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Occupational Exposure Assessment in Metal Degreasing and Dry Cleaning – Influences of Technology Innovation and Legislation

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Abstract

Besides numerous benefits, chemicals can also cause serious damage to human health and the environment. Thus, the use and release of chemicals needs to be regulated. For the regulation of a chemical, it is essential to know the volumes produced or imported, the known or suspected hazardous properties, the use patterns, and the resulting exposures. In order to evaluate these factors in their interplay, risk assessments have to be carried out.

The main aim of this thesis is the development of a method capable of representing, for an entire country, the risk of occupational exposure to solvents in different applications by integrating the complexity of activity patterns of workers and the temporal and spatial variability of machine technology and workplace conditions. To this end, the "Scenario-based risk assessment" (SceBRA) method was further developed. In SceBRA, a set of possible and plausible exposure scenarios is defined, based on expert knowledge, that reflects the real situation in a given country for a given year. The occupational risk is depicted for each scenario or cluster of scenarios by two indicators, the risk quotient, i.e., the ratio of airborne concentrations and an effect level, and the number of exposed workers. The usefulness and value of this method is demonstrated in this thesis through its application to two case studies, namely the occupational exposure to trichloroethylene (TRIC) and perchloroethylene (PERC) in metal degreasing and PERC in dry cleaning. Metal degreasing and dry cleaning are performed in highly variable settings, with metal parts of different size and shape and garments of different textile fibres, and with machines of different capacities and technological standards. Germany was chosen as model country because of the restrictive legislation, which has demanded since the 1970s major changes of machine technology (four to five subsequent generations of improved machine technology).

With a dynamic two-box model, the airborne concentrations in the near-field and far-field of the machines are calculated for different kinds of release (diffuse emission, release of contaminated air during loading and unloading, solvent release from cleaned metal parts or textiles). The concentration estimates, which are in good agreement with measured data, are compared to

maximum workplace concentrations (MAK values). The full set of scenarios represents the variability of the occupational exposure and shows for which situations MAK values were exceeded and how the transition from fully emissive open-top to closed-loop metal-degreasing machines and from vented to non-vented dry-cleaning machines reduced the exposure by about one order of magnitude to well below one-tenth of the MAK value.

In addition, numbers of exposed workers are estimated for different years. While more than 48'000 workers in the near-field were exposed to TRIC and PERC in metal degreasing and dry cleaning in 1985, the number declined to below 10'000 by 1996. For metal degreasing, this was mainly due to technology changes, rationalization, automatization, and replacement of TRIC and PERC by non-chlorinated solvents. For dry cleaning, the reduction resulted mainly from new textiles and improved wet-cleaning machines that reduced the need for dry cleaning.

The collected data for the dry cleaning case study are of good quality and suitable for statistical evaluation. Thus, a detailed statistical exposure assessment (Monte Carlo simulation of airborne concentrations) is carried out to compare the results with the SceBRA concentration ranges. The concentration ranges obtained with the two methods are in good agreement. While the concentrations are not assigned frequencies in SceBRA, the statistical method also provides the frequencies of certain output ranges.

Overall, it can be seen that the developed method is suitable for representing the large variability and the systematic reduction of the occupational exposure, which results from technology changes triggered by the legislation.

Zusammenfassung

Um negative Auswirkung auf Mensch und Umwelt zu vermeiden oder zu minimieren, muss die Herstellung und Anwendung von Chemikalien gesetzlich geregelt werden. Dazu benötigen Gesetzgeber neben den produzierten und importierten Stoffmengen Angaben zum Gefährdungspotential (Gefahrstoffdaten), zu den verschiedenen Anwendungsgebieten und über die effektive Exposition von Mensch und Umwelt. Um diese Faktoren und ihr Zusammenwirken zu beurteilen, müssen Risikobewertungen durchgeführt werden.

Der Hauptbestandteil der vorliegenden Arbeit ist die Entwicklung einer Methode, die es ermöglicht, das Arbeitsplatzrisiko durch Lösemittel in verschiedenen Anwendungen für eine ganze Region darzustellen. Dabei soll das Modell der zeitlichen und örtlichen Vielfalt der Anwendung unter Berücksichtigung der verwendeten Technologie und der Arbeitsplatzbedingungen gerecht werden. Hierzu wurde die szenarienbasierte Risikobewertungsmethode SceBRA (Scenario-Based Risk Assessment) massgeblich weiterentwickelt. Ausgehend von Expertenwissen wird eine Anzahl möglicher und plausibler Szenarien definiert, welche die zu betrachtende Situation zu verschiedenen gewählten Zeitpunkten widerspiegelt. Für jedes Szenario wird das Expositionsrisiko der Arbeiter ausgedrückt durch den Risikoquotienten (Verhältnis von Arbeitsplatzkonzentration zu MAK-Wert (maximale Arbeitsplatzkonzentration)) und die Anzahl exponierter Arbeiter. Die Anwendbarkeit und der Nutzen dieser Methode wird anhand von zwei Fallstudien aufgezeigt, und zwar der Anwendung von Trichlorethylen (TRIC) und Perchlorethylen (PERC) in der Metallentfettung und der Verwendung von PERC in der chemischen Textilreinigung. Beide Anwendungsgebiete zeichnen sich durch eine grosse Vielfalt an Reinigungsgütern, Reinigungsmaschinen sowie verwendeter Technologien aus. Deutschland wurde als exemplarischer Anwendungsfall gewählt wegen der strengen Gesetzesvorlagen, die seit den 70er Jahren einen starken Wandel der verwendeten Anlagen bedingt hat (vier bis fünf zunehmend verbesserte Anlagegenerationen).

Mit Hilfe eines dynamischen Zwei-Box-Modells wird die Arbeitsplatzkonzentration für das nahe und ferne Arbeitsumfeld berechnet, und zwar in Abhängig-

keit von emittierten Stoffmengen aus verschiedenen Quellen (diffuse Emissionen, Emissionen bei der Bestückung und Entleerung, sowie Emissionen aus den gereinigten Waren). Die berechneten Konzentrationen stimmen gut mit Arbeitsplatzmessungen überein. Die Gesamtheit aller Szenarien ermöglicht es, die hohe Variabilität der Exposition am Arbeitsplatz im Modell widerzuspiegeln. Das Modell liefert Angaben, bei welchen Szenarien es zu MAK-Wert-Überschreitungen kommt. Insgesamt konnte beim Übergang von offenen oder ausblasenden Anlagen zu den heute zulässigen ausblasfreien Anlagen mit geschlossenem Lösemittelkreislauf die Exposition der Arbeiter um mehr als eine Grössenordnung verbessert werden. Die heutigen Konzentrationen liegen maximal bei einem Zehntel des MAK-Wertes. In Jahre 1985 waren in Deutschland noch mehr als 48'000 Arbeiter im nahen Arbeitsumfeld der Anlagen exponiert, seit 1996 ist diese Zahl unter 10'000 Arbeiter gesunken. Bei der Metallentfettung kann diese Reduktion mit verbesserter Maschinenteknologie, Automation, Rationalisierungen und Substitution von TRIC und PERC durch nicht halogenierte Lösemittel begründet werden. Bei der Textilreinigung ist die Reduktion, bedingt durch neue Textilfasern und bessere Haushaltswaschmaschinen, hauptsächlich auf die geringere zu reinigende Warenmenge zurückzuführen.

Die gute Qualität der ermittelten Daten zu den Anwendungsbedingungen der Textilreinigungs-Maschinen, erlaubt bei dieser Fallstudie eine statistische Expositionsbewertung mit Hilfe von Monte-Carlo-Rechnungen. Auf diese Weise ist ein Vergleich der Konzentrationsbandbreiten der statistischen und der szenarien-basierten Methode möglich. Die Bandbreiten aus beiden Methoden zeigen eine gute Übereinstimmung. Während die szenarien-basierte Methode keine Häufigkeiten für das Auftreten bestimmter Konzentrationswerte liefert, ergibt die statistische Bewertung zusätzlich auch die Eintrittshäufigkeiten der einzelnen Konzentrationswerte.

Insgesamt wird gezeigt, dass die entwickelte Methode sehr gut geeignet ist, um die grosse Vielfalt sowie die systematische Reduktion der Exposition am Arbeitsplatz wiederzugeben, die sich durch den von der Gesetzgebung erzwungenen Technologiewandel ergeben hat, beziehungsweise ergeben wird.

Contents

1	INTRODUCTION	1
1.1	Motivation	1
1.2	Objectives	3
1.3	Structure	5
2	CHLORINATED SOLVENTS TRIC AND PERC	9
2.1	Physical and chemical properties	10
2.2	Toxicology	11
2.2.1	Acute toxicity data for TRIC and PERC	11
2.2.2	TRIC	12
2.2.3	PERC	14
2.3	Use of TRIC and PERC	16
2.4	Production and economical data for Germany	18
2.5	German regulations	19
2.5.1	2 nd BImSchV of 1986	19
2.5.2	2 nd BImSchV of 1990	21
2.5.3	Amendment of 2 nd BImSchV 1990 in 2001	22
2.5.4	Toxicological classifications	23
3	METHODS AND MODELS	25
3.1	Scenario-Based Risk Assessment (SceBRA)	26
3.2	System boundaries	27
3.3	Mass balance models	30
3.3.1	One-box model	30
3.3.2	Two-box model	31
3.4	Use of emission factors	34
3.5	Variability and uncertainty of exposure estimates	36
3.5.1	Deterministic versus statistical approach in exposure assessment	36
3.5.2	Model uncertainty	37
3.5.3	Parameter variability and uncertainty	38
3.5.4	Sensitivity analysis	39
3.5.5	Implementation of variability and uncertainty analysis in SceBRA	40
4	CASE STUDY: METAL DEGREASING	43
4.1	Technological development	44
4.2	Scenario definition	49

4.2.1	Machine parameters	49
4.2.2	Emission factors	50
4.2.3	Workplace parameters.....	55
4.2.4	Number of exposed workers	56
4.3	Results of occupational exposure assessment in metal degreasing	57
4.3.1	Dynamic concentrations	57
4.3.2	Parameter combination.....	59
4.3.3	Comparison of technologies	62
4.3.4	Cumulative risk	66
4.3.5	Validation	69
4.3.6	Sensitivity analysis.....	74
4.4	Conclusions	77
5	CASE STUDY: DRY CLEANING	79
5.1	Technological development	81
5.2	Scenario definition	85
5.2.1	Machine parameters	86
5.2.2	Emission factors	87
5.2.3	Workplace parameters.....	90
5.2.4	Number of exposed workers	91
5.3	Results of occupational exposure assessment in dry cleaning	92
5.3.1	Dynamic concentrations	92
5.3.2	Parameter combination.....	94
5.3.3	Comparison of technologies	97
5.3.4	Cumulative risk	99
5.3.5	Validation	103
5.4	Statistical exposure assessment and sensitivity analysis (Monte Carlo).....	106
5.5	Conclusions	116
6	CONCLUSIONS AND OUTLOOK.....	119
6.1	Conclusions	119
6.2	Outlook	124
	BIBLIOGRAPHY	127
A.	CHLORINATED SOLVENTS TRIC AND PERC.....	145
A.1.	Production of TRIC and PERC	145
B.	EXPOSURE MODELS.....	147
B.1.	Solutions of differential equation systems.....	147

B.2. Dynamic concentration	148
B.3. Long-term concentration	151
C. METAL DEGREASING	153
C.1. Metal degreasing process	153
C.2. Metal degreasing input data.....	154
C.2.1. Method for metal degreasing data collection	154
C.2.2. Machine parameters	155
C.2.3. Emission factors	159
C.2.3.1 Continuous emission factor for diffuse emissions	159
C.2.3.2 Continuous emission factor for cleaned metal parts	161
C.2.3.3 Periodic emission factor for loading and unloading.....	163
C.2.4. Workplace parameters.....	166
C.2.5. Number of machines.....	166
C.2.6. Number of exposed workers	169
C.3. Metal degreasing results.....	170
C.4. Concentration measurements in metal-degreasing facilities	179
D. DRY CLEANING.....	185
D.1. Dry cleaning input data	185
D.1.1. Method for dry cleaning data collection	185
D.1.2. Machine parameters	186
D.1.3. Emission factors	187
D.1.3.1 Continuous emission factor for diffuse emissions	187
D.1.3.2 Continuous emission factor for cleaned textiles.....	189
D.1.3.3 Periodic emission factor for loading and unloading.....	192
D.1.4. Workplace parameters.....	194
D.1.5. Number of machines.....	195
D.1.6. Number of exposed workers	196
D.2. Dry cleaning results	197
D.3. Dry cleaning validation data.....	202
D.4. Statistical exposure assessment for dry cleaning	206
D.4.1. Probability density functions (PDF) of input parameters	206
D.4.2. Output distributions.....	211
E. SYMBOLS	213
E.1. Abbreviations	213
E.2. Model parameters	215

Chapter 1

1 Introduction

1.1 Motivation

Chemicals bring numerous benefits on which modern society is entirely dependent, for example, in food production, as active ingredients in medicines, and in the production of consumer goods. On the other hand, some applied chemicals have caused serious damage to human health and to the environment. Thus, the use and release of chemicals must be regulated to ensure the protection of human health and the environment at a high level.

