEM using a flat fan spray nozzle (MMD>300 µm). The use of a flat fan spray nozzle resulted in airborne release rates of 0.8 g/s and release fractions of 9% for PTEO (Vp=80Pa). These slightly lower values are due to the coarser droplet spectrum of the flat fan nozzle accompanied with a smaller surface area and, thus, a lower evaporation rate of the substance. For low vapour pressure substances where exposure is aerosol dominated, such as OCTEO (Vp < 1 Pa), the effect of droplet spectrum on release rate is much stronger.

For the flat fan nozzle the release rate was 0.003 g/s i.e. a factor of 100 lower than for the spray gun with MMD=45 µm.

For the aerosol-dominated scenarios, the airborne release rate is proportional to the liquid mass flow of the spray device and its droplet size distribution. For liquids with vapour pressures above 80 Pa, the influence of the droplet spectrum and liquid mass flow on vapour release is weak. Vapour release is dominated by the saturation vapour pressure of the spray liquid. The volume of the spray cone is saturated with the vapour and the airborne release rate of vapour is proportional to the volume the spray cone is scanning per time (here: (0.5m x 1.2m x 2m) x 3 = 3.6 m³)[8]. This view is in accordance with the fact that the measured vapour phase concentrations in the 41.5 m³ control room is approximately 25% of the saturation concentration for both substances, irrespective of their vapour pressures which are 5 and 80 Pa, respectively. The measured release rate for PTEO is R_{PTEO}=1.25 g/s. Since for substances of high volatility the release rate is entirely driven by their vapour pressure, the following general extrapolation can be applied to calculate the release rate (in g/s) as function of the gas phase saturation concentration, C_s, of the substance under consideration:

$$\boldsymbol{R = 1.25 \cdot \frac{C_s}{C_{s,PTEO}}} \qquad \text{Eq. 6}$$

Dermal exposure was also measured by exposing patches to the airborne material. The values represent the material accumulated over a time of 3 minutes. During exposure time, T, and at a given airborne concentration (C_g) of the compound of interest, the mass, M_d, per surface area taken up by the skin is given by:

$$\boldsymbol{M_d = k \cdot C_g \cdot T} \qquad \text{Eq. 7}$$

Here k (m/s) is the mass transfer coefficient, from the gas phase in the room onto the skin surface. For vapours, it is determined by the transfer from air to skin by diffusion characterized by the mass transfer coefficient $k=d_V$ and aerosols by the droplet settling velocity, $k=v_d$.

For aerosols, dermal exposure is by droplet deposition onto the skin. In a conservative approach (exposure of horizontal surfaces such as hands), the mass transfer coefficient is simply the droplet settling velocity[9], v_d, independent of the chemical nature of the liquid[10]. In Table 5 the mass transfer coefficient is calculated from the measured mass density accumulated during the 3 minutes averaging time and the average airborne concentration using the above equation. Both measurements for the aerosol dominated scenario result in similar values, 39.6 and 50.4 m/h. A value of k= 50 m/h corresponds to a settling velocity of 22 µm droplets. This is quite reasonable for the overspray generated when using the spray gun producing a spray with median droplet spray of 45 µm; as the median droplet, size of the overspray is expected to be smaller. Vertical patches are virtually not loaded by aerosols.

For the vapour dominated scenario the mass transfer coefficient is expected to take lower values and is approximately the same for vertical and horizontal patches (within the measurement error). The deposition plates included in the experimental set-up of this study were sufficient to capture potential dermal exposure to aerosols, but not for dermal exposure to vapours. An additional experiment with horizontal deposition plates (petri dishes)

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[8] Distance between spray nozzle and plasterboard: 0.5 m; plasterboard height: 2 m; plasterboard width: 1.2 m; plasterboard was sprayed 3 times.

[9] $v = \frac{d^2 \cdot \rho \cdot g}{18 \cdot \eta}$ v – droplet settling velocity; d – particle diameter in [m]; g – gravity constant (9.807 m/s); ρ – particle density (1000 kg/m³); η - viscosity of air in 0.0000181 Pa s)

[10] It is assumed that the entire liquid material deposited on the skin will finally become systemically available.

n-hexane was conducted for the vapour dominated spraying scenario with PTEO. Potential dermal exposure was determined as 28 (± 6) µg/cm² (n = 6) compared to 1.9 (± 1.1) µg/cm² (n = 6), when empty petri dishes were used as horizontal deposition plates. In this case a transfer coefficient of =3.7 m/h would be applicable. These experiments aimed to simulate worst case, 100% transfer ($k=\infty$) of the vapour to the skin surface. The mass transfer is controlled by the diffusion process from the air to the surface (skin, here simulated by n-hexane). In a study by Weschler and Nazaroff (2014), the value for the "[...] mass-transfer coefficient for external transport of an organic compound from the gas phase in the core of a room through the boundary layer adjacent to the skin."[11], was taken as 6 m/h (please see supporting information in Weschler and Nazaroff; 2014). This is in good agreement with our finding revealing 3.7 m/h. However, depending on the phys.-chem. properties of the of interest only a certain proportion will permeate through the boundary skin corneum and become systemically available. Systemic exposure estimates will have to be carried out for each substance individually, considering their transdermal permeability coefficient, $k_{p\text{-}g}$. Julander et al.[12] cite the work of Potts and Guy[13] for the calculation of $k_{p\text{-}g}$ based on the two compound specific parameters molecular weight and octanol:water partition coefficient. They also point out that synergistic effects might enhance dermal uptake of individual substances mixtures. As systemic exposure is not within the scope of this study dermal exposure are limited to external exposure on the skin surface. For vapours these estimates are based on the mass-transfer coefficient, d_v, which is taken as 6 m/h and for aerosols on the droplet settling velocity, v_d, of 50 m/h (Table 9 and Table 10).

The use of n-hexane as sampling medium to determine the dermal exposure to vapours as well as the subsequent application of a mass-transfer coefficient of 6 m/h will result in an overestimation of dermal exposure. Reducing factors such as the evaporation of the from the skin surface were not taken into consideration. The phys. – chem. properties of the substance (e.g. vapour pressure, lipophilicity, molecular weight, etc.), (co-)formulant and the climatic conditions (e.g. temperature, humidity, etc.) of the work environment are two factors impacting on the evaporation of the substance of interest from the skin. The trapping of a substance in the fabric of either ordinary or protective clothes on the other hand, can lead to enhancement of dermal exposure. In real life scenarios, dermal exposure to substances applied by spraying activities will have multiple sources with varying contributions. In this the data presented in Table 9 and Table 10, should be viewed as a starting point for dermal exposure estimates; which will need adaptation to derive at exposure estimates that can reasonably be expected for industrial and professional spraying activities.

[11] In this study denoted as d_v.

[12] Julander A., Boman A.,Johanson G, Lidén C. (2018): The Nordic Expert Group for Criteria Documentation of Health Risks and Chemicals 151. Occupational skin exposure to chemicals. *Arbete och Hälsa*; 52:1-69.

[13] Potts R.O., Guy R. H. (1992): Predicting skin permeability. *Pharm. Res.*, 9:663-669.

Table 5 Results of concentration measurements in a test room of 41.5 m³ volume. Averaging time 3 minutes.

