Effectiveness of personal protective equipment against dermal exposure – a comparative survey

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

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Abstract

The efficiency of dermal personal protective equipment (PPE) may depend on several factors, such as the material and the thickness of the PPE or the behaviour of the user. Within this project, literature on the efficiency of dermal PPE was searched, compiled in a database and evaluated in order to examine – to the extent possible – the impact of these factors and to compare the results with default factors for the efficiency of dermal PPE. The literature search identified 410 datasets with data on the efficiency of dermal PPE, with only 13 datasets being based on biomonitoring studies and 397 datasets derived from dosimetry studies. Within the dosimetry studies, most of the datasets relate to protective gloves (N=142) and suits (N=150). After limiting the datasets to studies providing minimum information on the PPE investigated, average protection factors were 88 % (gloves) and 90 % (suits). The distributions of protection factors for both types of PPE suggest that the majority of values is higher than the calculated averages. Less than 10 datasets each were obtained for all other types of dermal PPE. No standardised method for the determination of the efficiency of dermal PPE by dosimetry was identified. Only few studies investigated the impact of the measurement method or the study design.

Several other differentiations, e.g. by the length and state (used vs. new) of protective gloves, were tested. Definitive conclusions on the impact of these factors could not be drawn from the comparison of groups within the database. However, additional information could be extracted from some individual studies.

Apart from the studies in the database, which reflect the occupational setting, both *in vitro* studies and experimental data generated for the purpose of model development were evaluated. While the *in vitro* studies did not allow drawing general conclusions, experimental data for protective suits identified some factors with an impact on the efficiency (e.g. thickness and surface tension of the chemical mixture tested).

In summary, the evaluations provide a comprehensive overview of studies on the efficiency of dermal PPE. Due to the problems described, the default factors for the efficiency of dermal PPE can neither be reliably substantiated nor disproven by the data generated. The problems identified in the evaluation can serve as a basis for future research projects.

Key words:

Dermal exposure, skin protection, dermal protective equipment, measurement methods

Schutzwirkung von persönlicher Schutzausrüstung gegen dermale Belastungen – eine vergleichende Untersuchung

Kurzreferat

Die Schutzwirkung dermaler Schutzausrüstung kann von einer Reihe verschiedener Faktoren, wie z.B. Material und Dicke der Schutzausrüstung oder Anwenderverhalten, abhängen. Im vorliegenden Projekt wurden Studien zur Wirksamkeit dermaler Schutzausrüstung recherchiert, in einer Datenbank zusammengestellt und ausgewertet, um – soweit möglich – den Einfluss dieser Faktoren zu untersuchen und an gängigen Standardfaktoren zur Wirksamkeit zu spiegeln. Die Literaturrecherche ergab insgesamt 410 Datensätze mit Angaben zur Effizienz der Schutzausrüstung, wobei nur 13 Datensätze aus Biomonitoring-Studien und 397 Datensätze aus Dosimetrie-Studien stammen. Innerhalb der Dosimetrie-Studien lagen die meisten Datensätze für Schutzhandschuhe (N=142) und Schutzanzüge (N=150) vor. Nach Einengung auf Datensätze mit Minimalangaben zur Schutzausrüstung ergaben sich mittlere Schutzfaktoren von 88 % (Schutzhandschuhe) und 90 % (Schutzanzüge). Die Verteilungen für diese beiden Arten von Schutzausrüstung legen nahe, dass ein Großteil der Werte über den berechneten mittleren Wirksamkeiten liegt. Für alle anderen Arten von Schutzausrüstung lagen weniger als 10 Datensätze vor. Es wurde keine standardisierte Methodik zur Bestimmung der Effizienz mit Hilfe von Dosimetrie identifiziert. Gleichzeitig gibt es nur wenige Publikationen, die den Einfluss der Messmethode oder des Studiendesigns untersuchen.

Verschiedene weitere Differenzierungen, beispielsweise nach Länge der Schutzhandschuhe und Zustand (alt vs. neu), wurden untersucht. Genauere Schlüsse über den Einfluss dieser Faktoren aus einem Vergleich von Gruppen innerhalb der Datenbank waren nicht möglich. Ergänzende Informationen konnten jedoch aus manchen Einzelstudien extrahiert werden.

Neben den in der Datenbank erfassten Studien, die die Situation an Arbeitsplätzen widerspiegeln, wurden sowohl *in vitro* Untersuchungen als auch für die Modellentwicklung generierte experimentelle Daten ausgewertet. Während die Auswertung der *in vitro* Studien keine verallgemeinere Aussagen lieferten, lassen die experimentellen Daten für Schutzkleidung generelle Einflussfaktoren für die Wirksamkeit (beispielsweise Dicke der Schutzkleidung, aber auch Oberflächenspannung des getesteten Gemisches) erkennen.

Zusammenfassend liefern die Auswertungen ein umfassendes Bild über Untersuchungen zur Effizienz dermaler Schutzausrüstung. Aufgrund der beschriebenen Probleme lassen sich die gängigen Standardfaktoren für die Wirksamkeit dermaler Schutzausrüstung mit den erhobenen Daten weder verlässlich belegen noch widerlegen. Die bei der Auswertung identifizierten Probleme, beispielsweise in Studiendesign und -durchführung, können als Grundlage für zukünftige Forschungsprojekte dienen.

Schlagwörter:

Dermale Exposition, Hautschutz, Dermale Schutzausrüstung, Messmethoden

1 Introduction

Exposure to hazardous chemicals in various sectors of use is a cause of occupational diseases. Skin diseases rank high in the list of occupational diseases, but typically these refer only to local effects caused by chemicals. In recent years, systemic dermal exposure under consideration of percutaneous absorption and personal protective equipment (PPE) has moved into the focus as well.

Gloves represent the most widely used type of dermal PPE (against both local and systemic exposure), but other types of dermal PPE, such as suits, aprons, boots and goggles are also used (see section 3). Sometimes, protective creams are used instead of protective gloves or clothing (WHO, 2014b).

Assumptions on the magnitude of the protective effect of PPE are generally based on considerations of the material used and the breakthrough times reported for specific chemicals. In this context, permeation of chemicals (i.e. transition of the chemical through the barrier itself on a molecular level) can be distinguished from penetration (i.e. transition of the chemical through needle holes, seams etc.) (SOUTAR et al., 2000b). However, these terms are often used interchangeably in the literature[1]. They are also very difficult – if not impossible – to separate in studies at workplaces.

Apart from chemical permeation or penetration through PPE, several other factors are meanwhile acknowledged to have an impact on the effectiveness of dermal PPE, such as the specific scenario considered and the handling of PPE (BROUWER et al., 2005; CHERRIE et al., 2004). Overall, the effectiveness of dermal PPE can be affected by factors, such as:

- The properties of the PPE, also in combination with the properties of the substance:
    - Form/type of the PPE and material properties, e.g. glove length, material thickness (MACFARLANE et al., 2013)
    - Use of new or already used PPE (GARROD et al., 2001)
- Properties of a substance
    - State of the substance at process temperature
    - Volatility of the substance
- Work tasks and processes
    - Exposure pattern and dermal loading (aerosol, splashes, immersion etc.)
    - Type of application (e.g. direction in spray applications)
    - Use frequency and exposure duration
    - Conditions of use (e.g. temperature (EVANS et al., 2001))
    - Instruction and training of workers, compliance by workers (CEBALLOS et al., 2011).

These factors are partly represented in the default factors for PPE effectiveness used in the regulatory area. The following table summarise the default effectiveness values generally applied in exposure assessments for chemicals (REACH) and biocides (BPR).

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[1] Some authors e.g. use the term penetration, when in fact permeation appears to be measured. For this report, we have generally chosen to use the term that the respective authors have chosen.

Table 1.1 Default effectiveness values for dermal PPE

Effectiveness	**Description**	**Context**
	Gloves	
80%	Chemically resistant gloves conforming to EN374	REACH (ECHA, 2012)[2], ECETOC TRA (ECETOC, 2012)
90%	Chemically resistant gloves conforming to EN374 with basic employee training	
95%	Chemically resistant gloves conforming to EN374 with specific activity training; industrial users only	
90%	For challenges by a liquid	BPR, HEEG Opinion 9 (EC, 2010)
95%	When new gloves for each work shift are used	
95%	For challenges by a solid	
	Protective clothing	
50%	Non-professionals wearing long-sleeved shirt and trousers or skirt with shoes; no gloves worn	Biocides, HEEG Opinion 9 (EC, 2010)
75%	Uncoated cotton coveralls; only for dry substances	
80%	Coated coveralls (coveralls designed to protect against spray contamination such as chemical protection clothing of type 6); e.g. spray application of insecticides (PT18), but may also be adequate for other scenarios for other PTs	
90%	Coated coveralls (coveralls designed to protect against spray contamination such as chemical protection clothing of type 6); e.g. post-application exposure for wood preservatives (PT8), but may not be adequate for other PTs	
95%	Impermeable coveralls; the challenge is 'considerable' (i.e. ≥ 200 mg in-use product/minute) on the whole of the body, not including the hands	
99%	Double coveralls, typically e.g. worn during spraying of antifouling products (long-sleeve, long-leg cotton coverall with a second coverall with a hood worn over the cotton coverall); outer coverall should be chemically resistant if exposure is to wet paint, spray mist or solvents	

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[2] The specific values are now included in the November 2015 draft update of the R.14 Guidance; according to this draft update, application of an efficiency of 98% for gloves is possible under certain conditions, but requires specific justification. This choice is currently not implemented in ECETOC TRA.

HEEG Opinion 9 clarifies that using the default effectiveness values for gloves assumes "*that the worker has a good occupational hygiene approach in his/her behaviour and uses, where appropriate, gloves with long sleeves to prevent exposure via the openings around the wrists. It is also assumed that gloves are taken off carefully, without touching the outside of the contaminated gloves with bare hands*" (EC, 2010).

Similarly, ECETOC TRA assumes that 'specific activity training' (95% effectiveness for gloves) can only be considered in the industrial setting, but not for professional workers (ECETOC, 2012). Consequently, when a professional setting is chosen in ECETOC TRA software (version 3.1), the selection of gloves with an effectiveness of 95% protection is impossible. The report also details that 'specific activity training' e.g. includes procedures for glove removal and disposal (ECETOC, 2012). The differentiation between the effectiveness levels in ECETOC appears to primarily reflect different levels of training/management. In contrast, HEEG Opinion 9 (EC, 2010) assumes a high level of training for all effectiveness values for gloves, the differentiation rather reflecting different states of a substance, with an additional input of new versus used gloves.

While the scope of default of effectiveness values for dermal PPE in the areas of chemicals (REACH) and biocides (BPR) shows some differences, the scientific basis of these default values and their justification is limited. In this context, an analysis of measured data on the effectiveness of dermal PPE at workplaces is considered helpful to substantiate or disprove the default values shown in Table 1.1. For example, dermal exposure measurements with and without dermal PPE can be used to derive values for the effectiveness of the dermal PPE in place.

Most of such measurements were performed during the use of agricultural pesticides and non-agricultural biocides, such as antifouling products and wood preservatives. This fact in itself limits the resulting values to specific type of application and conditions of use (often spray or brush applications performed outdoors) and to specific substances (active substances are generally non-volatiles).

In addition, such measurements may be performed by a variety of methods, which may involve problems that have an impact on the effectiveness values calculated from them. A comparison of these methods for measuring dermal exposure is the subject of the on-going SysDEA project.

This report focusses on measurement methods used to quantify the effectiveness of PPE against dermal exposure, i.e. the reduction of exposure by PPE. It addresses critical issues specific for (a) dosimetry studies (b) biomonitoring studies, (c) in vitro studies (laboratory experiments), and (d) mathematical models that aim at predicting penetration or permeation.
The terms "penetration" and "permeation" describe specific transition processes and therefore influence the exposure reduction by PPE. However, they should not be used as synonyms for the efficiency of protective equipment in real workplace situations.

Dosimetry defines studies measuring exposure outside of the body. This can refer to surrogate methods, which use patches or pieces of clothing as collection material, *in* *situ* methods which assess concentrations directly on the skin (e.g. via fluorescence marker) and removal methods (e.g. hand washing).

Studies using these methods were searched, retrieved and evaluated. Important information on dosimetry and biomonitoring studies as well as the protection factors derived from them were compiled in a Microsoft Excel® file. This report summarises the main findings of these evaluations. It also discusses in vitro studies as well as mathematical models that predict penetration. Details for these studies are not included in the Microsoft Excel® file, since the studies do not reflect workplace conditions. However, they provide insight into factors that may affect the effectiveness of dermal PPE, which are often not tested in dosimetry and biomonitoring studies.

2 Literature search and screening

In this part of the project, the following tasks were performed:

Literature searches

- Definition of search strategies
- Performing literature searches
- Curation of search results
- Compilation of a reference database

Screening of literature

- Identification of potentially relevant studies
- More in-depth appraisal of potentially relevant studies
- Final selection for data entry

Literature was identified mainly via research in the commonly known databases Pubmed, WebOfKnowledge and Scopus. A search strategy was developed using Pubmed and the list of results was checked for publications already known in order to get an impression of its quality and completeness. Keywords include as an example different types of PPE (apron, gloves etc.), terms such as "permeation" or "penetration" (see sections 1 and 3 for details on terminology) and terms related to the sampling strategy (e.g. "biomonitoring"). The detailed description of all search strategies has been summarised exemplarily for Pubmed in Appendix 1, Table 1-4.

Once a list of keywords and suitable combinations of keywords were established the overall four search strategies were adapted to WebOfKnowledge and Scopus. Due to a very high number of results (10000 and higher) for Scopus and WebOfKnowledge the area of research was limited to "Environmental Science" (Scopus) and "Public Environmental Occupational Health" (WebOfKnowledge). This restriction was based on test-wise screening of the results included in different areas of research and selecting the one(s) with the highest relevance. As an example, the area material science was noticed to include mainly publications about thermal properties (e.g. knitwear), fire protection or sportswear while papers found in the area of pharmacology / pharmacy / biochemistry tended to focus on the skin barrier function and skin penetration and not on exposure and the effect of personal protective equipment.

The search was limited to publications published since 2000 and the languages English and German.

All results were exported to EndNote and automatically scanned for duplicates, resulting in 3202 publications (see Table 2.1). Titles and abstracts were then further screened for relevance. Partly title keywords were excluded which had been identified as a marker of not relevant publications. Examples are "allergy" (referred often to latex allergy and qualitative information), asthma, rhinitis (mostly inhalation focussed), needlestick (information related to the probability of PPE damage in medical occupations) and frostbite (not exposure related). However, the main part of the identified publications were scanned individually via title and abstract for potential relevance using personal judgement and scientific knowledge of the authors.

308 publications were selected for closer review, which were amended by a number of cross reference.

In addition, a number of web pages were searched for "grey literature" such as project reports or other information. Examples are the web pages of TNO, HSE /HSL and the

US EPA. Search strategies were similar to the one described above, however, had to be adapted due to the variable nature of the search engines available.

All literature for which the whole document was screened (i.e. not only title and abstract) was collected in a Microsoft Excel file ("PPE dermal literature.xlsx") together with an indication if the publication contained information about models, dosimetry and/ or biomonitoring in relation to PPE reduction efficiencies or any other information of interest.
Publications of relevance were assigned to a responsible project partner for further evaluation and entering into the database if appropriate while the remaining sources of information were marked as discarded.

Cross references in the evaluated literature and known reviews or project reports (e.g. (GERRITSEN-EBBEN et al., 2007; SPAAN et al., 2014; TSAKIRAKIS, 2014)) have also been included into the literature list for further screening and evaluation. This also includes guidance documents such as the Technical Notes for Guidance (EUROPEAN COMMISSION, 2002; JRC, 2007) and the Biocides human health exposure methodology (ECHA, 2015). As far as possible and available, underlying data and publications were analysed if it was indicated in the TNsG / guidance document that they may include information about glove /clothing penetration and / or exposure both above and underneath protective equipment.

Unfortunately a lot of information in the TNsG is only of limited transparency (e.g. is "dermal exposure" related to body or hands), therefore for scenarios without the original documents no further reduction efficiencies could be identified.
All relevant publications identified in the TNO review and the corresponding EFSA addendum published in 2008 have been evaluated and included into the database if appropriate (GERRITSEN-EBBEN et al., 2007; HAMEY et al., 2008).

Table 2.1 Results of literature search: Number of publications found.

	Pubmed	**WebofKnow-ledge**	**Scopus**	**Overall results**
Search	Number of hits	Number of hits	Number of hits	
PSA-1	197	271	105	
PSA-2	307	312	175	
PSA-3	182	1225	302	
PSA-4	253	1098	345	
Total	939	2906	927	
No. of duplicates (within one database)	131	553	183	
remaining	**808**	**2353**	**744**	**3905**
without duplicates (between databases)				3202
after refinement (keywords / title in EndNote)				**308**

3 Different types of protective equipment and test standards

In general, personal protective equipment used to reduce dermal exposure can be classified according to its point of use and its design leading to the following rough categories:

- Gloves
- Overalls / coveralls; whole body garments
- Boots
- Aprons
- other equipment for single body parts (e.g. Tyvek hoods or sleeves)
- barrier creams

PPE can be re-useable or for limited / single use, whereas re-useable PPE may pose additional risks due to continuous contamination and possible exposure during the necessary washing and cleaning process. Commonly used materials are e.g. nitrile, PVC or Tyvek (especially for whole body garments). However, a number of other materials are possible depending on type of PPE used and the type of chemical met.
Normal clothing such as shirts or trousers (e.g. cotton, synthetic materials) have a protective effect as well and corresponding literature has been evaluated if available. However, as this is no personal protective equipment it will not be the focus of the investigation.
A special role take barrier creams, since they are no clothing or piece of equipment that can be taken off again. Barrier creams are products that can be applied directly to the skin in order to avoid skin irritation but also minimise exposure to chemicals. They can include a number of ingredients such as allantoin, cocoa butter or petrolatum at different concentrations (ZHAI et al., 2007).

Further classification of protective equipment can be done according to its protective properties which define the exposure reduction that can finally be achieved by wearing it.

The following parameters can be used to describe the materials of personal protective equipment (see e.g. (FORSBERG and LAWRENCE, 1999; WHO, 2014a))

- **Measured breakthrough time (MBT) / breakthrough detection time (MBT/BDT):** The time it takes the chemical to permeate through the protective material until it can be detected on the unexposed side of the material and reaches a specific flow rate
- **Steady-state) permeation rate:** Rate at which a chemical moves through a specific area of the material and reaches equilibrium with the material during a specified test period duration.
- **Penetration:** Intrusion of chemicals through openings (e.g., pores, needle holes, seams)
- **Permeation:** Intrusion of chemicals through the barrier itself on a molecular level.
- **Degradation**: Indicator of the deterioration (getting harder, getting softer or swelling) of the material on contact with a specific chemical.

In order to achieve a standardised categorisation system, norms and test standards have been developed that are used to test the equipment and corresponding materials. Further tests can be used to check the performance of whole garments (e.g. protective suits) and thus include possible sources of leakage such as seams and other openings. In this context it is often differentiated between permeation of chemicals (i.e. through the barrier itself on a molecular level) and penetration (i.e. though needle holes, seams etc.) (SOUTAR et al., 2000b). Although the two processes cannot be completely separated (i.e. if holes exist in the fabric, there will obviously be penetration; permeation will always be a side effect when penetration is present) it is possible to design test standards in a way that favours one over the other: A piece of material without holes is not expected to show penetration while permeation will be negligible as soon as openings are available (refers also to woven fabrics).

All parameters mentioned above have in common that, although standardised tests exist, they can so far not be used to derive a protection factor, i.e. an efficiency.

Furthermore, even if penetration is measured as a reduction efficiency in a permeation cell it will never be able to capture variables such as user behaviour, e.g. general movements during a task (T material stretch at some points) or contamination during PPE removal / change.

Commonly known test norms are e.g. ASTM, DIN EN or ISO (provided by the American Society for Testing and Materials, the German Institute for Standardization or the International Organization for Standardization) whereas further classification depends on the specific test, the substance and material to be tested.
The norms give a general overview of selection criteria in relation to a stressor. Chemicals are one of these stressors. Mechanical stress is another factor that can indirectly also influence the resistance to chemicals.

In Europe, certification procedures and minimum safety requirements for the use of protective devices at the workplace are regulated by Directive 89/686/EEC and 89/656/EEC, which have been amended by the Directives 93/95/EEC and the CE marking Directives 93/68/EEC and 95/58/EC (WHO, 2014a).

In the following sections a short overview of common test standards used in Europe and partly other countries will be given.

3.1 Test standards and classification of gloves

The regulatory system described above results in a number of test standards, whereas one of the most relevant in the context of chemical resistance is the standard EN 374:2003. EN 374-2:2003 and EN 374-3:2003 have recently been replaced by EN 16523-1:2015 (Determination of material resistance to permeation by chemicals – part 1: permeation by liquid chemical under conditions of continuous contact) and EN 16523-2:2015 (Determination of material resistance to permeation by chemicals – part 2: permeation by gaseous chemical under conditions of continuous contact) (WHO, 2014a). The publication of more parts related to intermittent contact, drops and penetration at seams, closures and material combinations is planned.

EN 374-1:2003 (Protective gloves against chemicals and micro-organisms. Terminology and performance requirements; still up to date) describes the terminology and performance requirements. PPE is divided into three categories for which different certification procedures are in place depending on their use and corresponding risks. The basis for this categorisation is Directive 89/686/EEC (EEC, 1989). Category III corresponds to irreversible or mortal risks and includes protection against chemical attack. Chemical protective gloves are all assigned to this category (Table 3.1) (IFA; MELLSTRÖM and CARLSSON, 2005).

Table 3.1 Glove and other PPE categories according to Directive 89/686/EEC (IFA; MELLSTRÖM and CARLSSON, 2005; WHO, 2014a)

Category	**Description**
I Simple design for minimal risks	To be used in situations where the end user can identify the hazards and level of protection required and where consequences are reversible. Examples: protection against cleaning materials of weak action, against heat (not above 50 °C) and other minor impacts and vibrations. A declaration by the manufacturer about compliance with the requirements of the Directive is sufficient for CE marking of the product.
II Intermediate design for intermediate risks	Examples of intermediate risks: general handling gloves requiring good cut, puncture and abrasion performance. Must be subjected to independent testing and certification by an approved notified body, which may issue a CE mark.
III Complex design for irreversible or mortal risk	Examples: protection against chemical attack or ionizing radiation, against heat (temperatures above 100 ◦C) and cold (temperatures below –50 ◦C) and against electrical risks (high voltage). An additional quality control system or a regular control of the production is necessary for CE certification, and the body carrying out this evaluation will be identified by a number, which must appear alongside the CE mark.

EN 374-2:2003 (Protective gloves against dangerous chemicals and micro-organisms – Part 2: Determination of resistance to penetration; German version) and 3 (Protective gloves against chemicals and micro-organisms - Part 3: Determination of resistance to permeation by chemicals) describe the permeation of chemicals.

EN 374-2:2003 defines an acceptable quality level (AQL, three categories) based on the number of defective gloves that have not passed a water and air leak tests. EN 374-3:2003 describes a technique for in vitro measurement of permeation of chemicals through the evaluated material, where the material is clamped between two chambers with one being filled with the chemical and one being filled with a collector medium. Depending on the minimum breakthrough time 6 performance levels can be defined.

Further details concerning the chemicals tested and the different results are given by pictograms and letter/number codes on the gloves (NORMENAUSSCHUSS PERSÖNLICHE SCHUTZAUSRÜSTUNG (NPS) IM DIN DEUTSCHES INSTITUT FÜR NORMUNG E. V., 2003, 2014).

The updates EN 16523-1:2015 and EN 16523-2:2015 include some rewordings and restructurings, e.g. the separation into liquid and gaseous test materials. Cell

dimensions are slightly changed, however, main parameters such as the suggested test temperatures (23 °C) and the flux of permeation used for the determination of breakthrough time (1 µg / (cm^2·min)) remain the same (NORMENAUSSCHUSS PERSÖNLICHE SCHUTZAUSRÜSTUNG (NPS) IM DIN DEUTSCHES INSTITUT FÜR NORMUNG E. V., 2015a, 2015b).
It is further advised to check the test sample for changes during the study (e.g. thickness, mass, hardness).
A separate test standard for further evaluation of this issue is also available (EN 374-4:2013: Protective gloves against chemicals and micro-organisms. Determination of resistance to degradation by chemicals) (WHO, 2014a).

Other standards describing physical and thermal resistance, radioactive hazard or biological hazard exist as well. However, although these factors may influence the final exposure reduction they are not directly related to chemical exposure and corresponding standards will therefore not be discussed here (ZUTHER).

Corresponding standards from the United States are mainly the ASTM F739-12 (permeation/resistance to specific chemicals), ASTM F903-10 (resistance of protective clothing to penetration by liquids) and ASTM F1383-12 (resistance of protective clothing materials to permeation by liquids or gases under conditions of intermittent contact). However, further standards for specific uses exist (e.g. chemotherapy drugs) (WHO, 2014a).

In case of ASTM F739-12, the breakthrough time is used for the comparison of different types of protective material. However, some differences can be found: As an example, the suggested test temperature is at 27 °C and the flux used for the determination of the breakthrough time is at 0.1 µg / (cm^2·min).
ASTM 1383-12 is used to evaluate visible permeation of a substance through material by application of ambient pressure (5 minutes), 2.0 psi (1 minute) and again ambient pressure (54 minutes) and noting the time when the first indication of liquid is observed. It may give an indication of protection against splash hazards (ASTM INTERNATIONAL, 2012).

Another standard that can be used for the determination of the breakthrough time is EN ISO 6530:2005 (Protective clothing - Protection against chemicals - Determination of resistance of protective clothing materials to permeation by liquids and gases (ISO 6529:2001); German version EN ISO 6529:2001).

3.2 Classification of other PPE

Protective clothing for chemical hazards is broadly categorised into six classes, whereas “PB” (partial body) is usually added after the marking for the type if a certain type of PPE only covers a part of the body (e.g. arms – sleeves) (MÄKELÄ and MÄKINEN, 2013). A summary of PPE classes and corresponding standards directly related to chemical exposure reduction is given in Table 3.2.

The classification includes gas tight suits (type 1), non-gas tight suits (type 2), liquid tight suits (type 3), spray tight suits (type 4), suits against solid particles (type 5) and suits offering limited protective performance against liquid chemicals (type 6). The

corresponding overview standard is EN 14325:2004 (BSI, 2004), which lists test standards e.g. for abrasion resistances, repellency to liquids and penetration and differentiates between the suit material, seams and connecting materials.
For gas tight suits 1a and 1b also variants for emergency teams (1a-ET, 1b-ET) are available. As these may be applied in extreme circumstances, usually stricter requirements have to be fulfilled.

Tests for chemical permeation are required for protective clothing types 1-4, whereas not efficiency but the breakthrough time is measured.

Concerning penetration for type 6 the so called “gutter test” (Protective clothing for use against liquid chemicals; test method: resistance of materials to penetration by liquids; German version EN 368:1992; now Protective clothing - Protection against liquid chemicals - Test method for resistance of materials to penetration by liquids (ISO 6530:2005); German version EN ISO 6530:2005) is performed by dispensing some liquid onto the surface of the clothing, which is laid in an inclined gutter at an angle of 45° (see e.g. SOUTAR et al. (2000b)). It is measured how much of the liquid will run off (repellency) and how much will penetrate the material (MÄKELÄ and MÄKINEN, 2013).

All standards listed in this subsection so far refer to the European classification standard (EN 14325:2004). However, additional classification systems such as the international ISO 16602:2007 (Protective clothing for protection against chemicals -- Classification, labelling and performance requirements) and the system drafted by the American National Standards Institute that has been issued as ANSI / ISEA 103 exist. Although these systems also refer to a six category classification system, subtle differences exist, e.g. partial body garments only considered for category 6 in the ANSI/ ISEA system while they also apply to category 3 and 4 for ISO 16602:2007 (ZEIGLER, 2011).

In Germany, an additional standard for PPE in plant protection applications processes exists (DIN 32781). It requires penetration testing (Protective clothing - Determination of resistance to penetration by sprayed liquid chemicals, emulsions and dispersions - Atomizer test; German version EN 14786:2006; max. 5%), and an evaluation of tear resistance, water vapour volume resistance and make / design and price. The atomiser test has been designed specifically for the plat protection product application in order to reflect more realistic conditions than the usually applied gutter test (ISO 6530:2005). Instead of dripping the substance on the material and letting it run over a gutter it is sprayed onto the test specimen from above while penetration is measured using a sorbens below the test material (HINZ and ERDTMANN-VOURLIOTIS, 2007).

Table 3.2 Classification of protective suites. (MÄKELÄ and MÄKINEN, 2013)

CPC types and pupose	**Application area**	**Standard**		**Main tests (see also (HSE, 2013))**
Type 1 gas tight suit: Type 1a	• Protection against hazardous gases, liquids, aerosols, and solid particles. • Breathable air supply inside suit.	EN 943-1:2002 (now EN 943-1:2015)	Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles - Part 1: Performance requirements for ventilated and non-ventilated "gas-tight" (Type 1) and "non-gas-tight" (Type 2) chemical protective suits" Recent update: Protective clothing against dangerous solid, liquid and gaseous chemicals, including liquid and solid aerosols - Part 1: Performance requirements for Type 1 (gas-tight) chemical protective suits; German version EN 943-1:2015 (Publication date: 2015-11, (BEUTH VERLAG GMBH, 2015))	• Test, how pressurised air is held by the suit (EN 464:1994) • Permeation (EN 14325:2004)
Type 1 gas tight suit: Type 1b	• Protection against hazardous gases, liquids, aerosols, and solid particles • Breathable air supply outside suit.			• Test, how pressurised air is held by the suit (EN 464:1994) • If mask is not joined with suit, also Inward leakage test (BS EN 943-1:2002). • Permeation (EN 14325:2004)
Type 1 gas tight suit: Type 1c	• Protection against hazardous gases, liquids, aerosols, and solid particles • Positive pressure of breathable air can be provided via air lines.			• Test, how pressurised air is held by the suit. (EN 464:1994) • Inward leakage test (BS EN 943-1:2002): not more than 0.05% • Permeation (EN 14325:2004)
Type 1 gas tight suit: Type 1a-ET	• Protection against hazardous gases, liquids, aerosols, and solid particles • For emergency teams.	EN 943-2:2002	Protective clothing against liquid and gaseous chemicals, aerosols and solid particles. Performance requirements for gas-tight (Type 1) chemical	• Test, how pressurised air is held by the suit. (EN 464:1994) • Permeation (EN 14325:2004)

CPC types and pupose	**Application area**	**Standard**		**Main tests (see also (HSE, 2013))**
Type 1 gas tight suit: Type 1b-ET	• Protection against hazardous gases, liquids, aerosols, and solid particles • For emergency teams.		protective suits for emergency teams (ET)	• Test, how pressurised air is held by the suit. • Inward leakage test (BS EN 943-1:2002): not more than 0.05% • Permeation (EN 14325:2004)
Type 2 air-fed non-gas-tight suits	• Protection against hazardous gases, liquids, aerosols, and solid particles • Positive pressure is provided via air lines or similar.	EN 943-1:2002 (now EN 943-1:2015)	Protective clothing against liquid and gaseous chemicals, including liquid aerosols and solid particles - Part 1: Performance requirements for ventilated and non-ventilated "gas-tight" (Type 1) and "non-gas-tight" (Type 2) chemical protective suits" Recent update: Protective clothing against dangerous solid, liquid and gaseous chemicals, including liquid and solid aerosols - Part 1: Performance requirements for Type 1 (gas-tight) chemical protective suits; German version EN 943-1:2015 (Publication date: 2015-11, (BEUTH VERLAG GMBH, 2015)) Non-gas–tight suits are no longer mentioned in EN 943-1:2015. However, since the DIN EN 14325:2004 was published in 2004 this type of suit should still be included.	• Test, how pressurised air is held by the suit. (EN 464:1994) • Inward leakage test. (BS EN 943-1:2002): not more than 0.05% • Permeation (EN 14325:2004)

CPC types and pupose	**Application area**	**Standard**		**Main tests (see also (HSE, 2013))**
Type 3 liquid-tight suit (and PB)	• Protection against pressurised liquids • Liquid tight connections between different parts of the clothing.	EN 14605:2009-08	Protective clothing against liquid chemicals. Performance requirements for clothing with liquid-tight (Type 3) or spray-tight (Type 4) connections, including items providing protection to parts of the body only (Types PB and PB)	• Not tested for gas or particles • Penetration test with compressed jets of water (EN ISO 17491-3): Clothing beneath the PPE is visually examined. (BERNER SAFETY, 2015) • Permeation (EN 14325:2004)
Type 4 spray-tight suits (and PB)	• Protection against sprayed liquids • Spray tight connections between different parts of the clothing. • Taped seams, otherwise same materials as for type 5.	EN 14605:2009-08	Protective clothing against liquid chemicals. Performance requirements for clothing with liquid-tight (Type 3) or spray-tight (Type 4) connections, including items providing protection to parts of the body only (Types PB and PB)	• Tested by spraying suit with water (EN ISO 17491-4): Clothing beneath the PPE is visually examined. (BERNER SAFETY, 2015) • Permeation (EN 14325:2004)
Type 5 suits against solid particles	• protection against dusts and solid particles	EN ISO 13982-1:2011-02	Protective clothing for use against solid particulates -- Part 1: Performance requirements for chemical protective clothing providing protection to the full body against airborne solid particulates (type 5 clothing)	• Total inward leakage is tested (overall mean penetration in sodium chloride aerosol atmosphere, EN ISO 13982-2:2004): measurements are taken at a test person during performance of a series of movements, not more than 15% for 8 of 10 test persons (MICROCHEM)

CPC types and pupose	**Application area**	**Standard**		**Main tests (see also (HSE, 2013))**
Type 6 suits offering limited protective performance against liquid chemicals (and PB)	• protection against e.g. minor splashes or irritant chemical	EN 13034:2009-08	Protective clothing against liquid chemicals - Performance requirements for chemical protective clothing offering limited protective performance against liquid chemicals (Type 6 and Type PB equipment)	• Tested by spraying suit with water (EN ISO 17491-4); similar spray test as for type 4 but only 10% of liquid load. Material efficacy is measured in % (type 1-4 in microg/cm^2) • Penetration test (EN 368:1992 (now replaced by ISO 6530:2005))

An extensive overview of available classifications and test standards for chemical protective equipment has been published by Li et al. in 2013 and includes a summary of main parameters (e.g. resistance to penetration) and corresponding differences for EN Standards (EN), ASTM standards, BS Standards, ISO standards, JIS standards (Japananese Industrial standards) and GB standards (China' Guo Biao). Main test parameters identified are tensile strength, trapezoidal tear resistance, puncture resistance, bursting resistance, abrasion resistance, flex cracking resistance, flex cracking resistance at low temperatures (-30 C°) and resistance to permeation by liquids / gaseous chemicals. Although the general categorisation is similar for all standardisation systems, differences concerning the requirements and test methods exist (LI et al., 2013).

3.3 Discussion and summary

Some publications have been identified in the course of the project in which different test standards have been compared and evaluated.

All sets of standards available for determination of the breakthrough time described in section 3.1 allow the user to select their own collection medium. CHAO et al. (2010) have used the ASTM F739 in vitro test method in order to gather information about the influence of the collection medium on the result of a permeation measurement. The permeation of dimethyl formamide and methyl ethyl ketone through neoprene were tested with methanol, ethanol, 2-propanol and acetone as collection medium. Clear differences were found whereas solubility parameters could be used for interpretation purposes. Methanol was suggested as collection medium while ethanol, water, and 2-propanol showed a low capacity for the permeating DMF.

Results found by Mäkela et al. (2003) demonstrate differences between the test standards ASTM F739 and EN374, which were used to compare breakthrough times and flow rates for surgical gloves. While breakthrough times according to the ASTM are already reached, according to the EN standard the flow rate is not high enough yet (example: formaldehyde solution).

This can be explained by the different fluxes used for the definition of breakthrough (0.1 vs. 1 $\mu g/cm^2 \cdot min$) (see also (DUPONT, 2012)). No method has been identified that can transform results of both techniques into each other. The authors consider it unlikely that such a method can be derived as the difference between both results depends on the substance and the slope of the permeation function.

While a long breakthrough time is usually considered to be good, a glove with a shorter breakthrough time according to a certain test standard can still show a better exposure reduction than one with a longer breakthrough time if the steady state permeation rate is lower (Figure 3.1). However, this is mainly relevant for gloves that are worn longer than the breakthrough time, which should not be the normal case as long as good occupational practice is in place.

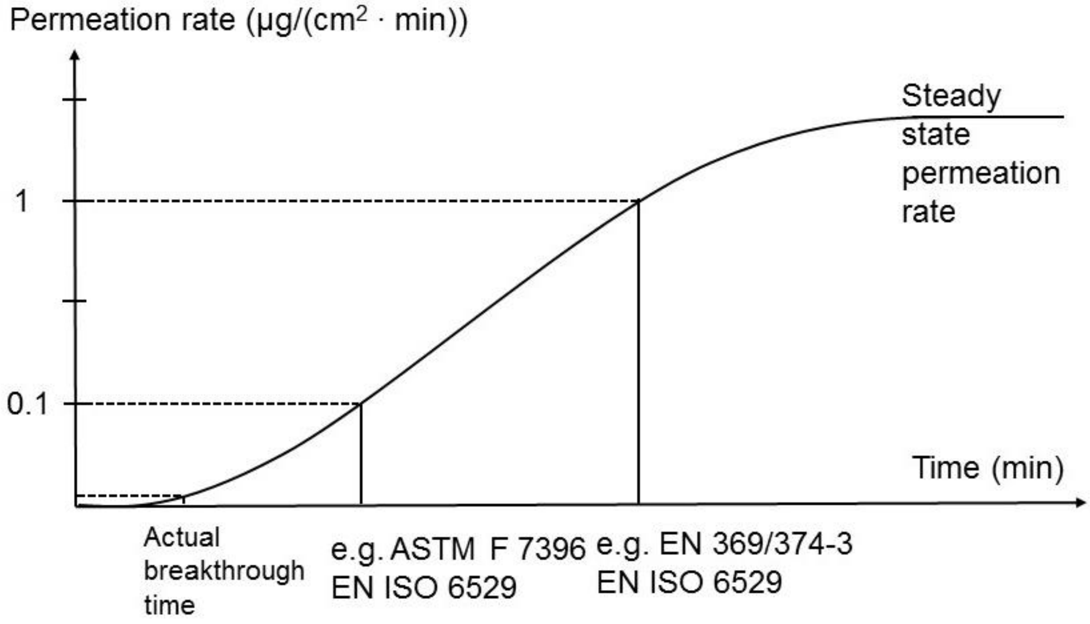

Figure 3.1 Permeation rate as a function of time. Different definitions of the minimum breakthrough time.

Another aspect has been evaluated by PERKINS and POOL (1997) who have measured the permeation rate at steady state, the breakthrough detection time (ASTM F1407), the cumulative permeation at 125 minutes and the glass transition temperature (Tg) for two makes of nitrile gloves in four batches. Considerable variation was observed batch-to-batch variability was statistically significant for all parameters except the breakthrough detection time, suggesting that the same might apply to the resulting exposure.

MICKELSEN and HALL (1987) compared breakthrough times for identical glove types (concerning material and thickness) of different manufacturers. They found that breakthrough times varied considerably (max. factor 10 difference). However, it was recognised that only the breakthrough time was evaluated while also other parameters influence the final protection. Reasons for these differences may be as an example different raw materials / mixtures, vulcanisation methods or different fractions of (material) layers in the gloves.

Furthermore it is often emphasized that conditions in these tests do not necessarily meet those found in reality. As an example, OPPL summarises findings of other authors who report temperatures above the test temperatures and higher elongation especially in the finger area of gloves. An elongation of 50% in pre experiments resulted in a breakthrough time which was reduced about a factor of 2.[3] Simulated hand movements (not permanent elongation) resulted in a reduction of the

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[3] Reference cited in OPPL 1999: Engler R, Heudorfer W: Prüfung der Chemikalienbeständigkeit von Schutzhandschuhen, Chemie in Labor und Biotechnik 48(1997)7, 286-291, sowie Engler R, Heudorfer W: Chemikalienbeständigkeit von Schutzhandschuhen, Sicherheit + Management (1997)3, 190-193; Leicher JP: Chemikalienschutzhandschuhe (CSH), Arbeitssch.akt. (1996)3, 8-10.

breakthrough time of 20-40%, whereas interval elongation in a permeation cell resulted in a longer breakthrough time (50-100% times longer)[4].
It is described that mixtures have partly shorter breakthrough times than the pure substance, resulting in other glove requirements[5].
As a consequence, OPPL suggests a review of the permeation test standards including the usage of higher test temperatures (35°C) , a test at 20% elongation of the material, exposures close to reality and in general substances found in reality (OPPL, 1999, 2003).
The corresponding experiments lead to a reductions of the breakthrough time for the combinations nitrile/ ethanol (152 vs. 137 or 136 min. constant or changing elongation at 35°C), chloropren / iso-octane (155 vs. 118 or 143 min. constant or changing elongation at 35°C), PVC / iso-propanol (153 vs. 36 or 59 min. constant or changing elongation at 35°C) and latex / ethanol (different results depending on type of elongation (area or length-wise elongation) in the pre experiments. Several workplaces and corresponding glove recommendations are discussed and tested as well (OPPL, 1999).
EVANS et al. found increased permeation rates and decreased breakthrough times with higher temperature (T body temperature). The difference between inside and outside of the glove caused by the body heat also may have a negative influence (butyl gloves, acetone and ethyl acetate as solvent). Butyl gloves were found to be impermeable to both solvents. For nitrile gloves and acetone a statistically significant influence was found, indicating increased permeation rates for a temperature difference (23/23°C vs. 23/35°C; 484 µg/cm^2·min vs. 591 µg/cm^2·min.) and increased overall temperature (23/23°C vs. 35/35°C; 484 µg/cm^2·min vs. 657 µg/cm^2·min.). Breakthrough times decreased (23/23°C vs. 23/35°C; 8.6 vs. 7.4 min.; 23/23°C vs. 35/35°C; 8.6 vs. 6.3 min.). The same tendency was reported for nitrile gloves and ethyl acetate (permeation rates of 91, 101, 125 µg/cm^2·min; breakthrough times of 22.9, 22, 13.7 min.). However, differences were reported to be not statistically significant (EVANS et al., 2001).

All mentioned aspects can significantly influence the measured breakthrough time, however, the most recent standards still recommend test temperatures of 23°C (NORMENAUSSCHUSS PERSÖNLICHE SCHUTZAUSRÜSTUNG (NPS) IM DIN DEUTSCHES INSTITUT FÜR NORMUNG E. V., 2015a, 2015b).

As a conclusion it can be said that although terms such as breakthrough time or the categorisation of PPE may seem straightforward, it should be kept in mind that differences may exist depending on the used standard and this can also influence the final exposure reduction. Exposure reduction measurements are occasionally required (e.g. gutter test, inward leakage test), however, often tests are not aimed at an estimation of efficiency values but of a concentration in µg / cm^2 or visual examinations. User variables such as behaviour cannot be reflected by in-vitro tests and only to a limited extent by other tests such as the spray test (EN ISO 17491-4).

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[4] Reference cited in OPPL 1999: Perkins JL, Rainey KC: The Effect of Glove Flexure on Permeation Parameters, Appl.Occup.Environ. Hyg. 12(1997)12, 206-210

[5] Reference cited in OPPL 1999: Rheker R: Schutzhandschuhe beim Umgang mit Gefahrstoffen, Sicherheitsing. (1998)3, 28-32; Packham CL, Spoors R, Rowell FJ: Performance of chemical protective gloves under actual working conditions: a preliminary study (to be published (according to OPPL)

4 Reduction efficiency database

4.1 Database development and structure

As already mentioned in section 2 publications containing suitable quantitative information about exposure reduction related to dermal PPE were collected in an Excel database (see external file "PPE dermal database.xlsx"). A summary of the database structure is given in Table 4.1 and includes information about the type of equipment, the workplace, the substance, study type and obviously the results.