The present EU chemicals policy distinguishes “existing substances”, i.e. chemicals declared to be on the market in September 1981, and “new substances”, i.e. those placed on the market since that date. For new substances, testing and assessment of their risks for human health and the environment according to Directive 67/548 are required. Their registration and classification is performed generally according to intrinsic hazardous properties identified in toxicological tests.

The European Commission proposed in the “White Paper on the Strategy for a Future Chemicals Policy” (COM, 2001) that, in the future, existing and new substances should be subject to the same assessment procedure under a single system. The proposed system is called REACH, for the **R**egistration, **E**valuation and **A**uthorization of **C**hemicals. The requirements of the REACH system depend on the proven or suspected *hazardous properties*, *use*, *exposure*, and *volumes* of chemicals produced or imported. As these parameters are normally not known, risk assessments have to be carried out.

According to the Technical Guidance Document (TGD) of the EU (TGD, 1996), a human health risk assessment consists of four parts, the *hazard identification*, *dose-response (or effect) assessment*, *exposure assessment*, and *risk characterization*. In the hazard identification and effect assessment stages, intrinsic hazardous properties and dose-response characteristics are identified and, whenever possible, a no observed adverse effect level (NOAEL) or at least a lowest observed adverse effect level (LOAEL) is established on the basis of animal testing or available human data. In the exposure assessment stage, human exposure to substances and the exposure of environmental compartments are described. In the risk characterization stage the incidence and severity of the adverse effects likely to occur due to actual or predicted exposure to a substance are estimated.

A lot of research has been carried out on effect assessment, but only relatively little on exposure assessment (Gundert-Remy, 2003). On page 15 of the White Paper, it is stated that: "Adequate knowledge about exposure is an absolute requirement for any reliable risk assessment" but that there is: "however, a general lack of knowledge on the exposure to the existing substances" (COM, 2001). From this it can be seen that there is an urgent need for further research on this field.

Exposure can be characterized according to two criteria: exposure of the total population and exposure of a specified, usually highly or maximally exposed individual (CRAHAP, 1994). In the case of exposure of the total population, it is necessary to know which group is exposed to which substance (e.g., workers in a specific field or consumers of a certain product).

The analysis of all situations in which exposure can occur is a first step in exposure assessment. The second step is the estimation of the quantity of toxic materials emitted by a given source. Emission characterization involves identification of the chemical components of emissions and determination of the rates at which they are emitted. In a third step, the effective exposure has to be determined.

As the available data describing human exposure to chemicals are of varying quality and scope (Northage and Marquat, 2001; Money and Margary, 2002), modelling is needed (Nicas and Jayjock, 2002). Models used in exposure

assessment can be classified into two broad categories: empiric models, which use measured exposure data and mechanistic models, which predict exposure (in units of concentration multiplied by time) or concentration (in units of mass per volume) (CRAHAP, 1994). Exposure models consider only exposure and not its consequences (TGD, 1996).

The magnitude of exposure and the number of exposed people is of common interest to regulators and, due to product liability, also to producers of chemicals and products and to insurance companies insuring the producers and formulators.

1.2 Objectives

The main aim of this thesis is the development of a method that is able to reflect, for a specific chemical in different applications, the occupational exposure of all exposed workers. This is done on the basis of two case studies: the use of trichloroethylene (TRIC) and perchloroethylene (PERC) in metal degreasing and the use of PERC in dry cleaning.

Effective control of human exposure to TRIC and PERC is highly important because these solvents cause a variety of toxic effects, possibly including cancer (BUA, 1993; BUA, 1994; ECETOC, 1994; ECETOC, 1999), and because they are widely used as degreasing and cleaning agents with a potentially high number of exposed workers.

Assessing occupational exposure is impeded by the complexity of the activity patterns of workers and the temporal and spatial variability of workplace conditions (Matthiessen, 1986; Jayjock and Hawkins, 1993; Fehrenbacher and Hummel, 1996). It is often impossible to ascertain exactly the conditions determining the exposure in a specific case. A second problem is the need to include the variability of a broad range of workplace conditions. With respect to the second problem, which is the focus of the present thesis, sufficiently flexible methods for covering the wide range of possible exposure situations are required. To this end, the method "Scenario-based risk assessment" (SceBRA), which was developed for characterizing exposure to chemicals used in a variety of applications (Scheringer et al., 2001), has been adapted to

the assessment of occupational exposure to TRIC and PERC in metal degreasing and PERC in dry cleaning. Metal degreasing and dry cleaning are performed in highly variable settings, with metal parts of different size and shape and garments of different textile fibres, and with machines of different capacities and technological standard. Therefore, the variety of scenarios employed in the SceBRA method is suitable for characterizing these solvent applications.

The study is restricted to Germany, where the strictest legislation in Europe regulating the use of TRIC and PERC is in force and where data on machine technology and numbers as well as working conditions are available.

The objectives of this study are:

- To develop a suitable occupational exposure model for metal degreasing and dry cleaning.
- To quantify reliably exposure levels resulting from the use of TRIC and PERC in various metal-degreasing and dry-cleaning machines, ranging from highly emissive machines used in the 1950s and 1960s to hermetically closed machines used since 1990.
- To reflect the occupational exposure risk for the entire population of metal-degreasing and dry-cleaning workers in Germany.
- To demonstrate the effect of technology development and stricter legislation on the two dimensions of risk considered in SceBRA, namely the risk quotient, i.e. the ratio of airborne concentrations and an effect level, and the number of exposed workers.
- To illustrate which factors strongly influence the variability of occupational exposure in metal degreasing and dry cleaning.
- To indicate the risks remaining today.

- To show which factors have driven long-term technology development.
- To compare the deterministic SceBRA method with a statistical exposure assessment approach.

1.3 Structure

After an introduction in *Chapter 1* to the presently required risk assessment (according to TGD) for new substances, which shall be expanded according to the “White Paper” for new chemicals *and* old chemicals, *Chapter 2* describes the two chlorinated solvents TRIC and PERC for which the exposure assessment with the SceBRA method is carried out. In a first section, the physical and chemical properties of TRIC and PERC are summarized. This is followed by a literature review of the toxicological findings for both substances. In a third section, the applications of TRIC and PERC are shown for the time between the 1970s and today. Next, the development of the German domestic consumption of TRIC and PERC used in solvent applications is given for the last 20 years. Finally, the German regulations laying down the use of TRIC and PERC are introduced and the requirements for the application of TRIC and PERC in metal degreasing and dry cleaning are listed.

Chapter 3 describes the method and models used for the occupational exposure assessment. In a first part, details about the SceBRA method are given. Then, the system boundaries for the two case studies are established. In a third part, the mass-balance models used for the exposure assessment are introduced. In the fourth part, the definitions of the three different emission factors used to describe solvent emissions into the workplace are described. In the last section of *Chapter 3*, the limits of a deterministic exposure assessment approach in contrast to a statistical approach are depicted, and the uncertainties of exposure estimates in terms of model uncertainty, parameter variability, and parameter uncertainty are discussed.

Chapters 4 and 5 present the results of the two case studies, occupational exposure during the use of TRIC and PERC in metal degreasing and occupational exposure during the use of PERC in dry cleaning. These

chapters can be read independently of each other and, therefore, include some redundancies.

In *Chapter 4*, the occupational exposure assessment for the use of TRIC and PERC in metal-degreasing machines is performed. First, the technological development from fully emissive open-top machines to hermetically closed machines is described and the machine types investigated are defined. In a second part, possible and plausible exposure scenarios for metal degreasing are defined according to variations in the machine parameters, the three emission factors, and the workplace parameters; the number of exposed workers is estimated for different years according to machine numbers. In the third part of Chapter 4, the results of the occupational exposure assessment in metal degreasing are presented, starting with the dynamic and the long-term airborne concentrations, both for the near-field and the far-field, for a working day of 8 hours. Then, the numerous scenarios derived from suitable parameter combinations are depicted and the influence of the different input parameters on the long-term ambient concentration is discussed. Next, the different machine technologies are compared in terms of near-field and far-field long-term exposure; for selected years, the number of exposed workers is combined with the risk quotients of different machine types and sizes. Then, the near-field long-term air concentration results are compared to measurements in metal-degreasing facilities, and the results of a local sensitivity analysis are discussed. Lastly, first conclusions are drawn for the metal degreasing case study.

Chapter 5 contains the occupational exposure assessment of PERC used in dry-cleaning facilities. After a short introduction into dry cleaning, the technological development of vented machines to machines that release no exhaust air is described, and the machine generations investigated in this case study are defined. In a second part, suitable SceBRA scenarios are defined according to the variability in machine parameters, the three different emission factors, and the workplace parameters. The number of exposed workers is estimated according to machine numbers for different years. In the third part of Chapter 5, the results of the dry cleaning case study are presented and discussed. First, the dynamic and the long-term air concentrations in the near-field and the far-field of dry-cleaning machines and,

second, the systematic combination of all independent input parameters leading to the exposure scenarios, and the contribution of the different input parameters to the long-term concentration are discussed. Third, the four dry-cleaning machine generations are compared in terms of occupational exposure risk. Then, for the different machines that were in use in certain years, the risk quotients are weighted with the number of exposed workers both for the near-field and the far-field. Lastly, the calculated near-field and far-field long-term ambient concentrations are compared to exposure measurements. In the fourth part of Chapter 5, the SceBRA results are compared to results obtained in a statistical exposure assessment and the results of a global sensitivity analysis are discussed. At the end, first conclusions are drawn about the dry-cleaning results and about the strengths and limitations of the SceBRA method in comparison to a statistical approach. In *Chapter 6*, the metal degreasing and the dry cleaning case studies are compared and the most important results are summarized. This is followed by a recommendation about when and how the SceBRA method should be implemented in an exposure assessment. Finally, ideas for further application of the SceBRA method and further research needs are discussed.

Chapter 2

2 Chlorinated solvents TRIC and PERC

The chlorinated solvents TRIC and PERC are highly suitable for dissolving numerous organic acids, as well as a variety of other organic substances such as fats, oils, rubber, tars, and resins, and they have according to standard methods no flash point. These are perfect properties for their use as cleaning agents. Stabilized TRIC and PERC, as provided commercially, can be used in the presence of air, water, and light, in contact with common materials of construction, at temperatures up to about 120°C for TRIC and 140°C for PERC (Wacker-Chemie GmbH, 1990; Hickman, 1993), and with textiles, leather and fur. However, there has been great concern about adverse health effects caused by high exposure concentrations, mainly in the 1980s and early 1990s (Greim, 1996; Greim, 1997).

In the first part of this chapter, the physical and chemical properties of the two solvents are listed. In the second part, a literature review of toxicological studies is given. The third part shows how TRIC and PERC have been used over the last 40 years and where they are still in use today. The production process of TRIC and PERC and some economical data about solvent consumption in Germany are described in the fourth part. Finally, German regulations laying down the uses of TRIC and PERC as degreasing and cleaning agents in metal degreasing and dry cleaning are given.

2.1 Physical and chemical properties

Trichloroethylene, $\text{CHCl}=\text{CCl}_2$, TCE, commonly called TRIC, is a colorless, sweet smelling, volatile liquid, and a powerful solvent for a large number of natural and synthetic substances. It is non-flammable under conditions of recommended use. The most important reactions of TRIC are atmospheric oxidation and degradation by aluminum chloride. The autoxidation is catalyzed by free radicals and is greatly accelerated by elevated temperature and exposure to light, especially ultraviolet radiation. The oxidation products, hydrogen chloride, carbon oxides, phosgene, and dichloroacetyl chloride are acidic, and corrosive. All commercial grades of TRIC are stabilized against autoxidation and AlCl_3 -catalyzed degradation with acid acceptors such as amines, alcohols, epoxides, and metal stabilizers (McNeill, 1979; Ullmann, 1986b, Mertens, 1993).

Perchloroethylene, also called tetrachloroethylene, $\text{CCl}_2=\text{CCl}_2$, commonly referred to as PERC, is a colorless heavy liquid with a mild odor. It is the most stable of the chlorinated ethylenes and ethanes, having no flash point and requiring only minor amounts of stabilizers. Under ultraviolet radiation in the presence of air or oxygen, PERC undergoes autoxidation to trichloroacetyl chloride. These reactions are inhibited in commercial products by the addition of alkylamines, phenols, or morpholine derivatives as stabilizers (Ullmann, 1986a; Hickman, 1993).