	0.7 Pa	7 Pa	80 Pa
	Experimental	Experimental	Experimental
	MV	MV	MV
Gas phase [mg/m³]	BLQ	45	1500
Percent of saturation concentration [%]	NA	25	22
Respicon inhalative [mg/m³]	295	385	NA
GSP (aerosol) [mg/m³]	338	313	NA (4.5)
Total average concentration [mg/m³]	317	349	1500
Total mass released, M_a [g]	15.8	17.4	74.7
Release rate, R [g/s]	0.27	0.29	1.25
Release fraction [-]	0.06	0.06	0.28
Dermal horizontal [µg/cm²]	65	88	1.9
Mass transfer coefficient [m/h]	39.6	50.4	0.25
Dermal vertical [µg/cm²]	#	4 (n=18)	0.7 (n=6)
Mass transfer coefficient [m/h]	-	2.27	0.09

BLQ – Below limit of quantitation; # - see **Table 6**

Table 6 Vertical deposition plates – Filter patches on operator

The release rates measured in our small control room can be used to model exposure to aerosol/vapour for other scenarios; using the software tool SprayExpo. The task of wall spraying is modelled exemplarily for various room sizes and release times using SprayExpo and a release rate of 1 g/s. The spraying scenario is shown in Figure 8. Two different process sequences were investigated: continuous spraying, and spraying with interruption without spray activities. The room sizes are varied by a factor of 44. The application time is adjusted to the treated wall area such that there is always the same surface coverage with spray liquid. Figure 9, shows the time-averaged concentration of the first process. Except from the very last one, all simulations are carried out for zero air exchange. The graphs show the exposure concentration averaged over the time starting with zero up to the x-axes value. Since the average concentration over time starts with a value of zero it quickly rises and finally, for large volumes, approaches a constant value of approximately 1200 mg/m³, nearly independent of the room size. The sprayer is in his personal vapour cloud generated locally, which moves with the sprayer as the work progresses. In this sense, the modelled exposure concentrations result in values independent of the averaging time when the spraying is carried out.

The simulation results shown in Figure 10 represent the same spraying scenarios as in Figure 9 with the modification that the worker resides for another 10 minutes in a place distant from the wall that has been treated. This is to simulate preparation, refilling or maintenance work. Exposure at this location is primarily related to the far field contribution resulting from the spray cloud after turbulent dispersion inside the room. In the examples, the two spraying times of 2 and 4 minutes cover 17%, respectively, 29% of the total simulation time (12 and 14 minutes). The mean concentration averaged over the entire simulation time decreases compared with the results of Figure 9 for continuous spraying without interruption. This decrease is most prominent for large rooms with large mixing volumes. According to Figure 10 a mean concentration of 500-600 mg/m³ would be a sufficiently conservative estimate that is applicable to rooms with a floor area larger than 100 m².

For the small 25 m²-room (floor area), where the concentration homogeneity is reached in shorter times, the reduction in mean concentration due to the non-spray period is smaller.

However, for a small room it is quite unlikely that the sprayer stays in the room during filling and preparation of the spraying system. If the concentration outside the room is assumed to be zero, the concentration averaged over the entire simulation time (2 or 4 minutes spraying + 10 minutes non-spraying) is just 17% and 29% of the mean concentration reached after 120 s and 240 s, respectively. This results in approximately 300 and 600 mg/m³ for an airborne release rate of 1 g/s. Assuming spraying and peripheral work are linked together suggests approximately 600 mg/m³ to be a conservative mean concentration averaged over the process time when the release rate of airborne material from the spray cone is 1 g/s as assumed in the simulation exercise.

These results serve as starting point for calculating the exposure to vapours with release rates determined from Eq**. 6**. For aerosol, dominated exposure a release rate of 0.3 g/s is suggested to be used since it represents a realistic worst case resulting from values of the spray droplet MMD and upper values of the liquid flow rate through the spray nozzle as discussed above.

Table 6 Vertical deposition plates – Filter patches on operator

	E1	E2	E3
	[µg/cm²]		
D1 (forearm - left)	269	184	179
D2 (forearm - right)	204	283	248
D3 (thigh - left)	48	68	11
D4 (thigh - right)	7	42	103
D5 (chest)	53	10	63
D6 (back)	51	17	65

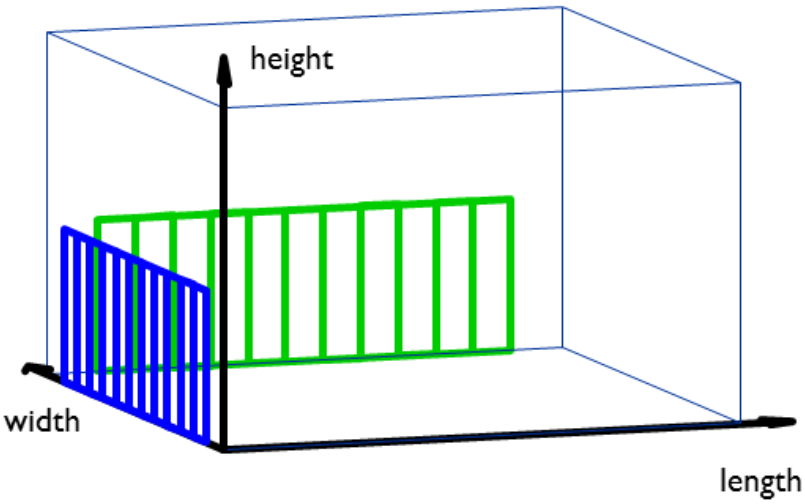
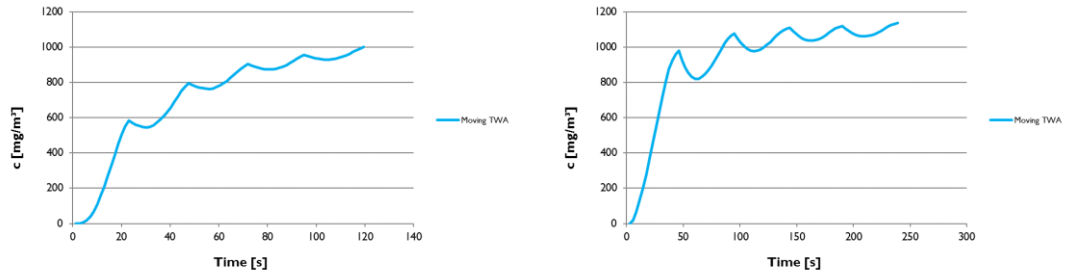
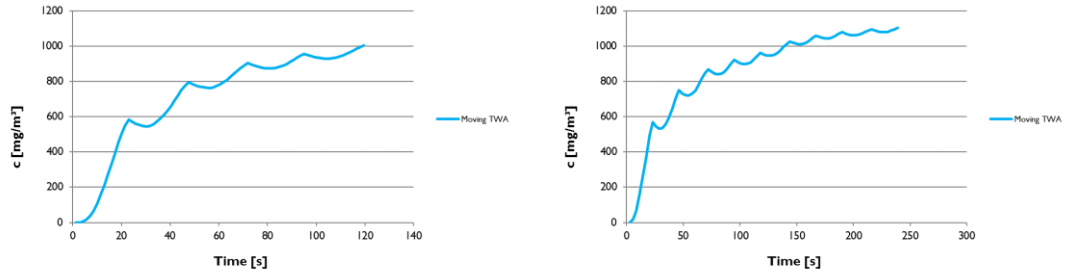


Figure 8 Wall spray scenarios used for SprayExpo simulations. The release rate is fixed at 1 g/s. Equal surface areas are treated in equal times.