Table 4.1 Database structure

PPE information	**PPE category**
	Reference
	Citation
	PPE description (material, form, …)
	PPE category according to HEEG opinion (agreed in TM I 2010)
	conditions of PPE application (usage once or several times, contact to substance during removal etc.)
	baseline information
Workplace information / operational conditions	industry area
	workplace situation / operational conditions (including influencing factors such as temperature)
	type of process /task (e.g. spraying, brushing)
	duration and frequency of task
	organisational / risk management measures influencing dermal exposure
	information about user / behaviour
Substance information	substances / substance groups, exposure related properties
	mixture properties (e.g. concentrations, other substances, emulsion, particles in liquid)
	physical state of product
	volatility (Pa) or dustiness of test substance
Study information	study type (laboratory vs. Workplace)
	sampling method (biomonitoring, removal method etc)
	details concerning sampling method (e.g. analyte)
	Contextual description / Abstract NO TO BE PUBLISHED
Results	Exposure reduction (%)
	Further information
	Quality of dataset (PPE description)
	Quality of dataset (workplace and task description)
	Quality of dataset (sampling quality)
	Quality of dataset (analysis and presentation / transparency)
	Comments

In order to give the reader a first impression of the quality of each dataset a scoring system was implemented describing the transparency (quality of PPE description, quality of workplace description, presentation and analysis of data) and the sampling methodology. The different categories were developed on the basis of available information and further adjusted during the evaluation process.
Explanations and examples are given below. There are however further examples available in the database.

Quality of PPE description: The evaluated equipment has to be described in the publication with a sufficient level of detail, otherwise the influence of certain PPE specific factors cannot be determined.

- Good: Complete description including manufacturer; Example: material, thickness, length (e.g. for gloves); material and design details (e.g. hood yes/no, cuff and seam design for coveralls)
- Medium: Some aspects are described but others are missing. Example: material, but no thickness or length (e.g. for gloves); material but no details about design of hood, cuffs, seams etc. (e.g. coverall)
- Poor: No material or any further details; e.g. “the worker wore gloves”

Quality of workplace description: The reasoning is similar to the PPE description. Without a description of sufficient level of detail it is not possible to define requirements for a certain PPE efficiency.

- Good: Complete and thorough description of all aspects included in the database (e.g. industry area, tasks and operational conditions (e.g. duration, further RMMs), user details (e.g. level of experience))
- Medium: Some missing aspects but still reasonable description of the main details (e.g. industry area, task, substance and duration but no user details or RMMs)
- Poor: hardly information available (e.g. only industry area and task)

Quality of dataset (analysis and presentation / transparency): This aspect does not represent knowledge about the workplace situation but the knowledge about the exposure reduction value, what it may represent and how it was derived:

- Good: Complete and thorough description of the efficiency or penetration factor derivation; available raw data
- Medium: Some missing aspects but still reasonable description of the main details
- Poor: obvious inconsistencies; basic information is missing (only efficiency given); calculation not reproducible

Quality of sampling strategy:

a) Dosimetry: The result of a PPE evaluation is also influenced by the chosen sampling strategy. However, as this also strongly depends on the quality of the sampling strategy in relation to dermal exposure alone and there is still a large demand of research in this area only a rough categorisation system has been chosen based on the assumption that it is favourable to use the same sampling technique for both scenarios (with and without PPE) and to maximise the sampled skin area in order to cover leaks at seams or cuffs. For gloves the use of cotton gloves as dosimeter is considered to be of lower quality than hand washing, since cotton is able to absorb much higher chemical doses than human skin.

- Good: e.g. whole body sampling (coverall), hand wash + extraction of protective gloves (gloves)
- Medium: e.g. large number of patch samples; whole body dosimeter in combination with large number of patch samples (coverall); cotton glove dosimeters (gloves)
- Poor: e.g. small number of patches (coverall); cotton glove dosimeter + protective glove extraction (gloves)

b) Biomonitoring: For biomonitoring studies the quality of the sampling strategy depends on:

- Controlled sampling (urine samples collected by study participants at home or under controlled conditions)
- Storage of samples until analysis (cooled in a fridge)
- Freezing of the samples till analysis
- Time after sampling until analysis

Further information was summarised in the “comments” field, if necessary.

Some identified efficiency data has not been included into the Excel database. Reasons for this were, as an example, if the level of detail of the available information was considered to be too low (e.g. conference abstracts, paper describes only “exposure reduction by clothing”) or if the information was only available via cross-references and the original publication could not be evaluated (e.g. because it was not available, not in English or German).
These datasets and values are described in the text of the corresponding sections and/ or summarised as separate tables if appropriate.

4.2 Database content

Overall, 410 data entries have been entered into the Excel database. Thereby often one reference has led to more than one entry, i.e. one exposure reduction efficiency, e.g. if more than one substance or type of PPE has been sampled. A list of publications and the assigned number of database entries is given in Table 4.2.

Table 4.2 Database entries: Number of entries and publications

	Number of database entries per publication		**Number of database entries per publication**
APREA et al. (1994)	7	LANDER and HINKE (1992)	2
APREA et al. (2004)	2	LAPPHARAT et al. (2014)	1
APREA et al. (2009)	2	LEAVITT et al. (1982)	1
BALDI et al. (2006)	2	LEBAILLY et al. (2009)	1
BALDI et al. (2014)	3	LESMES-FABIAN et al. (2012)	2
BELLO et al. (2008)	3	LINKS et al. (2007)	6
BERGER-PREISS et al. (2005)	1	MACHERA et al. (2003)	1
BIERMAN et al. (1998)	1	MACHERA et al. (2009)	2
BRADMAN et al. (2009)	2	MADDY et al. (1989)	1
BROUWER et al. (2000)	3	MANDIC-RAJCEVIC et al. (2015)	3
CASTRO CANO et al. (2000)	2	METHNER and FENSKE (1994)	4
CASTRO CANO et al. (2001)	1	NIGG and STAMPER (1983)	4
CASTRO CANO et al. (2001)	6	NIGG et al. (1986)	3
CAVALLARI et al. (2012)	16	NIGG et al. (1992)	7
CESSNA and GROVER (2002)	2	NIVEN et al. (1996)	3
CHANG et al. (2004)	2	NORTON et al. (1988)	2
CHANG et al. (2007)	2	OJANEN et al. (1992)	1
CHRISTOPHER and GALEA (2008)	3	POPENDORF (1988)	2
CREELY and CHERRIE (2001)	3	POPENDORF and SELIM (1995)	1
DAVIES et al. (1982)	6	POPENDORF et al. (1979)	1
ERIKSSON et al. (2004)	2	POPENDORF et al. (1995)	2
ESPANHOL-SOARES et al. (2013)	8	PRELLER and SCHIPPER (1999)	1
FENSKE (1988)	2	PUTMAN et al. (1983)	9
FENSKE et al. (1986)	4	RECH et al. (1989)	5

	Number of database entries per publication		**Number of database entries per publication**
FENSKE et al. (1990)	2	ROFF (1997)	2
FENSKE et al. (2002)	4	ROFF (2015)	3
FENT et al. (2009)	12	VAN ROOIJ et al. (1993)	1
FRANSMAN et al. (2004)	5	RUBINO et al. (2012)	4
FRANSMAN et al. (2005)	5	SCHEEPERS et al. (2009b)	1
FUSTINONI et al. (2014)	1	SCHIPPER et al. (1996)	4
GAO et al. (2014)	2	SHAW (2008)	2
GARRIGOU et al. (2011)	3	SHIH et al. (2009)	1
GARROD et al. (1998)	3	SOUTAR et al. (2000a)	6
GARROD et al. (1999)	3	SPEAR et al. (1977)	2
GARROD et al. (2000)	2	SPENCER et al. (1995)	1
GLASS et al. (2005)	7	STAMPER et al. (1989)	6
GOLD and HOLCSLAW (1985)	1	STONE et al. (2005)	3
GOLD et al. (1982)	1	TSAKIRAKIS et al. (2010)	2
GROßKOPF et al. (2013)	84	TSAKIRAKIS et al. (2011)	6
GROVER et al. (1986)	1	TSAKIRAKIS et al. (2014b)	3
HSE (1998)	4	TSAKIRAKIS et al. (2010)	1
HSL (2003)	7	TSAKIRAKIS (2014)	8
HUGHSON and CHERRIE (2001)	1	VAN DER JAGT et al. (2004)	4
JOHNSON et al. (2005)	1	VITALI et al. (2009)	2
KANGAS et al. (1993)	1	DE VREEDE et al. (1994)	1
KURTZ and BODE (1985)	42	WANG et al. (2006)	2
		WILLER and FELTEN (2006)	3
		Overall number of entries	**410**

The data entries represent information extracted from 93 publications.

The data cover a range of different types of PPE, however, there is a clear focus on coveralls / whole body garments and gloves. A summary of the types of PPE and used sampling techniques is given in Table 4.3. Definitions of the sampling techniques evaluated are given in the introduction. The category "other" has been used for one study applying gas phase measurements inside a gas tight hazmat suit and another combining two techniques (*in situ* sampling of the skin and extraction of substance from the worn garment) (BIERMAN et al., 1998; WILLER and FELTEN, 2006).
These datasets also include some evaluations where either negative efficiencies have been derived or some exposure values were below the limits of detection and could not be used for efficiency calculation purposes. Those entries were marked with "see further information" in the results field of the database. Details can then be found in the column beside the results. The corresponding datasets will be discussed separately and have not been used to for the derivation of average values in the following sections.

Table 4.3 Number of database entries per PPE type and sampling technique (all datasets included).

	biomoni-toring	**in-situ method**	**other**	**removal method**	**surrogate method**	**Number of entriesper PPE type**
apron (1 entry with efficiencies below 0 or LOD)					4	4
barrier cream	1	3				4
boots					1	1
gloves (4 entries with efficiencies below 0 or LOD)	9	1		76	65	151
gas tight hazmat suit[6] (1 entry with efficiencies below 0 or LOD)			3			3
hood				4	4	8
mixed equipment	3			4	23	30
normal clothing		3			55	58
overall/coverall (5 entries with efficiencies below 0 or LOD)		4	1	4	141	150
respiratory equipment				1		1
Overall number of entries per sampling technique	13	11	4	89	293	410

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[6] A hazmat suit is a piece of PPE made of impermeable material. The model evaluated by in the available study is gas tight and has therefore not been included into the category "overall/coverall" in the database.

A summary of datasets per physical state is given in Table 4.4. It seems at first sight that there is a comparably even distribution between solids, solid in solution and liquids. However, if the corresponding publications are analysed more closely it is determined that only very few have evaluated true solids but most of them wettable powders, suspensions or other, typical pesticide formulations.
"Unknown/different" has been chosen as category in cases where products of different physical states were reported together or the product was only reported as "pesticide product" or similar (not identifying if a solution, emulsion or suspension was used).

Table 4.4 Number of database entries per PPE type and physical state (all datasets included)

	different / unknown	**gas**	**liquid**	**solid**	**solid in solution**	**overall number of entries per PPE type**
apron (1 entry with efficiencies below 0 or LOD)	4					4
barrier cream			1		3	4
boots					1	1
gloves (4 entries with efficiencies below 0 or LOD)	35		30	43	43	151
hazmat suit (1 entry with efficiencies below 0 or LOD)		3				3
hood	3		1	1	3	8
mixed equipment	9		6	13	2	30
normal clothing	7		7	38	6	58
overall/coverall (5 entries with efficiencies below 0 or LOD)	24		41	28	57	150
respiratory equipment			1			1
overall number of entries per physical state	82	3	87	123	115	410

A summary of the number of database entries per study type is given in Table 4.5. There are very few laboratory studies, while the focus is clearly on the category "workplace (other)", which represents studies where potential and actual exposure have been sampled simultaneously at the same person. Thereby actual exposure describes the amount of substance which can be found under PPE (if PPE is worn), while potential exposure is the amount that would be found without any PPE (see also section 5.1).

Table 4.5 Number of database entries per study type (all datasets included**)**

Study type	**Number of database entries**
Experimental (2 entries with efficiencies below 0 or LOD)	19
workplace (intervention)	37
Workplace (Cross-sectional (a-posteriori design)) (3 entries with efficiencies below 0 or LOD)	111
Workplace (other) (6 entries with efficiencies below 0 or LOD)	243
Overall number of entries	**410**

Efficiencies have been included as exposure reductions in % (as opposed to penetration values). If possible the arithmetic mean has been used for the database entries. In cases where this was not possible, the geometric mean or median have been used and the choice was noted in the comments field of the database. A summary of the available results is given in Table 4.6. Further details will be discussed in chapter 5.

The efficiency values have been used as reported in the corresponding references or – if this was not possible or not considered reasonable – calculated from raw data with one of the following two equations (see also section 5.1; details are reported in the comment fields of the database):

(1) Efficiency (%) = 100 · (1- Skin exposure inside PPE / (Skin exposure inside PPE + Exposure outside PPE))
(used as an example for the combination of simultaneous sampling and PPE used as dosimeter)

(2) Efficiency (%) = 100 · (1- Skin exposure with/inside PPE / Skin exposure without/outside PPE)
(used as an example for the combination of simultaneous sampling and patch sampling; Intervention / cross sectional studies)

As the database entries have not been weighted for sample size and it was not possible to structure the result format in a completely homogeneous way (median / arithmetic mean etc.), all statistical output from the database should be seen with caution. For this reason it was also refrained from a detailed analysis (e.g. percentiles, standard deviation). However, parameters such as averages and ranges may give the reader a general idea of the database content and efficiencies to be expected for certain types of equipment.
The results show a large variability, however, this is not surprising considering the variability present within the rough categories of PPE shown in this overview and the age of some publications.

Table 4.6 Range of exposure reduction efficiencies for different PPE categories (without negative efficiencies and other not usable database entries (11 entries))

PPE type	Average exposure reduction (%)	Minimum exposure reduction (%)	Maximum exposure reduction (%)	Number of database entries
apron	50.9	0.0	87.6	3
barrier cream	63.7	40.0	82.9	4
Boots	64.0	64.0	64.0	1
gloves	84.1	4.4	100.0	147
hazmat suit	90.2	81.7	98.6	2
Hood	71.3	40.0	98.4	8
mixed equipment	70.9	8.7	100.0	30
normal clothing	70.5	4.0	97.7	58
overall/coverall	90.1	33.4	99.8	145
respiratory equipment (dermal exposure under RPE measured)	45.0	45.0	45.0	1
Overall result	82.5	0.0	100.0	399

5 Dosimetry

Overall 116 dosimetry studies of potential relevance have been identified in the course of the literature screening. Of these, 88 have finally been included into the database, resulting in 397 database entries.
Apart from this, some general points of interest concerning methodology have been evaluated.

5.1 Discussion of methodology

Only few published information is available on the methodology of PPE efficiency evaluation. In general there are a number of decisions which are necessary before an efficiency value can be derived. Although the available literature suggests that there is some experience in this area, often methods are used repetitive without further analyses or comparison. The questions arising during this process are also closely linked to the issue of dermal exposure sampling, which is often discussed in literature due to its complex nature (see e.g. (SCHNEIDER et al., 2000)).
In the following sections the following points will be discussed, based on the order in which they will appear in reality:

- choice of the study type and sampling technique
- how is the measured value presented; units,
- use of the measured exposure value for the derivation of an efficiency value

5.1.1 Study type and sampling technique

Study types found during this project include cross sectional and intervention studies at the workplace and experimental (laboratory) studies

While cross sectional studies consist of two defined groups (with and without PPE) that can be compared in order to define an exposure reduction efficiency, intervention studies measure exposure at different times. After a sampling period without PPE conditions are changed and measurements with PPE can be done. There are also studies, where actual and potential exposure have been sampled during same operational procedures at the same time and person (marked with “workplace (other)” in the database).
Laboratory studies can in theory be all of these types. However, during this project only simultaneous measurements (CREELY and CHERRIE, 2001; ESPANHOL-SOARES et al., 2013; GLASS et al., 2005; NORTON et al., 1988) and one intervention approach (CHRISTOPHER and GALEA, 2008) have been identified.

There often seems to be a consent that it is desirable to measure actual and potential exposure (with and without PPE) at the same time at the same person (e.g. pads below clothing and extraction of cotton overalls; see e.g. SPAAN et al. (2014)), but no publication has been identified where this approach has been compared to other approaches (e.g. intervention, cross sectional study). Simultaneous sampling is also represented at the majority of database entries (243 database entries).

Other study types may have a higher variability due to variations of the user behaviour or other factors. However, possible uncertainties induced by the simultaneous sampling will not be present (e.g. overestimation of potential exposure due to addition of exposure outside PPE and exposure inside PPE for potential exposure and disregard of removal effects such as dripping off).
It may be debatable if intervention studies would profit from the introduction of a control group as discussed in the context of biomonitoring studies (section 6). The sampled chemicals are usually substances to which the evaluated individuals are not exposed to in their daily life, therefore the baseline and the influence of other factors can be assumed to be negligible. However, changes concerning the workplace and the general exposure level cannot be excluded. No study has been identified where such a control group has been sampled. For cross sectional study designs no such setup is possible and for simultaneous sampling it is not necessary.

General discussions or recommendations of sampling techniques exist and have been published as an example by SCHNEIDER et al., who summarise the main problems of dermal sampling techniques as follows:

- the behaviour of a tracer in the transport process may differ from the behaviour of the substance of interest;
- transfer of mass depends on the amount of mass already present in the skin contaminant layer;
- skin stripping or washing with solvents cannot recover what has already penetrated to perfused tissue. Solvents influence the characteristics of the skin and can therefore not be used for repeated sampling;
- adherence of contaminants to patch sampler and real skin differs. Thus the amount on the patch sampler does not represent the amount actually present for uptake on the skin. Uptake is driven by concentration in the skin contaminant layer, not mass per skin surface area;
- patch samplers sample over small areas and therefore errors can occur when results have to be extrapolated to the whole exposed area;
- sampling efficiency of micro vacuuming is strongly dependent on sampling geometry and air flow rate. (SCHNEIDER et al., 2000).

In the following, SCHNEIDER et al. propose a dependency of recommended sampling methods on substance properties (volatility / skin penetration):
If a substance tends to evaporate or resuspend, removal or fluorescence techniques may lead to underestimations and biomonitoring may be a better choice. For high skin penetration rates removal techniques will lead to underestimations as they will not capture the amount already penetrated into the skin.

During this project, in most cases a variety of the surrogate method is used, especially for whole body garments (sampling gloves or pads / whole body dosimeters; 294 database entries), followed by removal techniques (tape stripping, wipes, hand washes; 92 database entries). Only a small number of in situ measurements and other techniques (gas phase measurements in gas tight suit; mixed sampling techniques) have been identified.

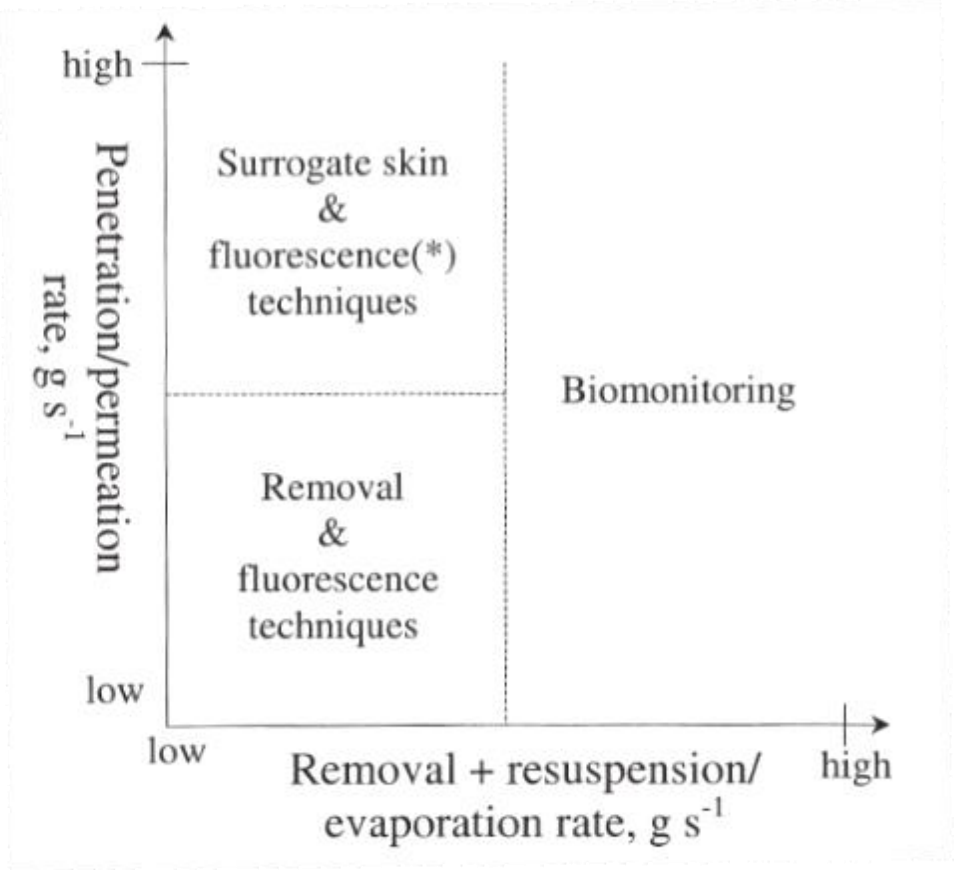


Figure 5.1 Proposed sampling methods to estimate dermal uptake as published by SCHNEIDER et al. The sampling conditions are characterised by the transport rates away from the skin contaminant layer. *UV tracers will have a low permeation penetration rate.

A general disadvantage of patches for the derivation of penetration values is their spatial limitation: Penetration of substance will not happen homogeneously at all points but more likely at seams and points of physical stress (BRODBERG and SANBORN, 1996; GARROD et al., 1999). Some authors describe only one pad above clothing and one below for the estimation of efficiency of a whole coverall (GARROD et al., 1998; HSL, 2003) while some use at least one patch per body part (OJANEN et al., 1992). In both cases only a fraction of the body will be sampled. Results extracted from the database so far do not suggest different efficiency values for both approaches (see section 5.2.9).

Moreover, an extrapolation to the whole body surface is often necessary, if this technique is combined with whole body dosimetry, or to body parts if other types of PPE than whole body garments are evaluated. Similar disadvantages may exist for wiping or tape stripping, if it is only practiced at limited points of the skin surface. However, only one publication using tape stripping for body exposure has been identified during the literature search, i.e. this does not seem to be a common solution (FENT et al., 2009).

Recommendations concerning the determination of dermal exposure in general or PPE efficiencies often seem to favour approaches which capture all substance regardless of its ability to stick to the skin in the sampled amounts or avoid diffusion and

evaporation e.g. by closing the cuff of a glove during sampling (BOENIGER and KLINGNER, 2002; MACHERA et al., 2002).
This is even stated to be the reason for the lack of penetration data for impervious coveralls: According to SPAAN et al. liquid will run off and not be absorbed properly, thus, these coveralls cannot be used as dosimeter (SPAAN et al., 2014).

However, while dosimeters made of absorbent material such as cotton will lead to exposures similar to the experienced exposure on skin for low loadings, much higher values can be measured for high exposure situations (e.g. immersion of hands into liquids). The interaction between actual and potential exposure can be quite difficult in these cases: While potential exposure may be overestimated dramatically, actual exposure, which is usually smaller, may be more accurate, leading to an overestimation of the protection factor.
Similar differences may appear when different dosimeter materials are used, e.g. because different suits have been evaluated. As an example, MACHERA et al. evaluated two woven coveralls (cotton and cotton/polyester), of which the cotton/polyester item was treated with a ResistSpills Finish. MACHERA et al. suggested in their publication that an underestimation of the potential dermal exposure may have happened for the water repellent coverall due to the run off. Indeed the potential dermal exposure was estimated to be almost twice as high for the cotton coverall. However, this can also be interpreted as an overestimation of the potential exposure in case of the cotton coverall compared to the treated coverall but also compared to human skin / a naked person (MACHERA et al., 2009).

A similar effect has been noticed in case of TSAKIRAKIS et al., who have compared a cotton coverall with a hydrofoil garment (50/50% cotton/polyester (Twill, 215 g/m^2 Hydrofoil®; treated with a water repellent finish attached at the nano (sub-micron) level to the fibres) and used cotton underwear for the sampling of actual exposure in both cases. Potential exposure was 1169 mg a.s./kg a.s. applied for the hydrofoil model, while it was 2089 mg a.s./kg a.s. applied for the cotton coverall. Actual exposures differed as well (9.2 mg/kg a.s. for the hydrofoil coverall vs. 57.7 mg/kg a.s. for the cotton model), leading to efficiencies of approximately 99% and 97 % (hydrofoil vs. cotton) (TSAKIRAKIS et al., 2010). Assuming a potential exposure of 1169 mg a.s. / kg a.s. applied for the cotton coverall as well would lead to an efficiency of ~95%, i.e. a factor of 1.7 more penetration.

It is not known to which extent this observation correlates with the partly discussed tendency to measure lower penetration factors with increasing outside loading. Another question is if there are alternatives to the penetration or efficiency (in %), that would be more reasonable and less dependent on other parameters. A flux (e.g. in mg/cm^2/h) is occasionally discussed, however this will probably also depend on the outside loading: If only a very limited exposure is available, the assumption of a constant flux can lead to very high overestimations.

In some publications single contamination paths that may have happened during a normal workday (e.g. during disrobing (GLASS et al., 2005)) may have been excluded from evaluation for some reason by the authors of this publication. The aim of this can be that the authors of a certain study wanted to evaluate solely the influence of permeation / penetration, and not contamination caused by user behaviour during disrobing. However, this does not represent reality and it may not always be obvious in a publication when this is the case during an experiment.

Some experimental recommendations concerning sampling are given in BOENIGER and KLINGNER (2002). However, evaluation of PPE efficiency focusses on the prevention of exposure and sampling of actual exposure. No recommendations directly related to efficiency derivation are given.
As an example, adsorbent materials are discussed for permeation measurements and it is pointed out, that there is a lack of standard test data for low volatility chemicals. As an alternative approach for field trials it is suggested to fix a sorbent directly to the inside of a glove instead of sampling the skin. Sealing the cuffs is suggested to avoid intrusion of volatile chemicals.
Equations for estimating the permeation rate (mass per area and time or mass per time) are given and explained.

It is recommended to test mixtures as well as the pure substance and to take into account increased temperatures, i.e. body temperature, when performing measurements of standard parameters (KLINGNER and BOENIGER, 2002) and some general guidance also exists at the manufacturers web pages on the appropriate choice of PPE, which however does not include the provision of exposure measurements.

In general it is known that significant differences exist (FENSKE et al., 1999; NG et al., 2014) therefore it is considered to be preferable to use the same technique for both measurements in case of efficiency calculations. This general idea has also been used as a basis for the scoring approach. However, there is still potential for research in this area and insights of other projects such as the SYSDEA project may further feed into a refinement of the provided draft scoring.

Comparisons of sampling techniques concerning evaluation of PPE have been done in studies published e.g. by ROFF and by SPAAN et al. in the course of the BROWSE project (ROFF, 1997; SPAAN et al., 2014; TSAKIRAKIS et al., 2014a).

ROFF, who evaluated wood impregnation, used the FIVES technique (in situ fluorescence monitoring) in comparison with hand washes. Using both sets of data, very comparable results were estimated (90.1% for FIVES vs. 91.0% for hand washes).

During the BROWSE project data for coveralls have been analysed separately for pads / patches and whole body dosimetry, coming to an average of 9.67% penetration for pads and 10.99% for the whole body dosimetry. At higher percentiles the differences are more noticeable (22.44 vs. 42.24% penetration for the 90th percentile, see Table 5.1). However, SPAAN et al. decided that all datasets would be combined for the later analyses (SPAAN et al., 2014).

A comparison of the patch and whole body dosimetry method done by DRIVER et al. in the course of their analysis of the PHED database did not show significantly different mean penetration values (8.21 (whole body) vs. 12.12% (patches)) as well (DRIVER et al., 2007).

Table 5.1 Overview descriptive statistics of analysis PPE and work wear migration factors (in %) based on whole garments, separate for data from the 3 involved databases – distinction in measurement methods applied and indication of scenarios that are left out of the analysis (re-entry and high-intensity)

Plot	**N**	**AM**	**SD**	**GM**	**GSD**	**P90**	**AM exposure reduction efficiency**
BROWSE pads/patches	106	9.67	12.83	3.61	5.34	22.44	90.33
BROWSE - whole body	98	10.99	15.13	3.79	5.30	42.24	89.01
BROWSE - re-entry	6	4.48	1.33	4.32	1.35	6.57	95.52

GROßKOPF et al. have compared handwash and cotton glove dosimeters and concluded that both techniques seemed to give similar penetration results for their evaluation of pesticides (emulsions, solutions, wettable powders, suspensions) (GROßKOPF et al., 2013). It should however be noticed, that cotton gloves were mostly only used under the protective gloves in this study, therefore not being exposed to large quantities of chemicals (only simultaneous sampling).

To our knowledge, all studies mentioned above except ROFF et al. use measurements done at the same persons at the same time, while ROFF chose a cross sectional study design that allows to compare different groups of workers (ROFF, 1997).

One publication by METHNER and FENSKE referred to different sampling techniques for actual and potential exposure (VITAE (video imaging technique for assessing dermal exposure) for skin exposure and patches for potential and actual exposure). Mean permeations measured with a combination of methods were about a factor of 10 higher than those measured only with patches. Partly even efficiency values above 100% were estimated, which suggests, that this approach may not be an ideal one (METHNER and FENSKE, 1994).
Another study using a similar combination of in situ method using a fluorescent tracer and whole body dosimetry resulted in a more reasonable efficiency of 89.3% overall (BIERMAN et al., 1998). However, no alternative sampling methods were available in this study which would allow a comparison of the results as in case of METHNER and FENSKE.

One study exists where one cotton glove above a protective glove was used on one hand and under the glove on the other side. The sides were switched halfway through the test to avoid any bias and resulted in efficiencies of > 98% for nitrile gloves used during wood impregnation (CREELY and CHERRIE, 2001). The technique has however not been compared to any other technique.

Overall it can be summarised that some studies exist where sampling methods such as patch or whole body dosimetry have been compared in relation to the derivation of PPE performance. No large differences were observed.
CREELY and CHERRIE found a comparably high efficiency (>98%) for their sampling technique, however, other studies using different techniques also identified high efficiencies above 98% for protective nitrile gloves (GROßKOPF et al., 2013; LINKS et al., 2007; TSAKIRAKIS et al., 2011) and no comparison with other sampling techniques has been done within the study by CREELY and CHERRIE. Thus, although

the reason for this high value may be an overestimation due to the cotton glove dosimeters, it is difficult to conclude on a specific reason.
No publication comparing different study designs has been identified.

5.1.2 Presentation of exposure value and derivation of result

Apart from the obvious choice of sampling method and study design, also a choice concerning the unit of exposure has to be made by the person documenting the results and/or the persons responsible for deriving the efficiency from these values.
Units of exposure found in the course of the project are:

- mass per piece of equipment or per patch
- mass per area
- mass per area and time (flux)
- mass per mass substance applied (especially for pesticides)
- mass per application or task

Depending on the further evaluation of the raw data, the choice of unit may influence the numerical result.

An excellent example for the variability that may be induced by these choices is a study published by BELLO et al. who have estimated skin exposure via wiping and have given exposure as ng/cm^2 but also as overall loading per sample. Highly different results are obtained for both approaches which suggests that the wiped skin area, which is used for the derivation of the mass per skin area exposure, is not identical for all wiping processes (e.g. 28.6 vs. 49.8% for gloves, spraying) (BELLO et al., 2008).

In addition, different results may be obtained due to mathematical reasons: If exposure values are evaluated for each person separately (individual efficiencies during intervention studies or simultaneous sampling of actual and potential exposure) the result may differ from the one obtained from averaged exposure values.

These influences are also connected to the units used to report exposure.
As an example, there will not be a difference between average efficiencies for different units (mg/cm^2, flux / mass per mass substance applied for simultaneous sampling of actual and potential exposure at the same individual) if an efficiency is estimated for each test subject individually and then averaged (units will be cancelled out). If, however, the flux values or mass values per area are averaged and then these averages are used for the efficiency calculation, there may be different results. An example based on hypothetical exposure data is given in Table 5.2 (77.1% for individual efficiency calculation vs. 78.8 and 82.0% for estimation of efficiency from average exposure values).
In case of intervention studies already for individual efficiency estimation and average calculation afterwards different efficiencies may be found for different exposure units (variability between “before” and “after” intervention scenario). An example based on hypothetical exposure data is given in Table 5.3 (77.1 and 76.8% for individual efficiency estimation vs. 78.8 and 78.2% for estimation from average exposures).

For cross sectional studies no estimation of efficiency for one selected individual is possible.

Table 5.2 Hypothetical exposure data and possible efficiency derivation (simultaneous sampling of actual and potential exposure)

Exposure given in mg / cm^2 (assumption: simultaneous sampling)						
Item #	**duration / h**	**exposure below PPE**	**duration / h**	**exposure above PPE**	**efficiency (%)**	
1	0.5	2	0.5	5	60.00	individual values
2	0.3	1	0.3	10	90.00	
3	1	3	1	11	72.73	
4	0.5	1	0.5	7	85.71	
					77.11	individual efficiencies averaged
		average exposure: 1.8		average exposure: 8.3	78.79	average exposures used for efficiency
Exposure given in mg / cm^2 / h (assumption: simultaneous sampling)						
Item #	**duration / h**	**exposure below PPE**	**duration / h**	**exposure above PPE**	**efficiency (%)**	
1	0.5	4.0	0.5	10.0	60.00	individual values
2	0.3	3.3	0.3	33.3	90.00	
3	1	3.0	1	11.0	72.73	
4	0.5	2.0	0.5	14.0	85.71	
					77.11	individual efficiencies averaged
		average flow: 3.1		average flow: 17.1	81.95	average flows used for efficiency

In addition, the use of these units may imply correlations with other parameters such as the duration or the amount of substance. As an example, a flux (mg / cm^2 / h) implies a linear relationship with the task duration while at the same time ignoring saturation effects or intermittent contamination. Especially in cases, where sampling durations differ very much these effects may significantly bias an efficiency result.
For the project database, if possible and if no efficiency value was provided in the publication, the exposure value in mg/cm^2 was used. However, not every study has been conducted in the same way and not all efficiency results are reproducible (see Excel database and corresponding comments).

Another example related to inconsistencies probably caused by different evaluation of measured data are the publications of VITALI et al. and PROTANO et al. Although the contextual information (e.g. weather data, wind speed, information about workers etc.) presented in both publications is identical for the sampled individuals and therefore suggests that identical sets of raw data were used, different penetration factors were derived (PROTANO et al., 2009; VITALI et al., 2009). This implies either an error, missing information or different evaluation of the raw data. As a consequence, only data published by VITALI et al. were entered into the database as a worst case and data published by PROTANO et al. into the “comments” field for information. The transparency of the publications is not sufficient to retrace the origin of the differences.

Table 5.3 Hypothetical exposure data and possible efficiency derivation (intervention study)

Exposure given in mg / cm^2 (assumption: intervention study)						
Item #	**duration / h**	**exposure with PPE**	**duration / h**	**exposure without PPE**	**efficiency (%)**	
1	0.5	2	0.4	5	60.00	individual values
2	0.3	1	0.5	10	90.00	
3	1	3	1.1	11	72.73	
4	0.5	1	0.5	7	85.71	
					77.11	individual efficiencies averaged
		average exposure: 1.8		average exposure: 8.3	78.79	average exposures used for efficiency
Exposure given in mg / cm^2 / h (assumption: intervention study)						
Item #	**duration / h**	**exposure with PPE**	**duration / h**	**exposure without PPE**	**efficiency (%)**	
1	0.5	4.0	0.4	12.5	68.00	individual values
2	0.3	3.3	0.5	20.0	83.33	
3	1	3.0	1.1	10.0	70.00	
4	0.5	2.0	0.5	14.0	85.71	
					76.76	individual efficiencies averaged
		average flow: 3.1		average flow: 14.1	78.17	average flows used for efficiency

Care should also be taken for the interpretation and simplification of the efficiency result. While efficiencies higher than 90% apparently often are reached and may look similar at first sight, seemingly small differences can still have a large effect on the exposure outcome. As an example, two efficiencies of 98.7% and 97.3% mean penetration factors of 1.3 and 2.7%, i.e. a factor 2 difference in terms of exposure (TSAKIRAKIS et al., 2010).

Therefore it can be summarised that a great number of possibilities concerning exposure units exists and is represented in the project database.
No official recommendation seems to exist. However, it seems reasonable to use the most simplistic approach (mg/cm^2) and document other parameters, which may influence the result.

Many database entries are based on a simultaneous sampling of potential and actual exposure at the same individual. While having the advantage of having identical scenario conditions for potential and actual exposure samples (→ lower variability), if actual and potential exposure are sampled at the same time it cannot be excluded that the two layers of exposure will influence each other. An often applied equation uses the assumption that exposure "without PPE" (=potential exposure) corresponds to the sum of exposure on skin (=actual exposure) and exposure outside of PPE or clothing (GROßKOPF et al., 2013; SOUTAR et al., 2000b):

(1) Efficiency (%) = 100 · (1- Skin exposure inside PPE / (Skin exposure inside PPE + Exposure outside PPE))
With: potential exposure = Skin exposure inside PPE + Exposure outside PPE

It may depend on the exposure loading and the substance in question if this is reasonable or can represent an overestimation of the efficiency, e.g. because in reality the excess of substance would evaporate or drip off the skin (influencing factors: vapour pressure, skin or PPE permeation, adsorption on skin / PPE).
This equation is not always practiced. Partly the efficiency is instead calculated by comparing the concentrations inside and outside the clothing or PPE without summing up (FENSKE et al., 2002; GARROD et al., 1999):

(2) Efficiency (%) = 100 · (1- Skin exposure with/inside PPE / Skin exposure without/outside PPE)
With: potential exposure = Skin exposure without PPE

In both equations the efficiency is derived by comparison of actual and potential exposure. The main difference is the general way how potential exposure is derived from measured exposure values. In studies where exposures with and without PPE have been sampled separately, i.e. separated either by time (intervention, different sampling time) or space (cross sectional, different individuals), potential exposure is usually measured directly, i.e. on a person without any PPE (equation (2)).
In cases of simultaneous sampling, however, exposure samples inside and outside PPE are often added up in order to derive the potential exposure. This is usually practiced in cases where the PPE has also been used as dosimeter (e.g. extraction of gloves or coveralls), i.e. it is assumed that the substance which can be detected outside of the PPE would have been additional skin contamination without using the PPE (equation (1)). In other words, the chemical that is already present on the skin is assumed to have been removed from the outside of the PPE, therefore exposure outside PPE does not represent the complete potential exposure.
In cases of simultaneous patch sampling (patches outside and inside PPE) it is usually assumed that patches are impermeable and all contaminants are collected on the outside patch, representing potential exposure. Thus, equation (2) is used.
However, not in all cases the calculations are completely transparent (GARROD et al., 1998) and if the patches are made of permeable material equation (1) may be more reasonable (see e.g. (KANGAS et al., 1993)). Some uncertainty cannot be excluded.

While for low penetrations the difference between both approaches is not large, it can be quite significant for high penetration rates. As an example, if the concentrations above and below protective gloves are identical, equation (1) will lead to an efficiency of 50%, while equation (2) will lead to no reduction efficiency at all.

5.2 Different PPE categories

In the following sections an overview of different PPE categories will be given and some aspects about which information can be drawn from the database or single publications will be discussed.
As the database entries have not been weighted for sample size and it was not possible to structure the result format in a completely homogeneous way (median / arithmetic mean etc.), all statistical output from the database should be seen with caution. However, in order to give the reader a general overview of the available data, some tables have been prepared in the following sections containing ranges and average values for some PPE categories, different industry areas and other properties, that might influence the exposure reduction efficiency.

5.2.1 Aprons

Chemical resistant aprons are a type of equipment that is frequently found in various industries. However, it has rarely been evaluated quantitatively in the past.

Identified sources of information have been published by STAMPER et al., NIGG AND STAMPER and HSE. All have been published before 2000 and are describing plant protection applications. The results are very variable (HSE, 1998; NIGG and STAMPER, 1983; STAMPER et al., 1989).

NIGG and STAMPER have concluded that no reduction of the flux (µg/cm^2/ h) for two mixers / loaders wearing a long, heavy duty rubber apron could be found. However, they compared sampling pads fixed to the forearms (= not covered by apron) with pads on the thighs (= covered by apron) for these conclusions, therefore they recognise that the conclusion may be clouded.

STAMPER et al. have followed a similar approach of comparing inside and outside flux of corresponding pads on three of four greenhouse pesticide sprayers and found non-detectable levels of fluvalinate on chest and thigh pads. It is stated that the data is insufficient to assess the effect of the apron on other compounds, however, there are indeed measured values available also for chlorpyrifos in the publication. Using these values and the given limit of detection mean exposure reduction efficiencies of > 87.6% for fluvalinate and -33.7% for chlorpyrifos can be derived (transmittance estimated by STAMPER et al. by comparing inside pad flux to that of the corresponding outside pad; efficiency of apron derived by comparison of transmittance of coverall and coverall with apron). For chlorpyrifos the exposure at the thighs is higher beneath the apron than above, however, it is not known why. It is also not explained why the data is considered to be insufficient to assess the effect of the apron.

HSE have published a study about exposure to chlorpyrifos in orchard spraying. Patch sampling was used with a detailed description of the clothing / PPE represented by the measured reduction. 10 subjects wore aprons which covered chest, thigh and ankle (compared with 36-37 without PPE, depending on location). Measured exposure is given as µg chlorpyrifos / day and HSE derived a median exposure reduction of 65% (range 35-80%; comparison of patches without PPE obstruction and patches below apron). No further details about the aprons (material etc.) have been published.

Concerning sampling techniques it is not surprising that only patch techniques have been used for the evaluation of aprons, since this piece of equipment covers only part of the body and is usually not suitable for a whole body dosimeter approach. However, this approach is not able to identify specific sources of exposure entry, which are – due to the "open" nature of aprons, most likely present (e.g. leakage around the edges). Another effect worthwhile evaluation might be the contamination of other body parts which are less protected by touching the outside of the apron (e.g. arms).

5.2.2 Barrier cream

Only one dosimetry study has been identified evaluating the effect of barrier cream, which is not surprising considering that dosimetry techniques are not usually suitable for this specific PPE.

The study has been published by CHRISTOPHER and GALEA (2008) and evaluates and compares five different barrier creams (hands first barrier cream, E45 (an emollient hand cream), Savlon barrier cream, DEB protect hand cream and Skinsure salon with five test subjects per cream. However, only for "hands first" cream and E45 cream separate results are available while for the remaining three test items results have been merged as they had to be anonymised. CHRISTOPHER and GALEA have used an in situ technique using fluorescent tracer that was evenly sprayed over the cream treated hands simulating an immersion event. By comparing the fluorescent area (= not protected) with the overall skin area a protection factor was derived for each test subject. No exposure experiment without cream application was performed. As a result, the "hands first" cream showed an efficiency of 69.8%, E45 resulted in 82.9%, while the last three products showed an average protection of 61.9%.

In addition to this quantitative study some recommendations on the use of barrier creams were found in the environmental health criteria on dermal exposure (WHO, 2014a) and in general some qualitative discussion exists on the topic of barrier creams (e.g. SADHRA et al. (2014)). Authors describe for example the effect of cream on skin dermatitis, however, quantitative information on the effect of barrier creams on exposure to chemicals has hardly been published.