Commercial grades of TRIC and PERC include a vapor degreasing grade; a dry-cleaning grade (only PERC), and an industrial grade for use in formulations. The various grades differ in the amount and type of added stabilizers. In Table 2.1, the physical and chemical properties of TRIC and PERC are summarized.

Table 2.1: Physical and chemical properties of TRIC and PERC (a: Broermann, 1991; b: McNeill, 1979; c: BUA, 1993; d: Ballschmiter et al., 1987; e: Wacker-Chemie GmbH, 1990; f: Verschueren, 1983; g: Roth and Weller, 2002; h: BUA, 1994).

Properties	TRIC	PERC
CAS no.	79-01-6	127-18-4
Molecular weight, g/mol	131.4 ^a	165.8 ^a
Melting point, °C	-73 to -88.0 ^a	-19 to -23.5 ^a
Boiling point at 1013 hPa, °C	86.7 ^b to 87.1 ^a	120.8 to 121.4 ^a
Density, kg/l	1.46 ^{a,b}	1.62 ^a
Vapor pressure, hPa at 20°C	77.2 – 78.0 ^a	18.6 – 19.0 ^a
Evaporation number (diethylether=1)	3.0 to 3.8 ^a	6.0 to 11 ^a
Flash point, °C according to DIN 51755/51758	non ^{b,c}	non ^d
Ignition temperature, °C	410 ^a	non ^a
Explosive mixture, vol%	7.9 to 90 ^a	non ^a
Diffusion coefficient in air at 1013 hPa and 25°C, m ² /h	0.073 ^e	0.067 ^e
Saturation concentration in air at 1013 hPa and 20°C, kg/m ³	0.415 ^f	0.126 ^f
Start of decomposition, °C	120 ^d	150 ^{d,e}
Threshold of odor, ppm	20 to 50 ^{a,f}	5 ^{d,e}
	40 to 100 ^g	20 to 40 ^g
Conversion factor (air) ppm into mg/m ³ at 20°C	5.46 ^c	6.89 ^h

2.2 Toxicology

2.2.1 Acute toxicity data for TRIC and PERC

Table 2.2 lists some acute toxicity data for several test species.

Table 2.2: Acute toxicity data (a: Smyth et al., 1969; b: Pozzani et al., 1959; c: Hayes et al., 1986; d: Tucker et al., 1982; e: Aviado et al., 1976; f: Dybing and Dybing, 1946; g: Siegel et al., 1971; h: Vernot et al., 1977; i: Bonnet et al., 1980; j: Kylin et al., 1962; k: Gradiski et al., 1978; l: Dupra et al., 1979; m: Friberg et al., 1953; n: ECETOC, 1999).

Acute toxicity:	TRIC	PERC
Oral LD ₅₀ rats, mg/kg body weight	7'183 ^a	2'629 ^b to 3'835 ^c
Oral LD ₅₀ mice, mg/kg body weight	2'400 ^d to 2'850 ^e	8'100 to 10'900 ^f
Inhalative LC ₅₀ rats, mg/m ³	4 h 12'500 ^g 1 h 26'300 ^h	6 h 28'250 ⁱ 8 h 34'200 ^b
Inhalative LC ₅₀ mice, mg/m ³	4 h 8'450 ^j	6 h 20'520 ^{k,l} 4 h 35'830 ^m
Inhalative LOEL wide range of animal species, ppm	n.d.	100 ⁿ

LD₅₀ dose resulting in 50% mortality
 LC₅₀ concentration resulting in 50% mortality
 LOEL: Lowest Observed Effect Level

For exposure of workers to PERC vapor with respect to neurotoxic symptoms and functional disturbance of liver, kidney or muscle tissue, a no-observed-effect level (NOEL) of 145 mg/m³ (21 ppm) was deduced from a study of employees in dry-cleaning facilities (time-weighted concentrations for an average of 6.4 years occupational exposure) (BUA, 1994). Another study carried out by the German Federal Environmental Office (UBA) deduced a NOEL for inhalation exposure to PERC (4 h/day on 4 consecutive days) on 28 test persons of between 68.9 and 344.5 mg/m³ (10 and 50 ppm) (BUA, 1994).

2.2.2 TRIC

TRIC is acutely toxic, primarily because it affects the central nervous system. Exposure to high vapor concentrations causes headache, vertigo, tremors, nausea and vomiting, fatigue, intoxication, unconsciousness, and even death. Exposure occurs almost exclusively by vapor inhalation, which is followed by rapid absorption into the bloodstream. At concentrations of 150–186 ppm, 51–

71% of the TRIC inhaled is absorbed (McNeill, 1979). Metabolic breakdown can occur via oxidation or reduction. So far only the oxidative metabolism has been described with kinetic data. There, TRIC is oxidized to chloral hydrate, followed by reduction to trichloroethanol, which is partly further oxidized to trichloroacetic acid (TCA) (McNeill, 1979; Mertens, 1993, Greim, 1996). Anesthetic effects have been reported at concentrations of 400 ppm after 20 min exposure (Mertens, 1993).

Early toxicological evaluations classified TRIC as a chemical of low toxicity. Acute intoxication was a rare event and only occasionally fatal (Hargarten et al., 1961). In 1976, the U.S. National Cancer Institute (NCI) published the results of a bioassay of TRIC administered in high doses by gavage, which indicated a tumorigenic potential in mice (National Cancer Institute, 1976). The technical samples of TRIC used in these experiments were stabilized with 0.1% epichlorohydrin and 0.2% epoxybutane, which are both mutagenic and carcinogenic compounds (Henschler et al., 1977). Additional carcinogenicity tests revealed negative or equivocal results with non-epoxide stabilized TRIC (Henschler et al., 1980; Henschler et al., 1984). However, new long-term gavage and inhalation studies with TRIC showed a low, but significant, increase in renal cell tumors in rats (Maltoni et al., 1988). In vitro tests of genotoxicity showed a weak mutagenic effect of high concentrations after metabolic activation (Greim, 1996). Inhalation studies of reproduction toxicity at foetotoxic levels (above 100 ppm) gave no indication of a teratogenic effect (Henschler, 1994, BUA, 1999).

Several epidemiological studies of exposed workers were negative in terms of carcinogenic potential (Tola et al., 1980; Barret et al., 1984; Shindell and Ulrich, 1985; ENSR, 1990; Spirtas et al., 1991; Stewart et al., 1991; Axelson et al., 1994; McLaughlin and Blot, 1997). However, with one exception (Axelson et al., 1994), these studies analyzed mortality and not morbidity, which is critical because the majority of kidney cancers are curable. In contrast, Henschler et al. (1995) reported that, of all types in their analysis, the incidence of kidney cancer was statistically elevated among a group of 169 men exposed to high levels of TRIC (much in excess of the common threshold limit value (TLV) of 100 ppm) for at least 1 year between 1956 and 1975.

Henschler et al. (1995) suggest that exposure to high concentrations of TRIC over prolonged periods of time causes renal tumors in humans. These new findings are in contrast to a report by the European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC) about human carcinogenic hazards (ECETOC, 1994) and a review article about several epidemiology studies of TRIC and the risk of renal-cell cancer (McLaughlin and Blot, 1997). Both studies concluded that exposure to TRIC does not present a carcinogenic hazard to man.

In a study of carcinogenic potential in humans, the International Agency for Research on Cancer (IARC) reviewed the data of three large cohort studies in the U.S. (Spirtas et al., 1991), Sweden (Axelson et al., 1994), and Finland (Anttila et al., 1995). They reasoned that: "There is limited evidence in humans for the carcinogenicity of trichloroethylene" (IARC, 1995b). A similar conclusion was drawn in a review article by Wartenberg et al. (2000), collecting information about 80 published papers and letters on cancer epidemiology of people exposed to TRIC. Wartenberg et al. strongly suggested an association of TRIC exposure with kidney, liver cancers, and non-Hodgins's lymphoma. They stated, however, that since few studies isolate TRIC exposure, results are likely confounded by exposure to other solvents and other risk factors. Therefore, they recommended further studies to elucidate the observed cancer risk (Wartenberg et al., 2000).

2.2.3 PERC

Exposure to PERC occurs almost exclusively by vapor inhalation, followed by absorption into the bloodstream. Only a very small amount of the absorbed PERC is metabolized and eliminated through the kidneys. Metabolic breakdown occurs by oxidation to TCA and oxalic acid. Approximately 70% of the inhaled PERC is exhaled unaltered (Keil, 1979; BUA, 1994; ECETOC, 1999). Overexposure to PERC by inhalation affects the central nervous system, the liver, and the kidneys. Dizziness, headache, confusion, nausea, and eye and mucous tissue irritation occur during prolonged exposure to vapor concentrations of 200 ppm (Hickman, 1993). It is estimated that concentrations of 1500 ppm cause loss of consciousness in less than 30 min

(Keil, 1979). Anesthetic effects have been reported at concentrations of 280 ppm after a 2-h exposure (Keil, 1979). Reversible central nervous system effects are observed following acute exposure to PERC at concentrations of 100 ppm and above (BUA, 1994).

Studies of the carcinogenic potential of PERC showed an increase in spontaneous tumor rates in long-term inhalation studies carried out with mice and rats. In mice, a significant increase in hepatocellular carcinomas was observed, while in rats the frequency of mononuclear cell leukemia was increased, although there was no clear dose dependency and the controls had a high rate of tumors as well. In addition, rats showed signs of damage to the renal tubules, which can be a pathogenic preliminary stage of tumor formation. In various in vitro mutagenicity tests carried out with pure PERC, negative results were obtained with both eukaryotic and prokaryotic organisms. Studies of reproduction toxicity with mice, rats and rabbits, involving inhalation exposure to PERC, provided no indication of an embryotoxic or teratogenic effect (BUA, 1994; ECETOC, 1999).

The BUA (1994) and ECETOC (1999) reports state that the available data on carcinogenic effects of PERC, obtained from animal experiments, seem to result from species-specific mechanisms and are, therefore, probably not applicable to humans (BUA, 1994; ECETOC, 1999). Kinetic models have been developed for PERC that describe general toxicological risk in terms of total metabolized dose and extrapolate between species by using species-specific physiology. According to the ECETOC report (1999), none of these models provide a full description of the pharmacokinetic behavior of PERC and, consequently, the carcinogenic or other toxicological risks to man are not fully predictable. The ECETOC report (1999) states further that the three cohort mortality studies of dry-cleaning workers, which provide the most relevant data for assessing the relationship between exposure to PERC and cancer risk (Blair et al., 1990; Ruder et al., 1994; Anttila et al., 1995), are insufficient in both their design and outcome to demonstrate a relationship between exposure to PERC and occurrence of cancer in humans (ECETOC, 1999). Further studies showed no increased frequency of liver or kidney cancer in humans (Weiss, 1995; Lynge et al., 1995).

In contrast to these studies and to the ECETOC report of 1999, an IARC review (IARC, 1995a) and an update of a mortality study in dry cleaning (Ruder et al., 2001) state that the evidence for cervical and esophageal cancer has become stronger.

2.3 Use of TRIC and PERC

In the 1970s, the main fields of application of TRIC were metal degreasing, degreasing of textiles (wool, cotton, silk, fur, and leather), and the extraction of oil fruits, coffee, resins, bones, glue, tobacco pressure residues, and residues of carcass. Additionally, TRIC was used as a spot remover and as a solvent in the coating industry (hot and cold dip coating). Smaller applications were the drying of wood products, production of soap, dehydration of alcohol, and use as a solvent for unvulcanized rubber, a refrigerating medium, and a cleaning agent in the optical industry (Hargarten et al., 1961; Ullmann, 1975c; Mertens, 1993). In the field of human and veterinary medicine, TRIC was used as a general anesthetic and analgesic and as a disinfectant for surgical instruments (Hargarten et al., 1961; Broermann, 1991).

The major applications of PERC in the 1970s were in dry cleaning, in vapor degreasing and cold cleaning of metals, and also, to some extent, in textile processing and finishing, as a chemical intermediate in the manufacture of several chlorofluorocarbons (CFCs), as an extraction solvent for carcasses, and in flaying houses (Ullmann, 1975b; Keil, 1979). In the field of human and veterinary medicine, PERC was used as an anthelminticum (Broermann, 1991; BUA, 1994; Niemann, 1998).

For the two main applications of TRIC and PERC, metal degreasing and dry cleaning, the domestic consumption in Germany (only fresh solvent) since the 1970s is given in Tables 2.3 and 2.4.