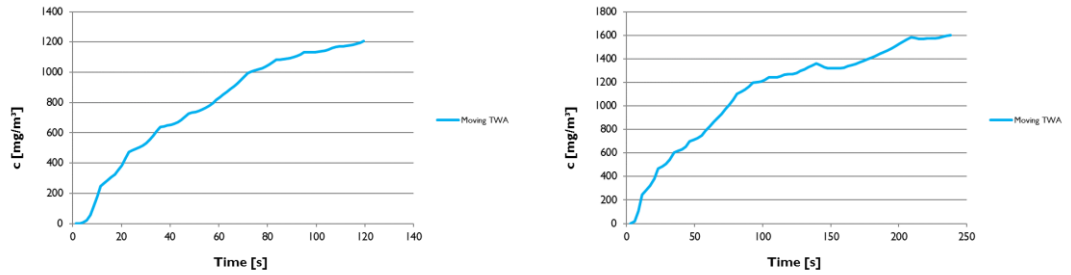
20 x 20 m², 1 g/s, 120 s spraying; 1-9 m wall length and 240 s 1-17 m wall length



10 x 10 m², 1 g/s, 120 s spraying,1-9 m wall length; 240 s 2 x 1-9 m wall length



5 x 5 m², 1 g/s, 120 s spraying, 2 x 0.5 – 4.5 m wall length; 240 s 4 x 0.5-4.5 m wall length



3 x 3 m², 1 g/s, 120 s spraying, 4 x 0.5 – 2.5 m wall length; right: 20 fold air exchange per h

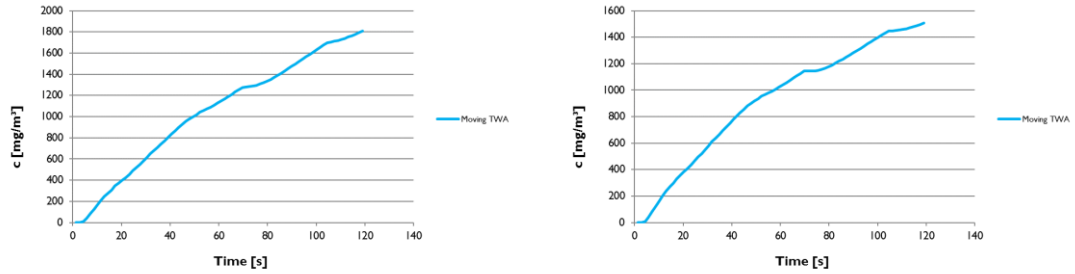
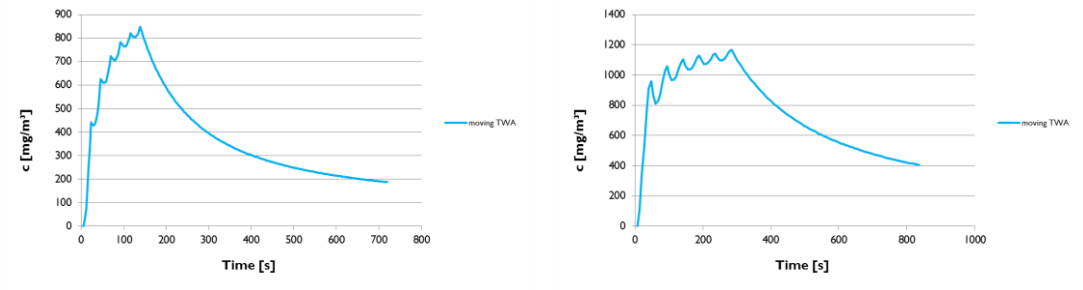
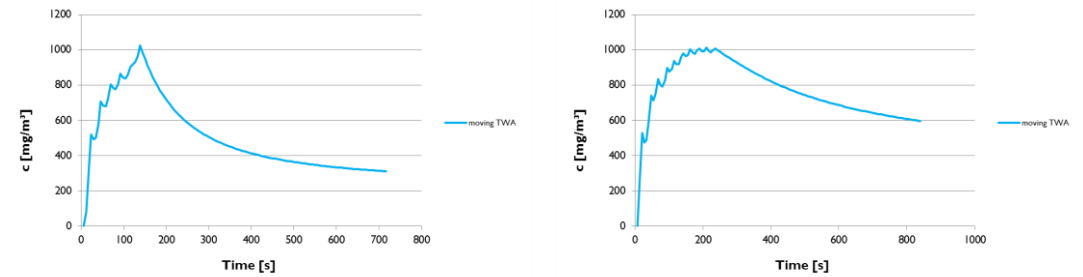


Figure 9 Average concentration values for wall spraying as calculated from the software tool SprayExpo. Moving average concentration over time means time averaging starts at t=0 and ends at the time point specified by the value on the abscissa. Simulation represents the spray cloud for a painter spraying on walls while moving as work progresses. For large rooms the average concentration quickly becomes stationary because the operator resides always in his personal cloud. The distance of the sprayer from the wall is 1.2 m. For small room sizes, there is accumulation of vapour mass due to the confined space leading to an increase in average concentration with time. In general the impact of the room size on the inhalation exposure is negligible.

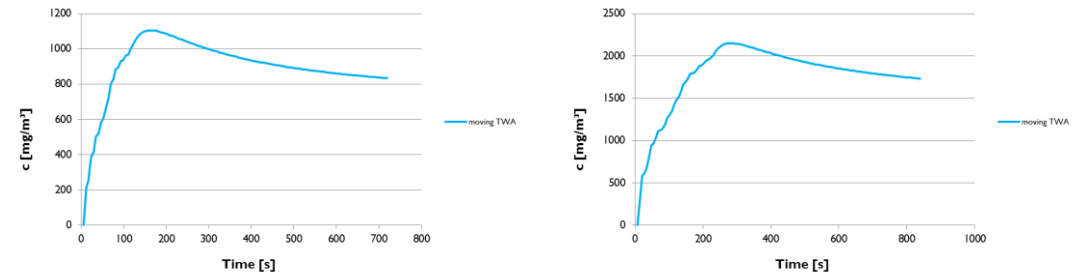
20 x 20 m², 1 g/s, 120 s spraying; 1-9 m wall length and 240 s 1-17 m wall length



10 x 10 m², 1 g/s, 120 s spraying,1-9 m wall length; 240 s 2 x 1-9 m wall length



5 x 5 m², 1 g/s, 120 s spraying, 2 x 0.5 – 4.5 m wall length; 240 s 2 x 0.5-4.5 m wall length



As above with 20-fold air exchange per h.

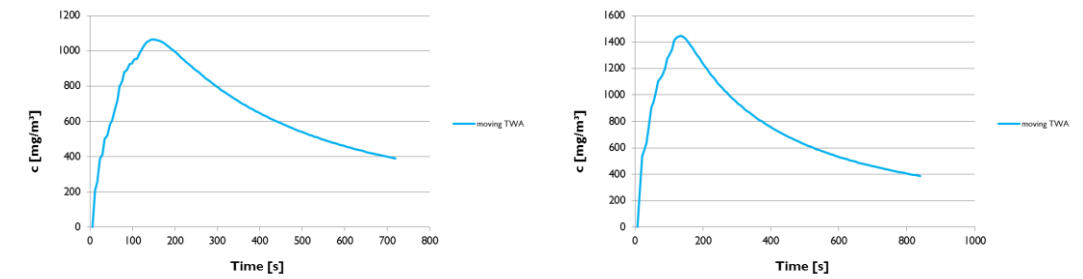


Figure 10 Average concentration values for wall spraying as calculated from the software tool SprayExpo. Moving average concentration over time means time averaging starts at t=0 and ends at the time point specified by the value on the abscissa. Simulation represents the spray cloud for a painter spraying on walls while moving as work progresses. The distance of the sprayer from the wall is 1.2 m. After the spraying (t=120), the worker moves away from the wall. He resides another 10 minutes at his new position.

5 Discussion

The aim of this project was to generate inhalation and dermal exposure data to assess aerosol and vapour phase contributions to inhalation and dermal exposure during (PROC 7- Industrial spraying) and professional spraying (PROC 11- professional spraying) activities.

The airborne release rate of solvent (as aerosol and vapour) during any spray activity is the key parameter influencing the exposure concentration. For high vapour pressure solvents, the release of vapour into the air is determined by the saturation concentration of the solvent, and the volume that the spray cone covers per time during application since it can be assumed that the entire spray cone is always saturated with the vapour due to the high surface area provided by the droplets independent of the droplet size distribution and the solvent flow rate through the nozzle. By contrast, for very low vapour pressure liquids where the exposure is aerosol dominated, the airborne release is controlled by the material mass flow and particularly by the droplet size distribution. Spray gun technology (MMD>=45 µm, mass flow =300 ml/min) results in highest release rates compared to other spray technologies such as flat and round spray nozzles operated without compressed air and having much coarser droplet distributions. Use of the spray gun is a realistic worst-case scenario. In this study upper limit, values of the release rates of aerosols and vapours have been determined experimentally. For aerosols a value of 0.3 g/s was measured, i.e. 1.7% of the total mass flow of the liquid through the spray nozzle. For the vapour phase, a release rate of 1.25 g/s was measured for PTEO (Vp: 80 Pa). The hypothesized release mechanism (saturation in the spray cone) leads to the extrapolation given by Eq.6 for substances with higher vapour pressures.