5.2.3 Boots

One database entry related to the use of boots was made based on the publication by VAN DER JAGT et al. (2004) that describes exposure during application of insecticides (hand-held spraying equipment to spray liquid on walls, floors and other surfaces). Exposure was measured via pads at lower legs and ankles in ng/cm^2 which were placed directly on the skin and therefore allowed a comparison between normal footwear (safety shoes) and chemical resistant boots which covered ankles and legs in the course of an intervention study. During the intervention part of the study the participants were also shown an instruction video. As a result, an exposure reduction of 65% was measured.

An additional piece of information is contained in an HSE report about reduction of chloropyrifos exposure by different types of PPE (HSE, 1998). The corresponding raw data were not considered to be sufficient for a database entry (only two data points with boots vs. 37 without), however, they suggest an exposure reduction of 97.1% on average based on patch samples placed at the ankle below rubber boots.

Again only the patch technique was employed. However, in this case it would at least theoretically be possible to use sampling socks in order to cover a larger skin area so improvements of the approach should be easily manageable.

5.2.4 Hoods / head protection

Some information has been identified on the exposure reduction efficiency related to the use of hoods.
Data published by VAN DER JAGT et al. can be used to evaluate the influence of a Tyvek hood and an instruction video including information about donning and removing PPE on the exposure level. A patch sample at the neck was used for the efficiency calculation, resulting in a mean reduction of 90.4% (baseline N=3, postintervention N=8). The spraying of insecticide has been evaluated in this publication (VAN DER JAGT et al., 2004).

Another study evaluating automotive spray painting has been published by FENT et al. (2009) and describes information about monomeric and polymeric 1,6-hexamethylene diisocyanate. Concentrations of hexamethylene diisocyanate, urethidone, biuret and isocyanurate are included and show exposure reduction efficiencies of 50%, 60%, 40% and 65.2%. Exposure has been measured by tape stripping at the neck (218 without vs. 86 samples with hood). No further information about the type of hood has been given.
A third example could be identified from the area of pesticide application (plant protection) (PUTMAN et al., 1983). The publication contains three datasets for mixing / loading / application (combined) of nitrofen in emulsion or wettable powder whereas the emulsion scenario is further split up into one scenario where dosing is done via pouring and one scenario where dosing is done via pumping. Workers wore amongst others a 3M White Cap helmet attached to a Model W-2801 air purification system sampled with pads inside and outside for exposure sampling. They were allowed to remove PPE themselves, i.e. contamination of pads during this process possible. Exposure efficiencies found are 78.0, 98.4 and 88.4% for emulsion with pumping for dosing, emulsion with pouring for dosing and wettable powder.
PUTMAN et al. also notice that the scenario including pouring shows a much higher potential exposure (~ factor 10) than the pumping scenario, which correlates with a higher protection factor.

Concerning head protection it can be summarised that although it is available as separate equipment (tyvek hood, helmet) and many types of coveralls have an integrated hood, it has only rarely been evaluated. Head exposure is often only sampled as potential exposure or not at all, resulting in no possibility to assess a separate efficiency (see e.g. GROßKOPF et al. (2013)).

5.2.5 Respiratory equipment

Respiratory equipment is not usually worn with the intention to avoid dermal contact. However, as it covers a portion of the face this can be a side effect. One publication has been identified were samples with and without respiratory equipment (negative pressure half face-piece cartridge respirators) have been compared via wipe sampling of the area covered by the respirator (BELLO et al., 2008). Exposure to isocyanates was evaluated for spraying tasks (primer, sealer, clear coating) in the autobody repair industry. In this case a negative efficiency of 45% was estimated using exposure values in ng/cm^2.

This publication is also an excellent example of different efficiencies that can be derived if exposure results in different units are used (see section 5.1).

5.2.6 Gloves

Gloves are one of the most common groups of PPE. A number of publications has therefore been identified that evaluates the influence of gloves on exposure via dosimetry.

Gloves without further PPE information

However, without giving further information about materials, length or other details, a glove basically can be anything ranging from thick protective nitrile or PVC gloves to cotton or working gloves without any real protective effect. An extract of the main database information is given in Table 5.4 and Table 5.5. All publications use the unprotected hand as a baseline, although BALDI et al. do not make a clear destinction between “no gloves worn” and “only worn half of day” (BALDI et al., 2014).

Overall an average exposure reduction of 63.7% has been found for this category, which is much lower than most commonly used default factors. Particular low values have been found in the autobody repair and finishing industry and the area of pesticide application.

The pesticide scenario has been published by BALDI et al. One main reason for the low exposure reduction value may be the lack of hand exposure values, as the publication only includes overall exposure in qualitative units. Exposure is not available in pairs per worker or directly as penetration / efficiency but only as overall, median result (BALDI et al., 2006).

Different average values have been found for removal and surrogate sampling methods. However, due to the different industry areas included (removal: autobody repair and finishing industry, construction industry, metal industry, Pesticide application (plant protection); surrogate: Antifoulant (consumers), construction industry, Pesticide application (plant protection), wood impregnation) and the lack of knowledge about the type of gloves used this may as well be a coincidence.

Apart from the lack of information about the PPE itself, most of the publications do not describe details about the use and handling of the gloves. The only exception is the evaluation by CAVALLARI et al., who state that gloves may not have been used 100% of the time (CAVALLARI et al., 2012). In case of the autobody industry (isocyanates exposure) again no paired values are available, however, hand exposure is given in the publication (BELLO et al., 2008). BELLO et al. did not discuss penetration through

PPE in depth and focussed instead on the sampling method and it is not known to which extent other, industry specific factors may have influenced the result.
One database entry based on the publication by BELLO et al. has been excluded from the overview table due to a negative efficiency (-305.9%). The reason for this negative value is not known. However, only three samples measured below PPE are available, which may explain unexpected results or high variability.

Gloves without any documented information about length, material and its thickness make it difficult to give a reliable estimate about necessary requirements for exposure reduction. A worst case could be cotton / working gloves used in a situation with exposure to liquid substances or other gloves not appropriate for the corresponding situation (e.g. very thin gloves, old gloves). Some of the low exposure reduction values might be explained by these factors. However, a detailed analysis remains difficult without further information.

Similar information can be drawn from Table 5.5: Differences between the physical states are obvious. However, considering the lack of knowledge and small number of database entries it is not possible to reach a conclusion. A high number of database entries is included in the “unknown/different” category for physical state, as no information has been identified in which form the substance has been applied as a (e.g. solid product or in solution).

Only HUGHSON and CHERRIE have sampled dusts (ZnO). The scenario corresponds to packing of ZnO and the efficiency of 78% has been estimated by comparing exposure of only two workers, i.e. the sample size is extremely small (HUGHSON and CHERRIE, 2001).

Table 5.4 Summary of database entries for gloves without further details about the type of gloves used: Sampling techniques (without negative efficiencies and other unusable results (1 entry))

Sampling method and industry area	**Average exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
removal method (BALDI et al., 2006; BELLO et al., 2008; CAVALLARI et al., 2012; FENT et al., 2009; HUGHSON and CHERRIE, 2001)	50.9	4.4	78.0	7
surrogate method (BALDI et al., 2014; CAVALLARI et al., 2012; GARROD et al., 2000; GOLD et al., 1982; HSE, 1998; RUBINO et al., 2012)	71.9	46.9	99.4	11
Overall result per category	63.7	4.4	99.4	18

Table 5.5 Summary of database entries for gloves without further details about the type of glove used: Industry areas and physical states (without negative efficiencies and other unusable database entries (1 entry))

Industry area / short task description	**different / unknown (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction efficiency per category (%)**	**number of database entries**
Antifoulant (consumers)				99.0	99.0	1
Mixing and loading, application by brush painting or paint roller (boat). (GARROD et al., 2000)				99.0	99.0	1
autobody repair and finishing industry		28.6			28.6	1
spraying (primer, sealer, clear) (BELLO et al., 2008)		28.6			28.6	1
construction industry (CAVALLARI et al., 2012)	54.2				54.2	8
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat); 127°C asphalt application temperature, Biodiesel substitute	46.9				46.9	1
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat); 127°C asphalt application temperature, unrestricted Diesel use	46.9				46.9	1
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat); 149°C asphalt application temperature, Biodiesel substitute	57.1				57.1	2

Industry area / short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average exposure reduction efficiency per category (%)	number of database entries
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat); 149°C asphalt application temperature, unrestricted Diesel use	51.0				51.0	2
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat); 127°C asphalt application temperature, Biodiesel substitute	66.7				66.7	1
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat) 127°C asphalt application temperature, unrestricted Diesel use	57.1				57.1	1
metal industry			78.0		78.0	1
Zn oxide packing in zind oxide and zinc dust manufacturing, packing into 25 kg sacks or IBCs (HUGHSON and CHERRIE, 2001)			78.0		78.0	1
Pesticide application (plant protection)	76.4		4.4	97.8	68.0	6
harvesting (BALDI et al., 2014)	76.4		4.4	97.8	68.0	1
mixing / loading / application (GOLD et al., 1982; HSE, 1998; RUBINO et al., 2012)				97.8	97.8	4

Industry area / short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average exposure reduction efficiency per category (%)	number of database entries
mixing / loading / application / cleaning (BALDI et al., 2006)	76.4				76.4	1
wood impregnation (GARROD et al., 2000)				99.4	99.4	1
mixing and loading, application by brush painting or paint roller (fence painting, house / shed painting). No surface preparation or brush cleaning tasks were measured. Consumer use				99.4	99.4	1
Average exposure reduction efficiency per category (%)	61.6	28.6	41.2	98.7	63.7	18
Number of database entries per category	12	1	2	3	18	

Gloves with documented properties

In this section database entries will be summarised which include a minimum of information, e.g. about glove length and material. Overall there are 123 database entries which fall into this category with an average exposure reduction of 88.1%.
Information about thickness has also been collected, however, is not considered sufficient for a categorisation, therefore it will not be discussed here in detail.
A short sub analysis has been done taking into account the publication date of the different data sets (not shown). There seem to be no clear tendency concerning higher exposure reduction efficiencies for more recent publications.
As can be seen in Table 5.6 there seems to be no significant difference between different sampling techniques. Only one author used an in-situ method for the evaluation of glove efficiency, whereas the remaining studies are almost evenly distributed between removal (mostly handwashing) and surrogate methods (mostly cotton gloves).

One negative efficiency has been identified using data published by CATTANI et al. and has been assigned to leather / rigger gloves. Considering the glove material the low, even negative efficiency is not surprising. The publication suggests that the workers' own PPE was used and although it is not known how old the gloves were at the point of the study it is noted that gloves were washed weekly by 60%, monthly by nearly 30% of the workers, and one worker never washed his gloves (general statement independent of glove type used). Thus, a daily decontamination of PPE will not take place in this company.
Occasionally a maximum of 100% protection has been reported (FRANSMAN et al., 2004, 2005). These values have been taken from the corresponding publications and are reported as, according to FRANSMAN et al., both values (above and below the gloves) are below the limit of detection.
These values (one negative efficiency and two efficiencies of 100%) have not been included into the summary tables in the following sections.

Table 5.6 Summary of database entries for gloves according to their sampling technique (without negative efficiencies and other unusable results (3 entries))

sampling technique	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
in-situ method (ROFF, 2015)	90.1	90.1	90.1	1
removal method (APREA et al., 1994; BRADMAN et al., 2009; BROUWER et al., 2000; CESSNA and GROVER, 2002; FENT et al., 2009; FRANSMAN et al., 2004, 2005; GROßKOPF et al., 2013; MADDY et al., 1989; MANDIC-RAJCEVIC et al., 2015; PRELLER and SCHIPPER, 1999; ROFF, 2015; SCHIPPER et al., 1996; SHIH et al., 2009)	87.4	11.9	100.0	67
surrogate method (BERGER-PREISS et al., 2005; CATTANI et al., 2001; CREELY and CHERRIE, 2001; GAO et al., 2014; GROßKOPF et al., 2013; LINKS et al., 2007; NIGG and STAMPER, 1983; POPENDORF and SELIM, 1995; POPENDORF et al., 1995; POPENDORF et al., 1979; PUTMAN et al., 1983; RECH et al., 1989; STONE et al., 2005; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	89.1	44.0	100.0	52
Overall result	88.1	11.9	100.0	120

Influence of material

It is known that the material of a glove is one of the main influencing factors of its exposure reducing potential, which is also why this material is usually tested for parameters such as degradation and the breakthrough time before it is recommended for a protective glove. However, protective properties are also substance specific and while a thin, disposable glove may be inappropriate for most chemicals there may be situations where it can be optimally suited, especially since other factors such as length, fit of the glove / wideness of cuffs and the general behaviour of the user will always influence the result.

It is therefore no trivial task to decide which factors are necessary to reach a certain protective factor, which factors are described only coincidental and if there are maybe factors that would be relevant but are not even mentioned in a publication.

The majority of datasets has been identified for nitrile (different lengths and thicknesses) and an average efficiency of approximately 90% has been identified.
Other gloves made of fabric such as nylon or cotton can also reach surprisingly high efficiencies (POPENDORF et al., 1979; RECH et al., 1989). However, it should be kept in mind that these materials can soak through and may quickly become contaminated on the inside. As will be discussed in section “Influence of prior use”, a continued use of gloves (as opposed to the use of new gloves), will certainly lead to lower efficiencies, especially if large spills of liquids can happen.
Database entries for other materials such as neoprene (CESSNA and GROVER, 2002), latex (FRANSMAN et al., 2004; RECH et al., 1989), rubber (APREA et al., 1994; CATTANI et al., 2001; MADDY et al., 1989; NIGG and STAMPER, 1983; PUTMAN et al., 1983) and PVC (CATTANI et al., 2001; CREELY and CHERRIE, 2001) and show efficiencies of 96%, 95% 87% and 81%. However, the numbers of database entries are much smaller which makes final conclusions or comparisons between the materials difficult.

A further comparison of glove materials has been done within the studies of KANGAS et al. and APREA et al. (APREA et al., 2004; KANGAS et al., 1993).
KANGAS et al. have evaluated mevinphos exposure to greenhouse spraying of ornamental flowers. Comparing three operators using thick polyvinyl chloride or nitrile rubber gloves with one operator using thin polyvinyl gloves led to an exposure reduction of 98.5%. This reduction however does not represent the efficiency of the polyvinyl or nitrile rubber gloves but only a relative influence of these two types in comparison with thin polyvinyl gloves.
APREA et al. have found that neoprene and rubber gloves showed similar protection during pesticide application at olive trees. One individual wore leather gloves and showed even lower exposure than individuals with protective gloves previously described (leather gloves 60.20 nmol per day, rubber gloves 333.5, neoprene 362.8).
In addition MÄKINEN et al. found workers’ hands wearing leather gloves significantly less exposed than those using leather / cotton mixture gloves (6.7 vs. 23 mg/h actual exposure; exposure to chromium during grinding of steel) (MAKINEN and LINNAINMAA, 2004).

No sample of the bare hands is available, therefore a derivation of an efficiency is not possible for this study.

Table 5.7 Summary of database entries for different glove materials (without negative efficiencies and other unusable results (1 entry))

Glove material	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
"protective gloves" (BERGER-PREISS et al., 2005; GROßKOPF et al., 2013; SHIH et al., 2009)	74.3	11.9	99.0	4
cloth (NIGG and STAMPER, 1983)	94.1	94.1	94.1	1
cloth, PVC, rubber (POPENDORF and SELIM, 1995; POPENDORF et al., 1995)	99.7	99.4	99.9	3
cotton (APREA et al., 1994; GAO et al., 2014; ROFF, 1997) (ROFF, 2015)	86.5	77.8	99.1	5
cotton (waterproofed) (APREA et al., 1994)	71.3	71.3	71.3	1
different (PRELLER and SCHIPPER, 1999)	97.4	97.4	97.4	1
latex (FRANSMAN et al., 2004; RECH et al., 1989)	95.4	88.9	98.7	3
latex / nitrile (FENT et al., 2009; FRANSMAN et al., 2005)	80.6	46.5	97.7	8
latex / rubber / other (SCHIPPER et al., 1996)	85.4	82.4	88.2	4
neoprene (CESSNA and GROVER, 2002)	96.0	96.0	96.0	1
neoprene / rubber (MANDIC-RAJCEVIC et al., 2015)	75.7	71.4	80.0	2
nitrile (BROUWER et al., 2000; CREELY and CHERRIE, 2001; FRANSMAN et al., 2004; GROßKOPF et al., 2013; LINKS et al., 2007; ROFF, 2015; STONE et al., 2005; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	89.5	19.3	100.0	73

Glove material	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
nylon (POPENDORF et al., 1979; RECH et al., 1989)	88.8	83.6	92.0	3
PVC (CATTANI et al., 2001; CREELY and CHERRIE, 2001)	81.2	63.5	99.0	2
rubber (APREA et al., 1994; CATTANI et al., 2001; MADDY et al., 1989; NIGG and STAMPER, 1983; PUTMAN et al., 1983)	86.9	44.0	99.8	7
non-latex (BRADMAN et al., 2009)	96.9	96.8	96.8	1
latex / nitrile / vinyl (ROFF, 2015)	96.8	96.9	96.9	1
Overall result per category	88.1	11.9	100.0	120

Influence of glove length and fit

In Table 5.8 a summary of the available glove datasets according to information about the length of the gloves has been prepared. Gloves have been categorised as “short” if they are approximately wrist long. If they are clearly longer (covering the forearms), they have been categorised as “long”. Again, there are only few database entries, where information was available on this specific feature. However, in this case a tendency seems to be visible. Considering the large variability within the database concerning tasks, industry areas and other factors this difference should be regarded with caution, however, the general tendency (92 vs. 77%) correlates with the expectations. Short gloves are expected to show less protection than long gloves, as chemicals can contaminate the edges or the forearms, run into the glove and contaminate the inside.

A low efficiency scenario seems to be the handling of urine described by FRANSMAN et al (19.3%). According to FRANSMAN et al. a possible reason for this may be that the forearms of nurses were not covered by clothing and therefore the hands might not have been fully protected by the gloves (FRANSMAN et al., 2004).

Table 5.8 Summary of database entries for different glove lengths (without negative efficiencies and other unusable results (3 entries))

glove length	Average exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
long (CESSNA and GROVER, 2002; CREELY and CHERRIE, 2001; MADDY et al., 1989; STONE et al., 2005)	90.0	65.3	99.8	8
no information (APREA et al., 2004; BERGER-PREISS et al., 2005; BRADMAN et al., 2009; BROUWER et al., 2000; CATTANI et al., 2001; FENT et al., 2009; FRANSMAN et al., 2004, 2005; FUSTINONI et al., 2014; GROßKOPF et al., 2013; LINKS et al., 2007; NIGG and STAMPER, 1983) (POPENDORF and SELIM, 1995; POPENDORF et al., 1995; POPENDORF et al., 1979) (PRELLER and SCHIPPER, 1999; PUTMAN et al., 1983; RECH et al., 1989; ROFF, 2015; ROFF, 1997; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	88.7	19.3	100.0	105
short (GAO et al., 2014; SCHIPPER et al., 1996; SHIH et al., 2009)	76.7	11.9	99.1	7
overall result per category	88.1	11.9	100.0	120

The lowest exposure value corresponds to information published by SHIH et al. (11.9%). It corresponds to exposure to 2-ethoxyethyl acetate in a commercial label silk screening shop that has been sampled with the tape stripping method in a cross sectional study. The glove material is not reported, however, it is described that the substance is absorbed via the skin. Thus, one reason for a possible high error may be that a (variable) part of the substance has already penetrated through the skin into the body. As the study is cross sectional by design and both scenarios (with and without PPE) are sampled directly on the skin it is however not known to which extent this could have influenced the result. Furthermore not the whole hand could be covered by the tape stripping process but only the palm and dorsal side of the hand which is an additional source of uncertainty (SHIH et al., 2009).

The highest efficiency value has been published by LINKS et al. and almost reaches 100% (rounded values). The study evaluates the influence of nitrile gloves on exposure to antifouling agent during the mixing / loading and application of paint. Exposure is sampled via cotton sampling gloves (LINKS et al., 2007). No information about glove length is available.

Additional information can be extracted from VAN DER JAGT et al., who have measured exposure at hands, wrists and forearms resulting in an effect of longer gloves of 84% exposure reduction (compared to short gloves) for the use of insecticides (VAN DER JAGT et al., 2004). Using only hand exposure leads to an exposure reduction of 80%.

SCHEEPERS et al. have evaluated coal tar application in a dermatology clinic by comparing tight fitting gloves and Tyvek sleeves with the use of loose gloves. A reduction of more than 97% was determined for this change for unpaired exposure results (median exposure for two different groups of individuals, one before and one after intervention), while for paired results >99% skin exposure reduction was determined (median exposure for the same group of individuals before and after intervention) (SCHEEPERS et al., 2009a).

Influence of industry area and physical state

In Table 5.8 a summary of all available datasets including information about the industry area and included products, in particular their physical states are included.

Again the previously identified studies of very high and very low efficiency are visible (LINKS et al., 2007; SHIH et al., 2009).

The majority of database entries (87) can be assigned to pesticide application (plant protection), followed by 10 entries in hospital scenarios published by FRANSMAN et al.

Concerning the various physical states there seems to be a focus on solids at first sight. However, it should be noted that only LINKS et al. have published data that may be related to exposure to solids in their natural form. Exposure to old layers of paint (sand blasting and grit filling, 12 samples) has been evaluated by LINKS et al. leading to 80 and 98.5% efficiency for nitrile rubber gloves (LINKS et al., 2007)). During this scenario grit and water were mixed for the sand blasting process. Since main exposure is reported to be dust by LINKS et al., it is assumed that this can be considered to be a “solids” scenario, however, some uncertainty remains.

All other scenarios are related to specific pesticide formulations such as wettable powders, dispersible granules or suspensions.

Overall, no clear difference between the physical states seems to be recognisable.

According to additional information provided by ROFF, who evaluated the short-term protective effects of ‘Non-PPE’ gloves used by greenhouse workers for waterproof gloves, protection was similar for dry and wet tasks. For cotton gloves, protection was lower for wet tasks, although this might have been consistent with that decreasing trend, because the ungloved hand challenges were higher for wet tasks than dry (ROFF, 2015).

Further information is available published by POPENDORF et al. describing the application of biocides (scenario: pouring and pumping of liquids vs. pouring of solids). Protection factors of 290 (liquids) and 155 (solids) were found for gloves (mixed materials), corresponding to efficiencies of 99.7 and 99.4% (POPENDORF et al., 1995). Unfortunately, the data for pouring liquids is not split up according to pouring and pumping.

Table 5.9 Summary of database entries for gloves concerning industry areas and short task descriptions (without negative efficiencies and other unusable results (3 entries))

Industry area / short task description	**different / unknown (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average efficiency (%)**	**Number of entries**
commercial silk screening shop (SHIH et al., 2009)		11.9			11.9	1
no information		11.9			11.9	1
Hospital		71.9			71.9	8
removal of sheets from CP treated patients beds (FRANSMAN et al., 2004, 2005)		52.0			52.0	1
washing od CP treated patients (FRANSMAN et al., 2004, 2005)		88.2			88.2	2
Cleaners, no medical staff, cleaning of CP treated patients' toilets. (FRANSMAN et al., 2004)		88.9			88.9	1
handling of CP treated patients urine (FRANSMAN et al., 2005)		46.5			46.5	1
oncology nurses, handling of CP treated patients urine (FRANSMAN et al., 2004)		19.3			19.3	1
preparation of CP (FRANSMAN et al., 2005)		93.4			93.4	1
Trained pharmacy technicians. preparation of CP (FRANSMAN et al., 2004)		98.5			98.5	1
Antifoulant (boats) (LINKS et al., 2007)	99.8		89.3		95.6	5
Grit filling (Cu)			98.5		98.5	1

Industry area / short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average efficiency (%)	Number of entries
Mixing / loading and application of antifouling paints via rolling	100.0				100.0	1
Paint filling (Cu)	99.9				99.9	1
Sand blasting (Cu)			80.0		80.0	1
Spraying of antifouling paints	99.5				99.5	1
Pesticide application (plant protection)	90.6	97.9	89.5	84.0	89.5	87
application (BROUWER et al., 2000; CESSNA and GROVER, 2002; GROßKOPF et al., 2013; MANDIC-RAJCEVIC et al., 2015; NIGG and STAMPER, 1983; STONE et al., 2005; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	86.6	96.7	85.0	86.3	87.3	40
harvesting (BRADMAN et al., 2009; BROUWER et al., 2000; MADDY et al., 1989; POPENDORF et al., 1979; RECH et al., 1989)	93.2	96.8	92.0		93.6	7
mixing (BROUWER et al., 2000; MANDIC-RAJCEVIC et al., 2015)	96.5		80.0		88.3	2
mixing / loading (GROßKOPF et al., 2013; NIGG and STAMPER, 1983; TSAKIRAKIS et al., 2014a)	97.4	99.6	95.3	81.7	93.2	27
mixing / loading / application (GAO et al., 2014; PUTMAN et al., 1983)	91.8		99.7	71.9	85.4	5
re-entry (APREA et al., 1994; ROFF, 2015)				87.5	87.5	6
automotive industry	93.0	90.0			92.3	4
automotive spray painting (FENT et al., 2009)	93.0	90.0			92.3	4
wood impregnation				97.1	97.1	4
application of insecticide / wood preservative, brushing + spraying				99.4	99.4	3

Industry area / short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average efficiency (%)	Number of entries
(CREELY and CHERRIE, 2001)						
brushing of wood preservatives, outdoor, non-professionals / amateurs ,(ROFF, 1997)				90.1	90.1	1
biocide application	92.3				92.3	1
application (BERGER-PREISS et al., 2005)	92.3				92.3	1
pesticide application (construction sites) (CATTANI et al., 2001)				66.7	66.7	2
Termite treatment: preparation (drilling of injection ports), application and clean up.				66.7	66.7	2
Disinfectant application (agricultural setting) (PRELLER and SCHIPPER, 1999)				99.9	99.9	1
mixing / loading / application				99.9	99.9	1
biocide application (different areas) (POPENDORF and SELIM, 1995)			99.4	99.7	99.6	2
pouring and pumping				99.7	99.7	1
pouring solids			99.4		99.4	1
Disinfectant application in meat industry (PRELLER and SCHIPPER, 1999)				97.4	97.4	1
disinfection of rooms in slaughterhouses and meat processing companies				97.4	97.4	1
disinfectant application in hospitals (SCHIPPER et al., 1996)				85.4	85.4	4
preparing a disinfectant solution				85.6	85.6	2
disinfecting activities - washing/cleaning				85.3	85.3	2
Average efficiency	92.2	84.2	89.7	86.0	88.1	120
Number of entries	23	22	41	34	120	

Influence of prior use

Another parameter of interest is the age of gloves, since gloves which are not completely new may be contaminated on the inside already at the start of a new shift. However, detailed information is only rarely included in the evaluated studies. For this reason some assumptions have been made:

- if it was pointed out in a publication that PPE was issued to the workers at the start of the study it was assumed to be new
- if PPE was not usually used in a company but evaluated in a study it was assumed that it was issued at the start of the study and it was new at this point
- if gloves were used as dosimeter, they were assumed to be new.

These points were marked as “assumption” in the database entries to keep them separate from information found in the publications.

A summary of the resulting average exposure reductions included in the database can be found in Table 5.10. It has however been found that not much information can be drawn from this categorisation. Although some assumptions could be made about situations when gloves are most likely new, there is still a large number of database entries where no information is available and only few where it is known that the gloves have already been in use before the study. Cases where it is mentioned or seems at least likely that the workers own gloves have been used have usually been included into the “no information” category, since this fact alone does not mean that the gloves are not new. The only exception is a publication by RECH et al, who compare the effect of nylon gloves on pesticide exposure during the harvesting of tomatoes using new gloves and the workers own gloves, thereby implying that the own gloves have already been in use for some time. As a result, for new nylon gloves an exposure reduction of 90.8% has been found while the workers’ own gloves only 83.6% could been identified (RECH et al., 1989). This corresponds to a factor of 1.8 higher penetration for used nylon gloves.

Table 5.10 Summary of database entries for gloves with different use status (without negative efficiencies and other unusable results (3 entries))

Use status	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
new (assumption) (BROUWER et al., 2000; GAO et al., 2014; GROßKOPF et al., 2013; NIGG and STAMPER, 1983; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	89.8	50.0	100.0	52
new (medical gloves, probably disposable) (FRANSMAN et al., 2004, 2005)	71.9	19.3	98.5	8
new (single use) (BRADMAN et al., 2009; ROFF, 2015)	93.3	81.1	98.3	4
no information (APREA et al., 1994; BERGER-PREISS et al., 2005; CATTANI et al., 2001; CESSNA and GROVER, 2002; CREELY and CHERRIE, 2001; FENT et al., 2009; GROßKOPF et al., 2013; LINKS et al., 2007; MADDY et al., 1989; POPENDORF and SELIM, 1995; POPENDORF et al., 1995; POPENDORF et al., 1979; PRELLER and SCHIPPER, 1999; PUTMAN et al., 1983; RECH et al., 1989; ROFF, 1997; SHIH et al., 2009; STONE et al., 2005)	89.4	11.9	100.0	48
new and used (MANDIC-RAJCEVIC et al., 2015)	75.7	71.4	80.0	2
new (RECH et al., 1989)	90.8	90.8	90.8	1
used (RECH et al., 1989)	83.6	83.6	83.6	1
new (medical gloves, probably disposable), also non-disposable gloves (SCHIPPER et al., 1996)	85.4	82.4	88.2	4
Result per category	88.1	11.9	100.0	120

Apart from that, MANDIC-RAJEVIC et al. describe in their publication a mixture of new and used gloves (5 used, 5 new pairs), resulting in an exposure reduction of 75.7% for for pesticide application (mixing / spraying) and a mixture of neoprene and rubber gloves (MANDIC-RAJCEVIC et al., 2015).

GARROD et al. have carried out measurements inside gloves for the application of non-agricultural pesticides (e.g. antifoulants, remedial products, insecticides) and the combination of values under old and new gloves can be used for a comparison: While the median for existing gloves is 1.52 mg/min it is only 0.67 mg/min for new gloves, i.e. there is approximately a factor of 2 difference which should also be represented in the corresponding exposure reduction efficiency (GARROD et al., 2001). It is also noted that better than 20-fold protection is offered by wearing protective gloves (type unspecified)" by comparison with other data published by IOM.

In 1999 GARROD et al. have evaluated wood preservatives, finding a reduction factor of 3.4 when comparing old with new gloves for arsenic containing products and 1.6 for permethrin (GARROD et al., 1999).

This scenario is quite similar to information published by HSE (1999) about timber treatment which suggests median exposure values under gloves for water based timber treatment of 787 mg/cycle and 135 mg/cycle (used and new gloves) and for solvent based timber treatment 14 and 23.6 mg/cycle (used and new gloves; median value for new gloves higher although exposure range suggests otherwise). This would result in an average factor of 3.2 between the skin exposure below old and new gloves.

Similar information can be drawn from ROFF, who has evaluated the use of chemical protective gloves to control dermal exposures in the UV lithographic printing subsector and recognised that underglove measurements for cleaning tasks showed small amounts inside the gloves on the first day, but higher levels on the second day, indicating either that the chemical was now permeating the glove, or that repeated donning and doffing transferred the chemical inside (or both) (ROFF, 2007).

Influence of user behaviour

Only rarely information about user behaviour is available in the included studies. If information of this type is available at all it is usually related to basic facts, e.g. if workers were allowed to remove gloves themselves or used their own gloves.

In most cases, no details about behaviour (e.g. good practice concerning glove handling, training) are described and only two studies have been identified where instruction videos were part of the study design (RAWSON et al., 2005; VAN DER JAGT et al., 2004).

An exception is a study by CREELY and CHERRIE, who have evaluated protection factors for gloves (nitrile and PVC, three different types) for the application of the wood preservative permethrin via brushing and spraying for messy and tidy workers using cotton gloves as dosimeters. A protection factor of 220 for messy workers (occasions when splashes and spills of concentrate and/or dilute solution occurred and the participant used very brisk brushing techniques) and 450 for tidy workers (occasions when no splashes and spills of concentrate and/or dilute solution occurred and a very controlled brushing technique was employed) was identified (i.e. efficiency 99.8 vs. 99.5%). For pump failure experiments only a protection factor of 32 could be found (efficiency of 96.9%). Differences were not significant according to ANOVA analysis. Thicker gloves were also found to have lower protection factors (96 instead of 200 or 470) which was concluded to have something to do with less dexterity and as a consequence, more spills and splashes. Individuals were also pulling the gloves up repeatedly and touching the insides of the cuffs while doing this. The glove with the highest protection factor was thin but also the best fitting (CREELY and CHERRIE, 2001).

A piece of qualitative information has been published by QUACH et al., who have evaluated the effect of worker training in nail salons on air exposure, knowledge about glove use and general health condition. Increased knowledge about glove use was noticed after the training as well as 47.4% more use of gloves and 21.2% less skin, throat and nose irritation prevalence (QUACH et al., 2013).

Another evaluation of the influence of re-use of gloves and routes of exposure has been published by RAWSON et al. NMP and a fluorescent tracer have been used. The experiment included cleaning and wiping of a fume cupboard, removing the gloves three times and donning them again whereas each time the hands where scanned for contamination. No quantitative exposure measurements were done but a qualitative evaluation of exposure (“high”, “medium”, “weak”) performed. In addition, the effect of an instruction video including explanations and practical demonstrations for donning and removing the gloves was evaluated. Without the video, 9 of 10 test subjects showed contamination of different levels after each glove removal. With the use of the video only one weak contamination was observed (RAWSON et al., 2005).

Exposure pathways

Concerning the question of exposure pathways a study published by SHIH et al. describing exposure to 2-Ethoxyethyl Acetate in a commercial label silk screening shop found correlations between the concentration in air and exposure levels on the skin (SHIH et al., 2009).
Similar indications were found by COCKER et al., who evaluated the efficiency of gloves used in printing and also identified a correlation between air concentrations and concentrations on skin (1-methoxy-2-propanol, used as wash up fluid; nitrile gloves). Sampling was done via cotton-carbon pads at fingers and palms for the 1-methoxy-2-propanol and an additional fluorescent tracer in the solvent. Taping the cuffs led to much lower exposure results (~1% of previous concentration). According to COCKER et al., although the gloves were too short for the task, an absence of fluorescence tracer on the hands of the test subjects suggests that no penetration, tears or running down the hands happened during the experiment. However, this finding was after handwashing to remove flock. Two instances of visible finger contamination of ink and solvent were found which were through careless removal of gloves.

PHALEN and HEE evaluated the influence of physical stress on glove performance using a robotic hand as model to study permeation and penetration through whole gloves (nitrile) with captan as a test substance. Captan was collected via wipe from the inner surface of the glove for analysis. Movement did not seem to influence permeation, but it did influence physical and/or chemical degradation resulting in glove failures (PHALEN and HEE, 2008).

Influence of duration

In the study published by ROFF in 1997 using the FIVES in situ technique datasets of two different formulation durations are included. Although they have been merged for the database entry, a separate consideration can be used for evaluation of the influence of duration on the exposure reduction efficiency. While for 0.5 h an efficiency of 92.6% for working cotton gloves has been found, for 1 h 87.2% have been estimated (ROFF, 1997). These efficiency values are derived from raw data given in the publication and not mentioned in the publication itself. Although two distinct groups of different durations are available in the publication other factors may therefore have differed and influenced the result. As an example, the exposure loading was very variable over the different measurements and 3.7 times higher for the one-hour tests (although only 1.6 as much wood was brushed).

In general it is considered likely that the relation between duration and exposure reduction also depends on the type of glove and the most relevant exposure pathway (permeation, penetration through holes or tears, contamination during removal of gloves). Permeation or penetration transport of the chemical may also be accelerated by movements of the worker. However, depending on the general protection level of the gloves this influence may be more or less evident.

If the main route of contamination is during removal of the PPE, the glove change (or removal) frequency is probably the most important parameter.

Influence of concentration / load

PUTMAN et al. have observed 44% efficiency for emulsion pesticide mixing/ loading and application (pump loading) and > 99% for pouring whereas the maximum exposure outside PPE was much higher for pouring (two orders of magnitude) (PUTMAN et al., 1983).

According to ROFF for cotton gloves the protection factor decreases with challenge (greenhouse workers), while for water proof gloves it increases with challenge (ROFF, 2015).

Further information on glove efficiency not included into the database

Additional exposure data not included into the database from the area of pesticide application were identified in the results of the BROWSE project (SPAAN et al., 2014; TSAKIRAKIS et al., 2014a), which includes an evaluation of available published data from literature about pesticide use as well as information from EUROPOEM and the southern greenhouse model database. Information is included for different types of gloves and coveralls and has been evaluated per body part (see section 5.3.1), formulation type and task. As the publications given in the BROWSE deliverables have been checked for availability and further evaluated if possible, a certain overlap with the database of the current project is likely. However, EUROPOEM data and information included in the Southern Greenhouse model are not publicly available, therefore main results have been included at this point for the sake of completeness. Further details are available in the corresponding project reports.

Measurements conducted in the course of BROWSE have been included into the EXCEL database and are not included in the analyses presented in this subsection.

Results for hand exposure are summarised in Table 5.11 and suggest mean exposure reduction efficiencies between 81.1 and 96.6%, depending on the glove material and

the database subset. The highest reduction has been found for nitrile gloves in the southern greenhouse model database and latex / PE / vinyl / PVC gloves in the BROWSE database (followed by nitrile gloves in the BROWSE database), whereas the lowest exposure reduction can be attributed to unspecified gloves.
This result is mostly consistent with values found in the database developed during this project.

Table 5.11 Overview descriptive statistics of analysis PPE and work wear migration factors (in %) based on individual body parts, separate for data from the BROWSE database and the Southern Greenhouse model database: Hands

Description	**N**	**AM**	**SD**	**GM**	**GSD**	**P90**	**AM exposure reduction efficiency (%)**
BROWSE database							
Hands - overall	317	6.71	14.7	1.04	9.85	18	93.29
Butyl / Neoprene gloves	1	9.09	-	9.09	-	9.09	90.91
Latex / PE / Vinyl / PVC gloves	91	4.5	10.6	0.59	10.1	10.8	95.5
Nitrile gloves	177	5.4	11.2	0.95	9.23	15.8	94.6
Plastic / Rubber gloves	22	11.8	24.8	1.91	9.35	24.4	88.16
Unspecified gloves	26	19	26.8	7.17	4.61	67	81.05
Southern Greenhouse model database							
Hands - Nitrile gloves	191	3.4	9.48	0.56	9.64	7.4	96.6

GARROD et al. mention a more than 20 fold reduction of hand exposure for the application of biocides during use of unspecified gloves (varying from disposable latex (for some public hygiene insecticide surveys) to well-used heavy duty gauntlets (generally in a reasonable condition). The efficiency is derived by comparison of data from two different studies (95.3, 97.4 and ~100.0% for insecticide, remedial biocide and antifoulant application). Sampling has been done via cotton dosimeters glove dosimeters under and above protective gloves (GARROD et al., 2001; TANNAHILL et al., 1996).

Summary

Overall 120 database entries for gloves with further PPE information available were made resulting in an average efficiency of 88.1% (3 excluded from evaluation). For gloves without information available only an average reduction of 63.7% (19 entries, 1 excluded from evaluation) could be found. Some glove related factors such as material or length have been analysed concerning their influence on the exposure reduction. However, as usually several factors differ between those categories it is often difficult to come to a final conclusion, e.g. in case of prior glove use.
Another problem is, that the database is biased, e.g. concerning pesticides (plant protection) and nitrile as a material, leading to small numbers of datasets for other categories. This may be an additional reason for inconclusive or surprising results. As an example cloth and cotton gloves partly show high efficiencies above 90% while

neoprene or rubber, which should have better protective properties, show only 76%. However, only two datasets for neoprene / rubber and five for cotton are available in contrast to seventy three entries for nitrile gloves.

In order to reduce at least the issue of variability a further refinement of the analyses has been done:

Gloves for which a minimum of information was available have been categorised into textile materials (cloth, cotton, waterproofed cotton, nylon), disposable gloves and protective gloves (nitrile, neoprene, rubber, PVC; gloves; assumed to be non-disposable except where additional information suggested otherwise) using the information about glove material and thickness stored in the database entries. All entries including several glove materials of different categories were discarded for this sub-analysis.

Results for gloves that can probably be counted under the category “protective gloves” are given in Table 5.12.

Concerning the use status a mixture of new and used gloves (neoprene / rubber) shows smaller efficiencies than new (nitrile, rubber or undefined material) gloves (76 vs. 90% efficiency, i.e. new glove result in 58% less skin exposure). Both sets of data have been derived from measurements in the area of plant protection products.

Data published by GARROD in 2001 and 1999 (2001: ~50% less skin exposure for new gloves; no protection factor available; 1999: protection factors of 3.4 and 1.6 for new and old gloves, i.e. ~53% less exposure) and HSE (no protection factors, 69% less exposure for new gloves than old gloves) suggest reductions of 38-69% when changing from used to new gloves (GARROD et al., 2001; GARROD et al., 1999; HSE, 1999) , which also includes the value derived from the database.

Overall this supports the so far used factor of two between used and new gloves (EC, 2010), while the overall efficiency values do not correlate very well with the defaults (90/95% for used and new gloves vs. 76/90% from the database). However, considering the age of most data and the lack of information concerning the type of glove used (GARROD et al., 2001; GARROD et al., 1999; HSE, 1999) additional information seems nevertheless advisable. Moreover, only few datasets in the database could be used for a comparison (only MANDIC-RAJCEVIC is known to have evaluated at least a mixture of old and new gloves) and it is not known to which extent further factors exist that are not reported but nevertheless are reflected in the resulting efficiencies.

Short gloves show a much lower efficiency than long gloves (89% less penetration). However, the one dataset for short gloves was measured in commercial silk screening shops using the tape stripping technique (SHIH et al., 2001), while data for long gloves stem from wood impregnation and plant protection products. The material of the short gloves is not known (marked as “protective gloves”).

The result is supported by VAN DER JAGT et al., who found a reduction of 84% (hands, wrists and forearms considered) for long gloves in combination with an instruction video compared to short ones (no instruction video) (VAN DER JAGT et al., 2004). If only hand exposure is considered an exposure reduction of 80% can be derived.

Thus, available data suggest that a significant reduction of exposure can be reached by using long instead of short gloves at least in some scenarios. However, considering the small database an evaluation of further scenarios may be reasonable.

Concerning the material neoprene gloves seemed to show the highest efficiency, followed by nitrile and rubber (96, 90 and 87%). All three datasets are at least partly based on plant protection products. It is not known to which extent the materials used are sufficient for the sampled products or how high the level of training is concerning glove use. The results seem also to be in contrast to results found by APREA et al., who identified similar protection for neoprene and rubber gloves (APREA et al., 1994). However, no thickness or length information is available. This or other unknown differences between the evaluated gloves or scenarios may explain the different results. Information obtained during the BROWSE project showed comparable average efficiencies for butyl / neoprene and plastic / rubber gloves (~91, 88%) while nitrile gloves led to 95% exposure reduction on average. However, differences are more pronounced when the 90th percentile is considered, suggesting 91 and 76% for butyl / neoprene and plastic / rubber and 84% for nitrile gloves. Latex / vinyl / PE / PVC gloves showed even higher value on average (~95%) which were however reduced to 89% in this project (SPAAN et al., 2014).

So far these results suggest high efficiencies especially for neoprene and nitrile, but also other materials. However, further, substance specific differences or not detected influences (e.g. behaviour / training) are possible. Concerning the detailed differences between glove materials no clear tendency can be identified at this point.

In general, the number of database entries for protective gloves is always small at least for one of the groups in question (i.e. new and used gloves; short gloves; neoprene). Thus, general statements based on comparisons of database subsets are difficult.