Table 2.3: Uses of the domestically produced “fresh” TRIC in Germany (a: Atri, 1985; b: BUA, 1993; c: BUA, 1999; d: Scholl et al., 1996; e: Adams, 1997; f: Nader, 2001c).

Year	Metal degreasing	Dry cleaning	Other uses
1970s	65-80% ^a	2-20% ^a	10-15% ^a
1986	90% ^b	-- ^b	10% ^b
1992	66% ^c	-- ^c	34% (21% adhesives and plastic processing, 2% varnish removal and paint stripping, 2% as process solvent) ^d
1994	68% ^d	-- ^d	32% ^d
1996	45% ^e	-- ^e	55% (24% adhesives and coatings) ^e
1999	16% ^f	-- ^f	84% ^f

Table 2.4: Uses of the domestically produced “fresh” PERC in Germany (a: Atri, 1985; b: Keil, 1979; c: Nolte and Joas, 1992; d: Niemann, 1998; e: Scholl et al., 1996; f: Adams, 1997).

Year	Metal degreasing	Dry cleaning	Other uses
1970s	~ 60-70% ^a	~ 20-30% ^a	~ 10-20% ^a
1976	13% ^b	66% ^b	21% (13% textile fabrication, 3% FCKW production) ^b
1986	60-64% ^c	32-36% ^c	4% electronics industry ^c
1989	~ 60-70% ^d	~ 20-30% ^d	~ 10% ^d
1992	68% ^e	16% ^e	16% (< 1% varnish removal and paint stripping) ^e
1994	66% ^e	n.d.	n.d.
1996	71% ^f	26% ^f	3% ^f

Today, the main uses of TRIC are metal degreasing, surface coating, and bitumen extraction in asphalt laboratories (Nader, 2001c). Since the 2nd BImSchV of 1986, the use of TRIC in dry cleaning, textile finishing and extraction has been banned (BImSchV, 1986). PERC is mainly used in metal degreasing (over 70%) and its second major application is in dry cleaning.

2.4 Production and economical data for Germany

The first synthesis of PERC was by Faraday in 1821 by thermal decomposition of hexachloroethane (Ullmann, 1975b; Hickman, 1993). TRIC was first prepared in 1864 by Fischer (Henschler et al., 1995). TRIC and PERC are typically produced as co-products by chlorination, oxychlorination and dehydrochlorination reactions of hydrocarbons or partially chlorinated hydrocarbons, and chlorine (further information on the production processes can be found in Appendix A.1) (Hickman, 1993; ECETOC, 1999).

Approximately 70% of the TRIC and PERC production volume is used as intermediates in the chemical and pharmaceutical industries; the remaining 30% are used as solvents. About 90% of the solvent is distributed via intermediate trade and only about 10% sold directly (Nader, 1993). In Figure 2.1, the sales figures for freshly produced TRIC and PERC used as solvents are shown for the Federal Republic of Germany (until 1991 only former Western Germany). Consumption of TRIC and PERC as solvents has decreased by over 90% since 1982. This is mainly due to changes in German environmental legislation, new non-venting closed-loop cleaning technology, rationalization, automatization, and replacement of TRIC and PERC by non-chlorinated solvents.

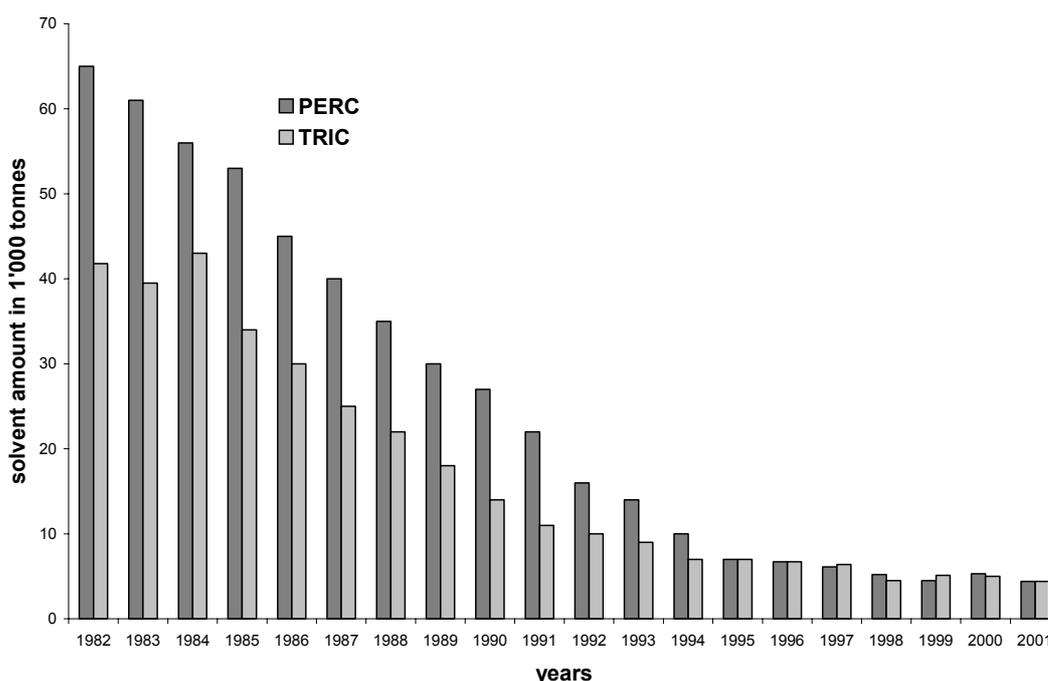


Figure 2.1: Consumption of freshly produced TRIC and PERC used as solvent in Germany (before 1992 only former Western Germany) (Nader, 1993; BUA, 1993; Nader, 2002).

2.5 German regulations

The most relevant German regulations covering the use of TRIC and PERC and, therefore, occupational exposure, are the German 2nd Federal Immission Protection Directive (“Zweite Bundes-Immissionsschutzverordnung”: 2nd BImSchV), starting with the 2nd BImSchV of 1974 (only for dry cleaning) (BImSchV, 1974), the 2nd BImSchV of 1986, the amended 2nd BImSchV of 1990, and the last amendment of the 2nd BImSchV 1990 in 2001. In the 2nd BImSchV of 1986, the 2nd BImSchV of 1990, and the revised version of 2001, the chemicals to be used in different applications are laid down together with technological standards for dry-cleaning and metal-degreasing equipments.

2.5.1 2nd BImSchV of 1986

The 2nd BImSchV enacted on 21 April 1986 regulated all surface-treatments (cleaning, greasing and degreasing, coating and coating removal, and surface

drying), dry-cleaning, textile-finishing, and extraction equipments using halogenated solvents or mixtures of solvents containing more than 1% of halogenated solvents that, according to §4 of the Federal Clean Air Act (“Bundes-Immissionsschutzgesetz”: BImSchG), required no permit.

Surface-treatment equipments

In this regulation, emissions were regulated for the first time. Equipments without exhaust systems and a solvent amount of up to 500 kg were not allowed to emit over 0.5 kg/h. For solvent amounts between 500 and 1500 kg, emissions were restricted to below 0.1% per hour of the solvent used. Equipments with solvent amounts above 1500 kg were restricted to releases of up to 1.5 kg/h. For devices with exhaust systems, the airborne concentration in the undiluted exhaust air was limited to a maximum of 200 mg/m³ for exhaust air volumes below 500 m³/h. For exhaust air volumes above 500 m³/h, a maximum of 100 mg/m³ was set. The use of up to 10-liter cold-cleaning equipments without exhaust air was not covered by the 2nd BImSchV of 1986. TRIC was only permitted when used in closed devices with exhaust air (BImSchV, 1986).

Dry-cleaning and textile-finishing equipments

For dry cleaning and textile finishing, equipments with and without exhaust systems were distinguished. Equipments without exhaust systems had to fulfill requirements relating to airborne concentrations in the drying air. The concentration in the drying air entering the cylinder was limited to 15 g/m³ and in the cylinder to 25 g/m³. For equipments already in use when the 2nd BImSchV 1986 was enacted, other limits were set: the maximum concentration in the drying air entering the cylinder was 28 g/m³, and in the cylinder not more than 42 g/m³. For devices with exhaust systems, airborne concentrations in the exhaust air were also specified. These were 200 mg/m³ for equipments with capacities of up to 30 kg and 100 mg/m³ for larger equipments. In all devices, the temperature of the treated textiles had to be above 30°C. The use of TRIC was forbidden in dry-cleaning, textile-finishing, and extraction devices (BImSchV, 1986).

2.5.2 2nd BImSchV of 1990

The amended 2nd BImSchV enacted on 20 December 1990, regulates all surface-treatments (cleaning, greasing and degreasing, coating and coating removal, and surface drying), dry-cleaning, textile-finishing, and extraction equipments using halogenated solvents or mixtures of solvents containing more than 1% of halogenated solvents that, according to §4 of the Federal Clean Air Act (BImSchG), require no permit.

The revised 2nd BImSchV of 1990 requires for all applications that loading and unloading of tanks be done according to the state of the art (e.g., gas-displacement device), and that chlorinated solvents and waste be transported and stored in closed containers with safety collection trays. Equipments are to be placed above metal safety troughs to prevent solvent leaks reaching the ground or the ground water. The airborne concentration in adjacent rooms is limited to 0.1 mg/m³. To this end, diffusion barriers are required where necessary. The use of TRIC is still forbidden in dry-cleaning, textile-finishing, and extraction equipments and the exception for TRIC used in surface-treatment equipments is removed. Transition arrangements ended on 31 December 1994.

Surface-treatment equipments

For surface treatment, closed or enclosed equipments with adsorption devices, concentration-monitoring devices for the unloading zone of the machine, and an automatic door interlock are laid down. The airborne concentration in the undiluted exhaust air is limited to 20 mg/m³. At the end of the drying step, the maximum concentration allowed in the cleaning chamber is defined as 1 g/m³. Cleaning chamber concentrations are to be measured continuously and an automatic lock installed that allows release of the treated parts when the concentration is below the required threshold. The special provision for small cold-cleaning equipments was suspended after the transition arrangements, which ended on 31 December 1992. From then on, all small equipments, basins, bins, vessels, etc. are considered as *equipments* that must comply with the amended 2nd BImSchV of 1990 (BImSchV, 1990).

Dry-cleaning and textile-finishing equipments

For dry-cleaning and textile-manufacturing installations, closed or enclosed equipments with adsorption devices, concentration-monitoring devices for the cylinder concentration, and an automatic door interlock are required. Cylinder concentrations are to be measured continuously and an automatic lock in use that allows release of the textiles only when the concentration is below the threshold of 2 g/m^3 . The temperature of the treated textiles have to be above 35°C at the end of the drying step. The airborne concentration in the undiluted exhaust air is limited to 20 mg/m^3 (BlmSchV, 1990).

2.5.3 Amendment of 2nd BlmSchV 1990 in 2001

The amendment of the 2nd BlmSchV 1990 enacted on 21 August 2001 implements the new directives of the European Parliament 1999/33/EG from 10 May 1999 and 2000/33/EG from 25 April 2000 (BlmSchV, 2001). In the following only the alterations to the 2nd BlmSchV 1990 enacted in 1990 are listed.

All surface-treatments, dry-cleaning, textile-finishing, and extraction equipments using halogenated solvents or mixtures of solvents containing more than 1% of halogenated solvents require official approval.

Substances classified as carcinogenic, mutagenic, or foetotoxic substances with the following R-sentences R 45, R 46, R 49, R 60 or R 61 have to be replaced if possible with less harmful substances. They do not need to be replaced if they are used in *surface treatment equipments* with hermetically-closed solvent tanks and pipes, which are operated under vacuum and for which the consumption is less than 1 metric ton per year. For these substances the airborne concentration in the undiluted exhaust air is limited to 2 mg/m^3 .

Transition arrangements for equipments installed before 25 August 2001 ended on 31 October 2007.

2.5.4 Toxicological classifications

The MAK value (“maximale Arbeitsplatz-Konzentration”: maximum workplace concentration) is defined as the maximum concentration in the workplace air of a chemical substance that generally has no known adverse effects on the health of employees and causes no unreasonable annoyance, even when the person is repeatedly exposed during long periods, given a 40-hour working week. The MAK is given as a time-weighted average concentration over an 8-h working period (TWA) (DFG, 2001). The historical development of MAK values for TRIC and PERC is shown in Table 2.5.

Table 2.5: Historical development of German MAK values for TRIC and PERC (Greim, 2002).