The experimentally determined release rates were used as inputs to the exposure model SprayExpo. Two scenarios for activities were modeled:

- The first one was a constant continuous spraying process where exposure is dominated by the near field concentration close to the spray cloud.
- The second scenario of a work process combines near field exposure during the spraying action and far field exposure during peripheral work (without spraying) such as refilling, maintenance etc. distant from the spraying location. Here two scenarios are considered, where spraying contributes 17%, respectively, 29% to the total time of the work process.

Simulations run with the exposure model SprayExpo predict exposure concentration of C_{sim} =1200 mg/m³ for an applied release rate of 1 g/s for the first scenario of continuous spraying and approximately C_{sim}=600 mg/m³ for the scenario taking into account non-spraying times during the working process.

According to this prediction, a base line concentration of

$$C_{ae} = C_{sim} \cdot 0.3 \qquad \text{Eq. 8}$$

is an appropriate upper limit exposure concentration for aerosol dominated scenarios (release rates 0.3 g/s), as was verified by laboratory based simulations in this study. For substances with higher vapour pressures (Vp > 80 Pa), where exposure is gas phase dominated (release rate 1.25 g/s), the base line concentration for inhalation exposure can be estimated as follows:

$$C_{vap} = C_{sim} \cdot 1.25 \cdot \frac{C_s}{C_{s,PTEO}} \quad . \qquad \text{Eq. 9}$$

This methodology has been applied to substances of different vapour pressures as listed in Table 7. The exposure concentrations as calculated from Eqs. 8 and 9 are listed in mg/m³ and, for vapours, in ppm. The two scenarios - continuous spraying as worst case and intermittent spraying as alternative worst case - are treated separately in Table 7 and Table 8. In Table 7 the activity is entirely spraying while, in Table 8, the activity covers both, spraying and peripheral work. If shorter activity durations (sum of all spraying activities) are considered, the estimates of this study have to be reduced according to Eq. 3 where we assume a shift duration of 8 h. The comparison with ECETOC TRA has been made with ECETOC TRA predictions listed for “Long-term Inhalation Exposure Estimate” based on “Duration of activity > 4h” and “Short-term Inhalation Exposure Estimate”. In this context, it has to be noted that ECETOC TRA estimates a shift exposure that will include a much more complex exposure profile than what is reflected by the experiments. For a meaningful comparison of the data sets more detailed information from “behind the scene” of ECETOC TRA are required.

For the estimates of the dermal exposure these values are inserted in Eq. 6 which for T=8 h (long term) and T=1 h (short-term) using values for an coefficient of 6 m/h for vapour and a deposition rate of 50 m/h for aerosol dominated scenarios (Table 9 and

Table 10). The estimates should be considered as conservative as neither the conceivable evaporation of the substances from the skin surface nor the wearing of clothes, ordinary or protective, are considered in the calculations. As for the inhalation exposure estimates a direct comparison between this study and ECETOC TRA should not be made at this point. The dermal exposure estimates presented in this report should be viewed as a starting point; which requires adaptation to derive at exposure estimates that can reasonably be expected for industrial and professional spraying activities.

6 Conclusion

This study has provided a first insight into the underlying parameter of inhalation and dermal exposure during spraying activities (PROC 7 and 11). Initial experiments demonstrated the impact of the spraying method, and therefore the droplet size distribution, for aerosol dominated spraying scenarios on the exposure concentration - the smaller the droplet size, the higher the aerosol concentration. Aerosol dominated exposure is to be expected for vapour pressures below 10 Pa. Above this value there exists a transition regime (10-100 Pa) characterized by simultaneous exposure to aerosols and vapours. For substances above 100 Pa, the saturation concentration of the vapour is the parameter controlling exposure. The measurements have shown a direct proportionality of estimated exposure concentration to the saturation concentration of the substance. The findings of this study indicate an underestimation of the inhalation baseline concentration by ECETOC TRA for high vapour pressure substances (>300 Pa). This underestimation increases with increasing vapour pressure, which also seems to hold true for dermal exposure. However, a direct comparison between the findings of this study and ECETOC TRA estimates could not be made, due to our limited knowledge of the data sets behind the ECETOC TRA exposure estimates.

7 Outook

There are still several remaining uncertainties of this analysis:

- The experimental basis for the derivation of Eq. 6 and, related to this, the extrapolation to high vapour pressure solvents was based on measurements with two substances only, with vapour pressure around 10 and 100 Pa, respectively.
- The results of the dispersion modelling was verified experimentally by carrying out measurements in a rather small room under laboratory-like conditions
- Only wall spraying processes were considered.
- No realistic industrial scenarios such as wall spraying in a large hall or spray treatment of surfaces at a fixed position (spray booth, surface coating of components) inside the hall were considered experimentally to validate the simulation results.

These gaps could be filled by performing a limited number of additional tests in a professional as well as industrial environment. Two different room sizes of 45 m² (10.7x4.2 m²) and 425 m² (17x25m²) are envisaged. Wall spraying (moving source) as well as spraying at a fixed location will be carried out using a solvent with very low vapour pressure simulating the aerosol dominated exposure and two solvents with vapour pressures of 100 Pa and 1,000 Pa. These experiments should be complemented by model calculations.

The data given in Table 9 and
Table 10 should be viewed as a starting point for dermal exposure estimates in mg/cm² over the given time periods. They are based on a mass transfer coefficient of 6 m/h for vapour as suggested by Weschler et. al 2014 and experimental work conducted in this study, deriving at a deposition rate of 50 m/h for aerosols. Additional experiments with solvent loaded horizontal deposition plate, provided first confirmation that 6 m/h is a reasonable mass transfer coefficient that can be applied for vapours. The use of solvent loaded horizontal deposition plates, however, poses the question of overestimating vapour deposition, as the solvent loaded deposition plate serves as a perfect sink which realistic surfaces do not. The exposure estimates should not be viewed as instantaneous loading of the skin with the given substance; but as the amount that comes into contact with the skin over the given time periods, 1 and 8 h respectively. Depending on for example the phys.-chem. properties (permeability coefficient) of the substance of interest a certain fraction will become systemically available, whereas the remainder will either be removed from or remains on the skin surface. But all fractions will have been in contact with the skin surface. The estimates in Table 9 and
Table 10 do not consider physical skin adherence or the implication of a maximum loading capacity of human skin towards vapours or aerosols. Maximum skin adherence and other modifying factors such as those outlined in the dermal conceptual model (Schneider et al.[14]) are not considered in the dermal exposure estimates given Table 9 and 10. Even though maximum skin adherence has been reported for solids and liquids, information on whether this concept is also applicable for vapours is currently not available, to our knowledge.
For aerosol dominated scenarios the short-term dermal exposure estimates reported in Table 9 and
Table 10 are in good agreement with the 2 mg/cm²/day baseline value stipulated by the ECETOC TRA tool; whereas the long-term estimates for aerosol dominated scenarios and

[14] Schneider T; Vermeulen R; Brouwer D H; Cherrie W; Kromhout H; Fogh C L (1999): Conceptual model for assessment of dermal exposure. *Occup. Environ. Med*.; 56:765-773.

vapour dominated scenarios (short- and long term) are clearly exceeding this value. Bearing this in mind two questions come into mind:

1. Is one baseline value for dermal exposure sufficient?-or do we need to take different fugacity bands into account? This question has already been addressed by Marquart et al.[15]; who came to the conclusion that not a single default value for dermal exposure estimates should be applied.