74 of the included datasets are derived from plant protection measurements and of these sixty three evaluated nitrile gloves, therefore a further refinement (e.g. concerning task or industry area) was not done.

Table 5.12 Protective gloves: Influence of prior use, length, material

	Average Exposure reduction (%)	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
Use status				
new (assumption) (BROUWER et al., 2000; GROßKOPF et al., 2013; NIGG and STAMPER, 1983; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	89.6	50.0	100.0	49
new and used (MANDIC-RAJCEVIC et al., 2015)	75.7	71.4	80.0	2
no information (APREA et al., 1994; BERGER-PREISS et al., 2005; CATTANI et al., 2001; CESSNA and GROVER, 2002; CREELY and CHERRIE, 2001; GROßKOPF et al., 2013; LINKS et al., 2007; MADDY et al., 1989; PUTMAN et al., 1983; SHIH et al., 2001; STONE et al., 2005)	88.5	11.9	100.0	35
Overall result	88.8	11.9	100.0	86
Glove length				
long (CESSNA and GROVER, 2002; CREELY and CHERRIE, 2001; MADDY et al., 1989; STONE et al., 2005)	90.0	65.3	99.8	8
no information (APREA et al., 1994; BERGER-PREISS et al., 2005; BROUWER et al., 2000; CATTANI et al., 2001; GROßKOPF et al., 2013; MANDIC-RAJCEVIC et al., 2015; NIGG and STAMPER, 1983; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b) (GROßKOPF et al., 2013; LINKS et al., 2007; PUTMAN et al., 1983)	89.7	44.0	100.0	77
short (SHIH et al., 2001)	11.9	11.9	11.9	1
Overall result	88.8	11.9	100.0	86

	Average Exposure reduction (%)	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
Glove material				
"protective gloves" (BERGER-PREISS et al., 2005; GROßKOPF et al., 2013; SHIH et al., 2001)	74.3	11.9	99.0	4
neoprene (CESSNA and GROVER, 2002)	96.0	96.0	96.0	1
neoprene / rubber (MANDIC-RAJCEVIC et al., 2015)	75.7	71.4	80.0	2
nitrile (BROUWER et al., 2000; CREELY and CHERRIE, 2001; GROßKOPF et al., 2013; LINKS et al., 2007; STONE et al., 2005; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	90.3	50.0	100.0	70
PVC (CATTANI et al., 2001; CREELY and CHERRIE, 2001)	81.2	63.5	99.0	2
rubber (APREA et al., 1994; CATTANI et al., 2001; MADDY et al., 1989; NIGG and STAMPER, 1983; PUTMAN et al., 1983)	86.9	44.0	99.8	7
Overall result	88.8	11.9	100.0	86

Results for disposable gloves are summarised in Table 5.13. Only a comparison of different materials has been possible, resulting in the highest efficiency for latex / nitrile / vinyl and latex gloves (97 and 94%). Works by FRANSMAN et al. are based on data measured in hospitals, while BRADMAN et al. and ROFF have sampled plant protection products. Considering the very limited number of database entries and the different settings no final conclusion is possible in this case.

Table 5.13 Disposable gloves: Influence of material (only new gloves, no length information)

Glove material	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
latex (FRANSMAN et al., 2004)	93.7	88.9	98.5	2
latex / nitrile (FRANSMAN et al., 2005)	69.0	46.5	93.4	4
latex / nitrile / vinyl (ROFF, 2015)	96.9	96.9	96.9	1
nitrile (FRANSMAN et al., 2004)	55.9	19.3	92.4	2
non-latex (BRADMAN et al., 2009)	96.8	96.8	96.8	1
Overall result	76.9	19.3	98.5	10

Results for textile gloves are summarised in Table 5.14. Concerning the material the highest efficiency has been found for "cloth", followed by nylon (94 and 89 %).
New gloves seem to show higher efficiencies than used gloves (91-93% vs. 84%, resulting in 44-54% reduction of exposure for the change from used to new gloves). This is in agreement with results discussed previously for protective gloves.
All database entries in this area are based on plant protection data except one dataset published by ROFF including information about cotton gloves (wood impregnation, no information about use status). Considering the small database no final conclusions should be made. However, due to the small relevance of textile gloves as PPE further research in this area is not considered to be of high priority.

The overall categorisation into protective, thin / disposable and textile suggests average efficiencies of ~89% for protective gloves, ~77% for disposable gloves and ~94% for textile gloves. The high efficiency for textile gloves seems surprising considering the high penetration potential of this material. The difference between thick (or assumed to be thick) gloves and thin disposable gloves on the other hand is with ~50% penetration reduction smaller than found by KANGAS et al. (98.5%; (KANGAS et al., 1993)). An additional possible factor, that could not be evaluated due to a lack of information, may be a shorter length of disposal gloves. As shown by the results of CREELY and CHERRIE, who found a higher efficiency for thin but well-fitting gloves (~80%), this effect may also be substance- or scenario specific (CREELY and CHERRIE, 2001).

Table 5.14 Textile gloves: Influence of material, use status (no sufficient length information)

	Average Exposure reduction (%)	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
glove material				
cloth (NIGG and STAMPER, 1983)	94.1	94.1	94.1	1
cotton (APREA et al., 1994; GAO et al., 2014; ROFF, 2015; ROFF, 1997)	86.5	77.8	99.1	5
cotton (waterproofed) (APREA et al., 1994)	71.3	71.3	71.3	1
nylon (POPENDORF et al., 1979; RECH et al., 1989)	88.8	83.6	90.8	3
Overall result	94.1	**71.3**	**99.1**	**10**
use status	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of entries (%)**
new (RECH et al., 1989)	90.8	90.8	90.8	1
new (assumption) (GAO et al., 2014; NIGG and STAMPER, 1983)	92.5	84.4	99.1	3
new (single use) (ROFF, 2015)	81.1	81.1	81.1	1
no information (APREA et al., 1994; POPENDORF et al., 1979; ROFF, 1997)	82.8	71.3	92.0	4
used (RECH et al., 1989)	83.6	83.6	83.6	1
Overall result	**86.4**	**71.3**	**99.1**	**10**

Concerning the dependence of the efficiency of the challenge it can be said that exposure reduction efficiencies apparently depend on the exposure load. This factor however interacts with PPE characteristics such as the material, therefore the general tendency might not always be clear, although often less migration at higher exposures is observed, especially for non-textile gloves (PUTMAN et al., 1983; ROFF, 2015).

The effect of user behaviour and training measures cannot be evaluated in detail due to a lack of information. The little information identified suggests a large influence (messy vs. tidy worker leads to 51% reduction). However, do not allow a final conclusion concerning its effects.

5.2.7 Mixed equipment

In some studies derived exposure reductions are available which cannot be assigned to one specific piece of equipment, usually because only an overall exposure for the whole body is available or because different individuals in a group wore different PPE. In these cases it is not possible to assign efficiencies to one specific type of PPE, however, values were collected for the sake of completeness.

A summary of the corresponding references assigned to relevant sampling techniques is given in Table 5.15. Differences concerning the average exposure reduction are obvious, however, considering the nature of this PPE category this is not surprising.

Table 5.15 Summary of database entries for mixed equipment: Sampling techniques

	Average Exposure reduction (%)	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
removal method (CAVALLARI et al., 2012)	36.6	36.2	37.0	4
surrogate method (CAVALLARI et al., 2012; HSL, 2003; KURTZ and BODE, 1985; NIGG et al., 1986; NIVEN et al., 1996; VAN DER JAGT et al., 2004; VAN ROOIJ et al., 1993)	76.6	8.7	99.8	23
Overall result	70.7	8.7	99.8	27

Influence of type of PPE

Concerning the baseline which has been used for comparison, one scenario using shorts and short sleeves included by KURTZ and BODE (1985) has been found. In addition, VAN ROOIJ et al. compared normal work clothes with Tyvek coveralls, gloves and socks (VAN ROOIJ et al., 1993). All other scenarios compare in some way to naked skin. No information about the presence of long sleeves on the sampling area is available in case of CAVALLARI et al.

Two publications should be pointed out in this context which have been published by KURTZ and BODE and HSE.

The work of KURTZ and BODE includes information about the influence of normal clothing (see also section 5.2.8) and gloves on pesticide exposure for consumer use. It is also one of the few studies which deal with exposure to solids (without further addition of water).

Table 5.16 Summary of database entries for mixed equipment: Different types of PPE (without negative efficiencies and other unusable results (3 entries))

Type of PPE	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**number of database entries**
Larger premises: occasionally respirators, visors and aprons to work during the sampling period. Smaller premises: safety glasses but no respirator or protective clothing apart from disposable nitrile or latex gloves (sampling via patches on the outside of the normal workwear and one inner patch on the chest inside the workwear) - > sampled part of equipment may be covered by overall / normal clothing + apron or only normal clothing (HSL, 2003)	22.9	8.7	37	2
Chemical-proof boots instead of shoes, to prevent exposure to ankles and lower legs. Long protective gloves (MSA 40 cm), to prevent exposure of wrist and forearms, especially during working above one's head. Tyvek hood (VAN DER JAGT et al., 2004)	99.8	99.8	99.8	1
Gloves or long sleeves, dosimeters were at wrist, therefore effect not clearly assignable to one of both. (CAVALLARI et al., 2012)	33.0	28.9	37	8
Maximum clothing (long sleeves + gloves + face mask) (KURTZ and BODE, 1985)	94.7	86.49	98.48	12
Men were issued long sleeved shirts, three pairs of long pants, and a belt. The shirts and pants were a regular permanent press industrial variety, woven into a Leno fabric from 65% Fortrel® polyester and 35% cotton by Washington Manufacturing Co„ P.O. Box 1470, Nashville, TN 37202. shirt + disposable coveralls (Abanda, Tyvek®, Style #1412,	95.0	95	95	1

Type of PPE	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	number of database entries
Disposable, Inc„ Decatur, IL 35601) sampled (Chest and forearm) (NIGG et al., 1986)				
overalls / boiler suit made of strong cotton material, waterproof trousers (either PVC or kimberly clark DP waterproof disposable), waterproof coat (either PVC or kimberley clark splashproof EP disposable) (NIVEN et al., 1996)	99.7	99.7	99.7	1
Safety shoes, protective gloves (usually short) (VAN DER JAGT et al., 2004)	99.5	99.5	99.5	1
Tyvek coveralls, gloves and socks of the same material (VAN ROOIJ et al., 1993)	68.6	68.6	68.6	1
Overall result	**70.7**	**8.7**	**99.8**	**27**

The authors have studied exposure using gauze pads at selected locations (face mask, shoulder tops, upper back, upper chest, forearm, hand, thigh, cuff, shoe, foot top) with a number of combinations of clothes and gloves (KURTZ and BODE, 1985). Thus, although the publication is comparably old and there may be more up to date work – and sampling techniques available today, this allows for a general comparison of the influence of an additional piece of clothing or gloves on overall exposure. Results are summarised in Table 5.18.
In addition, the influence of a change of baseline can be studies with such an experimental setup.

HSE have published a study about exposure to chlorpyrifos in orchard spraying. Patch sampling was used with one patch beneath the clothing and a detailed description of the clothing represented by the measured reduction. Not all data points have been included into the database due to small sample sizes and none for combined PPE types, however, information for several combinations of PPE such as aprons / boots or boots / coveralls are available as raw data in the report and may give additional indications for specific situations (HSE, 1998).

Influence of industry area and physical state

A summary of database entries per industry area and physical state is given in Table 5.17. The majority of datasets can be found in the area of plant protection products, however, also other areas are represented.
The lowest efficiencies have been identified by HSL and CAVALLARI et al. (approximately 23 and 33% on average) (CAVALLARI et al., 2012; HSL, 2003).

HSL describe the cleaning of objects in the engineering industry via dipping into a NMP bath and subsequent spraying with water (“spraying off”). The equipment sampled could represent a coverall or “normal” clothing or an additional apron. Only one patch beneath the clothing was used for sampling of the penetration, which may lead to a comparably high uncertainty.
CAVALLARI et al. describe scenarios related to paving, whereas the equipment sampled may represent gloves which are additionally covered with long sleeves or not. Hand washes and passive samplers at the wrist were used and it was stated that gloves may not have been used 100% of the time, which may explain the low efficiency. No further information about the glove material is given.

Only the study by KURTZ and BODE includes datasets measured with solids without further addition of water (no wettable powders, suspensions or similar products).

Summary

Some studies have been identified with information about the efficiency of mixed or combined equipment. Although this can be interesting in some cases in order to model the additional effect of a second piece of equipment (e.g. an apron over a coverall), the corresponding studies are usually difficult to interpret and the corresponding efficiencies apply only to specific situations.

Table 5.17 Summary of database entries for mixed equipment: Industry area and physical state

Industry area and short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average exposure reduction (%)	Number of database entries per category
construction industry (CAVALLARI et al., 2012)	33.0				33.0	8
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat). 149°C asphalt application temperature, Biodiesel substitute	32.9				32.9	2
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat). 149°C asphalt application temperature, unrestricted Diesel use	33.1				33.1	2
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat) 127°C asphalt application temperature, Biodiesel substitute	33.4				33.4	2
Screedman (typically stood at the back of the paver to control the depth and width of the asphalt mat) 127°C asphalt application temperature, unrestricted Diesel use	32.6				32.6	2
engineering industry (HSL, 2003)		22.9			22.9	2

Industry area and short task description	**different / unknown (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction (%)**	**Number of database entries per category**
dipping		37.0			37.0	1
spraying off		8.7			8.7	1
Insecticide application (NIVEN et al., 1996; NIVEN et al., 1993)		99.7			99.7	1
paddler (from NIVEN et al. (1993): manoeuvres sheep in the bath, lunges them under, ensures safe exit and handles dipping pole)		99.7			99.7	1
Pesticide application (plant protection)	95.0		94.7		94.7	13
application (KURTZ and BODE, 1985)			92.0		92.0	4
application / cleaning (KURTZ and BODE, 1985)			96.0		96.0	8
mixing / loading / application (NIGG et al., 1986)	95.0				95.0	1
wood impregnation (VAN ROOIJ et al., 1993)			68.6		68.6	1
impregnation of railroad crossties			68.6		68.6	1
use of insecticides (VAN DER JAGT et al., 2004)				99.7	99.7	2
mixing / loading / application				99.7	99.7	2
Average exposure reduction per category (%)	39.9	48.5	92.7	99.7	70.7	27
Number of database entries per category	9	3	13	2	27	

Table 5.18 Efficiency results based on data by KURTZ and BODE (1985)

Corn	**Dusting (solid)**			**Wettable Powder**			**Aqueous Suspen.**		
Clothing	**Mean exposure, mg**	**No clothes as baseline (%)**	**Short-sleeved and shorts as baseline (%)**	**Mean exposure, mg**	**No clothes as baseline (%)**	**Short-sleeved and shorts as baseline (%)**	**Mean exposure, mg**	**No clothes as baseline (%)**	**Short-sleeved and shorts as baseline (%)**
No clothes/ bare foot	9.9			7.7			11		
Shorts only/ bare foot	7.3	26.3		5	49.5		7.6	23.2	
Shorts + tank top	5.6	43.4		4.3	56.6		5.8	41.4	
Short-sleeved and shorts	3.7	62.6		2.4	75.8		3.8	61.6	
Long-sleeved	0.89	91.0	76.0	0.28	97.2	88.3	0.23	97.67	94.0
Maximum (long-sleeved + gloves + face mask)	0.5	95.0	86.5	0.18	98.2	92.5	0.15	98.5	96.1
Beans									
No clothes/ bare foot	10.2			5.4			6.8		
Shorts only/ bare foot	9.5	4.0		5.2	47.5		6.4	35.34	
Shorts + tank top	8.3	16.2		4.8	51.5		6	39.4	
Short-sleeved and shorts	5.2	47.5		3.1	68.7		3.7	62.6	
Long-sleeved	0.68	93.1	86.9	0.24	97.6	92.3	0.29	97.1	92.2
Maximum (long-sleeved + gloves + face mask)	0.46	95.4	91.1	0.19	98.1	93.9	0.24	97.6	93.5

5.2.8 Clothes

The exposure reduction potential of normal clothes is not the focus of this research. However, corresponding information has been collected for the sake of completeness. Overall 58 database entries have been made and an average exposure reduction of 70.5% has been estimated.

Table 5.19 Summary of database entries for clothes: Sampling techniques

Sampling technique	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
in-situ method (FENSKE et al., 1986; ROFF, 1997)	84.7	78.8	91.2	3
surrogate method (BALDI et al., 2006; BALDI et al., 2014; DAVIES et al., 1982; FENSKE et al., 2002; FENSKE et al., 1990; GOLD and HOLCSLAW, 1985; GROßKOPF et al., 2013; HSE, 1998; KANGAS et al., 1993; KURTZ and BODE, 1985; LAPPHARAT et al., 2014; LEAVITT et al., 1982; LESMES-FABIAN et al., 2012; NIGG et al., 1986; RECH et al., 1989; SPEAR et al., 1977; VITALI et al., 2009)	69.8	4.0	97.7	55
Overall result	70.5	4.0	97.7	58

Further information distinguishing between solids and liquids is available published by POPENDORF et al. describing the application of biocides (scenario: pouring of solids and liquids). Penetration through clothing for solids has been identified to be 6%, while for liquids 1.3% penetration where found.

Industry area and physical state

A summary of database entries for different industry areas and physical states is given in Table 5.22. The majority of datasets has been assigned to solid products. However, again only very few entries (FENSKE et al., 1990; KURTZ and BODE, 1985) include the use of solids without further addition of water.

The study published by KURTZ and BODE has already been discussed in one of the previous sections and describes the consumer application of plant protection products. FENSKE et al. have evaluated the treatment of seeds with lindane in a dust formulation. A cotton/polyester crew neck T-shirt, a cotton/ polyester long sleeve workshirt and cotton workpants have been worn and exposure has been sampled via the patch method (chest, back, shoulders, forearms, upper legs, lower legs; one inner and one outer sampling set). While the shirt and T-shirt provided 72.4% exposure reduction, 91.4% exposure reduction was reached by the workpants.

Influence of prior use

RECH et a. have evaluated the influence of new or used (workers’ own clothing) long sleeved shirts on pesticide exposure during tomatoe harvesting. While for an old shirt an exposure of 1961 µg/h on the arms was measured, only 767 µg/h were measured for a new long sleeved shirt and 699 µg/h for an old long-sleeved shirt, resulting in efficiencies of 60.9 and 64.4% (penetration of 39.1 and 35.6%) (RECH et al., 1989).

Influence of duration

SPENCER et al. have found no varying penetration factors for pesticide exposure through knitted T-shirts for harvesting of peaches with differing durations (2-7 h) (SPENCER et al., 1995).

User behaviour

ROFF et al. have evaluated dermal exposure of amateur of non-occupational users of wood preservative fluids (brushing) via fluorescence technique.
Differences between subjects behaviour gave rise to variations of a factor of 10 (ROFF, 1997).
Techniques used by the individuals included: holding the beaker by the base or the handle, leaving it on the ground, draining the brush against the beaker each time it was recharged, spreading each brushful further over the wood, brushing with greater vigour, standing close to, or at extended arm’s length from, the fence. However, a more detailed assignment of techniques to certain efficiencies is not possible based on the available information.

Further information on exposure reduction by clothes

Apart from the datasets included in the Excel database some information has been found, that was not included into the database due to a lack of information about the type of clothing worn or because it was only available in form of a review. These datasets are summarised in Table 5.23.
65.2-99.9% have been identified for normal, unidentified clothing in these references. However, usually the level of detail available in the publications does not allow further conclusions concerning the reasons for a certain value.

Table 5.20 Mean exposure reduction efficiency (%) for single layer clothing by PHED job classification category (patch and whole-body dosimeter samples; n = 2129) according to DRIVER et al. (DRIVER et al., 2007).

	n	**Efficiency / exposure reduction (%)**
Applicator	1117	88.97
Flagger	8	90.77
Mixing / Loading	513	84.65
Mixer / Loader / applicator	491	89.51

In addition, DRIVER and ROSS have evaluated the pesticide handlers exposure database (PHED) deriving penetration factors for single layer clothing (i.e., long-sleeved shirt, long pants; gloves are not included) for mixers / loaders, flaggers, applicators and found exposure reduction efficiencies of approximately 90% (84.65-90.77%; efficiency (%) = 100%- penetration (%)).
The effect of a single layer was also evaluated separately only for application for a number of different methods resulting in 75-96% (Rights-of-way sprayer vs. airless sprayer; see Table 5.20 and Table 5.21) (DRIVER et al., 2007).

Table 5.21 Mean percent penetration and exposure reduction efficiency (%) for single layer clothing for different application types (DRIVER et al., 2007). Only applicator samples considered.

Application type	**n**	**Efficiency (%)**
0 (Not Specified)	7	85.62
1 (Airblast)	403	91.47
2 (Groundboom Tractor)	178	89
3 (Groundboom Truck)	22	81.74
4 (Aerosol Can)	180	85.38
5 (Aerial - Fixed Wing)	25	79.59
7 (Low Pressure Hand Wand)	187	89.01
8 (Paint Brush)	75	89.51
9 (Backpack Sprayer)	50	91.31
10 (Airless Sprayer)	105	95.86
11 (Rights-of-way Sprayer)	40	75.03
13 (High Pressure Hand Wand (Greenhouse & Ornamentals)	43	85.8
16 (Termiticide Injection)	106	89.27
18 (Solid Broadcast Spreader (Belly Grinder)	139	89.23
22 (Hand Dispersion, granular bait)	6	91.29

A separate consideration of emulsifiable concentrate, aqueous solution, solution and undefined liquid pesticides resulted in penetrations of 15.12, 11.71, 19.98 and 14.62% (exposure reduction 84.88, 88.29, 80.02 and 85.38%), while a differentiation between the solid formulation types wettable powder, dry flowable and granule only resulted in small differences (penetrations of 10.40, 7.43 and 10.69%; 89.6, 92.57, 89.31% efficiency).

BRODBERG and SANDBORN (1996) have evaluated clothing penetration values of harvesters for pesticides. The highest penetration was found for forearms and upper arms (48 and 37%%), lowest for thighs and hands (7 and 9%) for phosalone (42,0 30, 9, 8 for azinphosmethyl). Reasons suggested include different fabrics used for gloves and a lower contact tendency or different movement patterns e.g. at thighs. Low exposure rate tends to give higher penetration. In general penetrations between 10 and 34 % (i.e. efficiencies between 66 and 90%) were observed and 75% exposure reduction is suggested as a default (see also Table 5.23). No influence of substance or clothing or crop was observed.

Summary

Overall 58 database entries with an average exposure reduction of 70.5% have been identified. The results suggest that the possible exposure values are very variable and depend on the type of clothing worn, the number of fabric layers and other usual parameters (product, task etc.). Efficiencies can reach 90% or more for long sleeves and trousers of sturdy material. However, this does not always seem to be the case, especially for shorts, t-shirts or other types of clothing that do not cover the whole body.

Table 5.22 Summary of database entries for clothes: Industry areas and physical states

Industry area and short task description	different / unknown (%)	liquid (%)	solid (%)	solid in solution (%)	Average exposure reduction efficiency per category (%)	Overall number of database entries per category
Pesticide application (plant protection)	71.7	78.9	67.0	79.7	70.2	57
application (DAVIES et al., 1982; FENSKE et al., 2002; FENSKE et al., 1986; GOLD and HOLCSLAW, 1985; GROßKOPF et al., 2013; KURTZ and BODE, 1985; LAPPHARAT et al., 2014; LEAVITT et al., 1982; LESMES-FABIAN et al., 2012)	97.1	85.4	65.2	92.2	73.4	21
application / cleaning (KURTZ and BODE, 1985)			68.2		68.2	20
harvesting (BALDI et al., 2014; RECH et al., 1989; SPEAR et al., 1977; SPENCER et al., 1995)	64.1	69.5		37.8	61.5	6
mixing (DAVIES et al., 1982; FENSKE et al., 1990)		72.4	81.9		78.7	3
mixing / loading (GROßKOPF et al., 2013)			95.6		95.6	1
mixing / loading / application (HSE, 1998; NIGG et al., 1986; VITALI et al., 2009)	70.9				70.9	3

Industry area and short task description	**different / unknown (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction efficiency per category (%)**	**Overall number of database entries per category**
mixing / loading / application / cleaning (BALDI et al., 2006)			10.4		10.4	1
re-entry (BALDI et al., 2014; KANGAS et al., 1993)		84.9		84.2	84.6	2
wood impregnation (ROFF, 1997)				91.2	91.2	1
brushing of wood preservatives, outdoor, non-professionals / amateurs				91.2	91.2	1
Average exposure reduction efficiency per category (%)	71.7	78.9	67.0	81.6	70.5	58
Overall number of database entries per category	7	7	38	6	58	

Table 5.23 Additional exposure reduction efficiencies for clothing (not included in database)

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
Brodberg, R. K. and J. R. Sanborn (1996). Compilation of Clothing Penetration Values: Harvesters. HS-1652, California Environmental Protection Agency. Department of Pesticide Regulation. Worker Health and Safety Branch. (BRODBERG and SANBORN, 1996)	Spencer, J.R., Sanborn, J.R., Hernandez, B.Z., and Margetich, S. (1990) Leng and short intervals of dermal exposure of peach harvesters to Azinphos-methyl residues. Department of Feod and Agriculture, Worker Health and Safety Branch, HS-1578.	Pesticide application Peaches, Azinphosmethyl	clothing	79
Popendorf, W.J., Spear, R.C„ Leffingwell, J.T. and Kahn, E. (1979) Harvester exposure to Zolone® (phosalone) residues in peach orchards. J. Occup. Med 21:189-194. (POPENDORF et al., 1979)		Pesticide application Peaches, Azinphosmethyl	clothing	81
Popendorf, W.J., Spear, R.C„ Leffingwell, J.T. and Kahn, E. (1979) Harvester exposure to Zolone® (phosalone) residues in peach orchards. J. Occup. Med 21:189-194. (POPENDORF et al., 1979)		Pesticide application Peaches, Phosalone	clothing	79
Brodberg, R. K. and J. R. Sanborn (1996). Compilation of Clothing Penetration Values: Harvesters. HS-1652, California Environmental Protection Agency. Department of Pesticide Regulation. Worker Health and Safety Branch. (BRODBERG and SANBORN, 1996)	Fong, H„ (1989a) Review of "Worker exposure to residues of Captan 50-WP during peach harvest". DPR Registration Doc. No. 103:227.	Pesticide application Peaches, Captan	clothing	90

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
Brodberg, R. K. and J. R. Sanborn (1996). Compilation of Clothing Penetration Values: Harvesters. HS-1652, California Environmental Protection Agency. Department of Pesticide Regulation. Worker Health and Safety Branch. (BRODBERG and SANBORN, 1996)	Fong, H„ (1989b) Review of "Worker exposure to residues of Captan 50-WP during strawberry harvest". DPR Registration Doc. No. 103:228.	Pesticide application Strawberries, Captan	clothing	66
Brodberg, R. K. and J. R. Sanborn (1996). Compilation of Clothing Penetration Values: Harvesters. HS-1652, California Environmental Protection Agency. Department of Pesticide Regulation. Worker Health and Safety Branch. (BRODBERG and SANBORN, 1996)	Fong, H„ (1989b) Review of "Worker exposure to residues of Captan 50-WP during strawberry harvest". DPR Registration Doc. No. 103:228.	Pesticide application Grapes, Captan	clothing	87
Brodberg, R. K. and J. R. Sanborn (1996). Compilation of Clothing Penetration Values: Harvesters. HS-1652, California Environmental Protection Agency. Department of Pesticide Regulation. Worker Health and Safety Branch. (BRODBERG and SANBORN, 1996)	Fong, H„ (1989d) Review of "Worker exposure to residues of Captan 50-WP during tomato harvest". DPR Registration Doc. No. 103:229.	Pesticide application Tomatoes, Captan	clothing	83
William Popendorf Mustafa Selim. Exposures While Applying Commercial Disinfectants. AMERICAN INDUSTRIAL HYGIENE ASSOCI ATION JOURNAL 56:1111-1120 (1995) (POPENDORF and SELIM, 1995)		Disinfectant application (high pressure spray) production building poultry, hog	clothing	99.9

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
William Popendorf, Mustafa Selim, Mary Q. Lewis. EXPOSURE WHILE APPLYING INDUSTRIAL ANTIMICROBIAL PESTICIDES. AM. IND. HYG. ASSOC. J. (56) I October 1995 (POPENDORF and SELIM, 1995)		Application of antimicrobial pesticides, pump application	clothing	92
William Popendorf, Mustafa Selim, Mary Q. Lewis. EXPOSURE WHILE APPLYING INDUSTRIAL ANTIMICROBIAL PESTICIDES. AM. IND. HYG. ASSOC. J. (56) I October 1995 (POPENDORF and SELIM, 1995)		Application of antimicrobial pesticides, pouring solids	clothing	94
William Popendorf, Mustafa Selim, Mary Q. Lewis. EXPOSURE WHILE APPLYING INDUSTRIAL ANTIMICROBIAL PESTICIDES. AM. IND. HYG. ASSOC. J. . (56) I October 1995 (POPENDORF and SELIM, 1995)		Application of antimicrobial pesticides, pouring liquids	clothing	99
Gao, B., C. Tao, et al. (2014). "Measurement of operator exposure to chlorpyrifos." Pest Manag Sci 70(4): 636-641. (GAO et al., 2014)		pesticide use / spraying (application) and mixing; maize, chlorpyrifos	clothing / no further information	65

Reference evaluated	**Cross-reference, if data was not from evaluated publication**	**Task / application**	**Type PPE**	**Exposure reduction (%)**
Garrod A.N.I., Guiver, R., Rimmer, D.A., (2000). Potential exposure of amateurs (consumers) through painting wood preservative and antifoulant preparations. Annals of Occupational Hygiene (44) 421-426.(GARROD et al., 2000)		wood preservative application. mixing and loading, application by brush painting or paint roller (fence painting, house / shed painting). No surface preparation or brush cleaning tasks were measured.	clothing / no further information	93
Garrod A.N.I., Guiver, R., Rimmer, D.A., (2000). Potential exposure of amateurs (consumers) through painting wood preservative and antifoulant preparations. Annals of Occupational Hygiene (44) 421-426. (GARROD et al., 2000)		wood preservative application. mixing and loading, application by brush painting or paint roller (boat). No surface preparation or brush cleaning tasks were measured.	clothing / no further information	94
Leavitt, J. R. C., Gold, R. E., Holcslaw, T., and Tupy, D. 1982. Exposure of professional pesticide applicators to carbaryl. Arch. Environ. Contam. Toxicol. 11:57-62. (LEAVITT et al., 1982)		pesticide application. power sprayer	clothing / no further information	89

5.2.9 Coveralls/ whole body garments

In this section database entries related to whole body PPE will be summarised. This may relate to cotton coveralls, however, chemically resistant garments as described in section 3 are also of great interest.

Coveralls without further information

Only two publications include information about efficiency of whole body garments without further defining the type of coverall that has been used. A summary of the relevant datasets is given in Table 5.24. Both belong to the area of pesticide application (plant protection) and describe mixing / loading and application tasks. The average exposure reduction is 83.3%, which seems a reasonable value considering the lack of information about the type of PPE. The physical state of pesticide product is unknown for both database entries.
Both sets of entries have been provided using surrogate techniques.

Table 5.24 Summary of database entries for coveralls without further details about PPE available

Industry area / short task description	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
Pesticide application (plant protection): mixing / loading / application	83.3	59.0	97.0	**3**
(HSE, 1999)	94.0	94.0	94.0	1
(RUBINO et al., 2012)	78.0	59.0	97.0	2
Overall result per category	83.3	59.0	97.0	**3**

Coveralls / whole body garments with documented properties

In this section database entries for coveralls / whole body garments will be summarised for which at least some additional information about the type of PPE is available. Overall 150 database entries are available matching this description.
A summary of the available datasets according to the used sampling technique is given in Table 5.25 and indicate a clear focus on surrogate techniques such as the whole body dosimetry or patch techniques. There are differences between the categories concerning resulting exposure reduction efficiency. However, numbers of database entries within most groups are small so it is likely that these are not caused by the difference concerning sampling.
Two authors referred neither to removal, nor in-situ or surrogate techniques: While WILLER and FELTEN used vapour measurements inside and outside a gas tight suit, BIERMAN et al. referred to a combination of in-situ measurements (on skin) and the

extraction of coveralls for the derivation of an efficiency (BIERMAN et al., 1998; WILLER and FELTEN, 2006).
Six database entries have been excluded from the further analyses due to negative efficiencies or sampled exposure values below the limit of detection (GARRIGOU et al., 2011; GROVER et al., 1986; NORTON et al., 1988; TSAKIRAKIS, 2014; WILLER and FELTEN, 2006).

Very high values of 100% efficiency have been found for Nylon / PTFE film and PVC by NORTON et al., one cotton coverall in combination with normal clothing by (GROVER et al., 1986) and another cotton coverall by TSAKIRAKIS et al. (NORTON et al., 1988; TSAKIRAKIS, 2014). All these database entries are based on comparisons of actual and potential exposure at the same individual and are explained by negligible exposure under the coverall reported in the corresponding publications without a usable limit of detection as alternative.

Some extreme negative outliers have been identified in the publication by WILLER and FELTEN, who evaluated a hazmat suit (type 1b equipment) by gas measurements inside and outside the suit.

No dermal exposure was directly evaluated. The material of the suit is unknown, however, this type of suit is supposed to be airtight and chemical resistant to a high degree. It is used (~1 year old) and was sampled for sulphuric acid during tank cleaning and various hydrogen carbons during other cleaning activities.
While average efficiencies of 98.6 and 81.7% were estimated for cleaning of sulfates from the tank and removal of oily-bitumen residues, a negative efficiency of -487300% was estimated for the cleaning of a heat exchanger. This value is the average of several samples for a number of substances (toluene, butyl acetate, ethyl acetate, butanone, limonene) which have all been measured in very low concentrations in the surrounding air and in higher concentrations inside the suit. WILLER and FELTEN however describe that the found substances are used in the cleaning agents used for the suits and the adhesives and maintenance materials used when the suit has to be repaired. The authors conclude that the evaluated suits probably often are gas tight at the start of a shift, however, leaks may appear during use due to physical stress e.g. at seams which also explains detected sulphuric acid during cleaning of tanks. Material degradation and the following permeation perhaps only play a minor role.

GARRIGOU et al. evaluated a type 4 coverall in a pesticide / plant protection scenario in a cross sectional study design with only one test individual. While for other parts of the application process a reduction of exposure was observed (mixing / spraying; ~88 and 97%) for cleaning higher exposure values were sampled when the suit was worn (negative efficiency of -450% estimated).
Further details will be discussed in the following sections.

Table 5.25 Summary of database entries for whole body PPE according to their sampling technique (without negative efficiencies and other unusable results (6 entries))

Sampling method	**Average exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
in-situ method (FENSKE, 1988)	61.0	45.0	77.0	2
other (BIERMAN et al., 1998; WILLER and FELTEN, 2006)	89.9	81.7	98.6	3
removal method (FENT et al., 2009)	94.9	89.7	99.8	10
surrogate method (APREA et al., 2009; APREA et al., 2004; BRADMAN et al., 2009; CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; CATTANI et al., 2001; CESSNA and GROVER, 2002; DAVIES et al., 1982; DE VREEDE et al., 1994; ERIKSSON et al., 2004; ESPANHOL-SOARES et al., 2013; FENSKE et al., 2002; FENSKE et al., 1986; FUSTINONI et al., 2014; GARRIGOU et al., 2011; GARROD et al., 1999; GARROD et al., 1998; GLASS et al., 2005; GROßKOPF et al., 2013; GROVER et al., 1986; HSL, 2003; JOHNSON et al., 2005; LEBAILLY et al., 2009; LINKS et al., 2007; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; METHNER and FENSKE, 1994; NIGG and STAMPER, 1983; NIGG et al., 1992; NIGG et al., 1986; NIVEN et al., 1996; NORTON et al., 1988; OJANEN et al., 1992; POPENDORF, 1988; PUTMAN et al., 1983; SHAW, 2008; SOUTAR et al., 2000b; STAMPER et al., 1989; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b; VITALI et al., 2009)	90.4	33.4	99.8	129
Overall result	90.3	33.4	99.8	144

Of these database entries, a further categorisation of surrogate methods into patch / pad sampling techniques, whole body methods and mixed sampling methods can be done. The results are shown in Table 5.26 and show a slight tendency to lower average exposure reductions for patch sampling (88 % for patch sampling vs. 93 % for whole body dosimetry). It is however not known to which extent this difference is significant. If it is further differentiated according to the sampling quality (small vs. high number of patches) the difference suggests a lower efficiency for a higher number of patches (86 vs. 89 %). Both whole body and patch sampling technique cover a large range of exposure reduction efficiencies ranging from 33/34% up to above 99%. Thus, so far the database contents only suggest minor differences.

Table 5.26 Summary of database entries for whole body PPE according to their sampling technique (without negative efficiencies and other unusable results (6 entries))

Sampling method	**Average exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
Patch (APREA et al., 2009; APREA et al., 2004; BRADMAN et al., 2009; CATTANI et al., 2001; CESSNA and GROVER, 2002; DAVIES et al., 1982; ERIKSSON et al., 2004; FENSKE et al., 2002; FENSKE et al., 1986; GARRIGOU et al., 2011; GARROD et al., 1999; GARROD et al., 1998; HSL, 2003; JOHNSON et al., 2005; METHNER and FENSKE, 1994; NIGG and STAMPER, 1983; NIGG et al., 1992; NIGG et al., 1986; OJANEN et al., 1992; POPENDORF, 1988; PUTMAN et al., 1983; STAMPER et al., 1989; VITALI et al., 2009)	87.9	33.7	99.8	58
Patch / whole body (SOUTAR et al., 2000b)	89.1	63.0	99.5	6
Whole body (CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; DE VREEDE et al., 1994; ESPANHOL-SOARES et al., 2013; FUSTINONI et al., 2014; GLASS et al., 2005; GROßKOPF et al., 2013; LEBAILLY et al., 2009; LINKS et al., 2007; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; NIVEN et al., 1996; SHAW, 2008; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	93.0	33.4	99.8	71
Overall result	90.7	33.4	99.8	135

A short sub analysis has been done taking into account the publication date of the different data sets (not shown). There seems to be no clear tendency concerning higher exposure reduction efficiencies for more recent publications.

Influence of material

As for gloves, also for whole body garments the material can have a large influence on the final exposure reduction potential. However, other than in case of gloves, the tendency to use non-chemical resistant materials is much higher in this case (see Table 5.27).

The majority of entries can be found for untreated cotton coveralls (53 entries), which may also be due to the fact that cotton is considered to be well suited as a dosimeter and penetration values are often more of a byproduct that can be derived from actual and potential exposure values. 30 entries can be found for polyester / cotton combinations and 17 for Tyvek. For 15 database entries no information on the garment material is available.

Overall this means that approximately 50% of the evaluated garments are made of classical, woven fabrics that may be sturdier than those used for normal clothing but not chemical resistant.

Average exposure reduction efficiencies range between 79 and 99% for all known materials.

Overall, no clear tendency such as lower efficiencies for woven fabrics seems to be visible.

Table 5.27 Summary of database entries for different coverall materials (without negative efficiencies and other unusable results (6 entries))

Material of coverall	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
cotton (APREA et al., 2009; BIERMAN et al., 1998; CATTANI et al., 2001; CESSNA and GROVER, 2002; DAVIES et al., 1982; ESPANHOL-SOARES et al., 2013; FENSKE et al., 1986; FUSTINONI et al., 2014; GLASS et al., 2005; GROßKOPF et al., 2013; LEBAILLY et al., 2009; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; NIGG et al., 1992; NIVEN et al., 1996; POPENDORF, 1988; SHAW, 2008; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	94.1	41.1	99.8	52
cotton (treated) (DAVIES et al., 1982)	99.4	99.4	99.4	1
Gore-Tex / Teflon / Nylon – Garment (PUTMAN et al., 1983)	79.3	76.8	80.7	3
Kleenguard non woven (GLASS et al., 2005; SOUTAR et al., 2000b)	86.8	60.2	99.5	4
no information (APREA et al., 2004; ERIKSSON et al., 2004; GARRIGOU et al., 2011; GARROD et al., 1998; GROßKOPF et al., 2013; JOHNSON et al., 2005; METHNER and FENSKE, 1994; NIGG and STAMPER, 1983; WILLER and FELTEN, 2006)	89.2	69.0	99.4	15
nylon / polyester; polyester ; polyester / cotton (FENT et al., 2009)	92.2	89.7	94.2	4
polyester / cotton (BRADMAN et al., 2009; ESPANHOL-SOARES et al., 2013; FENSKE, 1988; GLASS et al., 2005; GROßKOPF et al., 2013; HSL, 2003; MACHERA et al., 2009; SOUTAR et al., 2000b; TSAKIRAKIS et al., 2010; VITALI et al., 2009)	86.1	33.4	99.6	30

Material of coverall	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
polyester / cotton (treated) (NIGG et al., 1992; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014)	97.7	96.0	99.1	5
polypropylene non woven (METHNER and FENSKE, 1994) (FENSKE et al., 2002; NIGG et al., 1992)	96.2	93.9	98.1	5
Sontara (polyester / wood pulp) (CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; FENSKE et al., 2002; NIGG et al., 1992)	92.3	86.9	99.2	6
Tyvek (APREA et al., 2004; FENSKE, 1988; GARROD et al., 1999; GLASS et al., 2005; LINKS et al., 2007; METHNER and FENSKE, 1994; NIGG et al., 1986; SOUTAR et al., 2000b; STAMPER et al., 1989)	84.8	41.8	99.8	17
rubber and others, partly unknown (DE VREEDE et al., 1994)	90.6	90.6	90.6	1
CO / pyrovatex CP finished; polyamide / PTFE; PU/PA; CO/PA, PES/WO ; PES, PU/PA; Cotton (OJANEN et al., 1992)	78.0	78.0	78.0	1
Overall result per category	90.3	33.4	99.8	144

Type of garment / CE marking

Only very limited information is available about classification of coveralls as described in 3.2. The available information and corresponding datasets have been summarised in Table 5.28.
It is clear that the vast majority of datasets is without corresponding information (135 entries). One publication by WILLER and FELTEN includes some negative protection factors that have already been discussed in the previous section.
A type 4 coverall has been evaluated by GARRIGOU et al. for pesticide mixing, loading, application and cleaning, resulting in very variable results: While for mixing and application of pesticides a clear reduction of exposure could be identified (88.1 and 96.9%) for cleaning the exposure is actually higher when using the coverall, resulting in -450% “exposure reduction”. For the mixing scenario also a fume cupboard has been used instead of mixing directly on the field.
The only other study directly mentioning a CE marking has been published by GLASS et al. evaluating biocide spraying in a laboratory design simulating field conditions. While for the spray test (prEn13034) efficiencies of ~99.5% for both evaluated coveralls were found, only 78.4 and 69.7 could be identified for the field simulations.

Two further studies published by METHNER and FENSKE and NORTON et al. have evaluated coveralls without an indication about a CE label but gave the information that seams are sealed. METHNER and FENSKE came to an average exposure reduction of 99.8% for pesticide application in combination with a Tyvek suit (patch sampling) while in case of NORTON PVC and Nylon / PTFE film have been evaluated (see previous section) and all samples beneath the coverall are below the limit of detection (METHNER and FENSKE, 1994; NORTON et al., 1988).

In general it would be expected that coveralls with a CE marking or at least sealed seams show higher efficiencies than other coveralls. However, the categorised database entries so far do no give a clear picture. This may be due to a lot of reasons such as different tasks, industry areas, user behaviour or substance specifics as mentioned by WILLER and FELTEN. However, at this point no clear conclusion is possible.