Year	TRIC MAK value, ppm (g/m ³)	PERC MAK value, ppm (g/m ³)
1958	200 (1050)	200 (1350)
1961	100 (520)	100 (690)
1970	50 (270)	
1982		50 (345)

In Germany, the DFG commission (“Senatskommission der Deutschen Forschungsgemeinschaft”) evaluates occupational health hazards. New findings and prospective changes, if required from the scientific point of view, are published in “Occupational Toxicants” (“Toxikologisch-arbeitsmedizinische Begründung von MAK-Werten”), and are announced each year in the “List of MAK and BAT values”. Changes have then to be accepted by the committee for hazardous chemicals (“Ausschuss für Gefahrstoffe”: AGS).

Presently, the DFG commission is recommending a reclassification of both TRIC and PERC in accordance with new toxicological findings. The DFG commission suggests classifying TRIC as a carcinogen of category 1 (cancer category 1), which would require suspension of the pregnancy group and the MAK value, as carcinogens have no MAK values (Greim, 1996; Greim, 2000; Greim, 2001). For PERC, the DFG recommends suspending the MAK value until toxicological studies with humans determine whether genotoxic metabolites of the reductive metabolism occur at low concentrations (Greim, 1997).

In Table 2.6, the current toxicological classifications for occupational exposure and the suggested changes by the DFG commission indicated as “DFG-classification” are listed for Germany.

Table 2.6: Current toxicological classification of the European Union, Germany, and suggested changes by the DFG commission (a: Roth and Weller, 2002; b: 67/548/EEC, 2002; c: TRGS 900, 2002; d: DFG, 2001; e: Greim, 1997; f: Greim, 1996; g: TRGS 905, 2002).

	TRIC	PERC
Labeling	Xn ^a	Xn ^a
R-sentence	R45 ^b	R40 ^a
MAK (8-h TWA), ppm (mg/m ³)	50 (270) ^c	50 (345) ^c
- Germany	— ^d	— ^e
- DFG recommendation		
Cancer category		
- European Union	2 ^b	3 ^b
- Germany	*	3 ^g
- DFG recommendation	1 ^{a,f}	3
Peak limitation category		
- Germany	IV ^{a,c}	IV ^{a,c}
- DFG recommendation	— ^d	II,1 ^d
Pregnancy risk group		
- Germany	C ^a	C ^a
- DFG recommendation	— ^d	C ^d

* not indicated in TRGS 900 and TRGS 905

Xn: harmful to health

R40: Limited evidence of carcinogenic effect

R45: May cause cancer

IV: at no 15-min interval exposure exceeding four times MAK

II,1: max. 4 times per shift average value of two times MAK over 30-min interval

Cancer cat. 1: substance known to be carcinogenic

Cancer cat. 2: suspected of having carcinogenic potential to humans

Cancer cat. 3: possible carcinogenic effect to humans

C: no reason to fear a risk of damage to the embryo or fetus when MAK values are observed

Chapter 3

3 Methods and models

An exposure assessment is essential to evaluate the risk of occupational exposure to a chemical. As the available data describing human exposure to chemicals are of varying quality and scope (Northage and Marquat, 2001; Money and Margary, 2002), modelling is needed (Nicas and Jayjock, 2002). Models used in exposure assessments can be classified into two categories: empiric models, which use measured exposure data or epidemiological data, and mechanistic models, which predict exposure based on emission data and estimates.

Chemicals such as solvents, which are used in many different applications and with different application techniques, require a big dataset of exposure measurements for an empiric model. Therefore, mechanistic models are used to distinguish between the different applications and application techniques. The Scenario-Based Risk Assessment (SceBRA) method makes use of a large set of scenarios describing typical occupational exposure situations. The first part of this chapter introduces the SceBRA method, followed by the system boundaries for the occupational exposure assessment of TRIC and PERC used in metal degreasing and dry cleaning. A general introduction to the use of mass balance models (one-box model) is given in the third part, together with the two-box model distinguishing near-field and far-field exposition that is used in this study. In a fourth section, the different emission factors characterizing the variability in the release of chemicals from intermittent sources are described. In the last part of this chapter, the uncertainties of exposure estimates in terms of model uncertainty, parameter

variability, and parameter uncertainty are discussed. It is also shown for which case study a statistical exposure assessment is feasible.

3.1 Scenario-Based Risk Assessment (SceBRA)

The SceBRA method, originally developed by T. Vögl, is intended to describe the potential health risk of exposure to solvents and solvent-containing products during the various stages of product history, such as production, formulation, transport, and end-use (Vögl, 1999). SceBRA investigates a variety of exposure scenarios. The resulting risk is characterized by two indicators: (i) the risk quotient, r , which is the ratio of concentration and effect level, and (ii) the number of exposed workers, N (Scheringer et al., 2001).

SceBRA was developed in connection with the problem of product liability, which is of particular importance for manufacturers of chemicals and for insurance companies. Accordingly, the method is intended to cover a broad and rather diverse number of possible applications of solvents or solvent-containing products. In other words, SceBRA is a screening method that gives an overview and a first estimate of the number and kind of critical applications of a chemical. The main goals of SceBRA are to calculate the risk quotients and numbers of exposed individuals in the different scenarios, to compare the potential risks posed by different scenarios for a particular chemical, and to identify scenarios requiring a more specific assessment.

A similar method was developed by the United Kingdom Health and Safety Executive in the 1990s on the basis of measured exposure levels classified according to typical exposure scenarios (Friar, 1998). These exposure scenarios were defined according to use patterns and control patterns, as well as to the physicochemical properties of the substances. The “Estimation and Assessment of Substance Exposure” model (EASE) allows a structured access to the estimation of inhalative exposure and is applicable to a large variety of workplace situations (Bredendiek-Kämper, 2001). The main difference between the two models is that EASE is based on scenario measurements, whereas SceBRA is based on mass balance models to

estimate the airborne concentration after solvent emission. A further distinction is that SceBRA estimates how many people are exposed in certain scenarios.

In the present study, SceBRA was adapted to the industrial use of solvents to depict the occupational exposure in dry cleaning and metal degreasing. An exposure assessment is done in three steps: (i) analysis of machine technology; (ii) definition of scenarios; (iii) calculation of potential risk and number of exposed workers.

In the first step, machine technologies are analyzed for emission sources that emit into the surrounding workplace. Emissions occurring continuously over the whole working day and emissions occurring at certain periods of the degreasing and cleaning cycle are distinguished. In the second step, representative exposure scenarios are defined for all relevant machine sizes. Each scenario is characterized by a set of typical parameters, namely machine parameters, emission factors and workplace parameters. By systematically combining independent parameters, a broad spectrum of possible exposure situations is investigated. These scenarios represent idealized situations of solvent exposure during metal degreasing and dry cleaning. In the third step, the possible risk is quantified for all scenarios in terms of airborne concentration divided by a predicted no effect level, which results in the risk quotient and the number of exposed individuals.

In the present thesis, the SceBRA scenarios are defined with the aim of showing the differences in occupational health risk over a time period of several decades. For different years, only potential exposure scenarios are selected.

3.2 System boundaries

The occupational exposure to TRIC and PERC, used as cleaning solvents in industrial metal-degreasing and dry-cleaning facilities, is investigated over several decades with changing legislation and application technology. Germany is taken as a model country, because German legislation lays down not only the solvents to be used, but also technology standards for metal-

degreasing and dry cleaning devices (see also Chapter 2.5). In this respect, the German legislation is one of the strictest worldwide and can be taken as a standard for other countries that still use older technologies.

Here, only inhalative exposure to TRIC and PERC is investigated, as this is by far the major route of occupational exposure (see Chapter 2.2). Furthermore, only technology changes influencing the airborne concentration at the workplace and, therefore, the inhalative exposure are taken into consideration. The inhalative exposure is calculated with mass balance models for the vicinity of the machine (near-field) where the machine operators are present, as well as for the far-field, where other work is carried out. The workplace volume is divided into a fictitious working box with a volume of 100 m³ and a surrounding rest volume where other work not related to the degreasing and dry cleaning machines is done. According to Gmehling et al. (1989), a fictitious near-field of 100 m³ generates realistic results. To characterize the risk of exposure, information from the exposure assessment is combined with toxicity information to determine whether an emission could lead to an exposure above a particular predicted no effect level. Here, the German MAK (“maximale Arbeitsplatz-Konzentration”: maximum workplace concentration) values, corresponding to TLVs (threshold limit values), are taken. The MAK value is defined as the minimum concentration of a chemical substance (as gas, vapor or particulate matter) in the workplace air that generally has no known adverse effects on the health of the employee or causes no unreasonable annoyance even when the person is repeatedly exposed during long periods, given a 40-h working week (DFG, 2001). The airborne concentration, C , calculated as TWA for an 8-h working day, i.e. long-term concentration, is compared to the German MAK value, which leads to the risk quotient, r , given as:

$$r = \frac{C}{\text{MAK}} \quad (3.1)$$

The MAK values of 50 ppm (345 mg/m³) for PERC and 50 ppm (270 mg/m³) for TRIC have not been changed since 1982 for PERC or since 1970 for TRIC (BUA, 1994; BUA, 1993) (for further information, see Chapter 2.5). In order to

have a common basis for comparison of the different machine technologies, the current MAK values are used for all machine types and generations. For SceBRA calculations, a normal working day with the metal-degreasing and dry-cleaning devices continuously in use is assumed. Maintenance work such as filling of tanks, waste removal, desorption of carbon filters, cleaning of the machines or parts of the machines (such as valves, pump, still, condenser, or lint trap) are not taken into account. Additionally, good working practice is assumed, as there is few possibilities to abuse present-day metal-degreasing and dry-cleaning machines. For older machines, however, working practice in some instances may have differed significantly from good working practice. It has been reported that, under time pressure, cleaned parts and drycleaned textiles were taken out before they were entirely dry (Mannheim et al., 1979; Nolte and Joas, 1992; Leisewitz and Schwarz, 1994). However, because of lack of data, it was not possible to include poor working practice for older machines.

In Figure 3.1, the system boundaries of the SceBRA method for the industrial application of TRIC and PERC in metal degreasing and dry cleaning are shown.

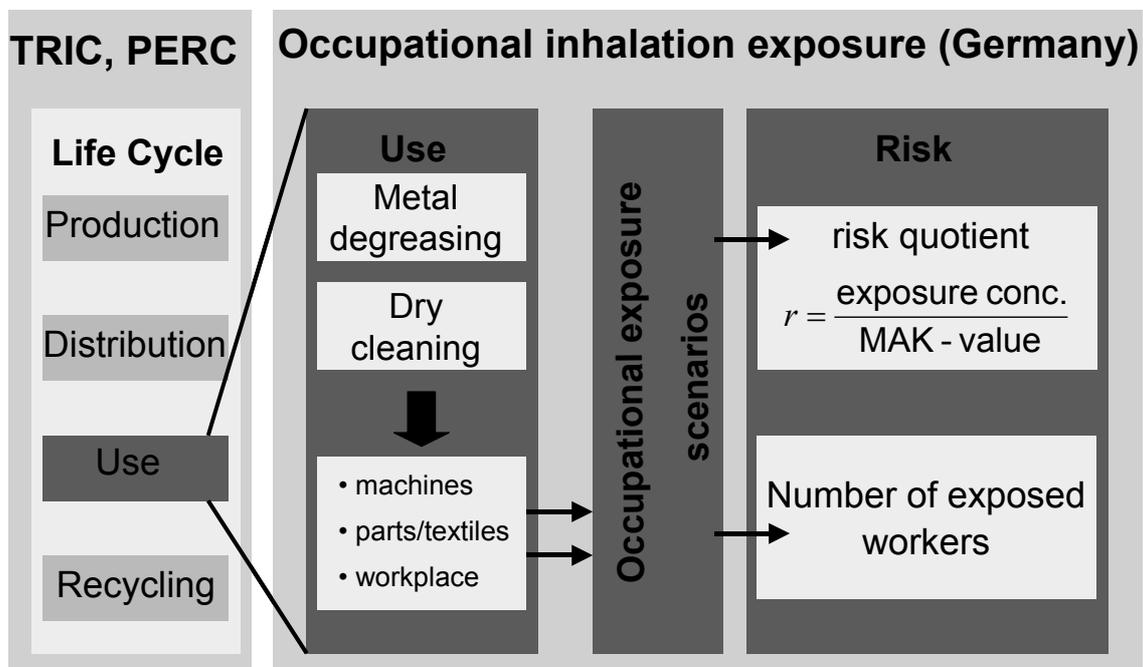


Figure 3.1: System boundaries of the SceBRA method for industrial application of TRIC and PERC in metal degreasing and dry cleaning.