2. Do we need time-weighted dermal exposure estimates? – considering that dermal exposure during spraying activities is seldomly an instantaneous event but occurs continuously over a given time period; with substance molecules moving to and from the skin surface, and the substance specific permeability coefficient being a measure for systemic uptake. The skin surface merely being a passing point and the dermal exposure estimate providing an indication for the amount of substance “passing by” during any given spray related task.

These two question as well as reducing and/or enhancing factors on dermal exposure estimates will require further investigation, either experimentally or desk based.

[15] Marquart H; Warren N D; Laitinen J, Van Hemmen J J (2006): Default values for assessment of potential dermal exposure of the hands to industrial chemicals in the scope of regulatory risk assessments. *Ann. Occup. Hyg*, 50:496-489.

Table 7: Inhalation exposure: Comparison of estimates based on this study and ECETOC TRA base line values (PROC 7). Exposure scenario 1. Scenario 1 is defined as constant continuous spraying process where exposure is dominated by the near field concentration close to the spray cloud.

Product data					Estimate for peak as well as > 4 h spraying activity*			Ratio to ECETOC based on mg/m³		ECETOC TRA v3 PROC 7 values			
	MW	Vp	Saturated air conc., C_s at 20 °C		Aerosol	Vapour		long-term (activity duration > 4h)	short-term	Long-term inhalation exposure estimate (activity duration > 4h)		Short-term inhalation exposure estimate	
Substance	**[g/mol]**	**[Pa]**	**[mg/m³]**	**[ppm]**	**[mg/m³]**	**[mg/m³]**	**[ppm]**	**-**	**-**	**[ppm]**	**[mg/m³]**	**[ppm]**	**[mg/m³]**
1-Bromopropane	123	14600	737192	143842	NA	163453	31893	63.8	15.9	500	2563	2000	10250
butan-2-one	72.11	10500	310819	103448	NA	68916	22937	45.9	11.5	500	1502	2000	6009
trichloroethylene	131.39	7760	418549	76453	NA	92802	16951	67.8	17.0	250	1369	1000	5475
propan-2-ol	60.1	4260	105101	41970	NA	23303	9306	37.2	9.3	250	626	1000	2504
Toluene	92.14	2910	110069	28670	NA	24405	6357	25.4	6.4	250	960	1000	3839
2-methyl-propan-1-ol	74.12	1180	35904	11626	NA	7961	2578	10.3	2.6	250	772	1000	3088
n-butyl acetate	116.16	1070	51023	10542	NA	11313	2337	9.3	2.3	250	1210	1000	4840
Xylene	106.17	670	29201	6601	NA	6475	1464	5.9	1.5	250	1106	1000	4424
1-methoxy-2-propyl acetate	132.16	310	16818	3054	NA	3729	677	6.8	1.7	100	551	400	2203
N-methyl-2-pyrrolidone	99.13	32	1302	315	400	289	NA	1.7	0.4	100	413	400	1652
PTEO	206	80	6765	788	NA	1500	175	1.7	0.4	100	858	400	3433
Ethylene glycol	62.07	5.3	135	52	400	30	NA	1.7	0.4	100	259	400	1035
Diethylene glycol	106.12	0.8	35	8	400	8	NA	0.9	0.2	100	442	400	1769

*These values are the maximum values. In case the activity duration, $T_{activity}$, are shorter than 8 h the TWA concentrations in these columns have to reduced according to Eq. 3.

Table 8: Inhalation exposure: Comparison of estimates based on this study and ECETOC TRA base line values (PROC 7). Exposure scenario 2. Scenario 2 is defined as a work process combines near field exposure during the spraying action and far zone exposure during peripheral work (without spraying) such as refilling, maintenance etc. distant from the spraying location.

Product data					Estimate for intermittent peak as well as > 4 h spraying activity*			Ratio to ECETOC based on mg/m³		ECETOC TRA v3 PROC 7 baseline			
	MW	Vp	Saturated air conc., C_s at 20 °C		Aerosol	Vapour		long-term (activity duration > 4h)	short-term	Long-term inhalation exposure estimate (activity duration > 4h)		Short-term inhalation exposure estimate	
Substance	**[g/mol]**	**[Pa]**	**[mg/m³]**	**[ppm]**	**[mg/m³]**	**[mg/m³]**	**[ppm]**	**-**	**-**	**[ppm]**	**[mg/m³]**	**[ppm]**	**[mg/m³]**
1-Bromopropane	123	14600	737192	143842	0	81726	15947	31.9	8.0	500	2563	2000	10250
butan-2-one	72.11	10500	310819	103448	0	34458	11468	22.9	5.7	500	1502	2000	6009
trichloroethylene	131.39	7760	418549	76453	0	46401	8476	33.9	8.5	250	1369	1000	5475
propan-2-ol	60.1	4260	105101	41970	0	11652	4653	18.6	4.7	250	626	1000	2504
Toluene	92.14	2910	110069	28670	0	12202	3178	12.7	3.2	250	960	1000	3839
2-methyl-propan-1-ol	74.12	1180	35904	11626	0	3980	1289	5.2	1.3	250	772	1000	3088
n-butyl acetate	116.16	1070	51023	10542	0	5656	1169	4.7	1.2	250	1210	1000	4840
Xylene	106.17	670	29201	6601	0	3237	732	2.9	0.7	250	1106	1000	4424
1-methoxy-2-propyl acetate	132.16	310	16818	3054	0	1865	339	3.4	0.8	100	551	400	2203
N-methyl-2-pyrrolidone	99.13	32	1302	315	200	144		0.8	0.2	100	413	400	1652
PTEO	206	80	6765	788	0	750	87	0.9	0.2	100	858	400	3433
Ethylene glycol	62.07	5.3	135	52	200	30		0.9	0.2	100	259	400	1035
Diethylene glycol	106.12	0.8	35	8	200	8		0.5	0.1	100	442	400	1769

*These values are the maximum values. In case the activity duration, $T_{activity}$, are shorter than 8 h the TWA concentrations in these columns have to reduced according to Eq. 3.

Table 9 Dermal exposure: Comparison of estimates based on this study and ECETOC TRA base line values. Scenario 1. Scenario 1 is defined as constant continuous spraying process where exposure is dominated by the near field concentration close to the spray cloud. External exposure on the skin, M_d, are calculated according to the following equation: $\boldsymbol{M_d = (c_{aerosol} \cdot T \cdot v_d/10000) + (c_{vapour} \cdot T \cdot d_v/10000)}$, *with $c_{aerosol}$ – airborne aerosol concentration in mg/m³; c_{vapour} – airborne vapour concentration in mg/m³; T – time in h; v_d – mass transfer coefficient for aerosols (droplet settling velocity) taken as 50 m/h; d_v – mass transfer coefficient for vapours, taken as 6 m/h.* **Please note: Dermal exposure estimates presented here, reflect only external exposure on the skin surface, without considering reducing factors such as the evaporation of the substance from the skin surface. Systemic exposure is determined by the phys.-chem. properties of the substance under consideration and has to be determined for each substance individually. The skin surface is viewed as merely being a passing point for the substance of interest and the dermal exposure estimate provides an indication for the amount of substance "passing by" over the given time period (e.g. 1 and 8 h).**