Influence of industry area and physical state

A summary of the available database entries sorted according to industry areas and task descriptions can be found in Table 5.29. Again the majority of datasets (106 of 144) can be found in the area of pesticide application (plant protection).
Concerning the physical state most data can be assigned to liquids or solids in solutions (41 and 56). Average exposure reductions vary between the categories but are often strongly influenced by the few extreme negative values already discussed.

Only two database entries for true solids are included that are based on exposure to chemicals contained in wood dust in sawmills (ERIKSSON et al., 2004). The coverall material is not given in the publication and efficiencies of 69 and 76% are estimated.

Table 5.28 Summary of database entries for different glove lengths (without negative efficiencies and other unusable results (6 entries))

Garment type / CE marking	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries
Sealed seams (METHNER and FENSKE, 1994)	99.8	99.8	99.8	1
CE marking Type 6+5 (GLASS et al., 2005)	83.8	60.2	99.5	4
CE marking: None (GLASS et al., 2005)	55.2	33.4	91.1	3
no information (all further database entries)	91.2	33.7	99.8	132
type 1b DIN EN 943-1 (WILLER and FELTEN, 2006)	90.2	81.7	98.6	2
type 4 (GARRIGOU et al., 2011)	92.5	88.1	96.9	2
Overall result	90.3	33.4	99.8	144

Table 5.29 Summary of database entries for coveralls / whole body garments concerning industry areas and short task descriptions (without negative efficiencies and other unusable results (6 entries))

Industry area / Short task description	**different / unknown (%)**	**gas (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction per category (%)**	**Number of database entries**
automotive industry	92.7		90.9			92.2	4
automotive spray painting (FENT et al., 2009)	92.7		90.9			92.2	4
Graffiti removal (HSL, 2003)			69.8			69.8	5
all wiping activities			93.3			93.3	1
brushing on			33.7			33.7	1
Hand spray on and wipe off			94.5			94.5	1
Spraying off			51.5			51.5	1
wiping on and off			75.9			75.9	1
Insecticide application (NIVEN et al., 1996)			98.6			98.6	2
sheep dipping: chucker (from (NIVEN et al., 1993): putting sheep into dipping bath)			99.4			99.4	1
sheep dipping: helper (from (NIVEN et al., 1993): general duties, can include chucking activities, rounding sheep up prior to dipping, transferring to holding pens following dipping and returning sheep to pasture)			97.8			97.8	1
no further information		90.2			96.7	94.1	5
cleaning (WILLER and FELTEN, 2006)		90.2				90.2	2

Industry area / Short task description	**different / unknown (%)**	**gas (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction per category (%)**	**Number of database entries**
spray test EN 13034 (GLASS et al., 2005)					96.7	96.7	3
paint application	99.6					99.6	1
Mixing / loading and application of antifouling paints via rolling (LINKS et al., 2007)	99.6					99.6	1
pesticide application (construction sites)					74.2	74.2	10
spray application (GLASS et al., 2005)					52.7	52.7	4
spraying and irrigation of pesticide (GARROD et al., 1998)					90.2	90.2	3
application preconstruction via sprinkling rose, Termite treatment: preparation (drilling of injection ports), application and clean up. (CATTANI et al., 2001)					69.2	69.2	1
post construction via injection into the ground or spraying onto the surface. Termite treatment: preparation (drilling of injection ports), application and clean up. (CATTANI et al., 2001)					95.5	95.5	1
under floor by crawling on hands and knees during application. Termite treatment: preparation (drilling of injection ports), application and clean up. (CATTANI et al., 2001)					95.9	95.9	1
Pesticide application (plant protection)	90.0		94.5	95.2	92.4	93.4	106

Industry area / Short task description	**different / unknown (%)**	**gas (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction per category (%)**	**Number of database entries**
application (APREA et al., 2004; BIERMAN et al., 1998; CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; CESSNA and GROVER, 2002; DAVIES et al., 1982; DE VREEDE et al., 1994; ESPANHOL-SOARES et al., 2013; FENSKE, 1988; FENSKE et al., 2002; FENSKE et al., 1986; GARRIGOU et al., 2011; GROßKOPF et al., 2013; LEBAILLY et al., 2009; MACHERA et al., 2003; MACHERA et al., 2009; METHNER and FENSKE, 1994; NIGG and STAMPER, 1983; NIGG et al., 1992; OJANEN et al., 1992; SHAW, 2008; STAMPER et al., 1989; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	88.7		94.7	95.3	93.3	93.6	74
harvesting (BRADMAN et al., 2009)			96.5			96.5	1
mixing (DAVIES et al., 1982; FENSKE, 1988; GARRIGOU et al., 2011)	82.6		96.2			89.4	4
mixing / loading (GROßKOPF et al., 2013; TSAKIRAKIS, 2014)			88.8	96.4	99.5	96.0	15
mixing / loading / application (FUSTINONI et al., 2014; GROVER et al., 1986; HSE, 1998; JOHNSON et al., 2005; NIGG et al., 1986; POPENDORF, 1988; PUTMAN et al., 1983; RUBINO et al., 2012; VITALI et al., 2009)	96.6			80.7	86.0	90.1	9

Industry area / Short task description	**different / unknown (%)**	**gas (%)**	**liquid (%)**	**solid (%)**	**solid in solution (%)**	**Average exposure reduction per category (%)**	**Number of database entries**
mixing / loading / application / cleaning (MANDIC-RAJCEVIC et al., 2015)				97.0		97.0	1
re-entry (APREA et al., 2009)					84.6	84.6	2
pesticide application (timber) (SOUTAR et al., 2000b)					89.1	89.1	6
application					96.3	96.3	3
mixing / application					82.0	82.0	3
wood impregnation (GARROD et al., 1999)					65.4	65.4	3
double vacuum process					55.9	55.9	2
vacuum pressure process					84.3	84.3	1
woodworking industry (ERIKSSON et al., 2004)				72.5		72.5	2
collection of boards in a sawmill				69.0		69.0	1
Sawing of wood in carpentry workshop				76.0		76.0	1
Average exposure reduction per category	90.9	90.2	91.6	93.5	87.6	90.3	144
Overall number of database entries	19	2	41	26	56	144	

Influence of prior use

For an evaluation of the use status and age of the various garments a similar categorisation as described in section 5.2.6 for gloves has been used.
The resulting summary of datasets assigned to the different categories is given in Table 5.30.
The database entries are focussed on the “no information” and “new (assumption)” categories (53 and 44 entries). There are however also some datasets assigned to new (22; 12 for single use) or used (12) garments or a mixture of both (1).
The efficiency for garments without further information on prior use is only slightly lower than that of the new garments (~86 vs. 88%). Used coveralls (90%), new single use garments (91%) and mixed property as well as garments assumed to be new (94% and 95%) follow closely.
Overall, the available data do not allow a conclusive statement.

Table 5.30 Summary of database entries for coveralls / whole body garments with different use status (without negative efficiencies and other unusable results (6 entries))

Age of garment / use status	**Average exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
5 used, 1 new (METHNER and FENSKE, 1994)	93.9	93.9	93.9	1
new (CATTANI et al., 2001; ESPANHOL-SOARES et al., 2013; FENSKE, 1988; GARRIGOU et al., 2011; GARROD et al., 1999; LEBAILLY et al., 2009; METHNER and FENSKE, 1994; NIGG et al., 1992)	87.6	41.8	99.8	22
new (assumption) (BRADMAN et al., 2009; CASTRO CANO et al., 2001; CESSNA and GROVER, 2002; DAVIES et al., 1982; FUSTINONI et al., 2014; GROßKOPF et al., 2013; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; PUTMAN et al., 1983; SHAW, 2008; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	95.0	76.8	99.8	53
new (single use) (CASTRO CANO et al., 2000; JOHNSON et al., 2005; LINKS et al., 2007; NIGG and STAMPER, 1983; NIGG et al., 1986; SOUTAR et al., 2000b; STAMPER et al., 1989)	91.4	66.0	99.6	12

Age of garment / use status	**Average exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
no information (APREA et al., 2009; APREA et al., 2004; BIERMAN et al., 1998; ERIKSSON et al., 2004; FENSKE et al., 2002; FENSKE et al., 1986; GARRIGOU et al., 2011; GARROD et al., 1998; GLASS et al., 2005; GROßKOPF et al., 2013; HSL, 2003; NIVEN et al., 1996; OJANEN et al., 1992; POPENDORF, 1988; SOUTAR et al., 2000b; TSAKIRAKIS et al., 2011; VITALI et al., 2009)	85.6	33.4	99.5	44
used (DE VREEDE et al., 1994; ESPANHOL-SOARES et al., 2013; FENT et al., 2009; GARROD et al., 1998; WILLER and FELTEN, 2006)	90.0	75.8	98.6	12
Overall result	90.3	33.4	99.8	144

Apart from the pure database analysis some additional information has been identified in the course of the literature search.
METHNER and FENSKE, whose evaluation of Kleenguard coveralls has been included as one entry into the database due to the otherwise small sample size have evaluated a group composed of used and new coveralls. The evaluated coveralls were composed of 100 percent nonwoven polypropylene; breathable, lightweight, and protects against oils, greases, resins, and water-based liquids. Pesticide exposure during greenhouse applications (contact with treated foliage) was evaluated. While for new coveralls only 0.05% penetration was found for used and washed coveralls 11.1% penetration was identified via the patch method (one worker with new coverall, five workers with used coveralls; Kleenguard™ liquid protection coverall (Kimberly-Clark): composed of 100 percent nonwoven polypropylene). It is not stated if the equipment used is intended to be disposable, however, one of the conclusions of the publication is that disposable garments should not be washed.
APREA et al. compared the stapling of ornamental plants in tunnels and greenhouses concerning exposure to pesticide for clean and used coveralls and first and second stapling of plants resulting in geometric means of 27.2 and 29.4% penetration for the first stapling and 4.7 vs. 9.2% for the second (APREA et al., 2009). The amount of vegetation differed in the two stapling scenarios: vegetation was more abundant and more plants are stapled at the second stapling (24 vs. 19 per hour for the first stapling), which may be a reason for the different penetration values. The exposure pattern over the body differs between the two stapling processes with anterior thighs being a major point of contamination for the second stapling. APREA et al. assume that this contamination may have happened during breaks (due to urination and/or the necessary during removal of the pants).

ESPANHOL-SOARES et al. have evaluated used and new cotton and polyester / cotton garments during the application of pesticide via whole body dosimetry. A summary of the results is given in Table 5.31 and indicates 95.9% efficiency for new garments and 89.9% for used garments, i.e. approximately 10 instead of 4% penetration for used coveralls (ESPANHOL-SOARES et al., 2013).

Table 5.31 Exposure reduction efficiency provided by used and new garments during the application of pesticide according to ESPANHOL-SOARES et al. (2013)

Garment	**Average Exposure reduction (%)**	**Number of database entries**
new	**95.9**	4
cotton garment	96.3	2
polyester/cotton garment	95.5	2
used	**89.9**	4
cotton garment	94.7	2
polyester/cotton garment	85.1	2

Some further testing strategies have been followed by other authors in order to evaluate the contamination potential of used coveralls / clothing after it has been cleaned.
As an example, according to NORTON et al., who evaluated the protectiveness of Gore-Tex and PVC spray suits laundering removed from 86 up to 100% of pesticide residues on Gore-Tex. Removal was greater when the garment was contaminated with aqueous suspension than with an oil emulsion (NORTON et al., 1988).
Other authors describe a removal of 89-99% of pesticide from a polyester coverall with some variability depending on the substance (LILLIE et al., 1981).
However, there are also authors who show that depending on the laundering protocols (cold wash, hot wash, sunlight exposure yes or no, no detergent on cotton and polyester / cotton) with chlorpyrifos, yielded in 1-50% residual substance still being in the fabric (FITZGERALD and MANLEY-HARRIS, 2005).

There also exists some research about self-decontaminating fibres containing magnesium oxide nanoparticles (LANGE and OBENDORF, 2012).

Overall it can be summarised that limited information about the change of protectiveness following the continued use of protective garments is available. A simple analysis of the available database did not give conclusive results while single studies partly predict large differences. General information about decontamination of PPE has been found.

Different baselines

Another important factor when the efficiency of a piece of equipment is evaluated is always the baseline against which this measure is compared. In case of gloves this baseline is usually the naked hand. However, in case of whole body garments other baselines are in general possible: Depending on the way the derived efficiency should be used at a later stage it can be derived by comparing potential and actual exposure directly, thereby defining the baseline as the naked body, or as some sort of non-PPE clothing such as shorts and T-shirt. While it is not considered to be a reasonable worst case to assume that a worker will work without any clothing in reality, such an efficiency might still be useful for certain modelling purposes. It cannot be reproduced by biomonitoring under normal circumstances. Choosing other baselines however allows the exposure assessor to estimate how much exposure can be reduced if normal clothing is exchanged for a certain type of PPE or amended by additional equipment.
In theory, there are different results expected for both efficiencies. However, since in the available database the focus is clearly on the comparison of potential with actual exposure, in this case the number of datasets per category is too small and other factors have too much influence to identify clear differences. The list described below is therefore merely fore information purposes.

Table 5.32 Summary of database entries for coveralls / whole body garments with baselines other than “no PPE (actual vs. potential exposure)” or similar

	Average Exposure reduction (%)	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**
cotton garments, it is not known if this refers to coveralls or T-shirt / trousers. (LEBAILLY et al., 2009; NIGG et al., 1992)	88.7	81.9	95.4	2
No PPE (actual vs. Potential exposure) (APREA et al., 2009; APREA et al., 2004; BIERMAN et al., 1998) (BRADMAN et al., 2009; CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; CATTANI et al., 2001; CESSNA and GROVER, 2002; DAVIES et al., 1982; ERIKSSON et al., 2004; FENSKE et al., 2002; FENSKE et al., 1986; FENT et al., 2009; FUSTINONI et al., 2014; GARRIGOU et al., 2011; GARROD et al., 1999; GARROD et al., 1998; GLASS et al., 2005; GROßKOPF et al., 2013; HSL, 2003; JOHNSON et al., 2005) (DE VREEDE et al., 1994; LINKS et al., 2007; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; NIVEN et al., 1996; OJANEN et al., 1992; POPENDORF, 1988; PUTMAN et al., 1983; SHAW, 2008; SOUTAR et al., 2000b; STAMPER et al., 1989; TSAKIRAKIS et al., 2011; TSAKIRAKIS et al., 2014a; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b; VITALI et al., 2009; WILLER and FELTEN, 2006)	90.7	33.4	99.8	138
outside, near the vine that was going to be treated, shorts and t-shirt (DAVIES et al., 1982)	92.5	88.1	96.9	2
workshirts made of a 50/50 cotton/polyester fabric (weight = 11.0 mg/crn 2), tshirt worn under workshirt (FENSKE, 1988)	61.0	45.0	77.0	2
Overall result per category	90.3	33.4	99.8	144

Temperature and humidity

Another piece of information worth mentioning has been published by APREA et al. who evaluate the exposure to imidacloprid during stapling of ornamental plants in tunnels or greenhouses. The influence of temperature on the permeation through coveralls is shortly discussed in this publication and it is stated, that higher temperature and humidity seem to promote greater penetration of active ingredient though clothing leading to greater contamination (APREA et al., 2009).

Influence of behaviour

In the same study by APREA et al. about stapling of plants in greenhouses and tunnels it is reported that the contamination is greatest at the anterior thighs and hips. According to APREA et al. contact may have happened during urination, i.e. removal of the coverall pants (APREA et al., 2009).
Apart from this, the study of ESPANHOL-SOARES et al. should be pointed out, who evaluated the influence of washing and use on two woven fabric coveralls treated for water repellency via ASTM F1359 method (spray method using a mannequin) and field trials with a knapsack sprayer. Above 90% exposure reduction were observed in all cases. However, the penetration increased by a factor of 2 or 4 (material A and B) for the mannequin (ASTM) test, but almost not or only by a factor of 2 (material A and B) during the field test in the course of the washing / use cycles. This difference may as an example be attributed to the experience of the users in the field trials. Different distributions of the penetration rates over the body were noticed as well for mannequins and field trials (ESPANHOL-SOARES et al., 2013).

Correlation between in vitro and field studies

Some publications have been identified in which both in vitro studies and field studies have been done for the same equipment. In the following paragraphs these studies will be shortly summarised and inconsistencies between results of both approaches pointed out.

SOUTAR et al. have evaluated the efficiencies of different coveralls during timber spraying and via in vitro study (EN 368 Protective Clothing - Protection Against Liquid Chemicals – Test Method: Resistance Of Materials To Penetrations By Liquids ('Gutter Method'). Sampling suits (cotton and polyester) have been used as whole body dosimeters for actual exposure and patches for potential exposure. The evaluated suits are a polyester cotton coverall, a Tyvek Pro Tech suit and a Kleenguard EP suit. As a result, while laboratory tests suggested Tyvek and Kleenguard suits to be more effective than the polyester cotton overall (41 vs. 1 and 4% penetration), field trials indicated that there was very little difference between the three types, although there is a small number of datasets which complicates general statements (SOUTAR et al., 2000b).

OJANEN et al. have evaluated the efficiency of whole body PPE during the spraying of herbicide for several coverall types with a non-standard in-vitro experiment that is described in the publication and field studies. While the field study suggests 11-33% penetration, only up to 1.2% are suggested by the in vitro result. Results of the field study are only given as a range, therefore no comparison of single types of PPE are possible (OJANEN et al., 1992).

Another study evaluating the effect of coveralls during pesticide application has been published by MACHERA et al. The evaluated types of PPE include one cotton/polyester coverall 50/50 (treated with Resist Spills®- repellent finish) and one cotton coverall, which have both been tested in vitro using the ISO 22608 (2004) standard. While for the cotton / polyester coverall the penetration rate after 15 launderings was 2.4% (in contrast to 0.4 in field experiments), it was 18.7% for the cotton product (2.3% in field experiments).

A further study by LLOYD also evaluated breakthrough times and permeation data in comparison with field tests and came to the result that there is no correlation between both (LLOYD, 1986).

It can be summarised that in vitro studies not necessarily correlate with results of field studies, neither in the order of magnitude concerning penetration nor the relative quality of suits. This can either mean that the chosen in vitro studies are not appropriate to estimate influences of the different exposure paths or that field trials and sampling techniques applied do not capture real skin exposure appropriately or a mixture of both aspects.

Influence of duration

METHNER and FENSKE have evaluated the influence of application time in their study on protection efficiency of coveralls during pesticide application, finding that by shortening the application time from 30 to 15 minutes and leaving the challenge (mass per area and time) identical, the penetration rate decreased about 60% (METHNER and FENSKE, 1994).

Influence of concentration / load

MACHERA et al., who have evaluated cotton and cotton / polyester coveralls during pesticide application have found that penetration increases with decreasing outside loading (MACHERA et al., 2009).

This is consistent with findings of the review of BRODBERG and SANDBORN (1996) and HAMEY et al. (2008), who have summarised clothing penetration values of harvesters for pesticides and other penetration values for pesticide scenarios: Low exposure rate tends to give higher penetration.

According to results of the BROWSE project about pesticide exposure it has been shown that higher dermal loading usually results in less migration of plant protection products through the PPE and work wear worn. However, this relationship was not found for all PPE and work wear types (i.e. polyester-cotton coverall and impermeable/waterproof clothing) (SPAAN et al., 2014).

The TNO review (citing Ross 1997) even mentions an approximation for the relation between loading and penetration through clothing: With linear regression analysis it appeared on the basis of the data used that percent penetration = 3.3 (outer loading in $\mu g/cm^2)^{-0.3}$ (GERRITSEN-EBBEN et al., 2007).
DRIVER et al. also conclude that different defaults for different challenges might be necessary (DRIVER et al., 2007).

Additional information on exposure reduction by coveralls / whole body garments not included into the database

There are some reviews especially for the area of pesticide application (plant protection products), from which information could be extracted. Results are summarised in Table 5.33 and indicate exposure reduction efficiencies between 58 and 100% for protective coveralls (mainly cotton coveralls).

Another source of information is the BROWSE project (SPAAN et al., 2014; TSAKIRAKIS et al., 2014a) which includes an evaluation of available published data from literature about pesticide use as well as information from EUROPOEM and the southern greenhouse model database. Information is included for different types of gloves and coveralls and has been evaluated per body part (see section 5.3.1), formulation type and task.

Table 5.33 Additional exposure reduction efficiencies for protective garments / coveralls

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
Glass C R, et l Final Report SMT4-CT96-2048 (GLASS, 2002)		Pesticide application	white cotton ET garment	94
Glass C R, et l Final Report SMT4-CT96-2048 (GLASS, 2002)		Pesticide application	white cotton ET garment	97
Glass C R, et l Final Report SMT4-CT96-2049 (GLASS, 2002)		Pesticide application	white cotton ET garment	100
Glass C R, et l Final Report SMT4-CT96-2050 (GLASS, 2002)		Pesticide application	blue cotton (Textulan) garment	68
Glass C R, et l Final Report SMT4-CT96-2051 (GLASS, 2002)		Pesticide application	blue cotton (Textulan) garment	76
Glass C R, et l Final Report SMT4-CT96-2052 (GLASS, 2002)		Pesticide application	green cotton (Bayer) garment	98
Glass C R, et l Final Report		Pesticide application	white Tyvek (Indutex) garment	58

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
SMT4-CT96-2053 (GLASS, 2002)				
Glass C R, et l Final Report SMT4-CT96-2054 (GLASS, 2002)		Pesticide application	white Tyvek (Indutex) garment	71
Glass C R, et l Final Report SMT4-CT96-2055 (GLASS, 2002)		Pesticide application	white Kappler (Proshield 2) garment	93
Moreira J F, Santos J, Glass C R, 1999. Personal protective equipment penetration during application of plant protection products. XIVth International Plant Protection Congress. Jerusalem, Israel, July 25 – 30 (MOREIRA J F et al., 1999)		pesticide application	Cotton coverall	98.3% efficiency. Highest penetration value 4.3% (right arm). Rest ranges 0.19-3.1 (abdomen) %.
BROWSE project (SPAAN et al., 2014)	Tacio, M. B., M. L. d. Oliveira, et al. (2008). "Efficiency of new clothes waterrepelent in the protection of the tractor-driver in pesticide spraying in guava orchards with the air-assisted sprayer." Revista Brasileira de Fruticultura 30(1): 106-111.	Pesticide application	coveralls (Agro light set and Azeredo set)	96.7% for the Agro Light set and 96.2% for the Azeredo set.
BROWSE project (SPAAN et al., 2014)	Tacio, M. B., M. L. d. Oliveira, et al. (2010). "Security in the preparation of pesticides of liquid formulations for guava	Pesticide application	coveralls (Agro light set and Kit Tratorizado)	92.8% for the Agro Light set and 94.2% for the Kit

Reference evaluated	Cross-reference, if data was not from evaluated publication	Task / application	Type PPE	Exposure reduction (%)
	orchards." Revista Brasileira de Fruticultura 32(3): 726-735.			Tratorizado.
Berger-Preiss, E., A. Boehncke, et al. (2005). "Inhalational and dermal exposures during spray application of biocides." International Journal of Hygiene and Environmental Health 208(5): 357-372. (BERGER-PREISS et al., 2005)		Spray application of biocides (antifouling, wood protection, veterinary hygiene, private area and public hygiene, Food and feed area disinfection)	coveralls (no further information)	80-90%

As the publications given in the BROWSE deliverables have been checked for availability and further evaluated if possible a certain overlap with the database of the current project is likely. However, EUROPOEM data and information included in the Southern Greenhouse model are not publicly available, therefore main results have been included at this point for the sake of completeness. Further details are available in the corresponding project reports.

Measurements conducted in the course of BROWSE have been included into the EXCEL database and are not included in the analyses presented in this subsection.

As presented in Table 5.34 efficiencies range – depending on the material – from 79.0 (cotton clothing) up to 92.4% (cotton coverall; 96.2% overall for Southern Greenhouse model).

Concerning tasks there seems to be more penetration for mixing/ loading than for application (15.6 vs. 6.2% AM penetration). For mixing and loading it has also been differentiated between liquids and solids with liquids showing higher penetration values (21.1 vs. 14.5% AM penetration). Further differentiations are discussed in the BROWSE report (SPAAN et al., 2014).

Table 5.34 Overview descriptive statistics of analysis PPE and work wear migration factors (in %) based on individual body parts, separate for data from the BROWSE database and the Southern Greenhouse model database: Body

Description	**N**	**AM**	**SD**	**GM**	**GSD**	**P90**	**AM exposure reduction efficiency**
BROWSE database							
Overall	1838	10.8	16.1	3	7.38	33	89.2
Per PPE type							
Body - overall	1521	11.7	16.2	3.74	6.42	33.3	88.3
Cotton clothing	80	21	17.1	14.5	2.56	48.5	79.0
Cotton coverall	581	7.63	12.5	2.51	5.73	21	92.4
Cotton-polyester clothing	30	9.16	13.4	1.15	25.9	33.9	90.8
Impermeable / waterproof clothing/coverall	41	10.8	14.3	3.07	8.01	25.4	89.2
Polyester-cotton coverall	86	8.24	16	2.8	4.52	20.1	91.8
Sontara coverall	88	19.9	19.6	10.9	3.68	49.1	80.1
Tyvek coverall	73	13.8	12.6	8.22	4.88	33.3	86.2
Unspecified clothing/coverall	542	13.9	18.3	4.05	6.76	41.8	86.2
Southern Greenhouse model database							
Body - Polyester-cotton coverall	689	3.79	6.47	1.61	4	8.71	96.2

According to SPAAN et al. (not included in database), internal data from ECPA estimated 99.8% exposure reduction (0.2% penetration) for a Cat. I water impervious rain suit based on the comparison of the 75th percentile of the potential dermal exposure levels measured on polyester-cotton coveralls with the 75th percentile of actual dermal exposure measured underneath the rain suit. Migrations of 0.1% or lower were suggested for Type 3 or 4 coveralls.

It is however noted that these values are only indicative as actual and potential exposure could not be measured at the same time at the same person, what would, according to SPAAN et al., be the preferred way of sampling. No raw data was available (SPAAN et al., 2014), however, exposure values are visualised in graphical form.

Summary

Overall 144 database entries have been made for coveralls / whole body garments with a minimum of information, while only 3 database entries have been made for coveralls with no information available. The average exposure reduction efficiency for coveralls with a minimum of information has been estimated to be 90.3% (83.3% without information). Exposure reduction efficiencies range between 33.4 and 99.8%.

The large variability concerning tasks, substances and probably further, unidentified factors complicates the identification of tendencies concerning industry areas, garment material or other factors.
A further categorisation of coverall materials / types, as done in case of gloves, seems not reasonable as the majority of database entries is based on woven or non-woven, penetrable materials. Few datasets concerning further types of PPE are available (see section “Type of garment / CE marking”), and while sealed seams seemed to result in an improved exposure reduction, CE marking Type 5+6, 1b or 4 led to similar or even lower values as unmarked garments. While cotton coveralls seem to provide 94% protection, Tyvek only shows an average of 85% exposure reduction and both materials cover similar efficiency ranges. The general tendency, i.e. high efficiencies for penetrable cotton material, does not seem to be reasonable. However, it may be an effect of the commonly applied sampling via absorbent patches or whole body dosimetry, where the garment itself serves as dosimeter. The absorbent material is usually able to absorb very large amounts of substance, hence leading to an overestimation of the potential exposure. Another possible explanation may be general low exposure rates. As long as the garment is able to absorb the contamination completely without releasing it onto the skin, it may still offer a certain protection even without being impermeable.
Overall, further information and measured data including increased knowledge about sampling methods and their possible influence on the result may be advisable.

Concerning the influence of prior use only minimal differences were found by comparison of the database entries. Other studies provide limited information (APREA et al., 2009; METHNER and FENSKE, 1994), since the evaluated garments are possibly disposable and should not be reused anyway or other aspects influencing the efficiency seem to exist within the scenario. ESPANHOL-SOARES et al. report a reduction of the penetration of ~60% when comparing used with new textile coveralls. Thus, overall only limited information is available on this topic and none on impermeable garments.

Only very general information was identified concerning the influence of behaviour (APREA et al., 2009; ESPANHOL-SOARES et al., 2013).

Concerning the influence of the challenge usually a decreasing penetration with increasing challenge is reported.

5.3 Other discussion points

5.3.1 Variability of the exposure reduction efficiency over the protected body part

This kind of analysis was not part of the original project database. However, in the area of plant protection products some previous publications are available which discuss how the penetration may vary over the body or the protected body part in general.
Theoretically, this variability will not influence the overall protection since no separate protection factors are derived for different parts of one garment. On the other hand, if it is known at which places for one specific garment leaks may occur for a certain task, the overall protection factor or efficiency can be increased by improving the

corresponding garment. However, as the penetration depends on a lot of factors including the exposure loading in general, contact with surfaces / physical stress at certain points and leakage points / seams, this topic is not trivial.
The following list of publications is not complete, as in general many studies which refer to patch techniques allow for a separate analysis of different body parts. However, the examples given may give an impression about the level of variability that can be expected.

Whole body garments

One large source of corresponding information is again the BROWSE project, whose database results split up according to different body areas are given in Table 5.35.
As areas of high exposure reduction efficiencies have the upper chest and abdomen been identified (~98%), while legs and lower legs only show ~90% exposure reduction (SPAAN et al., 2014).

Other information cited by SPAAN et al. also indicated that a considerable source of exposure may be contaminated gloves worn throughout the disrobing process and resulting in exposure at the chest and upper abdomen due to the unzipping process. The publication referenced did not derive penetration factors or efficiencies (GLASS et al., 2005). However, a comparison of chest contamination for individuals who removed gloves and individuals who did not do so before the unzipping process revealed 11.8 vs. 71.3 % of the total exposure in this area. Hand exposure tended to show opposite tendencies (19.1 vs. 1.7 % of the total exposure). Total exposure was approximately twice as high for those individuals who removed their gloves before the unzipping process (2.0 vs. 0.8 ml).

Table 5.35 Overview descriptive statistics of analysis PPE and work wear migration factors (in %) based on individual body parts, separate for data from the BROWSE database and the Southern Greenhouse model database

Description	**N**	**AM**	**SD**	**GM**	**GSD**	**P90**	**Average (AM) exposure reduction efficiency**
Overall	1838	10.8	16.1	3	7.38	33	89.16
Per body part							
Upper chest	3	2.17	3.53	0.24	27.3	6.25	97.83
Abdomen	11	2.33	0.71	2.12	1.77	2.8	97.67
Chest	400	13.8	18.1	4.88	6.15	38.3	86.18
Back	203	15	19.4	4.82	6.04	49.7	84.97
Torso	18	6.27	9.27	2.69	3.76	28.5	93.73
Upper arms	167	8.39	10.9	3.45	4.36	26.1	91.61
Forearms	203	12.6	17	4.85	5.14	35.9	87.39
Arms	55	10.9	15.7	3.5	6.61	31.7	89.06
Thighs	200	9.14	13	2.56	7.24	28.5	90.86
Lower legs	185	10.4	14.9	2.3	10.3	32.6	89.63
Legs	76	10.1	15.1	3.39	5.11	28.5	89.95
Hands	317	6.71	14.7	1.04	9.85	18	93.29

Table 5.36 Overview descriptive statistics of analysis PPE and work wear migration factors (in %) based on individual body parts, as published by (DRIVER et al., 2007a)

%CP by Body Part	n	Mean	SD	SE	95% CI of Mean		Average Exposure reduction efficiency
1 (Upper arm, right)	135.0	11.4	14.6	1.3	8.9 to	13.9	88.6
2 (Upper arm, left)	88.0	11.5	10.8	1.2	9.2 to	13.8	88.5
3 (Shoulders, right)	108.0	13.6	14.7	1.4	10.8 to	16.4	86.4
4 (Shoulders, left)	46.0	11.4	13.2	1.9	7.5 to	15.3	88.6
5 (Chest, right)	174.0	16.5	18.1	1.4	13.8 to	19.3	83.5
6 (Chest, left)	9.0	6.1	5.6	1.9	1.8 to	10.4	93.9
7 (Back, right)	153.0	16.6	15.3	1.2	14.2 to	19.1	83.4
8 (Back, left)	7.0	7.5	5.0	1.9	2.8 to	12.1	92.6
9 (Forearms, right)	297.0	12.4	16.4	1.0	10.5 to	14.2	87.6
10 (Forearms, left)	193.0	11.3	14.7	1.1	9.2 to	13.4	88.7
13 (Thighs, right)	238.0	9.3	12.3	0.8	7.7 to	10.9	90.7
14 (Thighs, left)	165.0	9.7	11.9	0.9	7.8 to	11.5	90.3
15 (Shins, right)	107.0	12.0	14.2	1.4	9.2 to	14.7	88.1
16 (Shins, left)	108.0	13.2	17.1	1.7	10.0 to	16.5	86.8
17 (Calves, right)	48.0	9.5	13.3	1.9	5.6 to	13.3	90.5
18 (Calves, left)	4.0	9.1	9.2	4.6	-5.6 to	23.73	90.9
19 (Ankles, right)	101.0	10.6	17.3	1.7	7.2 to	14.0	89.4
20 (Ankles, left)	48.0	12.7	16.4	2.4	7.9 to	17.5	87.3

Another source of information concerning pesticide data is the evaluation of the PHED database published by DRIVER et al.

A summary of penetration values is given in Table 5.36 and indicates high penetration values at the right side of the chest, while the left side only shows low values. This distribution may be related to specific movements during the application process. Another high penetration value has been identified at the back (right, 16.6%).

Gloves

For gloves only one work has been identified which discusses the variability of exposure reduction efficiency over the different parts of the hand.

STONE et al. have evaluated the efficiency of gloves for greenhouse pesticide applicators wearing cotton knit gloves under long nitrile protective gloves. A particularly low efficiency was identified for the index finger and palm, especially in case of the right hand (up to ~69%). The thumbs only showed 0-25% penetration (STONE et al., 2005). The penetration at the right hand seemed to be higher than at the left.

5.3.2 Influence of carrier substances

The majority of database entries has been measured with mixtures such as pesticide products. However, none of them has been evaluated explicitly for the influence of certain substances, i.e. carrier substances, on the efficiency.

Only some in-vitro studies were identified in the course of the project, which do however not allow to derive conclusions on the exposure reduction efficiency as they only evaluate the usual standard parameters such as breakthrough time or permeation flow and usually do not give information about the specific influence of certain substances on the behaviour of others (CHIN and BATTERMAN, 2010; MUNKSGAARD, 2000; TRAN et al., 2012).

NIELSEN and ANDERSEN have evaluated the dermal absorption of methiocarb, paclobutrazol and pirimicarb in combination with different gloves (nitrile, latex) via in vitro studies. For paclobutrazol and primicarb lower dermal penetration was measured upon the addition of nonylphenolethoxylate while for methiocarb penetration increased. Without glove protection, all substances showed reduced dermal penetration upon addition of nonylphenolethoxylate, although it was not statistically significant for methiocarb (NIELSEN and ANDERSEN, 2001).

LÖNNROTH and EYSTEIN RUYTER have published a study about breakthrough times for mixtures of methyl methacrylate, ethylene glycol dimethycrlylate and 1,4-butanediol dimethacrylate through medical gloves. 15 gloves types representing natural rubber latex, synthetic rubber material and synthetic polymer were tested (thickness 74-250 micrometers). Methyl methacrylate permeated within 3 minutes through all gloves materials. Wearing two different glove materials at the same time (double layer) with the first one being rinsed in water was found to increase the breakthrough time (LONNROTH and EYSTEIN RUYTER, 2003).
The raw data reported by LONNROTH and EYSTEIN RUYTER suggest that only for one evaluated glove (Metin, vinyl glove) breakthrough times seem to become shorter upon change from the pure substance to the mixture. Partly even longer breakthrough times were reported for the mixture. The breakthrough time of methyl methacrylate (shortest breakthrough time) does not seem to define the overall breakthrough time of the mixture.

Information published by RENARD et al. suggests that the presence of a solvent with a high permeation rate may increase the rate of other mixture components (1,6-hexanediol diacrylate measured 2-ethylhexyl acrylate as carrier solvent). However, permeation rates of the carrier solvent were not reached (RENARD et al., 1992 (Information from Abstract)). Similar results were found by GEORGOULIS et al. (evaluation of toluene / methyl ethyl ketone mixtures). While substances with high permeation rates increase the permeation rate of those with low rates in a mixture, the permeation rate of the highly permeating substance will in turn be decreased (GEORGOULIS et al., 2005). The same seems to apply for the breakthrough time in binary and ternary mixtures (CHAO et al., 2008).
However, there are also cases where both substances in a binary mixture may show decreased breakthrough times (e.g. methanol and n-butyl acetate). Chemically similar substances such as xylene and toluene on the other hand may show almost the same parameters as pure substances and in a mixture.

Overall it can be summarised that parameters such as the breakthrough time and the steady state permeation rate of mixture components will be influenced by other mixture components. Available results suggest that breakthrough times or permeation rates will not necessarily reach the level of other components but rather shift depending on their concentration. However, complex interactions are possible as well.

Another aspect somehow related to the concept of carrier substances is addressed by CHAO et al., who discuss the release of toxic substances from glove materials: If certain substances (e.g. carrier substances or substances with similar properties) permeate through the glove material, they may not only be able to increase the flow of chemicals from the outside but they may also be able to increase the release of other substances from PPE materials (CHAO et al., 2015).

5.3.3 Exposure pathways

As described in section 3 there are different possible paths of exposure. The main processes in relation to the material alone are penetration (intrusion of substance through holes / openings) and permeation (diffusion on a molecular level through the material). If PPE is in use also contamination during change or removal of PPE is possible (direct deposition (FENSKE, 1988)). Contamination through the cuff or other necessary openings may happen as well.

No study has been identified which compares the influence of these different pathways on the protective effect of PPE and only few publications give information about what they think is the main path of exposure.

Some publications may exclude the contamination during disrobing either by visual examination and exclusion of some contaminated areas or by assisting the study subjects during the PPE removal process (CESSNA and GROVER, 2002; GLASS et al., 2005) while some include this process into the evaluation (PUTMAN et al., 1983).

COCKER et al. have stated in their report about glove efficiency in the printing industry that no penetration had occurred as no fluorescent tracer stains had been found on hands or forearms (COCKER, 2006).

FENSKE on the other hand found in the course of his evaluation of workshirts and trousers that penetration played an important role (FENSKE, 1988).

Some authors use the term “penetration” or “penetration factor” without further discussion of the details (see e.g. (NIGG et al., 1992; VITALI et al., 2009)).

Exposure during disrobing / PPE change is often seen as a major influence on PPE efficiency (FENSKE, 1988; GLASS et al., 2005).

In general it can be stated that the usual sampling methods for field studies capture all pathways of contamination, therefore an assignment to a specific way is only possible via interpretation of exposure patterns (e.g. main contamination around cuffs or seams) and assumptions (SOUTAR et al., 2000b). As an example it is considered to be likely that for woven fabrics penetration will play a larger role than permeation due to the open structure of the material. For chemically resistant materials as are usually used for protective gloves (e.g. nitrile) both permeation and penetration should play minor roles as long as the PPE is used appropriately, i.e. not worn beyond the breakthrough time, no use of damaged gloves. However, in general measured exposure is always a combination of all exposure pathways.

5.3.4 Requirements for a good dosimetry study which can be used to derive reliable protection factors

Although a high number of database entries for dosimetry could be collected, only a small number of them has been categorised as high quality.

- Sampling techniques should be aligned to the type of PPE and the substance evaluated (see section 5.1). Techniques covering a large skin area are to be preferred over others.

- Sampling techniques used for potential and actual exposure should lead to comparable results in order to avoid bias. A calibration or pilot study may be advisable in case of doubt.

- Sufficient data (measurement points and/or participants) should be foreseen depending on the variability of the result (consultation of a statistician in the planning phase is recommended in this context).

- The correct application of the dermal protection equipment should be assured and monitored, in order to exclude data resulting from wrong handling of PPE. On the other hand, with adequate design and control of other parameters (exposure!) the influence of (non-)compliance with use instructions could be monitored as well.

- Detailed information about the evaluated PPE and the monitored tasks should be documented. This includes for example:

    - PPE material description (material type, thickness etc.)
    - PPE style (length, seams etc.)
    - PPE manufacturer and product name
    - Task description (what was done and were all tasks monitored)
    - Task duration, sampling duration
    - Other risk management measures in place
    - evaluated substance (main physico-chemical properties and applicability for evaluated PPE should be documented)
    - User behaviour (how often was the PPE changed, any special observations leading to contamination or variabiliity in efficiency)

- Evaluation of protection factors should preferably be done individually not based on group means.

5.4 Dosimetry: Summary and discussion

The dosimetry studies found in the course of the literature search were evaluated concerning information about exposure reduction efficiency datasets and methodological information about the evaluation of PPE efficiency.

Concerning the methodology it has been found that already the aspect of dermal sampling alone may lead to a large uncertainty depending on the skin permeation potential of the substance evaluated and its removal tendency (e.g. via evaporation). In addition, sampling techniques often tend to capture all exposure regardless of its ability to stick to human skin, leading to possible overestimations.
Overall a lot of datasets have been identified where actual and potential exposure has been sampled at the same individuals and the same time (e.g. hand wash and glove extraction). It is not known to which extent this or in general the use of different

sampling techniques or study designs may influence the efficiency result. Results of the database analysis and other sources of information so far were inconclusive or did not indicate large differences concerning the efficiency result (patch vs. whole body dosimetry).
Various possibilities exist to derive an efficiency value from raw data and depending on the exact calculation this may lead to different results. As it was not possible to use a homogenous calculation method for all database entries this represents an additional source of variability within the database (see section 5.1).
In addition two equations have been identified that can be used for the calculation and are applied depending on the sampling method and study design. Although there is a mostly systematic approach available concerning the use of these equations this also leads to uncertainty as it is not always known which equation has been used (section 5.1). Deviations caused by the choice of equation can significantly influence the final result.

The majority of database entries contains information about gloves (142 entries) and whole body garments/ coveralls (153 entries), followed by normal clothes (58 entries). Only few pieces of information were found concerning aprons, barrier creams and other pieces of PPE.

Concerning gloves an average efficiency of 88% was found. Overall efficiencies range from approximately 4 to almost 100%. The large variability can partly be explained by the lack of information at various points: There is a number of database entries where no information at all was available on the type of gloves used for the evaluation and even for the remaining entries often no material, length and/or thickness was available. Information on the use status was almost never available. As a result, differences between database entries may be present that cannot be detected due to a lack of information.
Nevertheless it was tried – after a separate discussion of gloves without further information available - to categorise glove types according to material, length and fit, prior use status, physical state and industry area, using some assumptions where necessary. It was however recognised that the database is heavily biased concerning plant protection products (87 of all glove entries with information on glove available) and nitrile as a material (73 of all glove entries with information on glove available). Within these subsets of data still a high variability was found that may probably be explained by other differences within the groups (e.g. different tasks, glove lengths). At the same time differences between categories (e.g. nitrile vs. PVC gloves) are usually hard to assign to a certain factor, since the included studies usually differ in more than one factor. Often only a small number of datasets is available for the categories formed, especially if it is tried to keep the variability within each category small by further separation into different types of gloves (protective (reusable) gloves / disposable gloves / textile gloves; see also section “Summary ” in section 5.2.6).
In addition to the comparison of groups within the database, further information on the effect of some factors (e.g. user behaviour, glove length, glove material) has been extracted from single studies.

As a consequence, it can be summarised that the difference between new and used gloves is found to be in the range from 38-76% exposure reduction for protective gloves. This conclusion is based on limited data including limited information on the glove in question (GARROD et al., 2001; GARROD et al., 1999; HSE, 1999; MANDIC-

RAJCEVIC et al., 2015). Thus, more information may be advisable for a final recommendation.

A change from between short to long gloves was found to lead to 80-89% exposure reduction, based on comparison of database entries and data published by VAN DER JAGT et al. (VAN DER JAGT et al., 2004). Only one database entry of limited quality for short gloves was available for comparison within the database and the number of entries for long gloves is small as well (eight), as often no information is available concerning the glove length.