3.3 Mass balance models

Very few measurements have been reported in the past and workplace exposure data vary markedly in quality (Northage and Marquat, 2001; Money and Margary, 2002). In addition, the available data often lack a detailed description of the machine technology and the surrounding workplace. Thus, it is necessary to use mathematical models for the exposure assessment of metal-degreasing and dry cleaning facilities (Nicas and Jayjock, 2002). Mathematical models used in exposure assessment can be classified into two broad categories: models that predict exposure (in units of concentration multiplied by time) and models that predict concentration (in units of mass per volume) (CRAHAP, 1994). Although concentration (or air-quality) models are not true exposure models, they can be combined with information on human time-activity patterns to estimate exposures.

Here the airborne concentrations are simulated with indoor air-quality models based on mass balance equations that attempt to account for incoming and outgoing material. Such models are used by the U.S. Environmental Protection Agency (EPA) for evaluating the risks associated with manufacturing, processing, use, and disposal of existing chemical substances (Matthiessen, 1986) or for assessing potential and unacceptable human health and environmental risks of new chemical substances prior to commercialization (Fehrenbacher and Hummel, 1996).

3.3.1 One-box model

A one-box model is adequate for many situations. These include complete mixing within the space being modeled, uniform source emissions throughout the space and long time-scale modeling. If these criteria are met, the one-box approach can often give quantitatively acceptable results (Jayjock, 1988). The mass balance equation for a one-box model reads (Braun, 1993):

$$\frac{dC(t)}{dt} = \frac{\dot{E}}{V} - k \cdot C(t) \quad (3.2)$$

where $C(t)$ is the pollutant concentration in air (g/m^3), t is time (h), \dot{E} is the emission rate (g/h), V the box volume (m^3), and k the overall loss rate constant (h^{-1}). If all production and loss mechanisms are constant with time, Equation (3.2) may be integrated to give:

$$C(t) = C^0 \cdot e^{-kt} + \frac{\dot{E}}{V \cdot k} \cdot (1 - e^{-kt}) \quad (3.3)$$

where C^0 (g/m^3) is the background concentration of the pollutant at time $t = 0$ and $\dot{E}/(V \cdot k) = C^\infty$ is the steady-state concentration.

In many cases, however, a simple one-box approach is inadequate. For room volumes larger than 500 m^3 , which are common in industrial metal-degreasing and dry cleaning facilities, complete mixing is often not fulfilled (Gmehling et al., 1989). Therefore, some studies have recommended the use of mixing factors to account for non-complete mixing (Drivas et al., 1972; Matthiessen, 1986; Jayjock, 1988). Another approach is to use a two-compartment mass balance model (Furtaw et al., 1996; Cherrie et al., 1996; Keil, 1998; Cherrie, 1999; Keil, 2000). Nicas discusses the advantages of two-box models versus the use of mixing factors (Nicas, 1996). In the present study, a two-box model instead of a one-box model with a mixing factor is used because of its better spatial resolution. By this means, occupational exposures in the vicinity of the source (near-field) and further away (far-field) can be discerned.

3.3.2 Two-box model

In a two-box model, the workplace is considered to consist of two well-mixed boxes, each box communicating with the adjacent one via transfer of air and pollutant. For each box, the model assumes a mass balance for air flowing between the boxes. This results in two coupled linear differential equations (see Equation (3.4)). A two-box model may still be insufficient to describe complex situations such as the breathing-zone concentration during spray painting. Under these conditions, additional boxes may be introduced to account for the complexity resulting in sequential box models (Haberlin and Heinsohn, 1993) or computational fluid dynamic models may be applied

(Nicholson et al., 2000; Flynn and Sills, 2000). However, the need for adequate measurements or estimates of the transfer coefficients preclude the use of full, multi-box models for many problems of practical interest (Ryan et al., 1988). Several studies have compared concentration estimates from simple one- and two-box models with results from more complex models (Keil, 2000; Feigley et al., 2002).

In this study, a two-box mass balance model is used to calculate the occupational airborne concentrations for the near-field and the far-field of metal-degreasing and dry cleaning devices (see Figure 3.2). In the simplest case, there is a constant mass flow \dot{E}_A (g/h) from the machine into the fictitious inner box A. The air exchange between box A with volume V_A (m³) and concentration C_A (g/m³) and box B with volume V_B (m³) and concentration C_B (g/m³) is given by the exchange rates k_A (h⁻¹) and k_B (h⁻¹). k_B and k_A are related by $k_B = \frac{V_A}{V_B} \cdot k_A$ as the airflow into and out of box A has to be the same.

The total room volume V is the sum of V_A and V_B . For the air exchange of box B with the environment, denoted by k_L (h⁻¹), it is assumed that the background concentration C_{air} (g/m³) of the fresh air can be neglected (typical background concentrations in urban areas in Germany are between 5 and 15 µg/m³ for TRIC (BUA, 1993) and between 0.1 and 7 µg/m³ for PERC (CEFIC, 1984a)). Furthermore, it is appropriate to assume total mixing within the two boxes. Firstly, molecular mass is not a factor that leads to separation in ordinary indoor conditions (i.e., radon with an atomic mass of 222 g/mol is easily distributed through buildings and in the outdoor air) (Nazaroff, 2001). Secondly, Jayjock (1994) reported that density fluctuations can be neglected for concentrations below 150 ppm (threefold MAK value).

Additional factors that can be neglected are: (i) sorption and desorption of solvent molecules to different materials (i.e., walls and carpets), because a steady state of sorption and desorption is reached in running facilities (Meininghaus et al., 2000; Hürlimann, 2001); (ii) diffusion through walls and ceilings, as this is negligible compared with the drag-out via exhaust systems (Meininghaus et al., 2000; Hürlimann, 2001); (iii) degradation of TRIC and PERC in the workplace environment (Hürlimann, 2001). Under these assumptions, the mass balance equations for the two boxes are:

$$\begin{aligned}\frac{dC_A}{dt} &= \frac{\dot{E}_A}{V_A} - C_A \cdot k_A + C_B \cdot \frac{V_B}{V_A} \cdot k_B \\ \frac{dC_B}{dt} &= C_A \cdot \frac{V_A}{V_B} \cdot k_A - C_B \cdot (k_B + k_L)\end{aligned}\quad (3.4)$$

Equation 3.4 represents a system of two coupled inhomogeneous first-order differential equations that can be solved for $C_A(t)$ and $C_B(t)$. The solution is given in Appendix B.1.

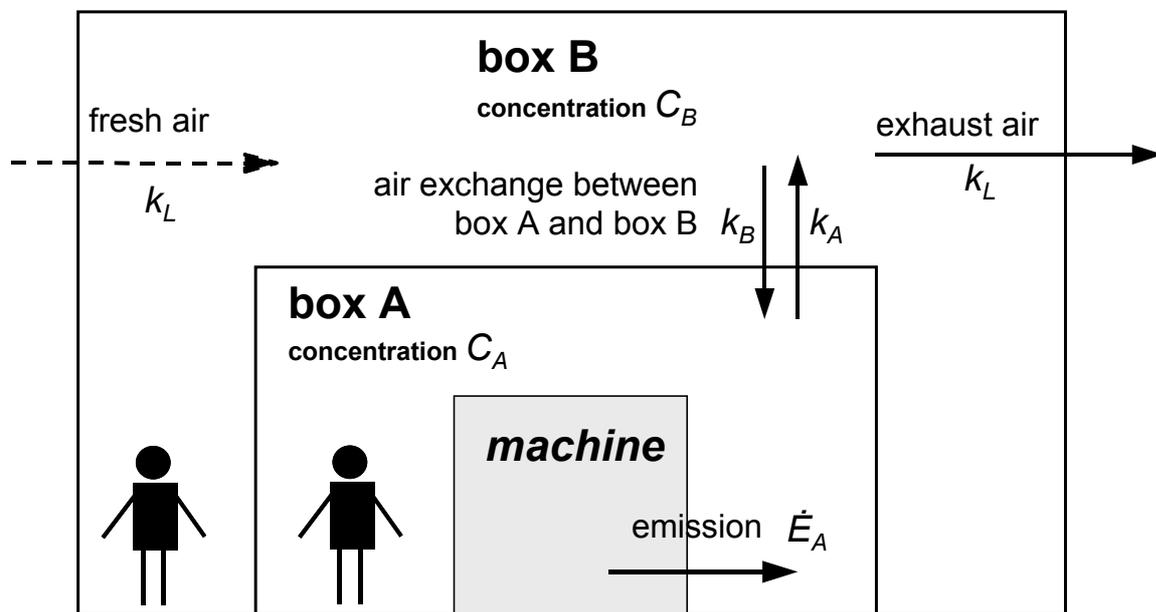


Figure 3.2: Two-box model with fictitious box A for the near-field of the machine and box B representing the far-field

For situations without a continuous emission term but with repetitive pulse emissions (release periods of less than 0.05 h are simplified as pulse releases), the homogeneous differential system for the two-box model is used. It is a simplification of the inhomogeneous system in which the constant mass flow \dot{E}_A is omitted. The system of two coupled linear homogeneous differential equations reads:

$$\begin{aligned}\frac{dC_A}{dt} &= -C_A \cdot k_A + C_B \cdot \frac{V_B}{V_A} \cdot k_B \\ \frac{dC_B}{dt} &= C_A \cdot \frac{V_A}{V_B} \cdot k_A - C_B \cdot (k_B + k_L)\end{aligned}\quad (3.5)$$

Each time a new pulse emission E_A (g) occurs, it is added to give the new background concentration $C_{A,i+1}^0$ for box A:

$$C_{A,i+1}^0 = C_A(t = i \cdot t_{\text{pulse}}) + \frac{E_A}{V_A} \quad (3.6)$$

where i indicates the number of pulses and t_{pulse} the time between the pulses. Equation 3.5 can be solved for $C_A(t)$ and $C_B(t)$. The solution is given in Appendix B.1.

3.4 Use of emission factors

Emission factors can be used to characterize the variability of the release of chemicals from intermittent sources and to discriminate the individual source contributions to ambient concentrations (Franke and Wadden, 1987; Wadden et al., 1991; Scheff et al., 1992; Conroy et al., 1995; Keil, 1998). The emissions depend on the chemical properties of the solvent (e.g., the vapor pressure), the atmospheric conditions (e.g., the temperature at the workplace), the type of machine (e.g., open-top machine), and the type of venting used. The release rate of different emissions can be calculated if the process rate of the source, source activity factors (e.g., mass or surface of cleaned part) and the emission associated with this process are known. Emission factors are characterized in terms of mass emitted per measure of process activity.

The exposure models for the use of TRIC and PERC in metal degreasing and PERC in dry cleaning include three different emission factors: (i) a continuous factor \dot{E}_{c1} (g/h) for diffuse emissions from open bath surfaces (open-top machines, only in metal degreasing), or from leakage of sealing; (ii) a second

continuous factor \dot{E}_{c2} (g/h) for emissions from cleaned metal parts and parts with cavities or cleaned textiles; (iii) a periodic factor E_p (g) for repetitive emissions from chamber air during loading and unloading. In a similar way, Wadden et al. (1989), (1991), Scheff et al. (1992), and Keli (1998) developed emission factors from measurements for solvent use in open-top and closed vapor degreasing and parts-washing processes. A comparison of the emission factors measured by Wadden et al. with the emission factors defined for the metal degreasing case study is given in Chapter 4.3.5.

For the two continuous emission factors, the inhomogeneous differential equation system is given by Equation 3.4, where \dot{E}_A is replaced by \dot{E}_{c1} or \dot{E}_{c2} . For the periodic emission factor, the homogeneous differential equation system is used, given by Equations 3.5 and 3.6, where E_A is replaced by E_p (g), i indicates the number of unloads and t_{pulse} is replaced by the batch time t_b .

With these three sets of equations, the airborne concentrations are calculated for an 8-h working day with the degreasing and dry-cleaning devices continuously in use. The dynamic concentrations in boxes A and B are obtained as:

$$\begin{aligned} C_A(t) &= C_{c1,A}(t) + C_{c2,A}(t) + C_{p,A}(t) \\ C_B(t) &= C_{c1,B}(t) + C_{c2,B}(t) + C_{p,B}(t) \end{aligned} \quad (3.7)$$

To this end, the time during which the three different emission factors are active or inactive needs to be known. More information about how the source code for the two-box model deals with this problem and at which times the different inhomogeneous and homogeneous differential equations are solved can be found in Appendix B.2.

The long-term concentrations in boxes A and B over an 8-h working day are obtained by summation of the integrals of the dynamic concentration curves of the three emission factors (for more details see Appendix B.3).

3.5 Variability and uncertainty of exposure estimates

Most risk assessments use mathematical models to estimate risk as a function of different inputs (e.g., machine parameters, emission factors, and workplace parameters). The models themselves are subject to large uncertainties, which stem partly from the limited ability of the model to properly represent reality and partly from variability and uncertainty in the input data. In many cases, knowledge about some or all of the inputs is insufficient and, consequently, so is knowledge about risk (Thompson and Graham, 1996).