			Estimate (this study)					ECETOC TRA v3 PROC 7 baseline
	MW	VP	Aerosol	Vapour		Dermal (long-term, 8h)	Dermal (short-term,1 h)	dermal
Substance	**[g/mol]**	**[Pa]**		**[mg/m³]**	**[ppm]**	**[mg/cm²]**	**[mg/cm²]**	**[mg/cm²/day]**
1-Bromopropane	123	14600	0	163453	31893	7 85	98,1	2
butan-2-one	72,11	10500	0	68916	22937	331	41,3	2
trichloroethylene	131,39	7760	0	92802	16951	445	55,7	2
propan-2-ol	60,1	4260	0	23303	9306	112	14,0	2
Toluene	92,14	2910	0	24405	6357	117	14,6	2
2-methyl-propan-1-ol	74,12	1180	0	7961	2578	38,2	4,78	2
n-butyl acetate	116,16	1070	0	11313	2337	54,3	6,79	2
Xylene	106,17	670	0	6475	1464	31,1	3,88	2
1-methoxy-2-propyl acetate	132,16	310	0	3729	677	17,9	2,24	2
N-methyl-2-pyrrolidone	99,13	32	400	289	70	17,4	2,17	2
PTEO	206	80	0	1500	175	7,20	0,90	2
Ethylene glycol	62,07	5,3	400	30		16,1	2,02	2
Diethylene glycol	106,12	0,8	400	8		16,0	2,00	2

Table 10 Dermal exposure: Comparison of estimates based on this study and ECETOC TRA base line values. Scenario 2. Scenario 2 is defined as a work process combines near field exposure during the spraying action and far zone exposure during peripheral work (without spraying) such as refilling, maintenance etc. distant from the spraying location. External exposure on the skin, M_d, are calculated according to the following equation: $\boldsymbol{M_d} = (\boldsymbol{c_{aerosol} \cdot T \cdot v_d / 10000}) + (\boldsymbol{c_{vapour} \cdot T \cdot d_v / 10000})$, *with* $c_{aerosol}$ *– airborne aerosol concentration in mg/m³;* c_{vapour} *– airborne vapour concentration in mg/m³;* T *– time in h;* v_d *– mass transfer coefficient for aerosols (droplet settling velocity) taken as 50 m/h;* d_v *– mass transfer coefficient for vapours, taken as 6 m/h.* **Please note: Dermal exposure estimates presented here, reflect only external exposure on the skin surface, without considering reducing factors such as the evaporation of the substance from the skin surface. Systemic exposure is determined by the phys.-chem. properties of the substance under consideration and has to be determined for each substance individually. The skin surface is viewed as merely being a passing point for the substance of interest and the dermal exposure estimate provides an indication for the amount of substance "passing by" over the given time period (e.g. 1 and 8 h).**

			Estimate (this study)					ECETOC TRA v3 PROC 7 baseline
	MW	VP	Aerosol	Vapour		Dermal (long-term, 8h)	Dermal (short-term, 1 h)	dermal
Substance	[g/mol]	[Pa]		[mg/m³]	[ppm]	[mg/cm²]	[mg/cm²]	[mg/cm²/day]
1-Bromopropane	123	14600	0	81726	15947	392	49.0	2
butan-2-one	72.11	10500	0	34458	11468	165	20.7	2
trichloroethylene	131.39	7760	0	46401	8476	223	27.8	2
propan-2-ol	60.1	4260	0	11652	4653	55.9	6.99	2
Toluene	92.14	2910	0	12202	3178	58.6	7.32	2
2-methyl-propan-1-ol	74.12	1180	0	3980	1289	19.1	2.39	2
n-butyl acetate	116.16	1070	0	5656	1169	27.2	3.39	2
Xylene	106.17	670	0	3237	732	15.5	1.94	2
1-methoxy-2-propyl acetate	132.16	310	0	1865	339	8.95	1.12	2
N-methyl-2-pyrrolidone	99.13	32	200	144		8.69	1.09	2
PTEO	206	80	0	750	87	3.60	0.45	2
Ethylene glycol	62.07	5.3	200	15		8.07	1.01	2
Diethylene glycol	106.12	0.8	200	4		8.02	1.00	2

8 Appendix A – Concentration data (on-line monitoring)

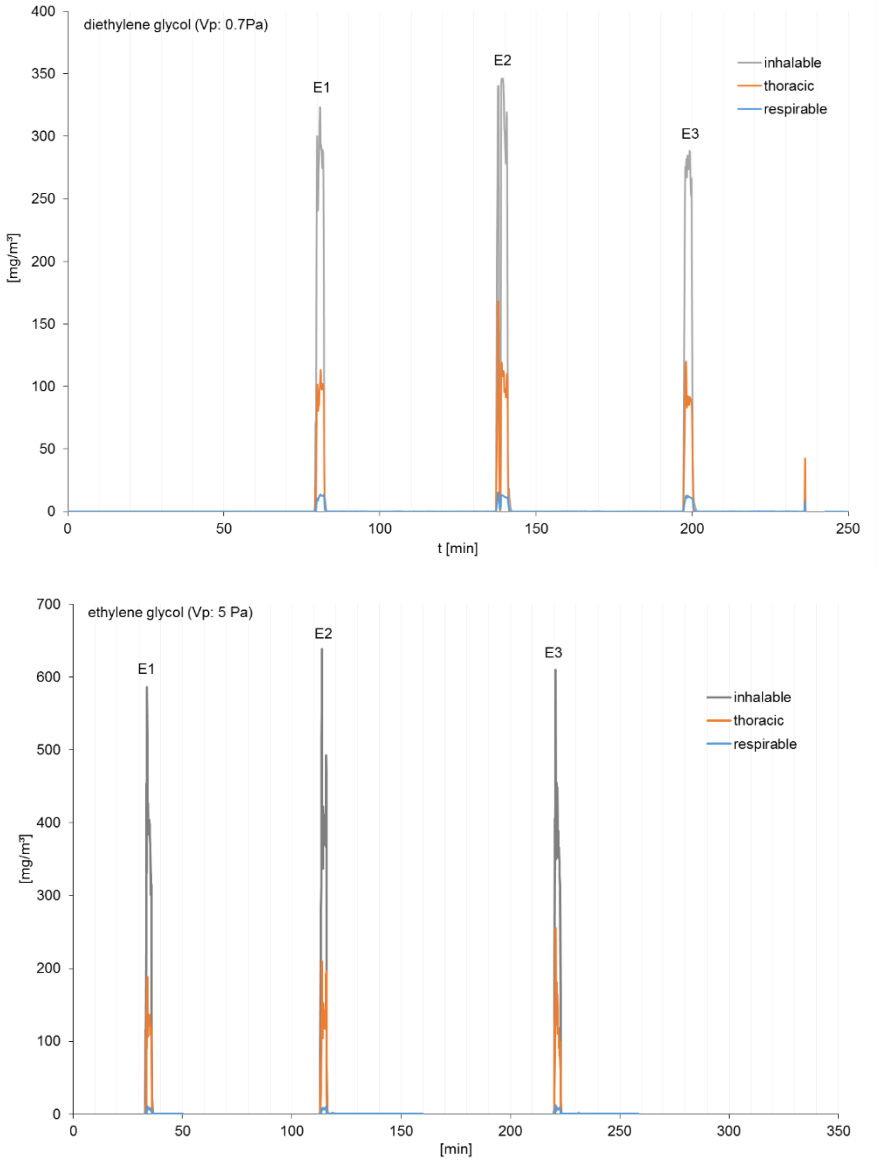


Figure 11 Aerosol data - Respicon data for diethylene glycol (top) and ethylene glycol (bottom).