Concerning the material mixed results were found. Although it was tried to categorise gloves into disposable gloves and non-disposable gloves (protective gloves) according to the available information (see also section 9.2) only limited information could be drawn from the comparison, as the database mainly includes nitrile gloves. Database entries and results of APREA and the BROWSE project suggest high efficiencies for nitrile, neoprene and rubber (APREA et al., 1994; SPAAN et al., 2014) (87-96% average according to database, 88-95% according to BROWSE).

Both database results and results of the BROWSE project suggest that thin gloves are able to reach high efficiencies as well. However, conditions under which this is possible are probably limited (e.g. only short term wearing (ROFF, 2015); specific substances). An advantage of thin gloves is often the increased dexterity and better fit compared to thicker glove types which may lead to less exposure and a higher efficiency.

Both influences (material / thickness) are in general hard to categorise as they heavily depend on the appropriateness of the glove in question for the substance evaluated and the task performed.

Textile gloves show a certain exposure reduction as well. However, they are not recommended as PPE as they will soak through and long-time effects are difficult to predict.

A dependency of the challenge is known suggesting higher efficiencies for higher exposure loads. However, this effect may also depend on the PPE material (textile vs. non-textile).

An additional important point is the dependence of the potential exposure value on other factors: How high or low the exposure load may be depends on a variety of task related parameters such as the duration, spray pressure, equipment used or task description in general. These parameters can at least partly also influence the efficiency directly (e.g. certain equipment may increase the probability of glove damage, certain activities may require frequent glove change / removal), which leads to a complex interaction.

Only little information concerning the influence of behaviour / training has been identified and is not considered sufficient for any kind of suggestions.

In addition to the tabular results, the number of database entries for several efficiency ranges has been summarised in Figure 5.2. The figures show a maximum above 99%. On the one hand this is encouraging as it suggests that high exposure reductions are possible and not unlikely. However, it is also surprising that no clear maximum can be identified. This may be a reflection of other influencing parameters that cannot be captured by the current approach (e.g. challenge dependency) and the lack of information about various parameters in the different studies (e.g. level of training, glove parameters).

Concerning clothes again a large range of possible efficiencies has been identified, leading to an average efficiency of ~71%. Partly this range also reflects the variety of clothing types reflected in the database and the presence of different baselines. A categorisation according to the industry area and physical state has been done. However, no meaningful conclusion can be drawn from this due to partly small numbers of datasets in the single categories and variability concerning other factors within these categories. Small differences concerning prior use were identified during a comparison of short sleeved and long-sleeved shirts (RECH et al., 1989).

For coveralls / whole body garments 144 database entries with a minimum of information about the type of garment were identified, resulting in an average of 90.3% exposure reduction (33.4-99.8%). The majority of garments evaluated are made of cotton (52) or polyester / cotton (30) materials followed by Tyvek (17). Differences between these materials are present but as in case of gloves the tendency of higher efficiencies for woven material seems surprising (94, 86, 85% efficiency). No additional studies on this topic have been identified.

Only very few database entries could be assigned to certain coverall types (CE marking) and again with inconclusive results: A gas tight suit showed lower efficiencies than one only with sealed seams. Efficiencies for the remaining whole body garments without CE marking were almost identical to this measurement. The corresponding datasets are not considered to be sufficient for a reliable differentiation.

The situation is similar for the influence of prior use. Only few datasets are available where it is clearly indicated that the coveralls had already been used before the study and differences between used and new coveralls are small (90 (used) vs. 93% (new and assumed new coveralls, datasets combined).

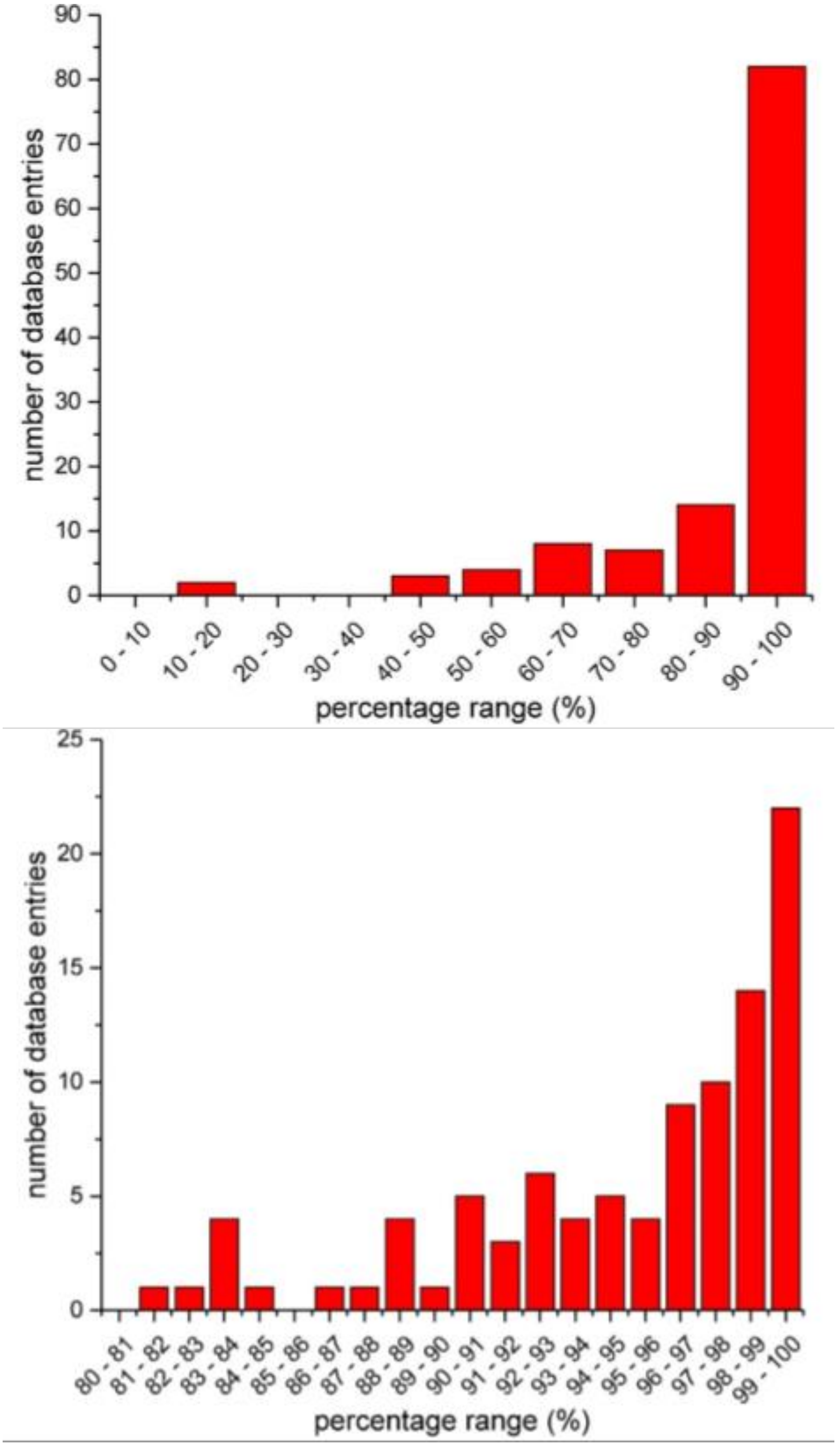


Figure 5.2 Number of database entries for different efficiency ranges for gloves with documented properties. The upper diagram shows the complete percentage range, the lower diagram contains a more detailed view on the percent range 80-100% of the same dataset.

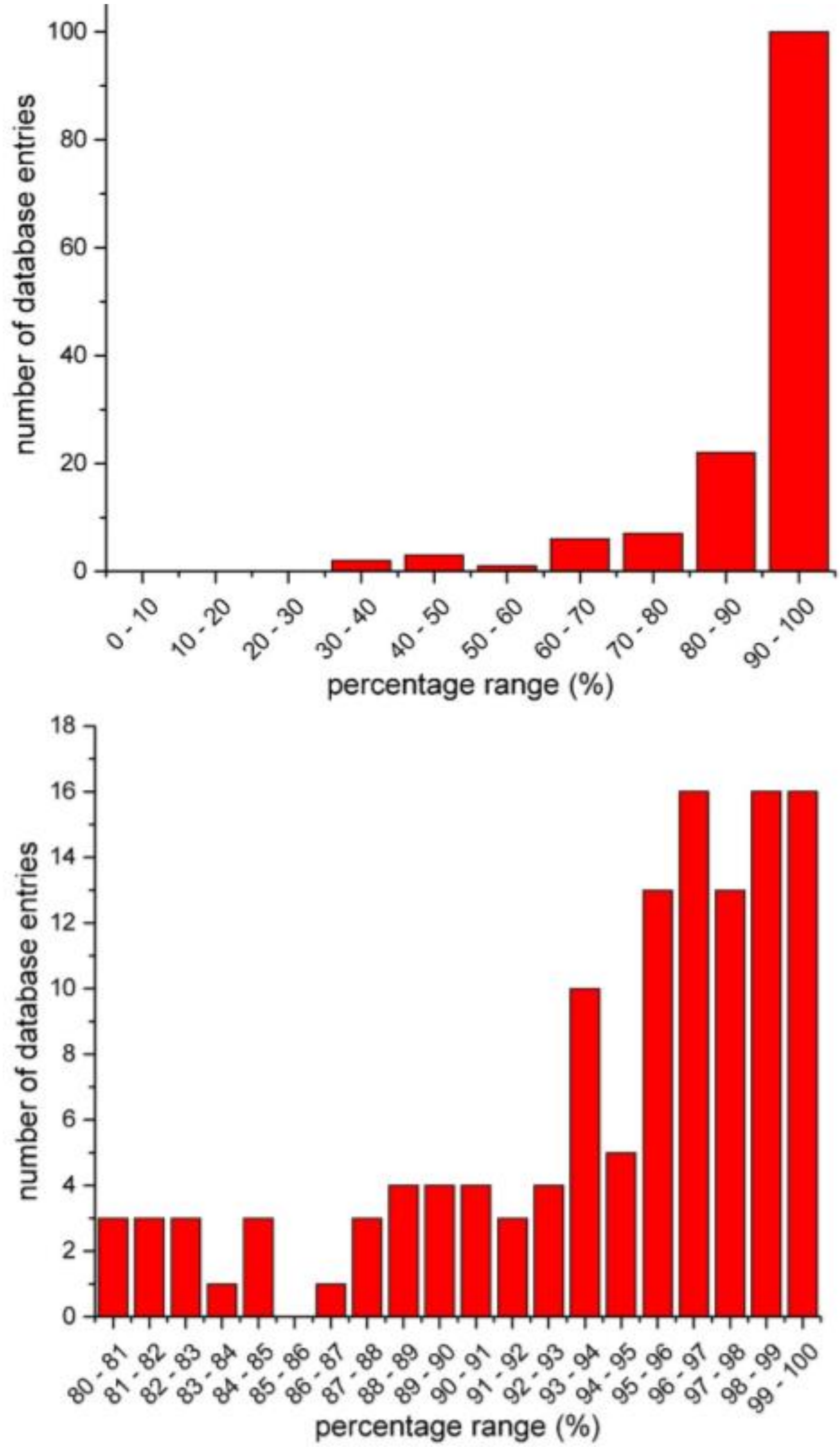


Figure 5.3 Number of database entries per efficiency range for coveralls / whole body garments with documented properties. The upper diagram shows the complete percentage range, the lower diagram contains a more detailed view on the percent range 80-100% of the same dataset.

Other studies evaluating this topic exist but the extracted information is only of limited value (APREA et al., 2009; METHNER and FENSKE, 1994), since the evaluated garments are possibly disposable and should not be reused anyway or other aspects influencing the efficiency seem to exist within the scenario. ESPANHOL-SOARES et al. report a reduction of the penetration of ~60% when comparing used with new textile coveralls.

In Figure 5.3 an overview of database entries per efficiency range has been summarised for whole body garments with documented information. As in case of the gloves, the maximum seems to be at very high efficiencies above 95%, suggesting other influencing parameters that may not have been taken into account yet. However, the trend is less defined than in case of the gloves.

Concerning the influence of exposure loading usually higher efficiencies with increasing loading are reported.

In addition to the comparison of studies within the database and related factors some general aspects were discussed. These are the influence of carrier substances, different exposure pathways and the distribution of penetration over the evaluated body area.

The distribution over the body area can be used to get information about possible exposure pathways and weak spots of the evaluated PPE. Depending on the task evaluated and other factors (e.g. how is the disrobing done? (GLASS et al., 2005)) it can be very variable due to different exposure distributions.

No information has been identified related to the influence of mixtures / carrier substances on efficiency. Information on material parameters such as breakthrough times or flow rates suggests variable effects depending on the substances evaluated. However, as the final efficiency is also influenced by other factors (e.g. contamination during glove removal) no conclusions concerning the efficiency should be drawn from these findings.

Concerning exposure pathways, the differentiation between permeation, penetration and direct deposition was discussed. Some assumptions can be made based as an example on the fact that textile fabrics by definition have holes that allow penetration of the substance. An interpretation of exposure patterns over the body is possible as well in order to identify major contamination pathways. However, most publications do not include corresponding information and as usual sampling methods in general capture all exposure pathways, a differentiation is not possible in most cases.

Currently, only eight dosimetry studies have been classified as “good” in the categories “sampling quality”, “workplace description” and “PPE description”. The corresponding database entries are summarised below. None of them includes details about the level of training that accompanies the PPE use other than a general statement if workers are “experienced” in some cases.
Data derived from the publication of GLASS et al. shows the lowest efficiency (37-76%). The publication describes a laboratory study aiming to represent spraying of a confined area such as the loft of a house (1.43 m (l) x 2.4 m (w) x 2.1 m (h)), which required the operators to spend a great deal of time stooped or crouched and a

significant proportion of the application time spent applying the tracer above head height. The comparably low efficiency may therefore be caused by the scenario itself (maybe a lot of contact with walls / floor and repeated stretching of fabric e.g. at knees) or the laboratory conditions which may have influenced the result somehow by differing from field conditions.

Efficiencies have been derived using equation (1) from section 5.1 (whole body dosimetry; extraction of coverall and sontara sampling coverall that was worn beneath).

MACHERA et al., SHAW et al. and TSAKIRAS et al. have evaluated the efficiency of coveralls as well.

MACHERA et al. referred to greenhouse application of pesticides via hand held spraying equipment using whole body sampling (equation (1)).

SHAW et al. describe the knapsack application of pesticides on cotton fields and TSAKIRAS et al. have evaluated knapsack spraying of olive trees (TSAKIRAKIS et al., 2011) and greenhouse sprayers (TSAKIRAKIS et al., 2010) (whole body dosimetry, equation (1)).

Glove data are included from ROFF, CESSNA and GROVER and MADDY et al. All publications evaluate plant protection scenarios, whereas ROFF describes hand weeding, pruning and cutting, while MADDY et al. evaluated strawberry harvesting. The efficiency values given for ROFF have been extracted directly from the publication (geometric mean protection factors) while data published by MADDY et al. have been evaluated using equation (2) (cross-sectional study). Efficiencies from CESSNA and GROVER have been derived from median exposure values with and without PPE using equation (2). According to this study contamination due to the PPE removal process has been excluded from the evaluation, as gloves were removed by other study team members in all cases where this was wished.

Table 5.37 Highest ranking dosimetry studies

	Average Exposure reduction (%)	**Number of database entries**
CESSNA and GROVER 2002 (gloves) (application, pesticides)	**96.0**	**1**
neoprene	96.0	1
MADDY et al. 1989 (gloves) (application, pesticides (plant protection))	**98.0**	**1**
rubber	98.0	1
ROFF 2015 (gloves) (re-entry, pesticides (plant protection))	**92.1**	**3**
fabric, rubber or plastic, nitrile, latex, polyvinyl chloride, neoprene, polyethylene, cotton	92.1	3
TSAKIRAKIS 2010 (overall) (application, pesticides)	**98.0**	**1**
50/50%, cotton/polyester treated with a water repellent finish	98.7	1
cotton	97.3	1

	Average Exposure reduction (%)	**Number of database entries**
GLASS et al. 2005 (coverall) (application, pesticides)	**52.7**	**4**
Kleenguard non woven	60.3	1
polyester / cotton	37.2	2
Tyvek	76.0	1
MACHERA et al. 2009 (coverall) (application, pesticides (plant protection))	**98.7**	**2**
cotton	97.7	1
polyester / cotton	99.6	1
SHAW 2008 (coverall) (application, pesticides (plant protection))	**88.9**	**2**
cotton	88.9	2
TSAKIRAS et al. 2011 (coverall) (application, pesticides (plant protection))	**98.5**	**4**
cotton	98.0	2
polyester / cotton (treated)	99.0	2

Overall it can be summarised that although a comparably large number of dosimetry datasets could be collected in the Excel database, the closer evaluation of possible influences and a detailed understanding of the resulting efficiency distribution is complicated by some factors:

1. The database is unbalanced concerning industry areas, PPE materials etc. leading to small numbers of datasets in many groups of PPE scenarios.

2. Within these groups there is often still a high variability concerning other, partly perhaps not even documented factors (e.g. task, glove thickness) that can only partly be compensated by further categorisation. Thus, it is difficult to identify the specific factors responsible for a difference between two efficiency studies.

3. Key information is often missing (e.g. glove thickness, length, use status), therefore assumptions are partly necessary for a categorisation into groups. This is also another factor leading to small numbers of datasets within certain groups of PPE.

4. It is often not known if the type of PPE evaluated is appropriate for substance and situation and if it has been applied correctly.

5. The level of training of the test individuals is usually not known. However, the range of publication years covered by the database suggests a high variability concerning work practices.

6. Very different sampling techniques and study designs have been applied and although it is assumed that there can be some influence on the efficiency result

there is so far no clear indication in which direction this influence may shift the results.

7. Due to the heterogeneity of the collected datasets a full statistical evaluation including percentiles and/or standard deviations was not possible.

As a result it has been possible to collect single pieces of information describing the influence of PPE age, challenge and other factors, but not to get a full understanding of influencing factors and the resulting efficiencies.
Only few studies scored as comparably high quality have been identified and even in these no information about the level of training is included.

Suggestions for these conditions that should be met for a high quality study have been summarised in 5.3.4 and include some recommendations concerning sampling and evaluation. However, the detailed and complete documentation of the study design and all related parameters including the use of PPE and the level of training the test subjects experienced before the measurement is of at least comparable relevance.
In order to derive a set of defaults to be used for regulatory purposes, the studies should ideally be designed in a comparable way. As an example, if the influence of glove materials is to be evaluated only this factor should be changed while all others should remain unchanged. In general, a small number of studies may be sufficient to gain a lot of information if the evaluated tasks and other scenario parameters are carefully selected and reasonable priorities are set concerning factors of interest to be evaluated. However, care has to be taken to document all necessary operational conditions, PPE descriptive parameters and aspects that may influence PPE efficiency.

With this, not only the derivation of a default, but a justified default would be possible, including all relevant aspects and factors influencing exposure. So far, the available studies are not sufficient for this purpose.

6 Biomonitoring studies

6.1 Limitations of the available biomonitoring studies

Despite the huge amount of biomonitoring studies found in the literature search for this project, the screening of the studies revealed only 42 potentially relevant studies that might be used as a basis for deriving a dermal protection factor based on biomonitoring data.
Mathematically such a dermal protection factor can be expressed in the following equation:

$$PF\ (\%) = \frac{post\ exposure\ value\ with\ gloves - pre\ exposure\ value\ with\ gloves}{post\ exposure\ value\ \ without\ gloves - pre\ exposure\ value\ without\ \ gloves}\ x\ 100 \qquad \textbf{(6.1)}$$

For very volatile substances, this equation may not be applicable since evaporation from the skin or the glove may be the determining factor (at least if the hands are not immersed in the substance).

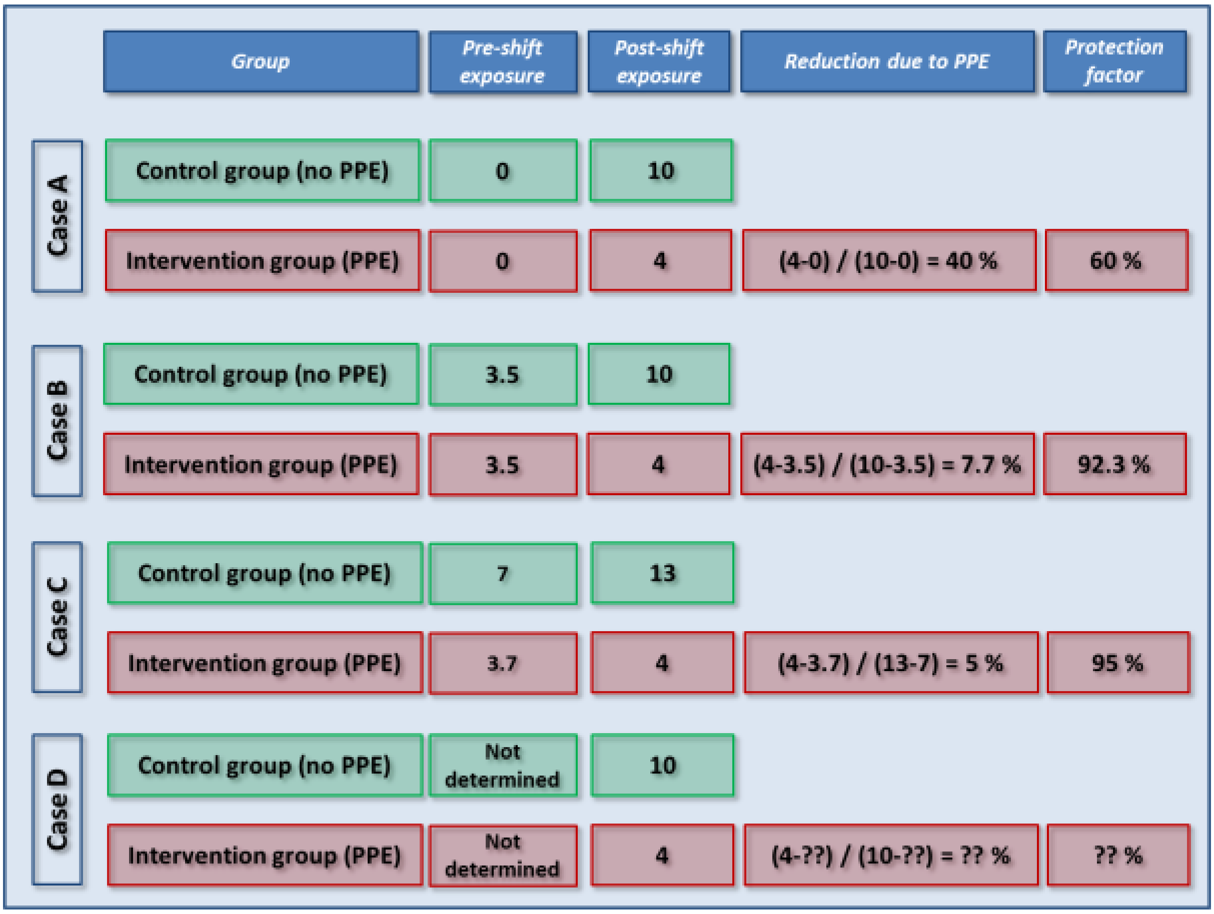
A more detailed look into these 42 studies revealed that only a small number could be used to derive a protection factor (PF). What are the reasons?

1) Many studies were not designed to test the effectiveness of dermal protection. Therefore, they do not assess the use of the substance with and without dermal protection. If a biomonitoring study is performed just to describe the current situation at the workplace, all workers usually wear the same PPE and no different groups (with/without PPE) are assessed (e.g. IOM, 1993).

2) Several studies monitor the current situation at a workplace (with dermal PPE) and try to show that an improvement (better/more PPE) would be beneficial. It is not possible to derive a protection factor in these cases, since the efficiency of the “old” PPE is not established, and the “new” PPE is just tested against the “old” and not against not using any PPE (e.g. van der Jagt et al. (2004)). How exactly a reasonable baseline (i.e. “no PPE”) may be defined depends on the scenario and the type of PPE evaluated.

3) A relevant criterion for deriving protection factors from biomonitoring studies is the availability of a pre-shift value. This value includes the background exposure (e.g. from food and smoking) to the substance investigated (or its metabolites). In case of an accumulating substance, the pre-shift value also reflects remains from exposures on the previous workday(s) (e.g. Weiss et al. (2011)).

Figure 6.1 illustrates the importance of the availability of pre-shift values. In case A, the pre-shift value is zero. The resulting protection factor is 60 % in this example. In case B, an identical pre-shift value is measured for the control and the intervention group. The resulting protection factor is considerably higher than in case A. If in case A the pre-shift value of zero was only assumed and not measured this would result in an underestimation of the protection factor. In case C pre-shift exposure is higher than in case B (e.g. due to previous exposure to the substance, which shows a long half-life) and differs for control and intervention group. The calculated protection factor is even higher than in case B. Case D shows what happens if no pre-shift value is derived: It is impossible to derive a protection factor in this study. Simply assuming that it was zero (case A), will potentially result in underestimates of the dermal protection factor offered by PPE.



	Group	Pre-shift exposure	Post-shift exposure	Reduction due to PPE	Protection factor
Case A	Control group (no PPE)	0	10		
	Intervention group (PPE)	0	4	(4-0) / (10-0) = 40 %	60 %
Case B	Control group (no PPE)	3.5	10		
	Intervention group (PPE)	3.5	4	(4-3.5) / (10-3.5) = 7.7 %	92.3 %
Case C	Control group (no PPE)	7	13		
	Intervention group (PPE)	3.7	4	(4-3.7) / (13-7) = 5 %	95 %
Case D	Control group (no PPE)	Not determined	10		
	Intervention group (PPE)	Not determined	4	(4-??) / (10-??) = ?? %	?? %

Figure 6.1 Illustration of the importance of pre-shift biomonitoring values

4) In almost every situation at the workplace dermal as well as inhalation exposure are relevant and contribute to the combined exposure of workers. In case of a biomonitoring study it is not known whether the measured metabolite exclusively reflects dermal exposure. In order to be able to derive dermal protection factors from biomonitoring studies, it is necessary to exclude or strictly control other exposure routes (oral or inhalation) (e.g. respiratory protection via mask). Some studies do not control for this (e.g. Bradman et al. (2009).

Current status

As a result of the problems mentioned above, the database currently contains only a limited number of 13 datasets from 6 biomonitoring studies.

6.2 Detailed study analyses

In this section the studies suitable for entry in the database are shortly described. Problems regarding the derivation of a protection factor are listed and explained.

6.2.1 Scheepers et al. (2009) *"The occupational exposure of dermatology nurses to polycyclic aromatic hydrocarbons – evaluating the effectiveness of better skin protection"*

Scheepers et al. studied the uptake of polycyclic aromatic hydrocarbons (PAH) in nurses who apply ointments containing coal tar (CTO) to patients in a dermatology clinic in the Netherlands. They also investigated the effectiveness of skin protection methods.

Study description parts (A) and (B):

A first study (A) aimed at determining the contribution of dermal and inhalation exposure to total PAH exposure. The levels of airborne pyrene and benzo[a]pyren (BaP), components of CTO, were below the limit of quantification. The authors conclude that exposure via this pathway during CTO application is very unlikely. During this study, all nurses wore loose-fitting polyethylene gloves during at least part of the CTO treatment.
In part (B) of the study three nurses were followed for three weeks and spot urine samples were collected for studying the relationship between work tasks and urinary excretion patterns of PAH-metabolites.

Study description part (C):

In the relevant study for this evaluation (C), 35 nurses were followed on two separate occasions involving CTO application. Nurses were asked to treat the same patient with and without loose-fitting polyethylene transparent gloves. Urine was sampled before treatment and for several hours after treatment. The urine samples were analyzed for 1-hydroxypyrene (1-OHP).

The authors calculated:

- The average reduction in the **total excretion** of 1-OHP (unit: µmol/24 h) (51.5%) (the difference in total excretion was not normalised to baseline)
- The change from baseline to the **maximum excretion** (unit: µmol/mol creatinine) within 10 h after CTO application (74% reduction wearing gloves compared to not wearing gloves) (this value is normalized to the baseline)

Limitations of part (C):

- As explained above for proper interpretation of biomonitoring studies it is of utmost importance to know and consider pre-exposure levels of biomarkers. In the current study (study C) baselines (pre-exposure levels) are given for the maximum concentrations of 1-OHP in urine, but not for total amounts excreted. Whereas the latter is actually the more relevant parameter, it cannot be corrected, as no baseline values are given. Maximum concentrations of metabolites generally vary between individuals and do not necessarily correlate with total amounts absorbed. Therefore, they comprise a high level of uncertainty.

- No information is available on amounts of CTO used for individual patients. It is indicated that each nurse noted the type of CTO (two types available with different composition) and weighted the container before and after each treatment to determine the applied amount. From the total amount of CTO and the type of CTO the total amount of pyrene and BaP were calculated. However, the exposure of the nurses is different but median values for the maximum excretion were used for the analysis.

- It is not reported, if nurses were instructed how to correctly use and pull off gloves. Exposure resulting from wrong handling of gloves or accidental contact with CTO on the forearm may contribute to total internal 1-OHP concentrations.

Study description part (D):

In the last part of the study (D) a new work practice was introduced for the nurses. Study (A) was repeated with the use of tight-fit vinyl gloves and Tyvek® narrow sleeves with elastic on the wrist. Three pads on the dominant hand were applied under the gloves and urine samples over 24 h were collected. The authors calculated a reduction of skin contamination of more than 97% (97.9 – 99.7% for pyrene, and of 97.0 – 97.5% for benzo[a]pyrene) compared to the situation before introducing the new work practice, based on the dosimetry data (measurement of pyrene and benzo[a]pyrene on skin pads). The total urinary excretion of 1-OHP was reduced by 56.9 % (paired analysis, same nurses in study part (A) and (D)) and 57.3 % (unpaired analysis, individuals from study parts (A) and (D) are different). Again, total urinary excretion was not compared to baseline values. Concentration of urinary 1-OHP concentrations were low in both groups (before and after introduction of the new practice), but introduction of the new practice resulted in approx. 40 – 50% lower concentrations. More details on the comparison of dosimetry results with biomonitoring results are described in section 6.4.2. These values are not included in the database for the following reasons:

Limitations of part (D):

- The effectiveness of the new PPE was tested against pre-existing work practices. For a calculation of PPE effectiveness this cannot be used as no “zero” value (no dermal protection at all) is available. This applies to the dosimetry as well as for the biomonitoring part of the study.

- Whereas with dosimetry a huge decrease in exposure was observed, the relative reduction of the OHP urinary concentration was smaller; but it should be noted that the OHP concentrations in the group before introducing the new technique was very low - close to the baseline level in study C.

- Three smokers were included in this study

Conclusions:

The study emphasises the need to normalise biomarker concentrations to pre-exposure levels (50% reduction by wearing gloves was obtained for not-normalised values for total amount excreted, but 74% for normalized maximum concentrations of bomarker OHP). Unfortunately, for the most relevant parameter “total amount of OHP excreted” no baseline values are given. The result of 74% reduction due to wearing gloves is therefore considered to be indicative, but of high quantitative uncertainty. Both types of biomonitoring values (total amount and highest concentration of OHP) show a high individual variability in the group without gloves (with ranges covering more than one order of magnitude).
Correlation between dosimetry and biomonitoring (study D) is poor, as dosimetry shows a near complete reduction in exposure due to the newly introduced technique, whereas biomonitoring results show a reduction in exposure, but starting from a very low exposure level (OHP urinary concentration in the group before introducing the new technique is close to the baseline level in study C).

6.2.2 Chang et al. (2007) *“Field protection effectiveness of chemical protective suits and gloves evaluated by biomonitoring”*

Study description:

In this intervention study, Chang et al. studied 15 male spray painters at a ship coating factory in Taiwan for two weeks. The painters used an airless spray gun to apply ethyl benzene- and xylene-containing paints.
In the first week, workers wore no protective clothing, in the second week they were provided with protection suits and gloves. During both weeks all workers wore respirators during spray painting.
The protective suits were airtight and made of two layers of polyethylene. The breakthrough time for toluene was < 5 min and the steady-state permeation rate was 3.3 mg/m²/s, with a thickness of 0.36 mm. The gloves (37 cm long with 0.65 cm thickness) were made of nitrile. The protection grade was A (excellent to good) for xylene and B (average) for toluene (no information provided for ethylbenzene) according to information retrieved by the authors.

Urine samples were collected before and after each work shift. Urine was screened for mandelic acid (MA, a metabolite of ethyl benzene) and methyl hippuric acid (MHA, a metabolite of xylenes).
Air samples were collected during both weeks. Analysis of air samples showed major differences in the concentration of ethyl benzene and xylene in both weeks. Concentrations were much higher for both substances in the second week compared to the first week.
The authors corrected for changes in urinary MA and MHA concentrations caused by inhalative exposure to different concentrations of ethyl benzene and xylene.
Mean decrease in biomarkers while wearing protective suits and gloves were calculated to be 69 % (MA) and 49 % (MHA). These values were calculated by the authors and are indicated as biomarker decreasing factors (BDFs).

Limitations of this study:

- In the discussion part of the study the authors mention that one subject refused to wear protective clothing through the entire spray painting task. Study conditions seem not to be completely controlled.

- Authors describe that painters changed the organic vapor filter whenever they experienced irritation during their work shift. This implies that workers despite wearing respirators were exposed to ethyl benzene and xylene via the inhalation route.
  The unknown amount of substance taken up by inhalation leads to an underestimation of the protection factor.

- Correction for changes in urinary MA and MHA concentrations were only calculated for post-shift values. For comparison between first and second week, pre-shift values were not considered. Reported pre-shift values indicate that pre-shift values differ for the two weeks:

Table 6.1 Comparison of 1st week and 2nd week pre-shift values

	1st week pre-shift value	2nd week pre-shift value
MA	70 mg/g creatinine	75 mg/g creatinine
MHA	82 mg/creatinine	141 mg/ g creatinine

- However, in the discussion part of their publication, the authors calculated BDFs for MA and MHA considering also the pre-shift value (post-shift minus pre-shift, corrected for the inhalative exposure). The resulting BDFs are slightly above the values which result when the pre-shift value is not considered: 72.4 % (MA) and 53.6 % (MHA). It is not clear, why the authors decided to report the values without consideration of the pre-shift value in the result part.

- Workers were exposed to different concentrations in weeks 1 and 2. The authors assume a linear correlation between air concentration of substance and the biomarker concentration in urine, which is difficult to verify experimentally (in general in biomonitoring studies). They also assume a linear correlation between air concentration and dermal exposure.

- The glove material may not be appropriate (see discussion in section 9.1).

Conclusions:

Inhalation exposure was not completely excluded. Further, at least one study subject did not comply with wearing dermal protective equipment in week 2 (the authors do not state whether this subject was excluded or not).
Further uncertainty was introduced by vastly differing exposure concentrations in week 1 and 2.
The study further shows that information on pre-shift values is important to calculate reliable protection factors.

6.2.3 Chang et al. (2004) *"Evaluation of the protective effectiveness of gloves from occupational exposure to 2-methoxyethanol using the biomarkers of 2-methoxyacetic acid levels in the urine and plasma"*

Study description:

Chang et al. evaluated the protective effectiveness of gloves from occupational exposure to 2-methoxyethanol (2-ME) and examined the association of 2-methoxyacetic acid (MAA) in urine and plasma collected simultaneously from low 2-ME exposure and high 2-ME exposure workers in a semiconductor copper laminate circuit board manufacturing plant in Taiwan. 74 workers were categorized in two exposure groups: regular operations and special operations with higher exposure. 80 non-exposed workers from the administration of the same plant were used as a control group.

Eight hour time weighted average personal breathing zone 2-ME monitoring was performed and biological samples (urine and plasma) were taken at the end of the last workday in the week.

Workers either used cotton gloves, rubber gloves or no gloves at all during work. The protective effectiveness of the gloves was determined by using the protective effectiveness index (PEI). PEI is defined by the ratios of the differences in the body burden indices between those not wearing gloves and those wearing gloves over the body burden indices for those not wearing gloves. Only for rubber gloves PEI values showed a protective effect:

Urinary PEI was 74.76 %, plasma PEI 68.9 %. Cotton gloves did not provide constant protection.

Limitations of this study:

- Airborne concentrations of 2-ME are measured, but not considered for calculation of PEI. This is a major deficit since authors declare that all workers refused to wear respirators due to the hot and humid environment at work. In the introduction part of the study, authors deliver a summary of data which support the assumption that skin uptake is more relevant than uptake via the inhalation route. However, this information is not sufficient to leave out the inhalation exposure in the assessment of biomonitoring data.

- One major deficit of the study is the absence of a pre-shift value. Authors do not even address this problem. Exposure levels in non-exposed subjects were below the detection limits of MMA in urine and plasma, therefore a relevant background concentration by non-occupational sources does not seem to exist. But relevant levels from the previous week cannot be ruled out, taking into consideration the half-life of MAA in humans of 77 hours (WHO, 2009)

- PEI for rubber gloves are based on very limited data (n=3 with rubber gloves and n=7 barehanded).

- Calculation of PEI cannot be reproduced since MAA concentration is presented only graphically.

We did not identify many studies which describe the derivation of a protection factor based on biomonitoring data. Chang et al. derived PEIs. However, neither exposure via inhalation nor a pre-shift value is considered for derivation.

Conclusions:

Despite these major limitations, the study was included in the database as this study is a good example to show the limitations of biomonitoring studies. Major limitations of this study are the absence of pre-shift values and the absence of a correction for inhalative exposure. Since workers refused to wear respiratory protection, the inhalative exposure route contributes to the body load with MAA and has to be considered.
Besides, the study results are based on very limited data (n=3 and n=7). For a significant evaluation more data should have been collected.
The calculated protective effectiveness indices (PEI) cannot be regarded as reliable.

6.2.4 Wang et al. (2006) *"Evaluation of the effectiveness of personal protective equipment against occupational exposure to N,N-dimethylformamide"*

Study description:

Wang et al. studied the protective effectiveness of various personal protective equipment against N,N-dimethylformamide (DMF) in a synthetic leather factory in Taiwan. Fifteen workers were selected and asked to do their work a) without personal protective equipment on the first day, b) barrier cream on the second, c) butyl rubber gloves on the third and d) rubber gloves plus respirator on the fourth day.
No pre-shift value of urinary N-methylformamide was collected before the shifts.

Protective effectiveness index (PEI) was used to evaluate different glove effectiveness. The authors calculated PEIs for barrier cream (40 %) and rubber gloves (49 %). Results were corrected for different airborne concentrations between exposure days.

Limitations of this study:

- As outlined already for the study of Chang et al. (2004), a major deficit of this type of study is the absence of pre-shift values. No pre-shift values were taken prior to the start of the study and before each intervention day (four days in a row). Authors do not even address this problem.

- The urinary metabolite concentration is quite high on day 1 (without PPE): In the high exposure group concentrations were more than two-times above the German BAT and in the intermediate group 71 % of the BAT value. With half-lives in the range of 5 hours for urinary NMF (WHO, 2001) and variable exposures the days before this might have led to substantial body burdens at the beginning of the next shift. In combination with 1) (no pre-shift values measured) this is major cause of defect of this study.

Conclusions:

Comparable to the study by Chang et al. (2004, see section 6.2.3) Wang et al. did not determine pre-shift values of their study participants. This is a critical limitation since due to the exposure situation high biomarker levels at the beginning of the next shift cannot be excluded. The calculated PEIs (40% for barrier cream and 49% for rubber gloves) cannot be regarded as reliable.

6.2.5 Lander and Hinke (1992) *"Indoor Application of Anti-Cholinesterase Agents and the Influence of personal protection on Uptake"*

Study description:

Lander and Hinke studied the relationship between plasma cholinesterase and the uptake of anti-cholinesterase agents (organophosphate insecticides) in greenhouse workers in Denmark. The study group included 117 men and 14 women. Blood samples were taken thrice: in August and September 1988 (time in the year in which greenhouse workers apply insecticides) and in January 1989 for the baseline value. A standardized interview was done in combination with the sampling in August. Workers indicated if and what kind of protection they wore during their activities with the insecticide.

Blood samples were analyzed for Cholinesterase (ChE) activity. Differences between baseline and August plasma-ChE activities were calculated. The workers were divided into two groups: Group 1 was exposed less than once a month during the last 3 months, group 2 was exposed more than once a month over the last three months before blood collection. Three kinds of protection were considered: wearing a face mask, wearing gloves or wearing whole-body clothes. Based on the data given in the publication, protection factors for the three different types of protection equipment could be calculated, this was not done by the authors themselves:

Table 6.2 Protection factors for gloves, face masks and whole-body clothes

	Protection factors – All exposed workers	Protection factors – Exposed less than once a month	Protection factors – Exposed more than once a month
Wearing face mask	91.9 %	92.6 %	85.4 %
Wearing gloves	53.8 %	83.3 %	7.69 %
Wearing whole-body clothes	100 %	40 %	100 %

Data based on exposure which occurred less than once per month over the study period is highly unreliable. In a worst case assumption it includes a person highly exposed on the day before the measurement and a person exposed 90 days ago. Therefore data obtained from workers exposed less than once over the last three months are not presented in the Excel table with the results. The protection factors calculated for all workers are also not included.

The statistical analysis done by the authors revealed that only the wearing of whole-body clothes had a significant influence on the plasma ChE.

The authors also performed an evaluation of a subgroup of 44 greenhouse sprayers which included 21 individuals wearing whole body protection, 6 individuals wearing aprons only around the body and 17 individuals without any protective clothing. Results are shown in a figure in the publication. It can be seen that wearing aprons provided better protection than wearing no equipment at all, but wearing whole body protection provides substantially better protection.

Due to some limitations of the study (see below) not all of these values were reported in the separate Excel table for the data evaluation.

Limitations of this study:

- The value for $ChE_{basline}$ – ChE_{August} is very low for workers wearing gloves. To measure a reliable difference from an already low value is difficult and not reliable (note: with protection a decrease is expected).
- Authors indicate that due to a highly significant correlation between wearing of whole-body clothes, gloves and face masks a detailed analysis of the protective influence of the equipment separately was not possible. The separate influence of the protection equipment cannot be described, since protection factors for individual protection equipment cannot be determined from the study design.
- Besides, information on wearing dermal protection is based on interviews. Workers had to give details on their PPE worn over the last three months. This is subjective.

Conclusion:

The study by Lander and Hinke has significant limitations. The baseline value is not a true pre-shift value since it was obtained afterwards. Besides, wearing of protection equipment was not monitored. Information was collected in interviews, which referred to the last three months. Combination of protective equipment at least by part of the workers has to be assumed. The separate influence of the protection equipment cannot be described, since protection factors for individual protection equipment cannot be determined from the study design. The reliability of the factors derived is therefore questionable.

6.2.6 Aprea et al. (1994) *“Biological monitoring of exposure to organophosphorus insecticides by assay of urinary alkylphosphates: influence of protective measures during manual operations with treated plants”*

Study description:

Aprea et al. studied a population of 12 workers exposed to chlopyrifos-methyl and azinphos-methyl during work (thinning immature peaches) in a previously sprayed peach orchard presumably in Italy. Urine samples were taken on the Monday before work (pre-shift) and over the whole monitoring period (one week). Samples were analyzed for various dialkylphosphates, but only results for dimethylalkylphosphates were reported. In parallel, the active ingredients were analyzed every day in hand wash solution (95% ethanol) collected over one working day.

Workers were divided into four groups based on the type of protection they were wearing:
Group 1: rubber gloves + felt face-mask (2 women)
Group 2: waterproof cotton gloves + felt face-mask (2 women)
Group 3: cotton gloves + felt face mask (2 women)
Group 4: Cotton gloves (5 women)

One worker (male) who did not wear any kind of protection apart from his normal clothes was also monitored. It is not described in detail what a “felt face-mask” is and what level of protection was provided by this respiratory protection device.