In the present study, the occupational risk is determined in terms of numbers of exposed workers, N , and risk quotients, r . The latter is the quotient of exposure estimates and MAK value. The German MAK is a predefined value that is not called into question within the scope of this study. As MAK values are not properly predicted no effect levels, they are used here as a proxy measure for the height of occupational exposure. Therefore, the following discussion focuses on the variability and uncertainty of the exposure estimates and, thereby, primarily on the variability, as this is known to be large for both exposure measurements and exposure estimates (variable over space and time) (Boleij et al., 1995). First, it is of interest to learn how large the actual variability and uncertainty in the exposure estimates are and to consider what consequences arise for the comparison of different machine technologies and sizes. Second, it is of interest to identify those input parameters that “drive” the model results in order to learn how additional efforts in data collection and measuring should be focused (Jayjock, 1997).

3.5.1 Deterministic versus statistical approach in exposure assessment

Two distinct approaches exist using a mathematical model for quantifying risk that differ considerably in their abilities to distinguish variability and uncertainty. On the one hand, there is the “point estimate” or “deterministic” approach, and on the other hand there is the “statistical” or “distributional” approach (Finkel, 1990; Thompson and Graham, 1996). Using the “point

estimate” approach, risk assessors consider the available information, select a single number for each of the model inputs, and then generate a point estimate (single number) of risk. Thereby, risk assessors unavoidably ignore variability and uncertainty in the risk estimate. In contrast, in the “statistical” approach, frequency distributions are used to characterize variability and/or uncertainty in some or all of the model inputs. The purpose of these distributional representations is to define the range of values that a parameter can take on and to assign a probability of obtaining any particular value within that range. The input distributions are then propagated through the model to produce frequency distributions that convey variability and/or uncertainty in risk. While the two approaches are conceptually different, a mixture of both approaches may be used in the risk assessment. For example, the process may start with a screening assessment, which uses generic numbers (“defaults”) for many inputs in the point-estimated approach, and progress to a highly refined variability and uncertainty analysis, which characterizes risk using frequency distributions that treat variability and uncertainty explicitly. The question of how far a statistical approach is reasonable and feasible, in other words how many and which input parameters are described by probability density functions (PDF) and propagated through the model, is strongly dependent on the existence and quality of the input parameters needed.

3.5.2 Model uncertainty

When a model is built up to evaluate occupational exposure, the problem is to specify which components are relevant to the situation at hand and how these components interrelate. Models may fall prey to oversimplification, or may be appropriately detailed but fail to capture important nuances about the situation under investigation. Generally, models are selected on the basis of physical principles, for their ability to describe or make sense of a limited set of observational data.

Common types of model uncertainties include relationship errors (e.g., incorrectly inferring the basis for correlations between, for example, the size of the machine and the amount of cleaned textiles) and errors introduced by oversimplification (e.g., use of one-box models for room volumes bigger than

1'000 m³). Moreover, models can be incomplete if they exclude one or more relevant variables (e.g., emissions from cleaned parts), or if they use surrogate variables for ones that cannot be measured (e.g., using the air exchange rate of the entire room volume as a proxy for air exchange rates between near-field and far-field) (Finkel, 1990; Morgan and Henrion, 1990; CRAHAP, 1994). In Chapter 3.3, it could be shown that mass balance models are appropriate for evaluating risks associated with chemical substances. Within mass balance models, two-box models have the great advantage of discerning between near-field and the far-field exposure (see Chapter 3.3.1 and 3.3.2), which is of major importance when analyzing the occupational exposure in metal degreasing and dry cleaning. Model uncertainties, therefore, are not investigated further in this study.

3.5.3 Parameter variability and uncertainty

The main focus of the variability and uncertainty analysis in this thesis is on parameter variability, which is known to be high in exposure assessments (Boleij et al., 1995), and, secondly, on parameter uncertainty. True parameter variability stems from variation in the data, which is due to the fact that some input variables take on different values in time and space (e.g., different workplace surroundings, different amounts being degreased or cleaned, etc.). In contrast to true parameter variability, parameter uncertainty stems from a variety of sources. Uncertainties may arise from measurement errors (often from the imprecision of analytical devices (Evans et al., 1984)), systematic errors (e.g., weighting the amount of residual solvent on metal parts without considering a residual of oil and fat). A second type of parameter uncertainty arises when generic or surrogate data are used instead of analyzing the desired parameter directly. Other potential sources of error in estimates of parameters are misclassification, random sampling error (too small sample size), and non-representativeness (e.g., developing emission factors for a dry-cleaning device based on samples from a leaking machine) (Finkel, 1990; CRAHAP, 1994).

Typical parameters in this thesis with both a large variability and uncertainty are the air exchange rates. They vary very much between different workplaces

(variability) and may also include uncertainties such as measurement errors and non-representativeness. This is in contrast to parameters describing machine technology (e.g., emission factors assigned to different machine types or generations) and machine size (e.g., parameters that are load dependent). These parameters have variability between different distinct values but have relatively low uncertainty. They define distinct “cases” of exposure, namely occupational exposure with a machine of a certain technology type and size. In such a case, it is pointless to describe the variability with PDFs, as this would involve a loss of information. Therefore, no parameter variability and uncertainty analysis is carried out for parameters describing machine type and size.

For all other parameters, true parameter variability and parameter uncertainty is propagated through the model in a Monte Carlo simulation (IAEA, 1989). In this study, the parameter variability and uncertainty analysis comprises five main steps: (i) identification of parameters that contribute significantly to the variability and uncertainty of a predicted outcome; (ii) construction of a PDF for each parameter (indicating the range of possible values and their probabilities); (iii) accounting for dependencies (correlations) among parameters; (iv) propagation of the variability and uncertainty through the model to generate a distribution of predicted outcome values; (v) derivation of confidence limits and intervals from the PDF of predicted outcome variables in order to provide a quantitative statement about the effect of parameter variability and uncertainty on the model predictions.

3.5.4 Sensitivity analysis

The goal of a sensitivity analysis is to rank the input parameters on the basis of their contribution to variance in the output. Sensitivity analysis can be either global or local. A global sensitivity analysis quantifies the effects of variation in the parameters over their entire range of values. A global sensitivity analysis requires a variability and uncertainty analysis as a starting point. The variance in the outcome is compared to the variance of the input. A local sensitivity analysis is used to examine the effects of small changes in parameter values at some defined point in the range of outcome values (Morgan and Henrion,

1990). Local sensitivity analysis can be performed for any deterministic calculations and for a preliminary sensitivity ranking in statistical calculations.

In the sensitivity analysis, each input parameter, x_i , is modified individually (e.g., increased by a certain amount Δx), while all other input parameters are kept constant and the sensitivity, a , of the outputs y_i , are calculated by (Morgan and Henrion, 1990):

$$a = \frac{\Delta y}{y_i} \cdot \frac{x_i}{\Delta x} \quad (3.8)$$

An a value of 0.1 indicates that a 1% change in one of the input parameters leads to a 0.1% change in one of the output parameters. The disadvantage of the sensitivity analysis is that it cannot account for the influence of simultaneous changes in several input parameters, nor does it include any information on the existence of variability or uncertainty in different input parameters.

3.5.5 Implementation of variability and uncertainty analysis in SceBRA

The SceBRA method as applied in this study does not provide single-point estimates, but point estimates for a broad range of possible exposure situations for one metal-degreasing or dry-cleaning activity. Therefore, it depicts the range of possible risk values but, as a deterministic tool, it fails to reflect the frequencies within this range. To compare and verify the SceBRA method and its ranges of predicted outcome and to depict the variability and uncertainty caused by variable and sometimes uncertain inputs, a statistical exposure assessment was carried out for the dry cleaning case study. To this end, @Risk (Palisade, 2002), a commercially available simulation software, is used to perform the variability and uncertainty analysis based on the Latin Hypercube sampling technique. Latin Hypercube and random or pseudo-random sampling techniques differ in the number of iterations required until sampled values approximate input distributions. Latin Hypercube sampling

converges faster on the true statistics of the input distributions than random sampling (Palisade, 2002).

In the exposure assessment of the *dry cleaning case study*, PDFs are defined or fitted for all variable and uncertain input parameters based on literature data, data from surveys, or best estimates deduced from expert opinions (explicit definitions of PDFs for 5th generation machines can be found in Appendix D.4). The results of the Monte Carlo simulations and the according global sensitivity analysis, as well as the comparison with the SceBRA calculations, are described in Chapter 5.4.

For the *metal degreasing case study*, lack of data did not permit definition of PDFs for the majority of input parameters and, therefore, only the ranges of exposure are determined by SceBRA and a local sensitivity analysis is done to depict which input parameters “drive” the model results (see Chapter 4.3.6).

Besides the risk quotient, r , the number of exposed workers, N , is introduced as a measure of how many workers are exposed in the various metal-degreasing and dry-cleaning scenarios. The aim is to get, in a broad overview, a first estimate of the number of workers possibly exposed to emissions from certain types and sizes of machines, this for both the near-field and the far-field. The quality of the data on the number of employees in metal degreasing and dry cleaning, when available at all (available only for dry cleaning), is very poor. The data consists of estimates for the whole dry-cleaning sector, which cannot be assigned to different machine technologies and sizes. N can be taken as a best estimate for an average number of exposed workers and, therefore, no statistical variability and uncertainty analysis was carried out (further information about the estimation of N can be found in Chapter 4.2.4 and 5.2.4).

Chapter 4

4 Case study: Metal degreasing

In this chapter, the adapted SceBRA method is used to identify how the occupational exposure towards TRIC and PERC in metal degreasing has decreased with changing legislation and developing machine technology (von Grote et al., 2003). It will be shown how the operation of the machines influences the airborne concentrations in the near-field and the far-field of the running machine over an 8-h working day and at what time steady state is reached. Answers will be provided to further questions: What are the main emission sources? How much is the exposure influenced by parameters such as size of the machine, batch time and room volume? What technology changes have there been and how was exposure reduced with new machines? Finally, for selected years, it will be shown how many and to what extent workers in both the near-field and the far-field were or are still exposed. Metal degreasing is widespread in the metal-processing industry. Whenever parts need to be transported or stored, they are greased to prevent them from corrosion until their final treatment, such as painting and coating, before which they have to be degreased. This can be done with either aqueous systems, hydrocarbons, or chlorinated solvents. Chlorinated solvents are often used in degreasing equipment for difficult cleaning tasks, such as with metal parts that need to be totally dry, are very small, are temperature sensitive, or have lots of cavities (Leisewitz and Schwarz, 1994). Degreasing can be done by immersion in a cold or heated bath (major mode of application in the 1960s and 1970s) or by vapor degreasing.

The fact that TRIC and PERC are both under suspicion of causing cancer (see Chapter 2.2) has led to several revisions in the German law regulating their

use. The 2nd BImSchV of 1986 (BImSchV, 1986), the 2nd BImSchV of 1990 (BImSchV, 1990), and the amendment of the 2nd BImSchV 1990 in 2001 (BImSchV, 2001) lay down not only the chemicals to be used in different applications but also the technological standards of metal-degreasing machines, which have changed substantially over the last 30 years (see Chapter 2.5). The technological development of metal degreasing is described in the first part of this chapter (Chapter 4.1). In Chapter 4.2, the different model inputs describing the exposure scenarios are introduced. These are divided into machine parameters, emission factors, workplace parameters, number of machines, and number of exposed workers. The results of the occupational exposure assessment answering the above-mentioned questions are described and discussed in Chapter 4.3. In Chapter 4.4, some initial conclusions are drawn regarding the metal degreasing case study.

4.1 Technological development

Metal Degreasing is a two-step process including a cleaning step (sometimes spray cleaning) with hot or cold solvent and a vapor degreasing and drying step. For heavily contaminated parts, an additional solvent pre-cleaning step may be integrated. At the start of the degreasing process, a basket is manually loaded with metal parts and then placed into the machine. Metal parts are pre-cleaned and/or cleaned in a hot or cold cleaning medium (sometimes with additional spray cleaning). During the vapor degreasing step, continuously vaporized solvent condenses on the cold metal parts and washes down the unwanted matter. Condensation stops as soon as the parts reach the temperature of the boiling solvent and, thereafter, the dried parts can be taken out. Vapor degreasing, distillation of fresh solvent, and drying of the metal parts is included in a single energy-saving process. Afterwards, the still hot parts can be taken out dry. A schematic representation of a metal-degreasing process for a closed one-chamber machine can be seen in Figures C.1 and C.2 in Appendix C.1.