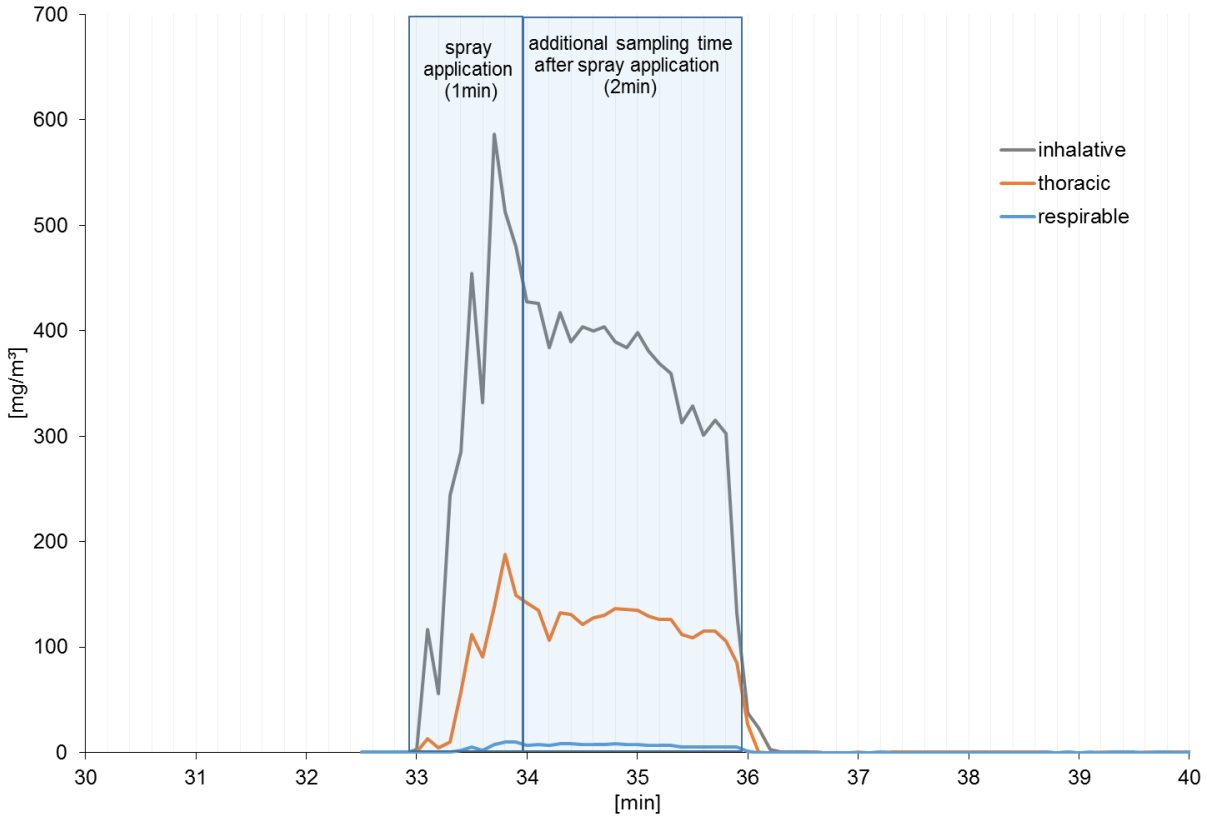


Figure 12 Ethylene glycol – Enlarged time resolved concentration data for the spray application (1 min) and the additional residence time (2 min) after spray application.

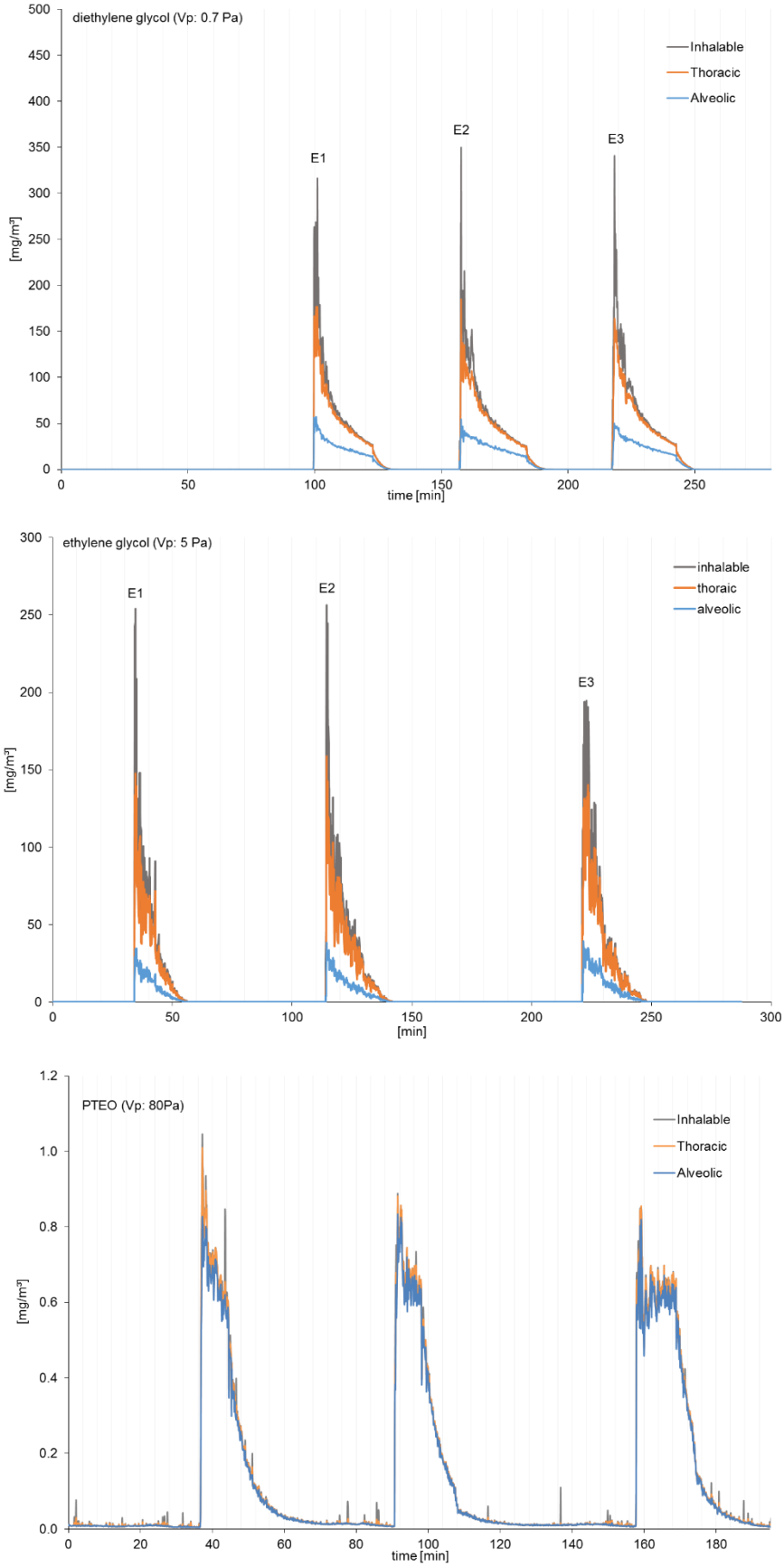


Figure 13 Aerosol data – Grimm (aerosol spectrometer) data for diethylene glycol (top), ethylene glycol (mid) and PTEO (bottom).