Based on the comparison of the mean urinary excretion of dimethylalkylphosphates between Groups 1 – 4 respectively and the one worker without any kind of protection, dermal protection factors for the gloves were derived. This was not done by the study authors and only calculated in the context of the present evaluation. For the calculation the pre-shift value calculated for the group was subtracted from the mean value calculated for the group. This was compared to the result obtained for the one person without dermal protection (minus pre-shift value of the whole group).
For group 1, a protection factor of 87.8%, for group 2 a PF of 85.3% and for group 3 a PF of 98.4% was calculated. For these three groups, inhalation exposure was controlled by wearing a felt face-mask. For limitations of these masks please see below. For group 4 a PF of 90.3 % was calculated, but in this group inhalation exposure was not controlled with masks. In addition to the mean values authors also provide the geometric mean (GM) and the median for each group. Using the GM for calculation of protection factors leads to a value of 92 % for group 2 and 99 % for group 3. This shows that calculated protection factors are highly dependent on the initial values.

Limitations of the study:

- The number of datasets is very limited. Only one worker was studied who did not wear any protection and who served to compare with protected workers. Groups 1 – 4 consisted of two or five workers. This small amount of datasets is reflected in the range of the measured values (e.g. group 3: 47.0 – 1432.0 nmol dimethylalkylphosphates /g creatinine).

- The pre-shift value is averaged for all 12 participants (range 27.6 – 1602.2 nmol/g creatinine). There is a possibility that the worker wearing no protection at all may have higher levels of dimethylalkylphosphates in the pre-shift urine sample. This would also influence the calculation of the protection factors. In general, pre-shift values for exposed individuals were higher by a factor 2 than for a control group (99 individuals not occupationally exposed to organophosphorus insecticides).

- The efficiency of the felt face-masks worn by groups 1 - 3 is not reported and cannot be estimated since the authors do not describe what a felt face-mask is. Therefore, it has to be assumed that protection from inhalative exposure is not 100%, and exposure may also have resulted from inhalation.

- Based on the study results inhalation seems to be a relevant exposure route. Absorption via inhalation is less than via dermal exposure. The authors are surprised by this observation because the application of the insecticides was 20 days (chlorpyrifos.methyl) and 7 days (azinphos-methyl) before workers entered the orchard.

- The low exposure of workers in group 3 is surprising since they wear the least efficient protection (cotton gloves). Authors conclude that compliance of workers in the other groups was bad, because rubber gloves and waterproof gloves are not so pleasant to wear and are frequently taken off for brief periods.

- All workers divided over the four groups were women. The one worker not wearing any protection at all was a man. No information on gender differences for the metabolism of chlopyrifos-methyl and azinphos-methyl in the body are reported in the paper. However, it is possible, that these differences exist. In combination with the limited number of subjects this is a major limitation of the study.

Conclusion:

The major limitation of the study by Aprea et al. is the small cohort. Only one individual represents working without any protection equipment and also the other exposure groups consist of only two or five workers. In addition, the efficiency of the felt face-mask is not clear and exposure via inhalation cannot be ruled out. Besides, the compliance of workers to wear dermal protection was not ideal.

6.3 Results

The resulting protection factors from the six biomonitoring studies described in detail in section 6.2 are listed in Table 6.3. Due to the limitations of the studies all of the listed protection factors have to be considered with reservation and an overall conclusion is not possible.

All of the evaluated studies considered the dermal protection by gloves made of different materials. In one case (Wang et al, 2006) barrier cream was also evaluated, Landers and Hinke studied the effect of whole body clothes.

No relevant studies were identified which could be used as a basis for deriving dermal protection factors for coveralls, shoes or aprons explicitly.

Table 6.3 Dermal protection factors derived from biomonitoring studies

Study author and year of publication	**gloves**	**Barrier cream**	**Whole body clothes**
Scheepers et al, 2009	**74 %**	-	-
Chang et al, 2007	**49% (53.6%)** (methyl hippuric acid)	-	-
	69% (72.4%) (mandelic acid)	-	-
Chang et al, 2004	**74.76%** (metabolites in urine)	-	-
	68.9 % (metabolites in plasma)	-	-
Wang et al, 2006	**49 %**	**40 %**	-
Landers and Hinke, 1992	**7.69 %**	-	**100 %**
Aprea et al 1992	**87.8 %** (rubber gloves)	-	-
	85.3 % (waterproofed cotton gloves)	-	-
	98.4 % (cotton gloves)	-	-
	90.3 % (cotton gloves, no control of inhalation exposure)	-	-

6.4 Discussion

6.4.1 Requirements for a good biomonitoring study which can be used to derive reliable protection factors for dermal PPE.

The number of biomonitoring studies which can be used to derive dermal protection factors is very limited. Few biomonitoring studies actually have been undertaken with the aim to derive protection factors for the dermal protection equipment worn.

Based on the extended literature search performed and the analysis of the studies with a limited design, criteria for a biomonitoring study suitable for deriving dermal protection factors are established. The following points should be considered:

- First of all, it is assumed that the study complies with the general requirements on a good epidemiological and a good biomonitoring study (no further details described in this context; for requirements on a biomonitoring study, see (ROSS et al., 2008)).

- Sufficient data (measurement points and/or participants) should be foreseen depending on the variability of the result (consultation of a statistician in the planning phase is recommended in this context).

- Depending on the substance monitored, a potential background exposure of the participants (e.g. smokers) should be avoided. Participants should be selected carefully.

  Detailed information about the evaluated PPE and the monitored tasks should be documented (see section 5.3.4).

- The correct application of the dermal protection equipment should be assured and monitored, in order to exclude data resulting from wrong handling of PPE. On the other hand, with adequate design and control of other parameters (exposure!) the influence of (non-)compliance with use instructions could be monitored as well.

- Reliable pre-shift values are mandatory. Pre-shift as well as post-exposure values have to be determined individually.
  The German “MAK Commission” suggests BW values in biological matrices such as blood and urine (“Beurteilungswerte in biologischen Materialien”) for a list of substances. For most of these substances, the following time points for sampling of biological material are suggested and should be considered (DFG, 2015):

  a) no limitations in sampling
  b) end of exposure or end of shift
  c) for long-term exposure: after several shifts

- Evaluation of protection factors should preferably be done individually not based on group means.

- Other exposure routes than dermal (inhalation/oral) should be excluded or strictly controlled. In case they cannot be avoided, exposure via these routes has to be measured and considered when calculating dermal exposure.

- If several pieces of dermal protection equipment are combined (e.g. gloves and a coverall), study design should allow for assigning the results to the specific PPE (e.g. by measurement of different data points: pre-shift, exposure with gloves only, exposure with coverall only, exposure with both PPEs, exposure without any PPE).

6.4.2 Comparison of biomonitoring results and dosimetry results concerning dermal protection factors obtained in the same study

Ross et al. (2008) compared absorbed dose estimates from passive dosimetry measurements with results from biological monitoring obtained in the same study. The intention was to validate passive dosimetry results. The authors examined fourteen studies (both proprietary and public) in this context and concluded that there is an excellent correlation between passive dosimetry and biomonitoring results. However, in the context of dermal protection factors the work of Ross et al. cannot be evaluated because the selected studies were not designed to derive protection factors.

As shown in chapters 6.1 and 6.2 and in the Excel file with the list of relevant studies, the number of biomonitoring studies which can be used to derive dermal protection factors is quite limited.
Only two of these studies (Scheepers et al., 2009 and Aprea et al., 1994) report both, results from biomonitoring and dosimetry experiments. As a consequence, only these two studies can be evaluated in the context of a comparison between PF derived from biomonitoring and dosimetry results.

A detailed description of the studies by Scheepers et al. (2009) and Aprea et al. (1994) can be found in sections 6.2.1 and 6.2.6.

Part (D) of the Scheepers study involves the calculation of dermal protection factors from dosimetry as well as from biomonitoring result. However, please note that in this study part exposure before and after introduction of an improved skin protection protocol was compared (and, therefore, no protection factors for using/not using PPE can be derived). Scheepers et al. compare results from handling CTO formulations with loose fitting gloves (part A of the study) against an improved work practice with Tyvek® narrow sleeves with elastic on the wrist. With this procedure, they obtain a reduction of at least 97% with the “new” method compared to the “old” method, based on dosimetry measurements (PAH concentrations on skin pads).
In the biomonitoring part of study (D), evaluation showed a reduction of 56.9 % in a paired analysis (same nurses in study part (A) and (D)) and 57.3 % (unpaired analysis, individuals from study parts (A) and (D) are different). The total urinary excretion was not compared to baseline values and the concentration of urinary 1-OHP was low in both groups (before and after introduction of the new practice).

Results from the dosimetry and biomonitoring approach show substantial discrepancies. But a comparison of the results from these two studies is difficult due to the limitations of the study design and the analysis.

- Authors could not exclude that the applied collection and storage methods of urine led to a loss of 2-OH-BaP glucuronide.
- Three smokers were included in the study.
- BaP is a substance with a high background exposure from food and air, depending on eating habits and lifestyle.

In the study of Aprea et al. (1994) urine samples were analysed for dialkylphosphates. In the same study the active ingredients were analyzed every day in hand wash solutions (95% ethanol) collected over one working day. Based on the study design, it was possible to derive dermal protection factors from the dosimetry as well as the biomonitoring part of the study. The results do not show any consistency:
For group 1 (details in section 6.2.6), PF derived from dosimetry was 99.6%, result from biomonitoring part was 87.8%.
For group 2, the biomonitoring part of the study yielded higher protection factors than the dosimetry part: 71.3% (dosimetry) vs. 85.3 % (biomonitoring). In the groups protected with cotton gloves (group 3 and 4), biomonitoring resulted in higher protection factors again (77.8% from dosimetry vs. 98.4% and 90.3 % from biomonitoring results).
Based on the limitations of this study (mainly: only one individual without any protection and two or five with protection), no distinct conclusion on the correlation between results from dosimetry and biomonitoring can be stated.

6.4.3 PBTK (physiologically-based toxicokinetic) modelling in relation to PPE efficiency

Within an exposure and risk assessment of substances, it is common to use models to predict the external exposure from various sources and by different routes, probably reduced by PPE. After that, the uptake has to be taken into account for deducing internal concentrations. In combination with toxicokinetic models it should be possible to predict chemical concentrations in easily accessible human matrices such as urine or blood that are routinely sampled in human biomonitoring studies. However, for a good toxicokinetic model a number of substance specific parameters (e.g. information about metabolism, blood/fat partition coefficient) has to be known.

In recent years, several projects have been carried out to investigate the relationship between external exposure and concentrations in urine and blood samples from human biomonitoring. For example the CEFIC LRI project Integrated External and Internal Exposure Modelling Platform (INTEGRA) tried to bridge the gap between external and internal concentrations by developing a unified computational platform (CENTRE FOR RESEARCH AND TECHNOLOGY et al., 2016).

In the literature, only data for a limited number of chemicals is available for external and internal exposure values and the toxicokinetic parameters needed for the prediction of e.g. blood concentrations on the basis of external exposure. Validated toxicokinetic models are only available for some well-known chemicals (e.g. benzene, N-methyl-pyrrolidone (JONGENEELEN and TEN BERGE, 2011)).

In conclusion, to derive efficiencies for PPE from biomonitoring data, the toxicokinetic has to be understood. If aspects such as bioaccumulation are not fully understood for a certain substance, misinterpretation of available data may happen.
At the best, an accepted and validated PBTK modelling the substance of interest should be available. However, these models are limited to some well understood chemicals and as a consequence, efficiencies derived from biomonitoring may include some uncertainty resulting from this lack of knowledge.

7 In vitro Studies

Studies evaluated in this chapter are dealing with penetration of chemicals through dermal PPE, such as protective clothing materials, glove materials and skin protection creams. However, most of the *in vitro* studies do not allow deducing a protection factor or values for the effectiveness of the PPE (e.g. CHAO et al., 2008; DOLEZ et al., 2011; GOLANSKI et al., 2009; HENRIKS-ECKERMAN and MAKELA, 2015; HENRIKS-ECKERMAN et al., 2015). Another major disadvantage is that such studies do not reflect real work scenarios. Yet some experiments include certain characteristics to mimic more realistic exposure conditions, e.g. weight put on exposed glove samples to mimic pressure of grip (HENRIKS-ECKERMAN and MAKELA, 2015; HENRIKS-ECKERMAN et al., 2015), higher air flow velocity to mimic movement with protective clothing (GOLANSKI et al., 2009). Despite the limitations, these studies are suitable for comparative assessment of different protective materials as well as different chemicals. In addition, they provide valuable insight into some basic parameters influencing penetration in general. Only studies providing information on protection factors are described in more detail below. Note that protection factor in this context must be understood as barrier efficiency of the PPE, since other factors cannot be addressed by this kind of study. They are divided according to protective equipment used.

Parameters typically identified in such studies are visualised in the scheme below. In the scheme the possible outcome of an experiment using two different PPE materials under the same exposure conditions (e.g. chemical, concentration, and temperature) is depicted.

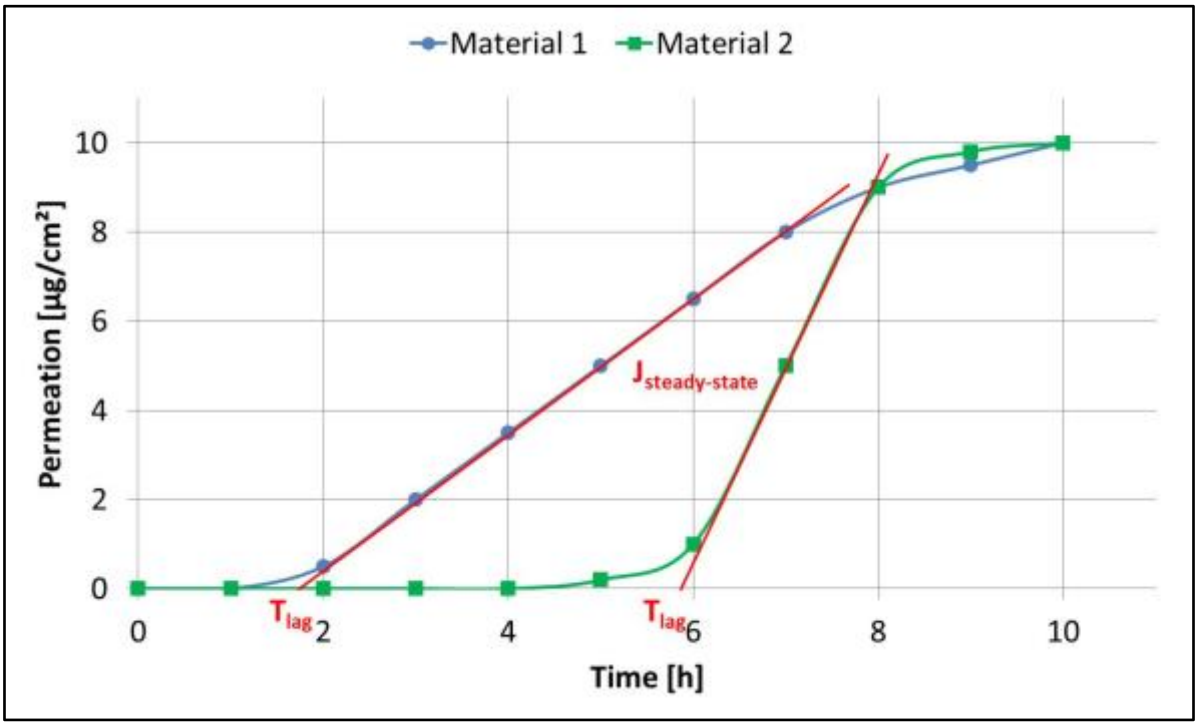


Figure 7.1 Schematic representation of steady-state flux (Jsteady-state) and lag time (Tlag)

The steady-state flux ($J_{steady\text{-}state}$; [µg/cm²/h]) represents the slope of the cumulative amount absorbed per unit skin area versus the time. Lag time (T_{lag}; [h]) is represented by the interception point between the flux curve and the x-axis representing the time. The permeability coefficient (K_P; [cm/h]) can be calculated by Fick's first law: ratio of steady-state flux (J) to the concentration of the initial topical dose applied [µg/cm³], but is not depicted above.

7.1 Clothing materials

Berthet et al. (2014) performed *in vitro* permeation assays using flow-through diffusion cells. Tests were performed with either freshly prepared full-thickness human skin, protective clothing suit materials[7] or combination of both with clothing overlaying human skin probes. In experiments with skin only, permeation of two active ingredients (bentazon and isproturon) at two different concentrations as well as two biocidal formulations of each active ingredient (bentazon: Basagran®, Basamais®; isproturon: Arelon®, Matara®) were tested. For experiments with suits or combination of suits and skin only the biocidal formulations were used. Tests were performed at 32 °C. In each experiment infinite doses were applied and steady-state flux (J; [ng/cm²/h]), the permeability coefficient (K_P; [cm/h]) and the lag time (T_{Lag}; [h]) were determined. The authors provided steady-state flux rates for skin alone or in combination of protective materials with skin for both biocidal formulations, having these data the authors of this report calculated protection factors for different protective materials (Protection factor (%) = 100 % - (100% / $Flux_{Formulation\ on\ skin}$) * $Flux_{+protective\ material}$). Protection factors ranged from 0 – 59 % protection for Microgard® 2000 Plus Green sample and from 0 - 63% for the AgriSafe Pro sample, with both materials being exposed for 8 to 15 hours. High protection was provided by the two other types of suits (Microchem® 3000: ~96 – 100 %; Proshield®: 75 – 100 %) with exposure times in between 5 and 8 hours.

Moore et al. (2014) investigated the protection provided by everyday clothing (cotton shirt) against low level exposure, as expected for the general population, to the organophosphates chlorpyrifos[8] and dichlorvos.[9] For this study, PTFE flow-through diffusion cells were mounted with dermatomed human breast skin, which was kept at a temperature of 32 °C. The test materials were applied as finite doses (10 µl/cm²) to either 'unclothed' or 'clothed' skin. Clothing means that a cotton shirt piece (1 cm²) was put above the skin and held at a small gap between skin and cotton (approximately 1 mm). In every scenario an additional decontamination step (i.e. washing of skin with respective washing solution) was included, either directly after exposure (i.e. 4 h for chlorpyrifos or 30 minutes for dichlorvos) or 24 hours later. Thus a total of three scenarios were tested: a) unclothed skin sample, decontaminated directly after substance exposure (i.e. either 4h or 30 minutes), b) clothed skin sample, after end of respective exposure period removal of clothing followed by an immediate skin surface decontamination, and c) clothed skin sample, after end of respective exposure period removal of clothing followed by skin surface decontamination at 24 hours. The authors provided figures showing cumulative absorption over 24 hours, recovery of the dose

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[7] Protective clothing suit materials: two 3–4, 5 types including a specific suit for pesticide application (Microchem® 3000 from Microgard® and AgriSafe Pro from HF Sicherheitskleidung) and two 4, 5, 6 types including also a suit specific to agricultural use (Proshield® from DuPont™ and Microgard® 2000 Plus Green from Microgard®)

[8] 0,5 µg/cm²; lipophilic solid; applied in two different solvents

[9] 5 µg/cm²; moderately lipophilic liquid; applied in three different solvents

applied in various compartments ([% of dose applied]), and tables giving the mass balances of the compounds applied to skin per vehicle for each scenario. As expected by the study authors, they found that clothing significantly reduced absorption through skin regardless of the application vehicle. Having the mass balances for the three scenarios described above, the differences in fractions recovered (unabsorbed on skin + penetrated) were used to calculate a protection factor for clothed skin with immediate washing only. Protections factors obtained for chlorpyrifos were in the range of 92 – 97 % (exposure time 4 hours) and 76 - 84 % for dichlorvos (exposure time 30 minutes). Immediate skin surface decontamination after removal of clothing from skin had an additional protective effect compared to decontamination at 24 h (post exposure). As expected, decontamination of skin in all three scenarios resulted in lower total absorption compared to 24 h continuous exposures (measured elsewhere, but mentioned in this study).

You et al. (2005) designed an *in vivo* animal model to examine suitability of protective clothing before actual application on humans, which would be most beneficial when testing hazardous chemicals. The authors designed protective vests fitting rats made from commercially available protective clothing materials. Rats were either left ‘unclothed’ or dressed in a vest made a) from regular clothing (cotton underlayer, polyester overlayer) or b) Tyvek® 1422A protective clothing (spanbond nonfabric of polyolefin class). Immobilised rats were exposed to fenitrothion for 4 hours (500 mg/kg spread over an area of 4 x 4 cm on the back). Four hours after exposure, penetration of the pesticide was measured as pesticide plasma concentration ([µg/mL]) and specific physiological response to this organophosphate insecticide (acetylcholinesterase (AchE) activity; [U/L]). Fenitrothion was found at approximately the same concentrations in the blood of ‘unclothed’ or ‘regular clothed’ rats, indicating no protection at all from regular clothing in this case. No pesticide was detectable in the rats, which were dressed with the Tyvek® vest (100 % protection after 4 hours of exposure). Confirming these results, AchE activity in rats wearing Tyvek® 1422A protective clothing was similar to the activity in untreated rats, while ‘unclothed’ rats and those rats wearing regular clothing showed significantly decreased AchE activity.

7.2 Glove materials

In a publication by Nielsen and co-workers (2012) static diffusion cells were used to investigate protective effects of two different glove types (nitrile, latex) against benzoic acid applied at two different concentrations (4 mg/mL and 40 mg/mL). Full thickness human breast skin was kept at approximately 32 °C. The experimental set-up contained a) skin only or b) glove material only or c) glove materials mounted on skin samples as membrane within the diffusion cell. For each experimental set-up the authors provided substance recovery data from different compartments ([µg], 48 hour exposure), lag-time information ([h]) and calculated maximal flux (J; [µg/h/cm²], based on initial 6 to 8 hours exposure). A substantial amount of the test chemical was recovered from the glove material, thus indicating a reservoir effect of the material (expressed as [% of the applied dose]; low concentration: nitrile 64 %, latex 27 %; high concentration: nitrile 29 %, latex 8 %). Moreover, these examples illustrate that increase of applied substance concentration also had an effect on relative distribution to different compartments, which varied between glove materials.[10] Regardless, the amount of chemical residing between glove material and skin is low and not dependent on glove material or concentration applied. This result was expected based on the observations made from the experiments with gloves or skin only, as the glove material was identified to be rate limiting for overall permeation (max. flux [µg/h/cm²] skin only: 13.1, nitrile only: 1.5, latex only: 11.2). Overall, the results obtained showed that for benzoic acid, nitrile gloves yielded a higher protection factor than latex gloves did (low concentration exposure, nitrile 96 % versus latex 50 %; calculation based on data for maximal flux during the initial 6 to 8 hours of exposure, according to the equation provided in paragraph Berthet et al., 2014). However, protection efficiency was reduced at higher chemical concentration (nitrile 71 % versus latex 38 %; calculation same as above).

Two studies dealt with permeation of cytotoxic agents through gloves (BOCCELLINO et al., 2010; PIERI et al., 2013). In the study of Pieri and colleagues four different, commercially available types of gloves (two natural rubber type gloves from different producers and two nitrile gloves with a thickness of 0.1 and 0.3 mm) were exposed to 1 mL of epirubicin in neutral or acidic solution (2 mg/mL) for 0 (control), 0.5, 1 or 8 hours. For each experimental set-up, one pair of gloves was used. Permeation was determined based on the external swipe of one glove compared to the internal swipe of the other glove under the same conditions. The authors reported that all types of gloves were able to prevent permeation of epirubicin for up to 8 hours under physiological (neutral) conditions. Under acidic exposure conditions differences in protection were detected: rubber gloves and 0.3 mm nitrile gloves were able to prevent epirubucin permeation, but 0.1 mm thick nitrile gloves showed non-negligible permeation immediately during substance application which increased up to 1.4 % within 8 hours.

In the study described by Boccellino et al. (2010), the experimental set-up was the same as in the study described by Pieri et al. (2013). Instead of epirubicin, doxorubicin was tested and only three types of gloves were used (the same two types of rubber gloves and one nitrile glove (thickness not mentioned)). All glove types were sufficient to prevent permeation up to 8 hour exposure to neutral doxorubicin solutions. As already seen for epirubicin, only rubber gloves were able to prevent permeation during the 8 hour exposure under acidic conditions, whereas for the nitrile gloves permeability increased over time (with 0.56 % after 8 hour exposure). While in both studies results show a protection of at least > 98 %, this is considered insufficient in the case of the specific substance (cytotoxic substances). In conclusion, these experiments showed that the pH of solutions can influence permeation through gloves.

The following study is described in detail, despite the fact that no protection factor is given. However, the study by Chao and colleagues (2011) not only investigated permeation of N,N-dimethylformamide (DMF) and methyl ethyl ketone (MEK) through neoprene gloves, but also desorption of chemicals from contaminated gloves and the usefulness of two decontamination procedures. For permeation assays the authors used ASTM F739 test cells. Permeation assays were carried out until a constant permeation rate occurred (steady state, J_S; [µg/cm²/min]). For desorption assessment, glove materials were taken from the first permeation cell when steady state permeation rate was reached, external surface was decontaminated and the sample material was

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[10] For latex gloves 10-fold concentration increase e.g. led to a 12-fold increase in skin deposition, but only to an approximate 3-fold increase in glove deposition at 48 h; 16-fold increase of maximal flux
For nitrile gloves 10-fold concentration increase e.g. led to a 20-fold increase in skin deposition, but only to an approximate 4-fold increase in glove deposition at 48 h; 95-fold increase of maximal flux

mounted into a second permeability cell (no further chemical challenge). DMF/MEK measured in the collection media of the second cell thus resembled desorbed chemical from the glove sample. The suitability of two decontamination methods was investigated with glove samples being contaminated, decontaminated and then re-exposed. These tasks were repeated on 5 consecutive days to simulate use of protective gloves within one working week. Breakthrough time and steady state permeation rates were determined after each cycle. Decontamination procedures compared were either a) rinse for 1 minute with water and then air-dry at 25 °C overnight or b) various thermal decontamination protocols (heating for 2 or 10 h up to 40, 70 or 100 °C with aeration overnight before re-exposure). The results state that for both chemicals permeation rates through skin (available from literature) were lower than through neoprene gloves (DMF: ~2-fold; MEK: 30-fold), thus permeation into skin is rate limiting. The authors concluded that for an assessment of health risk associated with use of protective gloves both variables should be available. Desorption from contaminated gloves was shown to occur, showing the importance of decontamination before re-use. However, simple rinsing with water and aeration overnight significantly decreased the breakthrough time after the third re-exposure due to reservoir effects. Thermal decontamination procedures were only effective, if heated up 70 or 100 °C. Nevertheless one has to bear in mind that thermal decontamination might also change the microstructure of the gloves (observed in this study).

7.3 Skin protection creams/products (‘Barrier creams’)

Skin protection creams can be classified as ‘non-specific’ (i.e. passive, physical diffusion barrier) or ‘chemically neutralising’ (i.e. reactive, active) and are used to protect skin from various chemicals, e.g. cutting oils, solvents and epoxy resins (CHILCOTT et al., 2002; KRESKEN and KLOTZ, 2003). Moreover, some of these creams have a regenerating effect, thus reinforcing the natural barrier function (ZUR MUHLEN et al., 2007). They are only to be used for non-toxic, non-carcinogenic and non-sensitising low grade irritants and cannot replace other PPE such as gloves. Skin protection creams have to be applied before and during work, skin regeneration/conditioning is performed after work (KRESKEN and KLOTZ, 2003).

The aim of the *in vitro* study by Chilcott et al. (2002) using diffusion cells was to evaluate the influence of a large number of passive and active barrier cream formulations with regard to absorption of the chemical warfare agent sulphur mustard through human skin. A total of 17 barrier cream formulations were prepared. Additionally, 7 pure substances (5 reactive powders and 2 reactive liquids) were applied to the skin. A static diffusion cell system was used and epidermal membranes, prepared from human breast skin, were kept at a dermal membrane surface temperature of 30 ± 2 °C. In general, 200 µl of barrier cream were applied to epidermal membranes, which lead to a nominal thickness of 0.78 mm (according to the authors: minimum practical thickness that could be achieved in diffusion cell, most likely in excess to thickness achieved *in vivo*). After pre-treatment for 2 hours, radioactively labelled sulphur mustard was added either under occlusive or non-occlusive exposure conditions. The authors determined the maximum penetration rates (flux; J_{max}; [µg/cm²/h]), T_{Lag} (results not provided in the publication), and further calculated a retardant index ($RI = J_{max\ control}/J_{max\ pre\text{-}treated}$) and the percentage of control dose penetrated ($\%CD = (Amount_{pre\text{-}treated}/Amount_{control}) * 100$). For occlusive conditions, the authors reported J_{max} values for 20 experiments using some kind of barrier as well as respective controls (exposure times ranged from 9 to 33 hours). For non-occlusive conditions, 14 J_{max} values were given in addition to respective controls (exposure times tanged in between 9 to 42 hours). From these data the authors of this report calculated the protection factors for barrier creams or reactive compounds in these experiments (according to equation provided in section 8.1). Under occlusive conditions the protection factors calculated ranged from 7.5 to 79.4 % (exposure times up to 27 hours in the experimental set-ups providing the highest and the lowest protection). In four cases, the J_{max} value for pre-treated samples was slightly above the control value and in one case the J_{max} value was 2.5-fold higher than control (meaning that higher penetration occurred when skin was pre-treated). Under non-occlusive conditions, only 4 barrier formulations provided protection (protection factors calculated ranged from 58.8 to 94.6 %, exposure times up to 21 hours in the experimental set-ups providing the highest and the lowest protection). In all other instances J_{max} values were above control values.

7.4 Overall conclusions

Protection factors – in the sense of barrier efficiencies – obtained from *in vitro* studies differed vastly (0-100 %) - depending on the material tested, the chemical investigated and the experimental set-up.

However the studies of Pieri et al. (2013) and Boccellino et al. (2010) demonstrate that protection factors alone might not be a sufficient read-out for worker safety. In order to draw meaningful conclusions, data from *in vitro* experiments must be interpreted under consideration of several parameters, e.g. J, K_P, T_{Lag} (BERTHET et al., 2014).

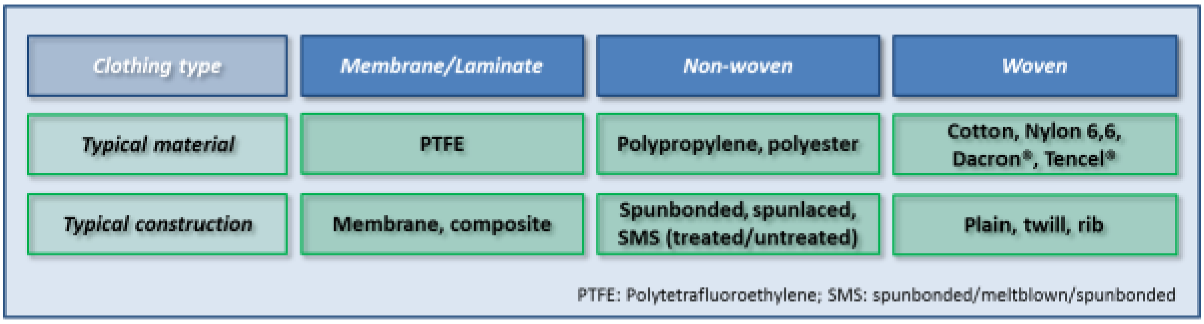
The studies described here investigated parameters influencing penetration of one or two chemicals through one or two PPE materials with a specific experimental set-up. These set-ups varied most often notably. Overall, no general conclusions (e.g. like “pH or concentration is always crucial” or “one experimental setup yields always higher protection factors than another experimental set-up”) can be drawn from these studies as there are too little intersecting data. The predictions of penetration are always only valid for a specific chemical or mixture in combination with a specific sample material. For example, penetration into skin was rate limiting for DMF/MEK in combination with neoprene gloves (CHAO et al., 2011), while glove materials were identified to be rate limiting in the case of benzoic acid penetration through nitrile and latex gloves (NIELSEN and SORENSEN, 2012). Also comparing experimental results for cotton clothing from the experiments of Moore et al. (2014; protection factor >75 % after 30 minutes exposure to dichlorvos and >90 % after 4 hours exposure to chlorpyrifos) and You et al. (2005; no protection after 4 hours exposure to fenitrothion) revealed that protection by this material is highly specific to the chemical applied and may vary significantly.

8 Mathematical models predicting penetration

Mathematical models aim at predicting penetration of a chemical through gloves or protective clothing on the basis of properties of the substance or the material through which penetration is assessed. This section describes some of the basics of mathematical models dealing with the penetration of protective clothing.

8.1 Protective clothing

Protective clothing can broadly be separated into three different types as shown in Figure 8.1 (based on LEE and OBENDORF, 2007). These range from typical work clothes made of woven cotton (or synthetic fibres) to membrane material made of polytetrafluorethylene (PTFE), either alone or as composite material on a non-woven material. In between these two materials are non-woven fabrics, often made of polypropylene, polyester, polyethylene or a mixture of polyester and wood pulp. These fabrics can be corona treated or finished with fluorocarbon compounds. For woven and non-woven materials, a variety of construction techniques are applied for specific needs.



Clothing type	*Membrane/Laminate*	*Non-woven*	*Woven*
Typical material	PTFE	Polypropylene, polyester	Cotton, Nylon 6,6, Dacron®, Tencel®
Typical construction	Membrane, composite	Spunbonded, spunlaced, SMS (treated/untreated)	Plain, twill, rib

PTFE: Polytetrafluoroethylene; SMS: spunbonded/meltblown/spunbonded

Figure 8.1 Overview of principal types of protective clothing

When mathematical models are developed, the protection offered by the equipment is generally related to one or several properties. The relevant properties can be broadly divided into (a) physico-chemical properties of the chemical or chemical mixture applied and (b) properties of the fabric material.

In this section, we discuss the findings of a research group at the Department of Fiber Science and Apparel Design at Cornell University (Ithaca, New York, USA) for the following reasons:

- This group has investigated penetration through all three types of protective clothing, covering common materials, such as e.g. several of DuPont's Tyvek® coveralls.

- The authors have used a large number of samples: 18 woven fabrics, 14 non-woven fabrics and 4 membrane/laminate materials.

- They have used the ASTM F-2130-01[11] standard for the testing of all materials, allowing meaningful comparisons between different types of clothing.

- The authors have used different pesticide formulations. This allows analysing the impact of some physico-chemical properties, although these evaluations are limited to pesticides and their formulations.

The tests performed and subsequent statistical analyses by these authors provide some insight into important factors that influence penetration of a substance through protective clothing:

- Low (<10%) to none penetration occurred through membrane/laminated fabrics. Detectable penetration was generally associated with pesticide mixtures of low surface tension and high viscosity, illustrating the importance of the properties of the liquid (LEE and OBENDORF, 2007).

- A fluorochemical finish on non-woven fabrics led to a penetration of 0 to ≤ 1%. This high protection efficiency is attributed to the decrease in surface energy provided by the finish, resulting in a high negative surface tension difference against the pesticide mixture (LEE and OBENDORF, 2001).

- For untreated non-woven fabrics, penetration ranged between 0 and 100% and is impacted by several factors, in particular (in decreasing order based on regression analyses):

    - surface tension difference
    - solid volume fraction of the fabric (negatively correlated)
    - fabric thickness (negatively correlated)
    - viscosity of the pesticide mixture

  The final statistical model developed by the authors is a polynomial model incorporating only the first three parameters, since the impact of the viscosity of the pesticide mixture on penetration turned out to be insignificant at the 5% level (LEE and OBENDORF, 2001).

- For woven fabrics, penetration ranged between 0 and 80%. Again, penetration is the result of several factors, with the most important ones being (in decreasing order based on regression analyses):

    - fabric cover factor (negatively correlated)
    - fabric thickness (negatively correlated)
    - yarn twist factor (negatively correlated)
    - wicking height (negatively correlated)
    - viscosity of the pesticide mixture
    - surface tension of the pesticide mixture (negatively correlated)

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[11] Standard Test Method for Measuring Repellency, Retention, and Penetration of Liquid Pesticide Formulation Through Protective Clothing Materials

> Interestingly, fabric thickness was an important determinant when used as a single factor and fabrics with a thickness above 0.8 mm showed no penetration regardless of other properties of the woven fabric. However, once other fabric parameters are entered into a more general model (covering lower thicknesses as well), the influence of the thickness decreases and became insignificant at the 5% level. The final statistical model developed by the authors consists of five parameters, with the cover factor and the yarn twist factor having the highest impact (LEE and OBENDORF, 2005).

The statistical models derived from these data are based on experimental studies. Therefore, they do not consider typical occupational activities and work routines and any possible decrease in efficiency that may emanate from work-related factors. The studies nonetheless provide valuable insight into the different properties that have an impact on the protection offered by protective clothing.

The research described is focused on the development of new materials and therefore includes many different parameters. In practice, it will be difficult to obtain values for these parameters for any given work cloth. The only exception is probably the fabric thickness that is readily available from manufacturer’s website. Information on the surface tension and viscosity of chemicals or mixtures should be available in many cases.

Therefore, the original data (penetration in % together with basic parameters, such as material thickness) from the studies cited above and two additional studies (JAIN and RAHEEL, 2003; ZHANG and RAHEEL, 2003) that also used the ASTM F-2130-01 standard test method were entered into a Microsoft Excel® file that can be used to analyse the impact of several basic parameters. The file contains 213 datasets and therefore allows differentiation by at least one parameter. Examples by the options of differentiation are shown in the following table.

Table 8.1 Experimental clothing penetration: differentiation by impact factors

	Mean penetration (%)	**Number of datasets**
No differentiation		
Total	37	213
Differentiation by fabric type		
Non-woven	30	87
Woven	42	126
Differentiation by material thickness		
>0.5 mm	5	27
<0.5 mm	42	186
Differentiation by treatment of clothing material (not provided for most materials)		
Treated (fluorocarbon finish)	0.33	12
Untreated	39	27
Differentiation by method of penetration analysis		
Gravimetric	50	108
Gas chromatography (GC)	24	105
Differentiation by fabric AND method of penetration analysis		
Non-woven fabric and GC analysis	27	39
Woven fabric and GC analysis	22	66
Non-woven fabric and gravimetric analysis	33	48
Woven fabric and gravimetric analysis	64	60

These data show for example that woven materials showed a mean penetration of 42 % under experimental conditions using a standard test method. In contrast, materials with a fluorocarbon finish (applied only to non-woven fabrics) showed almost no penetration (>99 % protection), although these materials have a thickness <0.5 mm.

The results are also impacted by the method used to analyse penetration. The comparatively high penetration results from studies using gravimetric analysis. When the method of penetration analysis is combined with the differentiation by fabric type, an even higher penetration is found for woven fabrics. However, the gravimetric method was considered by the authors to overpredict penetration (ZHANG and RAHEEL, 2003).

8.2 Gloves

Several authors have developed models to estimate chemical permeation (i.e. diffusion) through protective gloves. In principle, such models aim at estimating the diffusion coefficient for the permeation of a liquid chemical (generally solvents) through gloves (generally polymer materials). In order to estimate the diffusion coefficient, the solubility of the chemical in the glove is an important parameter that can be modelled or determined by immersion tests. From the diffusion coefficient the permeation can be estimated and compared with permeation obtained in standard test methods (such as the ASTM method F-739; diffusion coefficients can also be compared directly).

One group of researchers investigated model predictions with experimental results from tests performed according to ASTM method F-739 (CHAO et al., 2006; CHAO et al., 2004). These authors used nitrile and neoprene gloves in combination with several organic solvents (benzene, toluene, ethylbenzene, styrene and p-xylene). In one of these studies the solubility obtained from immersion tests did not adequately predict solvent permeation through gloves (CHAO et al., 2004). In the other study, there was a good correlation for nitrile gloves, but not for neoprene gloves (CHAO et al., 2006).

In similar approaches, ZELLERS (1993) found in an analysis of 40 solvents that solubility values obtained from immersion tests cannot be used directly in their model, but needed an additional weighting step. In addition, more advanced modelling requires input values, such as the polymer cross-link density, a parameter that is often not available.

Most of the models screened so far are primarily concerned with correctly predicting solubility parameters (see e.g. QUE HEE, 1996). These primarily relate to solvent-polymer interactions and are therefore not generally applicable. In contrast to the studies on clothing penetration discussed above, the studies screened so far also do not allow deriving more generalised conclusions.

Finally, the relevance of these models in the regulatory context is limited, since the exposure assessment under REACH e.g. requires gloves tested according to EN374 if a certain protection factor is applied (see Table 1.1). Large glove manufacturers provide sometimes detailed information on their gloves from laboratory testing.

In the light of these considerations, the value of studies on glove permeation models is small in the context of this project.

Apart from mathematical models predicting penetration, more far-reaching models have been developed for the assessment of dermal exposure. For example, SCHNEIDER et al. (1999) developed a conceptual dermal exposure model consisting of six compartments (ranging from source to the skin contaminant layer) and eight different mass transport processes with more than 30 individual parameters. This conceptual model served CHERRIE et al. (2004) as the basis for developing a proposal for the evaluation of the effectiveness of gloves in reducing dermal exposure. These authors proposed a new 'workplace protection factor', which they defined as the mass uptake of the chemical through the skin when no protection is worn divided by the 'mass uptake of the chemical through the skin while the gloves are worn.

This approach is intriguing in that it appears to cover many of the factors affecting the effectiveness of dermal PPE identified above. For example, the behaviour of the worker will be covered by this assessment. However, the proposed approach resembles more an exposure model in that the uptake of the chemical is also included in the calculations. The authors propose calculating the uptake with *in silico* methods, such as the SKINPERM model (CHERRIE et al., 2004). Such models have their own applicability domain and are not adequate for several substances. For example, irritating or corrosive substances or chemicals that are able to remove lipids from the stratum corneum are not covered by the model (TIBALDI et al., 2014). In addition, such skin permeation models are typically dependent on the log K_{ow} of a substance and are therefore not suited for inorganic substances.

The paper by CHERRIE et al. (2004) also reported several theoretical calculations that demonstrate lower hypothetical protection factors of gloves, when exposure is for longer periods than the breakthrough time of the material (specific for the substance) and when splashing of the substance into the glove (i.e. directly onto the skin) occurs. The lowest hypothetical protection factor obtained by these authors when both use beyond the breakthrough time and direct splashing on the skin was assumed, was about 5 (20% efficiency). Both cases represent a wrong selection of gloves, i.e. the wrong material has been selected for the longer task duration and the gloves are not long enough if splashes just above the gloves occur and reach the inside of the glove. Such cases are known to occur in the real world, but it is difficult to attribute them to the effectiveness of dermal PPE, since they primarily appear to be an issue of compliance with legal obligations and general industrial hygiene practice..

The hypothetical considerations by CHERRIE et al. (2004), however, suggest that some of the dosimetry and biomonitoring studies with low protection efficiency (see sections 5 and 6) may in fact reflect cases, where inappropriate PPE was used. This issue is also discussed in section 9.1.

9 Comparison of database entries with default values

9.1 General remarks

The default efficiency values both in the HEEG recommendations and in ECETOC TRA assume that the correct type of PPE (e.g. material, breakthrough time) has been selected for the task to be assessed. Correct selection of the type of PPE is within the responsibility of the company and has to consider the chemical risk, the workplace, the specific tasks as well as other parameters.

When comparing the efficiency values generated from the database with default values, it must be noted that the studies evaluated may also reflect situations, in which incorrect PPE types may have been selected. An example can serve to illustrate this point.

In the biomonitoring study by CHANG et al. (2007; see section 6.2.2), nitrile gloves (MAPA Ultranile 491) were used for tasks involving exposure to ethyl benzene and xylene. According to the authors, the protection grade was A (excellent to good) for xylene and B (average) for toluene. While this information is more detailed than in most other studies, there are several flaws.
First, the authors did not discuss why they provided data for toluene (not used at the workplace), rather than for ethyl benzene (actually used). Second, and more importantly, the grading suggesting “excellent to good” or at least “average” protection is hard to follow for the following reasons:

- Nitrile is unsuitable for protective gloves for protection against ethyl benzene and xylene because of degradation, severe swelling or low permeation time according to information in the GESTIS database[12].

- More specifically, the glove manufacturer provides information on the specific glove (MAPA Ultranile 491) showing that it is “not recommended” for xylene and toluene and is “not fully tested” for ethyl benzene[13].

- In fact, the glove manufacturer only recommends fluoropolymer-based gloves for high exposure or repeated contact to these chemicals, which is in agreement with the recommendations of the entries in the GESTIS database.

This example suggests that inappropriate gloves were selected for the workplace investigated in the study. The discrepancy between the information provided by the authors in 2007 and the more recent information retrieved from the glove manufacturer cannot be resolved.
An evaluation of the type presented for this example is only possible for studies with well-documented information on the PPE type, including the name of the PPE (manufacturer and specific product). For the studies in the database, this information

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[12] http://www.dguv.de/ifa/GESTIS/GESTIS-Stoffdatenbank/index.jsp, accessed: April 2016
[13] http://www.mapa-pro.net/our-gloves/protections/chemical-protection.html, accessed: April 2016

is rarely available. Such an evaluation is also time-consuming and could not be performed for other studies.

The example nonetheless illustrates that inappropriate PPE may lead to lower efficiency values (about 50-70%) compared to the default values (at least 80% for gloves made of appropriate material). Since the database contains (an unknown number of) studies which reflect inappropriate PPE, lower values from the evaluation of database entries compared to default values (which assume appropriate PPE) can be expected. However, the size of this effect remains unknown.

9.2 Correlation to HEEG categories

Under the biocides regulation, different types of PPE are categorised according to the HEEG opinion about default protection factors (EC, 2010) (see Table 1.1). In order to allow a comparison with these categories and to simplify the selection of example datasets for specific scenarios all database entries were assigned to one the corresponding categories if possible.
For this purpose some assumptions and considerations had to be used:

1. Thin gloves / single use gloves are not considered as protective gloves. This assumption has been used for the sake of simplicity and it is expected to apply in most cases. However, the exposure reduction potential of a glove always depends on the situation and the substance in question. Therefore thin gloves may nevertheless offer appropriate protection in some situations. A case by case decision may be necessary in these cases.

2. If no thickness information was available the decision was made based on the available information on a case by case basis.

3. Coveralls made of cotton / polyester mixtures were classified as cotton coveralls, as it is assumed that the protective properties of both materials (i.e. woven fabrics) will be similar.

4. Solids in solution were treated as liquids as they will soak or drip through openings in the same way liquids will and are expected to wet and contaminate surfaces in a similar way.

5. Wet solids (e.g. wettable powders) were assigned to the solids category, except in cases where the corresponding HEEG category and the corresponding efficiency was only applicable for dry substance.

6. If the physical state was unknown, the liquid category was used as a worst case.

7. The baseline was not considered for the categorisation in the Excel database. The corresponding information should however not be neglected during risk assessment. Therefore only datasets where actual and potential exposure have been compared in some way have been included into the data summary in this section.

8. Coated coveralls according to the HEEG opinion are coveralls designed to protect against spray contamination such as chemical protection clothing of type 6. However, since rarely information about the type number is available categorisation was based on descriptive information; all coveralls coated with a water repellant product were assigned to this category.

9. According to the HEEG opinion "'Impermeable' coveralls should provide a high degree of protection against heavy contamination by being relatively resistant to the penetration of the biocide through the material of which the coverall is made." Materials such as PVC or nylon / PTFE film were assigned to this category.

Apart from this it has already been discussed that a number of test standards exists that have to be applied before PPE can be brought onto the market (see section 3). These categorisations could not be used at this point as hardly specific information has been found in the corresponding database entries. Therefore especially for coated and impermeable coveralls a high uncertainty concerning the assigned categories exists, as the final protection level of coveralls depends not only on the material but also the overall style of the garment (e.g. sealed seams).
A summary of the result can be found in Table 9.1. A large fraction of the available datasets has been assigned to "no category" due to missing information or lack of an appropriate HEEG category. In general, it is again obvious that the different categories span large efficiency ranges. Most HEEG suggestions (impermeable coveralls, protective gloves) tend to be higher than average efficiencies derived from the database. However, for gloves at least the general tendency seems to correspond to the expectations (83% liquids, 89 and 91% solids, 92% liquids (new gloves for each shift)). Coated coveralls show clearly higher efficiencies than suggested (98% instead of 80 or 90%) and also the exposure reduction reached by long sleeves and trousers seems to be higher than anticipated (89% instead of 50%). Impermeable coveralls, which should show higher efficiencies than coated garments, seem to show lower efficiencies (98 vs. 83%) according to database outputs which suggest either wrong category assignments or issues within the study design and evaluation. While no specific reason can be selected as solely responsible for this unexpected tendency it can be assumed that factors such as the variable age of the studies or sampling methods (often patches for whole body garments) may also be a part of the reason. In addition only two studies included datatsets assigned to the "coated coveralls" category, leading to six database entries.

Overall this results in a mixed picture concerning consistency between database output and HEEG suggestions.

Overall, this comparison suggests that there is on the one hand some potential for improvement concerning the available measured data in order to increase the number of assignable datasets, in particular for coated coveralls (only 6 database entries). Moreover, as assumptions had to be made in order to assign HEEG categories, there is some uncertainty concerning the different categories. As an example, although materials such as cloth / cotton have already been excluded it is not known if all glove types / PPE were appropriate for the substance assessed. A number of uncertainties concerning the assignment of database entries to HEEG categories exists (e.g. usage of new gloves, exact type of protective garment). The variable format of the database entries (e.g. different numbers of measured data, arithmetic mean vs. geometric mean) so far does not allow a derivation of meaningful percentiles or standard deviations. Therefore so far only a limited comparison and evaluation of the level of conservativeness of the proposed HEEG categories is possible. Thus, in order to fully understand the applicability of the available default categories, an improvement of the available information would be necessary.

Table 9.1 Assignment of database entries to HEEG categories (EC, 2010) (without negative efficiencies and other unusable results (11 entries))

Assigned HEEG category	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**	**HEEG recommendation (%)**
Coated coveralls (coveralls designed to protect against spray contamination such as chemical protection clothing of type 6) (HEEG recommendation 90% or 80%) (NIGG et al., 1992; TSAKIRAKIS et al., 2010)	98.0	97.0	99.2	6	80 or 90 depending on task / challenge
Impermeable coveralls (GARROD et al., 1999; GLASS et al., 2005; LINKS et al., 2007; METHNER and FENSKE, 1994; NIGG et al., 1986; NORTON et al., 1988; PUTMAN et al., 1983; SOUTAR et al., 2000b; STAMPER et al., 1989; WILLER and FELTEN, 2006)	84.3	41.8	99.8	20	95
no HEEG category available (APREA et al., 2009; APREA et al., 1994; BALDI et al., 2006; BELLO et al., 2008; BIERMAN et al., 1998; BRADMAN et al., 2009; CASTRO CANO et al., 2001; CASTRO CANO et al., 2000; CATTANI et al., 2001; CAVALLARI et al., 2012; CESSNA and GROVER, 2002; CHRISTOPHER and GALEA, 2008; DAVIES et al., 1982; DE VREEDE et al., 1994; ERIKSSON et al., 2008; ESPANHOL-SOARES et al., 2013; FENSKE et al., 2002; FENSKE et al., 1986; FENT et al., 2009; FRANSMAN et al., 2004, 2005; FUSTINONI et al., 2014; GAO et al., 2014; GARROD et al., 2000; GARROD et al., 1998; GLASS et al., 2005; GOLD et al., 1982; GROßKOPF et al., 2013; GROVER et al., 1986; HSE, 1998; HSL, 2003; HUGHSON and CHERRIE, 2001; JOHNSON et al., 2005; KURTZ and BODE, 1985; LEBAILLY et al., 2009; LESMES-FABIAN et al., 2012; MACHERA et al., 2003; MACHERA et al., 2009; MANDIC-RAJCEVIC et al., 2015; METHNER	81.6	0.0	99.9	224	-

Assigned HEEG category	Average Exposure reduction (%)	Minimum Exposure reduction (%)	Maximum Exposure reduction (%)	Number of database entries	HEEG recomme n-dation (%)
and FENSKE, 1994; NIGG and STAMPER, 1983; NIGG et al., 1992; NIGG et al., 1986; NIVEN et al., 1996; OJANEN et al., 1992; POPENDORF, 1988; POPENDORF and SELIM, 1995; POPENDORF et al., 1995; POPENDORF et al., 1979; PRELLER and SCHIPPER, 1999; PUTMAN et al., 1983; RECH et al., 1989; ROFF, 2015; ROFF, 1997; RUBINO et al., 2012; SCHEEPERS et al., 2009a; SCHIPPER et al., 1996; SHAW, 2008; SOUTAR et al., 2000b; SPEAR et al., 1977; SPENCER et al., 1995; STAMPER et al., 1989; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b; VITALI et al., 2009; WANG et al., 2006)					
Nonprofessionals wearing long-sleeved shirt and trousers or skirt with shoes – no gloves worn (FENSKE et al., 2002; FENSKE et al., 1990; FENSKE et al., 1986; GOLD and HOLCSLAW, 1985; GROßKOPF et al., 2013; HSE, 1998; KANGAS et al., 1993; KURTZ and BODE, 1985; LAPPHARAT et al., 2014; LEAVITT et al., 1982; NIGG et al., 1986)	88.5	39.0	97.7	19	50
Protective gloves (liquids) (APREA et al., 1994; BERGER-PREISS et al., 2005; CATTANI et al., 2001; CHANG et al., 2004; CREELY and CHERRIE, 2001; GROßKOPF et al., 2013; LINKS et al., 2007; MADDY et al., 1989; PUTMAN et al., 1983; SHIH et al., 2009; STONE et al., 2005; WANG et al., 2006)	83.4	11.9	100.0	28	90
Protective gloves – new gloves for each work shift – solids (BROUWER et al., 2000; GROßKOPF et al., 2013; NIGG and STAMPER, 1983; TSAKIRAKIS, 2014)	88.8	50.0	100.0	31	95

Assigned HEEG category	**Average Exposure reduction (%)**	**Minimum Exposure reduction (%)**	**Maximum Exposure reduction (%)**	**Number of database entries**	**HEEG recomme n-dation (%)**
Protective gloves (solids) (GROßKOPF et al., 2013; LINKS et al., 2007; MANDIC-RAJCEVIC et al., 2015; PUTMAN et al., 1983)	90.5	71.4	99.7	15	95
Protective gloves – new gloves for each work shift – liquids (CESSNA and GROVER, 2002; GROßKOPF et al., 2013; TSAKIRAKIS et al., 2011; TSAKIRAKIS, 2014; TSAKIRAKIS et al., 2010; TSAKIRAKIS et al., 2014b)	91.5	51.2	100.0	16	95
Overall result per output category	83.9	0.0	100.0	356	

9.3 Exposure tools currently used under REACH and applicability of database results

The main dermal occupational exposure tools currently used under REACH are ECETOC TRA. and (sometimes) RISKOFDERM (ECHA, 2012).

Of these, only ECETOC TRA offers the option to include gloves as an exposure reducing method. The tool does not estimate body exposure, therefore an implementation of further types of dermal PPE is not possible.

Glove efficiencies according to ECETOC TRA v.3 are given in Table 9.2.

As previously described, only very limited information about user training and its influence on exposure reduction could be identified, suggesting a reduction of ~50% for ”tidy” workers compared to “messy” workers. However, it is not known to which extent this also describes the glove removal / change.

Datasets for comparison from the database are only those marked as protective gloves (see chapters “Summary ” in section 5.2.6 and 9.2).

For this category 86 database entries for dosimetry and 4 for biomonitoring have been identified. While for the biomonitoring studies an average of 70.1% (49.0-87.8%) has been found, for dosimetry 88.8% (11.9-100.0%) could be identified, resulting in an overall average of 87.1%, which does however comprise a large variety of glove types, substance types (e.g. different volatility, physical state) and general scenarios. One study by BALDI et al. has been removed as no clear baseline was identified (“no gloves or only half of day”) (BALDI et al., 2006).

As no sufficient information on worker training is available in these database entries, an assignment to the corresponding ECETOC categories proves to be difficult. Considering that the evaluated publications span a large range of years, usual work practice is likely to vary as well. If it is assumed that all database entries that have been assumed to fall under the category “protective gloves” correspond to ECETOC category “b” (gloves with available permeation data, no additional training), the comparison with database outputs suggests a conservative tendency of the model efficiency. However, the large range of efficiencies found in reality and the lack of information about the corresponding level of training also indicate a high level of uncertainty.

Additional factors may be the industry area and corresponding tasks, which are mainly focussed on plant protection products. REACH tools do not cover pesticides; on the other hand, it is so far not certain to which extent the industry area influences the efficiency result. Furthermore some tasks or uses may be very similar for REACH and pesticide scenarios (e.g. painting, mixing).

Overall, more information would be needed for an overall impression and closer evaluation of the categories proposed by ECECTOC TRA. So far the available information is neither sufficient to confirm the suggested default efficiencies, nor is it sufficient for a counterproposal.

Table 9.2 Glove efficiency categories implemented in ECETOC TRA v.3.

Dermal Protection Characteristics	Indicated Efficiency %	Affected User Groups
a. Any glove/gauntlet without permeation data and without employee training	0	Applies to both industrial and professional users
b. Gloves with available permeation data indicating that the material of construction offers good protection for the substance	80	
c. Chemically resistant gloves (i.e. as #b above) with ‘basic’ employee training	90	
d. Chemically resistant gloves in combination with specific activity training (e.g. procedures for glove removal and disposal) for tasks where dermal exposure can be expected to occur	95	Industrial users only

10 Summary and conclusions

10.1 Results of literature evaluation

In the previous sections available information about the estimation of protection factors for different pieces of PPE using dosimetry, biomonitoring, in vitro studies or mathematical models have been compiled.

Concerning dosimetry studies, a large number of studies was identified that can theoretically be used to derive an exposure reduction efficiency value. The highest numbers of datasets were identified for gloves and whole body garments. However, the range of efficiency values for each category of personal protective equipment is large and it is hardly possible to identify a reason, why certain studies lead to higher or lower efficiency results. The transparency of the various publications is often low, resulting in data gaps concerning PPE properties and the assessed scenario. It is often not known if the PPE in question can be considered appropriate for the situation and the assessed substance (see also Figure 10.1).
Only few publications evaluating the methodology of PPE efficiency were found, leading to mostly inconclusive results concerning sampling method and study design. However, as it is already known that variability in dermal exposure can be induced by different sampling methods (see e.g. NG et al. (2014)), an influence on efficiency results seems likely. So far no general recommendation concerning sampling methods can be made, as there are also substance- and situation specific aspects to consider. Additional variability can be added by different ways of evaluating the raw data. As an example the exposure data can be reported in different units (e.g. mg/cm^2, mg/cm^2/h) or differ concerning statistical evaluation (evaluation of single efficiency values to derive efficiency values vs. average exposures used for derivation of efficiency value; see section 5.1).
Thus, overall the available data are able to give a general idea on efficiencies that can be expected for certain types of PPE (Table 10.1, see single chapters for further details and discussion).

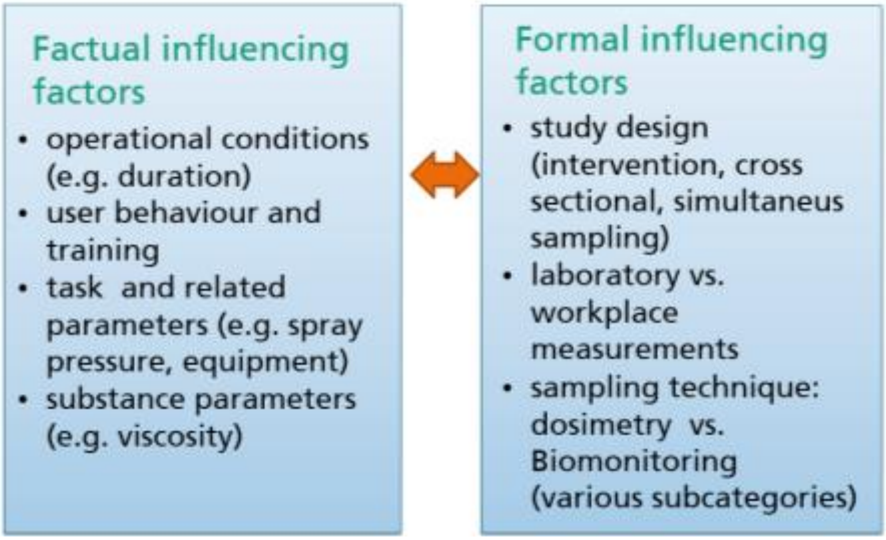

Figure 10.1 Factors influencing the final efficiency value.

Table 10.1 Range of exposure reduction efficiencies for different PPE categories (without negative efficiencies and other not usable database entries (11 entries))

PPE type	Average exposure reduction (%)	Minimum exposure reduction (%)	Maximum exposure reduction (%)	Number of database entries
apron	50.9	0.0	87.6	3
barrier cream	63.7	40.0	82.9	4
Boots	64.0	64.0	64.0	1
gloves	84.1	4.4	100.0	147
hazmat suit	90.2	81.7	98.6	2
Hood	71.3	40.0	98.4	8
mixed equipment	70.9	8.7	100.0	30
normal clothing	70.5	4.0	97.7	58
overall/coverall	90.1	33.4	99.8	145
respiratory equipment (dermal exposure under RPE measured)	45.0	45.0	45.0	1
Overall result	82.5	0.0	100.0	399

In addition various, isolated pieces of information about aspects influencing efficiency have been identified, such as

- the challenge of exposure (deposit),
- personal behaviour or
- PPE characteristics (e.g. glove length, use status (old vs. new)).

However, a detailed differentiation and evaluation of the factors which are necessary to reach a specific efficiency value has not been possible. Thus, although isolated pieces of information could be identified a full understanding of the summarised efficiency values is not possible and comprehensive advice leading to a specified efficiency cannot be given.

One of the aspects that are essential for PPE efficiency is the ability to function as a barrier against a challenging substance. The material can be passed either on a molecular level by permeation or on a more macroscopic level, i.e. through pores, holes, damaged material, seams etc. by penetration (see Figure 10.4). A number of studies focus on the evaluation of these barrier properties.

Regarding *in vitro* studies (with animal or human skin samples) dealing with permeation or penetration of chemicals through dermal PPE, no general conclusions on protection factors can be derived. The main reasons for this finding are that

a) these studies do not reflect real-life work scenarios and
b) barrier efficiencies identified in these study types differed vastly (0-100 %) - depending on

- the respective material tested,
- the chemical investigated and
- the experimental set-up.

Thus, **the predictions are always only valid for a specific chemical or mixture in combination with a specific sample material.** Despite the limitations, these studies are suitable for comparative assessment of different protective materials as well as different chemicals.

Similar to *in vitro* studies, mathematical models that aim to predict penetration through dermal PPE do not reflect real-life conditions at workplaces. They nonetheless provide insight into factors that may have an impact on penetration through dermal PPE. For example,

- the surface tension difference (between protective clothing and chemical) and
- fabric parameters such as
  - thickness and
  - the yarn twist factors (i.e. twists per inch or turns per inch)

were identified as important model parameters predicting clothing penetration. The experimental data generated for model development were also analysed as such and showed important parameters for experimental penetration of protective clothing, such as

- fabric type (e.g. cotton, polyethylene, polyester) and
- fabric thickness.

Regarding biomonitoring studies, the literature search for this project revealed a large amount of studies. However, only six biomonitoring studies could be used to derive dermal protection factors in the context of this project. The main reasons for this limited number of evaluated biomonitoring studies are the lack of pre-shift values, the lack of an assessment with and without dermal protection, or the study design of the biomonitoring study in general. Even the evaluated studies have major deficiencies.

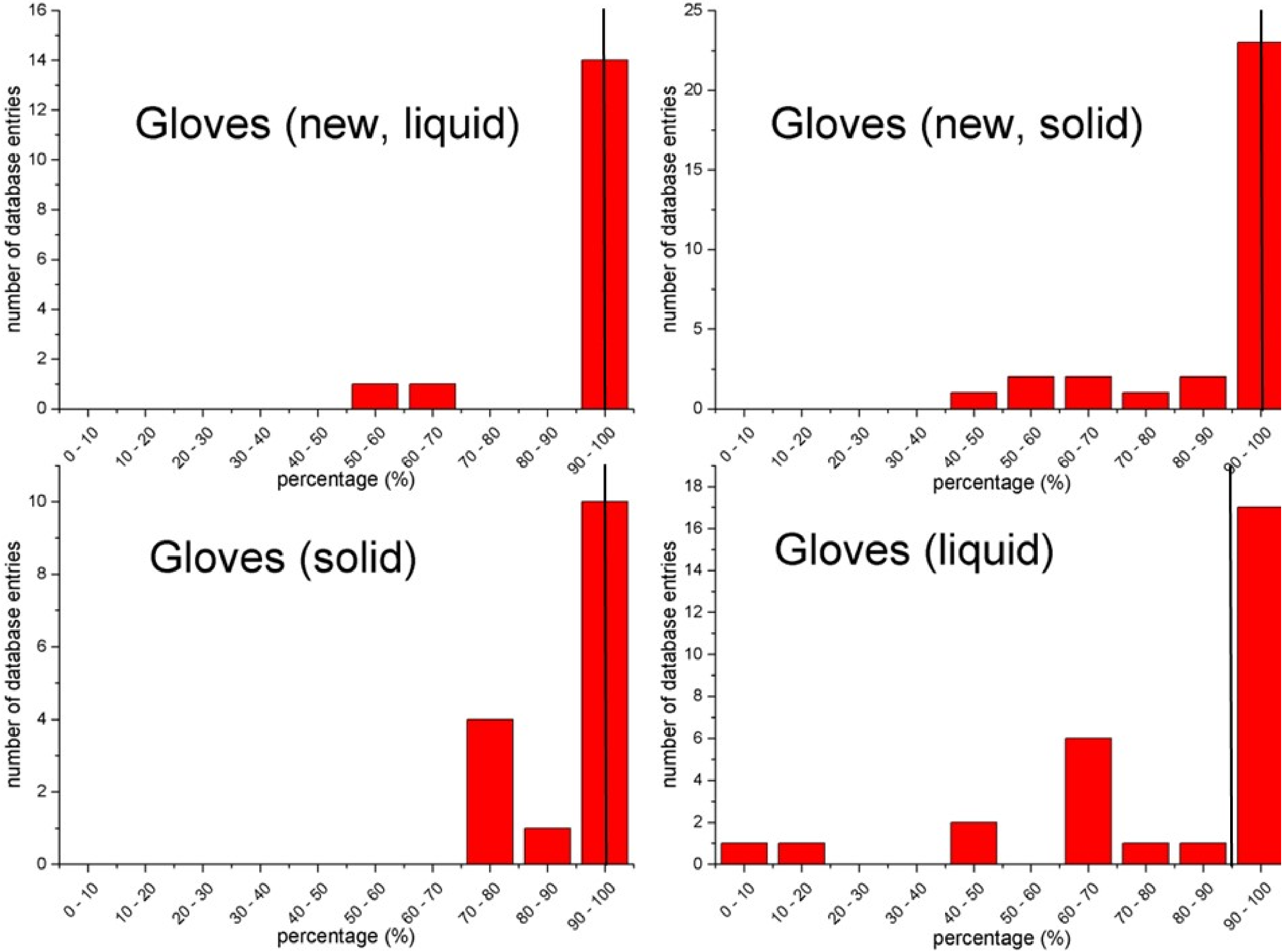

Figure 10.2 Distribution of efficiency values for HEEG glove categories. The current HEEG default is marked by a black line.

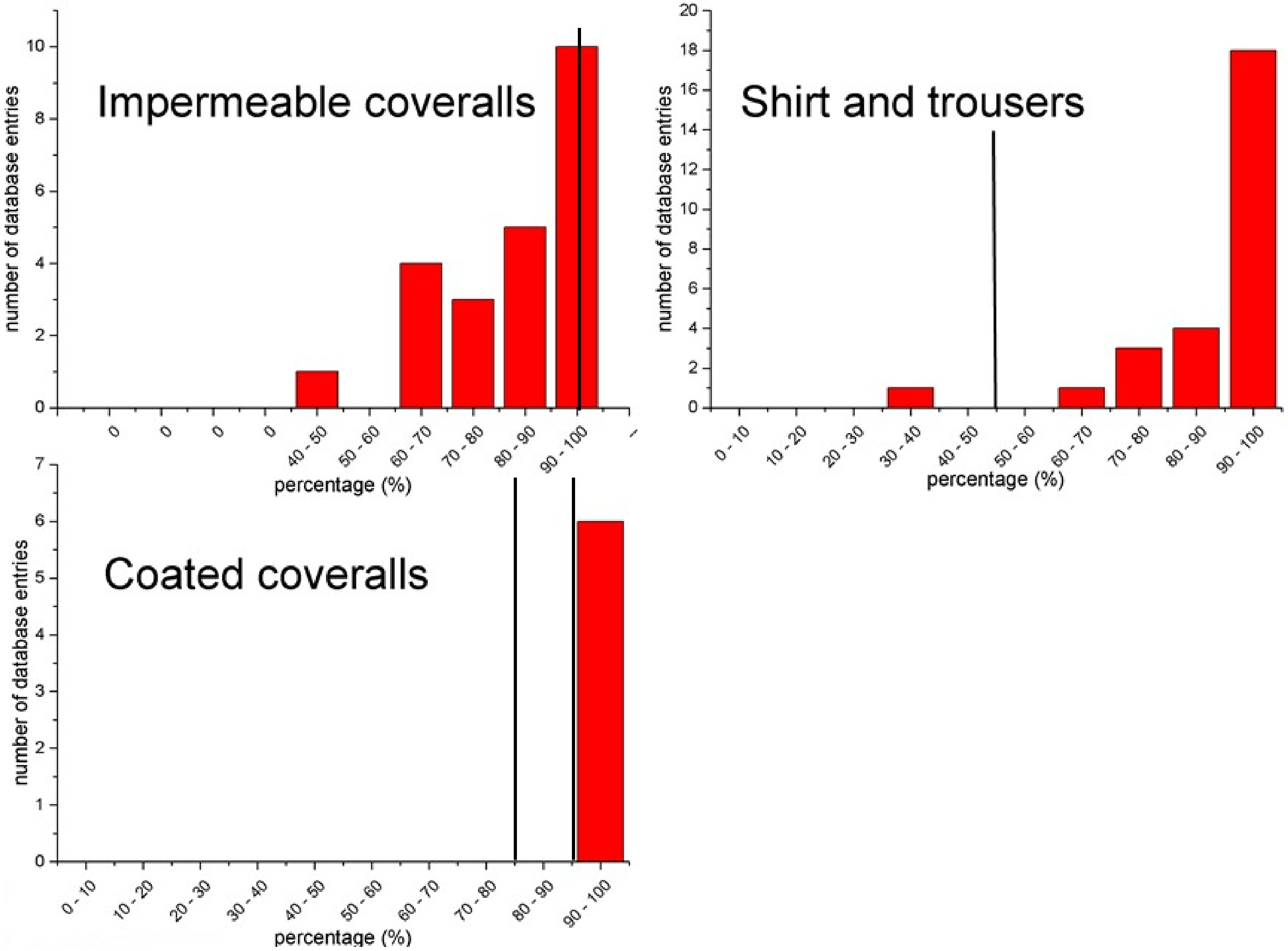

Figure 10.3 Distribution of efficiency values for HEEG whole body garment categories. The current HEEG default is marked by a black line.

Due to the limitations of all the studies evaluated, the derived dermal protection factors (see section 6.3) have to be considered with caution, and a general conclusion is impossible.

Only two studies were identified reporting results from both biomonitoring and dosimetry experiments. These two studies were evaluated in the context of a comparison between protection factors derived from biomonitoring and dosimetry results. It was concluded that for these studies a comparison of the results obtained with different methods was not possible due to study limitations (see chapter 6.4.2)
When the results from the literature evaluation are compared with default efficiencies of the HEEG opinion or ECETOC TRA, exposure reduction due to PPE is sometimes higher based on literature data and sometimes lower (depending on the PPE considered) (see Figure 10.2-Figure 10.3 and further figures in section 5.2). However, such a comparison involves substantial uncertainty for several reasons. For example, it cannot be excluded that the literature data may reflect (to an unknown degree) studies with inappropriate PPE for the scenario assessed. Furthermore, studies generally do not document the level of training in handling PPE, which, however, is important in the default efficiencies assumed. As a worst case it may be assumed that all studies refer to a good level of training and general occupational hygiene as long as no further information is documented. It is, however, expected that this approach will lead to underestimations of the final efficiency values and should therefore be amended by further research as soon as possible.

In particular three factors were identified which are considered to be of high relevance for the understanding of efficiency values but have so far not been evaluated:

1. Influence of the challenge of exposure
2. Influence of personal behaviour / level of training
3. Substances enhancing passage through PPE (not skin) / carrier substances.

These factors will be further discussed in the following section.

10.2 Suggestions for further research

As already described in sections 5.3.4 and 5.4 there are some general requirements that should be met for a good and usable dosimetry study, including a sufficient number of test subjects and a detailed and complete documentation of all operational conditions, PPE parameters and information about the user.
In addition, improved knowledge about the available dermal sampling methods may be essential in order to choose an appropriate technique for substance and scenario and will minimise the overall error.
Studies should be designed in a comparable way, and factors of interest that are to be evaluated should be carefully selected.
During the evaluation of dosimetry studies the following factors were identified which may influence the efficiency value. They are considered of high relevance but have so far not been evaluated:

1. Influence of the challenge of exposure

It has been indicated in several publications that the challenge will have an influence on the efficiency outcome (1996; DRIVER et al., 2007; GERRITSEN-EBBEN et al.,

2007); HAMEY et al. (2008); (MACHERA et al., 2009; PUTMAN et al., 1983; ROFF, 2015; SPAAN et al., 2014). However, this factor is difficult to evaluate, as the exposure also depends on other factors which may have a direct influence on the efficiency. This is illustrated in Figure 10.4: Influencing factors can be roughly categorised into operational conditions, task description and related parameters, substance parameters and user behaviour and training. While parameters of these categories certainly have an effect on the dermal exposure itself, they can also influence the efficiency directly. As an example doing a certain task for a longer time will usually lead to higher exposure values which often correlates with higher efficiencies. On the other hand a longer duration will also increase the probability that the tested individual will change or remove their gloves/PPE during this time which in turn often leads to a lower efficiency value due to contamination during removal. In order to evaluate only the influence of the challenge itself, other values would have to stay constant, i.e. there may be cases where the influencing factor of the efficiency would rather be assigned to a separate parameter (e.g. duration), and not the challenge itself.
Furthermore the efficiency is always a result of the combination of permeation, penetration and direct deposition during removal. The three processes can usually not be separated completely during field studies.

It may also be a possibility to use efficiency values only within certain limits (e.g. below a certain exposure value) and substance flux values above a certain exposure value. Such an approach could compensate for the influence of exposure on the efficiency. However, a reliable exposure estimation method is necessary for its application.

2. Influence of behaviour / level of training

It is recognised that this factor is of high relevance (MARQUART et al., 2003).
As an example, RAWSON et al. found a clear reduction of contamination after showing a video with instructions on donning and removal of gloves, although only semi-quantitative results are reaported. Further indications concerning the relevance of this parameter are published by other authors. However, quantitative information of sufficient quality is not available (APREA et al., 2009; ESPANHOL-SOARES et al., 2013; RAWSON et al., 2005; VAN DER JAGT et al., 2004)(CREELY and CHERRIE, 2001)(QUACH et al., 2013; RAWSON et al., 2005).
While information on training may be surveyed by questionnaires, video documentation of the tasks measured may help in elucidating behavioural factors in future dosimetry studies.
Ideally, the information gathered in the course of these further studies may even be used to develop a two-step model that can be applied for calculating final protection factors by implementing parameters representing the user behaviour and different levels of training.

3. Substances enhancing passage through PPE (not skin) / carrier substances

Only *in vitro* data were identified concerning this aspect that cannot be directly used for efficiency calculations. However, the evaluation of this aspect should probably be done after reliable results for pure substances have been established. If the major route of exposure is direct dermal contact during glove removal, the influence of carrier substances may only be of minor relevance.

In addition to these general aspects, there are some types of PPE for which the number of datasets was found to be especially low. These include suits with CE marking, aprons and other types of PPE which cover only a part of the body (e.g. Tyvek hoods, Tyvek sleeves, hoods, boots).

Partly, an evaluation of these three and further aspects (e.g. material, thickness, wearing time) may also be done via comparison of different situations (and individuals) that are typical for certain industry areas, as the level of training, experience and the type of glove/ PPE used will often differ. However, care should be taken to nevertheless document all details of the scenario, as factors influencing efficiency may not only be the industry area or task but other parameters arising from the specific scenario (e.g. temperature, ventilation, persons involved). As a consequence, an industry area with comparably low glove efficiency value will reach higher levels of protection if corresponding changes of the work environment are implemented.

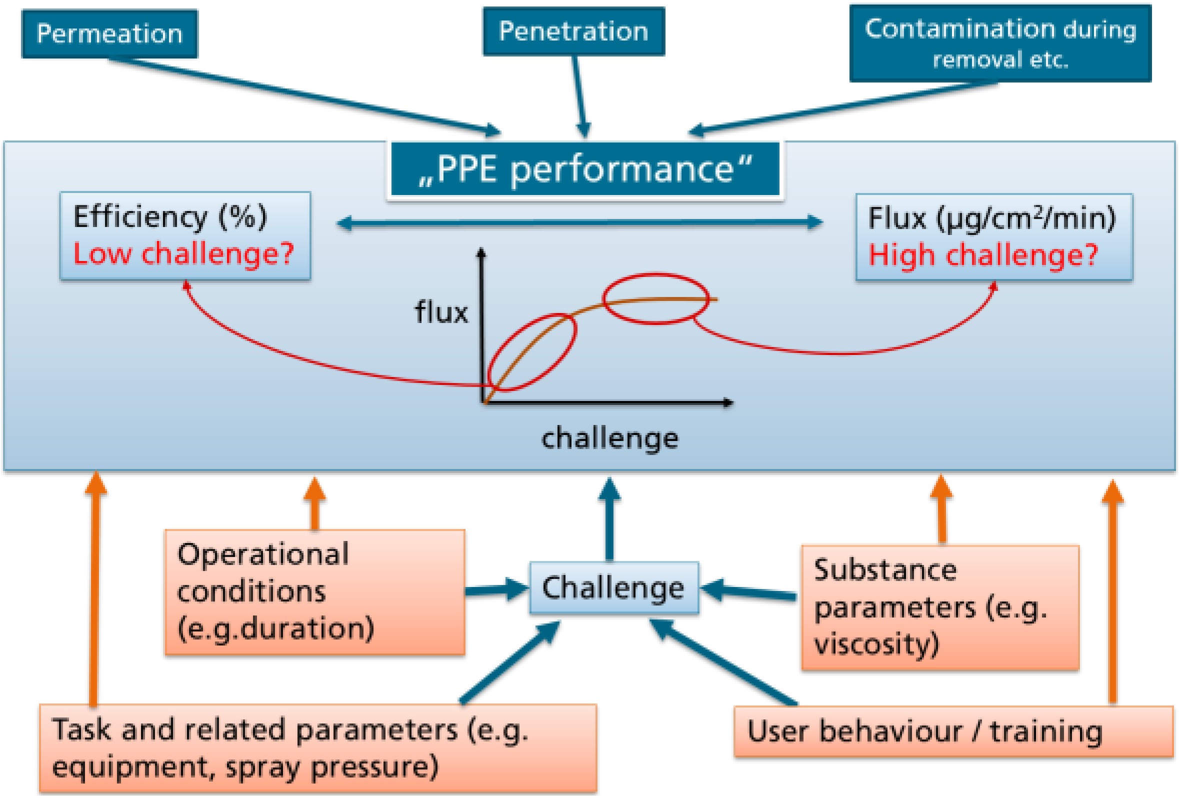

Figure 10.4 Performance of personal protective equipment

In relation to any future biomonitoring studies, a set of criteria that allow assessing the efficiency of PPE was already defined in section 6.4.1. If such a study is envisaged, substances should be assessed for which a biomonitoring method is available. The list of substances with BW values in biological matrices established by the German “MAK Commission” can serve as a starting point for candidate substances, since a valid biomonitoring method is available. However, some of the substances are no longer in use (e.g. pentachlorophenol) or are highly volatile (vapour pressure above 5000 Pa at ambient temperature). Since the latter can be expected to rapidly evaporate from PPE, they may be more difficult to study. As a consequence, substances with a comparatively low vapour pressure were selected for the following examples. In addition, a high REACH registration tonnage and (preferably) many industrial and professional uses of the substance were set as criteria to derive a list of substances that may be studied in future biomonitoring programmes. The table shows adequate substances but the list is not exhaustive.

Table 10.2 Candidate substances with available biomonitoring method

Substance name	CAS number	Vapour pressure (Pa)*	Tonnage (tpa)**	Uses***
Manganese	7439-96-5	Solid	>1 000 000	Many industrial & professional
Phenol	108-95-2	20	1 000 000-10 000 000	Many industrial & professional
N-Methylpyrolidone	872-50-4	32	10 000-100 000	Many industrial & professional
2-Butoxyethanol	111-76-2	80	100 000-1 000 000	Many industrial & professional
Cyclohexanone	108-94-1	700	1 000 000-10 000 000	Many industrial & professional
Hexamethylene diisocyanate	822-06-0	0.7	10 000-100 000	Industrial only
Aniline	62-53-3	40	1 000 000-10 000 000	Industrial only
Ethylbenzene	100-41-4	1000	1 000 000-10 000 000	Industrial only

* Vapour pressure at ambient temperature (20-25 °C) from REACH registration dossiers (key studies); ** REACH registration tonnage band in tonnes per annum (tpa); *** Uses according to REACH registration dossier

Furthermore, more data need to be assessed, e.g. on dermal absorption before such substances are selected for any future biomonitoring study.

As already stated for dosimetry studies above, video documentation of the tasks performed may help to identify behavioural differences between workers, but also any unforeseen events, such as accidental spills. In contrast to dosimetry studies (measuring, e.g., a task over 60 minutes), video documentation during biomonitoring studies, however, would need to be conducted over the entire shift.

It is tempting to evaluate one and the same scenario (use of a specific chemical at a specific workplace) by both dosimetry and biomonitoring. This would allow a comparison of both study types and identify any systematic differences. Such a comparison, however, would require a sufficiently high number of datasets (i.e. different scenarios) in order to check for a general correlation between both study types. Due to the high costs involved, especially for biomonitoring studies, this may not be a feasible option. With budget constraints in mind, a higher number of well-conducted and well-documented dosimetry studies may be the preferred approach.

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Appendix 1: Literature Search Strategy

Appendix 1, Table 1 Pubmed search strategy 1

	Pubmed
Search	Query
#8	Search #5 AND #6
#7	Search #5 AND #6 Filters: Publication date from 2000/01/01
#6	Search (skin[Title/Abstract] OR percutaneous[Title/Abstract] OR dermal[Title/Abstract]) Filters: Publication date from 2000/01/01
#5	Search #3 AND #4 Filters: Publication date from 2000/01/01
#4	Search (permeation OR permeability OR barrier OR penetrat*) Filters: Publication date from 2000/01/01
#3	Search #1 OR #2 Filters: Publication date from 2000/01/01
#2	Search protective equipment[Title/Abstract] Filters: Publication date from 2000/01/01
#1	Search (cloth*[Title/Abstract] OR glove[Title/Abstract] OR gloves[Title/Abstract] OR coverall[Title/Abstract] OR coveralls[Title/Abstract] OR overall[Title/Abstract] OR overalls[Title/Abstract] OR suits[Title/Abstract] OR fabrics[Title/Abstract] OR apron[Title/Abstract] OR aprons[Title/Abstract]) Filters: Publication date from 2000/01/01
	Refinement
#9	sun[Title] OR ultraviolet OR radiation OR transplantation OR surgery OR virus
#10	#8 NOT #9
	Limited to English and German (German articles already selected based on relevance)

Appendix 1, Table 2 Pubmed search strategy 2

	Pubmed
Search	Query
#5	Search #3 AND #4
#4	Search (skin[Title/Abstract] OR dermal[Title/Abstract] OR percutaneous[Title/Abstract]) Filters: Publication date from 2000/01/01
#3	Search #1 AND #2 Filters: Publication date from 2000/01/01
#2	Search (effectiveness OR efficiency OR efficacy OR performance OR "exposure reduction" OR "protection factor") Filters: Publication date from 2000/01/01
#1	Search ((cloth*[Title/Abstract] OR glove[Title/Abstract] OR gloves[Title/Abstract] OR coverall[Title/Abstract] OR coveralls[Title/Abstract] OR overall[Title/Abstract] OR overalls[Title/Abstract] OR suits[Title/Abstract] OR fabrics[Title/Abstract] OR apron[Title/Abstract] OR aprons[Title/Abstract])) Filters: Publication date from 2000/01/01
	Refinement
#6	sun[Title] OR ultraviolet OR radiation OR transplantation OR surgery OR virus
#7	#5 NOT #6
	Limited to English and German (German articles already selected based on relevance)

Appendix 1, Table 3 Pubmed search strategy 3

Pubmed	
Search	Query
#7	Search #5 AND #6 Filters: Publication date from 2000/01/01
#6	Search (method OR methodology OR methodologies OR methods OR model OR models OR concept OR concepts) Filters: Publication date from 2000/01/01
#5	Search #3 AND #4 Filters: Publication date from 2000/01/01
#4	Search (skin[Title/Abstract] OR dermal[Title/Abstract] OR percutaneous[Title/Abstract]) Filters: Publication date from 2000/01/01
#3	Search #1 AND #2 Filters: Publication date from 2000/01/01
#2	Search (worker[Title/Abstract] OR workers[Title/Abstract] OR occupational[Title/Abstract] OR occupation[Title/Abstract] OR workplace[Title/Abstract] OR professional[Title/Abstract] OR employee[Title/Abstract])
#1	Search (exposure monitoring[Title/Abstract] OR dermal exposure[Title/Abstract] OR dosimetry[Title/Abstract] OR protective[Title/Abstract] OR potential exposure[Title/Abstract])
	Refinement
#8	sun[Title] OR ultraviolet OR radiation OR transplantation OR surgery OR virus
#9	#7 NOT #8
	Limited to English and German (German articles already selected based on relevance)

Appendix 1, Table 4 Pubmed search strategy 4

	Pubmed
Search	Query
#5	Search #3 AND #4
#4	Search (worker[Title/Abstract] OR workers[Title/Abstract] OR occupational[Title/Abstract] OR occupation[Title/Abstract] OR workplace[Title/Abstract] OR professional[Title/Abstract] OR employee[Title/Abstract]) Filters: Publication date from 2000/01/01
#3	Search #1 AND #2 Filters: Publication date from 2000/01/01
#2	Search (skin[Title/Abstract] OR dermal[Title/Abstract] OR percutaneous[Title/Abstract])
#1	Search ("biological monitoring"[All Fields] OR "biomonitoring"[All Fields]) OR "biomarker"[All Fields]) OR urine[Title/Abstract] OR plasma[Title/Abstract] OR blood[Title/Abstract])
	Refinement
#6	sun[Title] OR ultraviolet OR radiation OR transplantation OR surgery OR virus
#7	#5 NOT #6
	Limited to English and German (German articles already selected based on relevance)