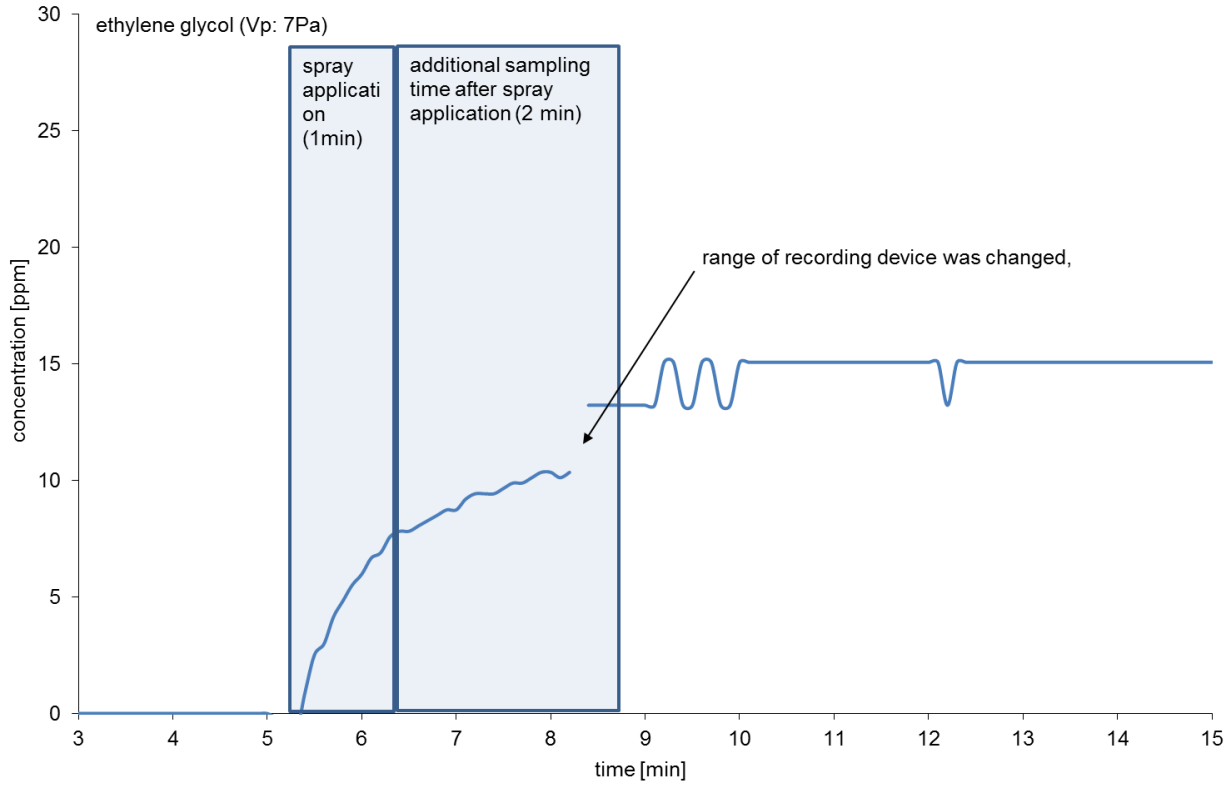


Figure 14 Gas phase data – On-line FID signal: Ethylene glycol

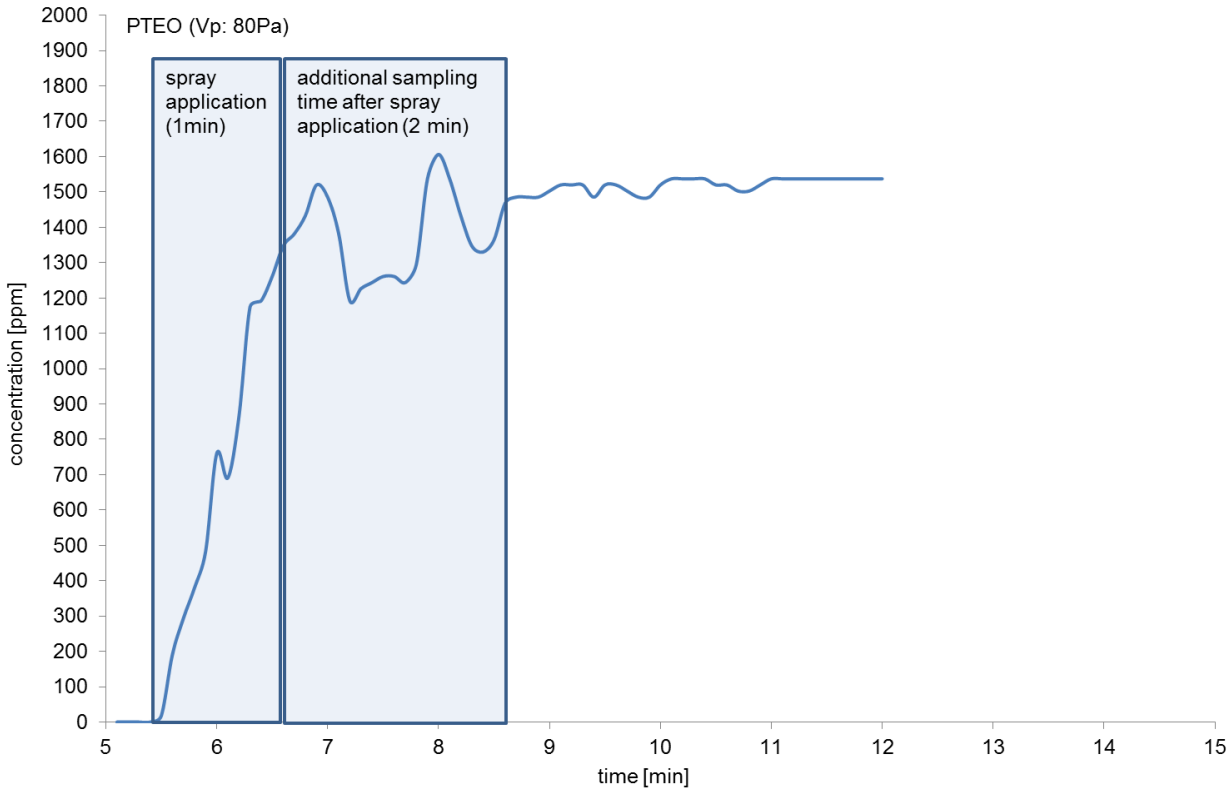
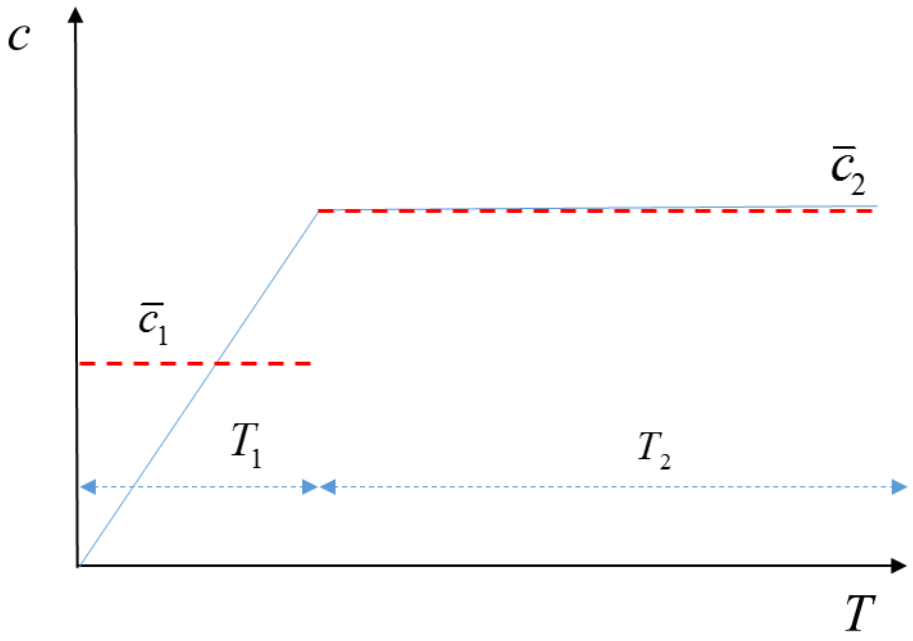


Figure 15 Gas phase data – On-line FID signal: PTEO

9 Appendix B - Derivation of the airborne release rate from the measured average concentration



The average concentration is given by:

$$\bar{c} = \frac{1}{T_1 + T_2}\left(T_1 \cdot \bar{c}_1 + T_2 \cdot \bar{c}_2\right) \qquad \text{A1}$$

where

$$\bar{c}_1 = \frac{1}{2} \cdot \frac{R_a \cdot T_1}{V} \quad \text{and} \quad \bar{c}_2 = \frac{R_a \cdot T_1}{V} \qquad \text{A2}$$

Inserting into A1 and solving for R_a :

$$R_a = \bar{c}\,\frac{T_1 + T_2}{T_1 \cdot \left(0.5 \cdot T_1 + T_2\right)} \cdot V \qquad \text{A3}$$

and

$$M_a = R_a \cdot T_1 \qquad \text{A4}$$