The technological development of metal-degreasing machines can be summarized in terms of five machine types, starting with fully emissive open-top machines with several baths and leading to closed-loop one-chamber machines (see Figure 4.1). Information on the different types was taken mostly from sales brochures provided by European manufacturers such as PERO, ROLL, FISA, DÜRR, MULTIMATIC, HÖCKH, ILSA, and EMO (Manufacturers, 1960-2001).

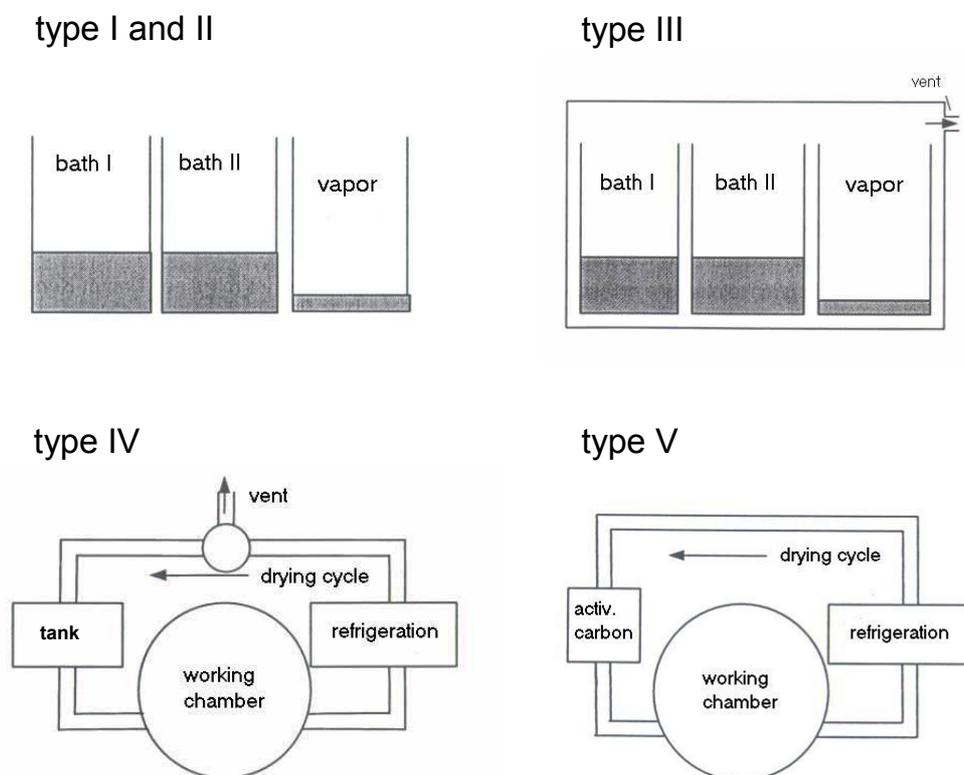


Figure 4.1: Technological progress of metal-degreasing machines represented by five different machine types.

Type I machines are fully emissive open-top machines with water-cooling at 15°C. They consist of several solvent baths and a vapor bath and have a suction device at the rim of the baths.

Type II machines are very similar to type I machines. The only difference is that these open-top machines with rim exhausters integrate an electro-cooling to cool the solvent to 2°C.

Type III machines have the baths and the vapor chamber encased to prevent evaporation from open baths.

Type IV machines are the first one-chamber metal degreasers; for the first time the solvent is brought to the metal parts and not vice versa. The machines are equipped with an integrated recirculated air dryer condensing the solvent and a recycling loop. The parts are dried with refrigeration cooling at temperatures between -20°C and -40°C. Type IV machines and some upgraded type III machines fulfill the 2nd BImSchV of 1986.

Type V machines (see Figure 4.2), which are in use today, are closed-loop one-working-chamber machines with closed loop drying and recycling systems with refrigeration cooling where the cooled air is additionally directed over activated carbon before reentering the working chamber to dry the metal parts. These type V machines do not release any exhaust air into the environment. The chamber concentration is monitored continuously and the metal parts are only released when the concentration in the cleaning chamber is below 1 g/m³. This technological standard was laid down in the 2nd BImSchV of 1990 (see Chapter 2.5).

The amendment of the 2nd BImSchV 1990 requires for PERC machines with hermetically-closed solvent tanks and pipes, which are operated under vacuum and for which the consumption is less than 1 metric ton per year (BImSchV, 2001). These machines are called type V B machines.

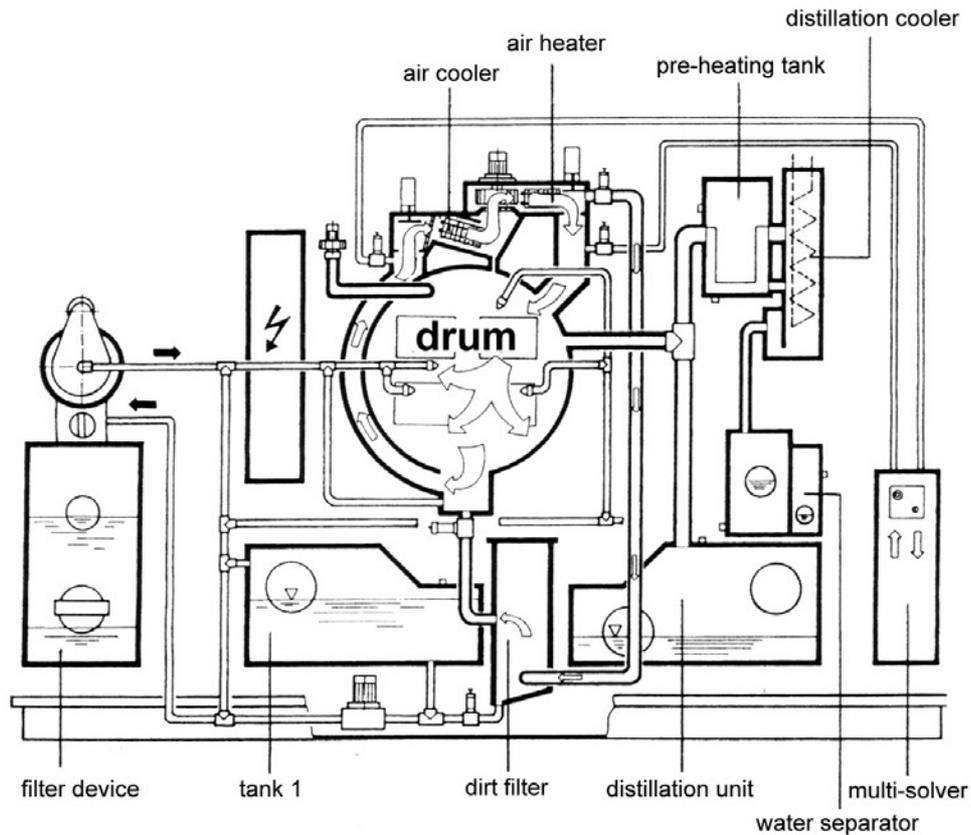


Figure 4.2: Technical drawing of a closed-loop type V machine (MULTIMATIC, 1990; Ziegler, 1991)

To account for small differences in each type due to different manufacturers, subtypes are defined that vary in the number of baths (type I and II), in the cooling temperature (type IV) or in the existence of a vacuum drying device (type V) (see Table 4.1).

Table 4.1: Characteristics of metal-degreasing subtypes.

Types and subtypes	Characteristics
I A	two baths
I B	two baths and vapor degreasing
II A	two baths
II B	two baths and vapor degreasing
III	no subtypes
IV A	cooling temperature PERC -20°C , TRIC -30°C
IV B	cooling temperature PERC -40°C , TRIC -40°C
V A	no vacuum drying
V B	vacuum drying

The fully open type I machines were first built in the early 1950s and type II machines in the middle of the 1950s. The encased type III machines were developed in the middle of the 1960s. These three types of machines were in use until the 2nd BImSchV was enacted in 1986. Type IV machines fulfilling the standards of 1986 came up in the middle of the 1970s. After 1986 and after the transitional regulation, only type IV machines and upgraded type III machines were allowed (in this study upgraded type III machines are grouped with type IV machines as they fulfill the same standards). In the late 1980s, type V machines were developed. The regulations of 1990 (BImSchV, 1990) require closed-loop type V machines for all metal-degreasing installations using PERC and the amendment of the 2nd BImSchV 1990 in 2001 requires for TRIC type V B machines, which are operated under vacuum. In Figure 4.3, the chronology of metal-degreasing technology triggered by the German 2nd BImSchV regulations is shown.

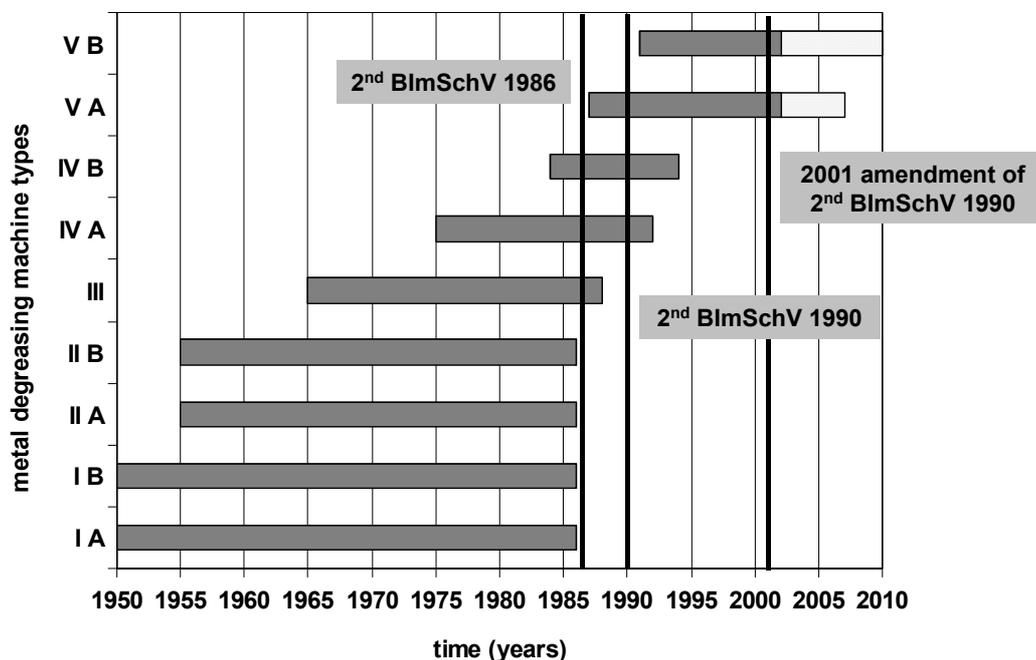


Figure 4.3: Chronology of metal-degreasing machine types triggered by the German 2nd BImSchV regulations.

4.2 Scenario definition

To represent the different exposure situations in metal degreasing, a range of possible and plausible use scenarios is defined. The scenarios are described by machine parameters (such as size, technology type, and machine load) and emission factors. Another factor that influences occupational exposure is the workplace surrounding, which is described by workplace parameters such as room size and air exchange rate. The number of machines of a certain technology used in a specific year and the number of workers needed to operate the machines are also important parameters.

4.2.1 Machine parameters

Machine technology has changed fundamentally since the 1950s. Therefore, five types and some subtypes of machines are defined according to information from sales brochures (Manufacturers, 1960-2001) (see Chapter 4.1). Each machine is manufactured in different sizes adjusted to specific purposes. For this study, the five most common sizes are chosen. These range from small size 1 machines with a load of 40–50 kg to large size 5 machines with loads of more than 1000 kg (Manufacturers, 1960-2001). Of the different sizes, size 3 machines are most commonly used. The batch time t_b depends on the material, geometry, and weight of the parts to be cleaned (during vapor degreasing the parts are heated until they have the same temperature as the vapor; condensing then stops and the vapor degreasing process is finished (Mannheim et al., 1979)). Therefore, size 5 machines have longer batch times than size 1 machines (see Table 4.2) (Manufacturers, 1960-2001).

Table 4.2: Characteristic loads and batch times for the five machine sizes (Manufacturers, 1960-2001).

Machine size	Load (kg)	Batch time t_b (h)
1	40 – 50	0.08 – 0.12
2	50 – 60	0.1 – 0.17
3	120 – 150	0.14 – 0.2
4	approx. 600	0.33 – 0.5
5	approx. 1000	0.5 – 1

4.2.2 Emission factors

In this chapter, the three emission factors used for the SceBRA calculations of the metal degreasing case study are explained in detail: (i) continuous emission factor for diffuse emissions; (ii) continuous emission factor for cleaned metal parts; and (iii) periodic emission factor for loading and unloading. In Figure 4.4, the different emission sources are depicted in a schematic drawing for an open-top machine.

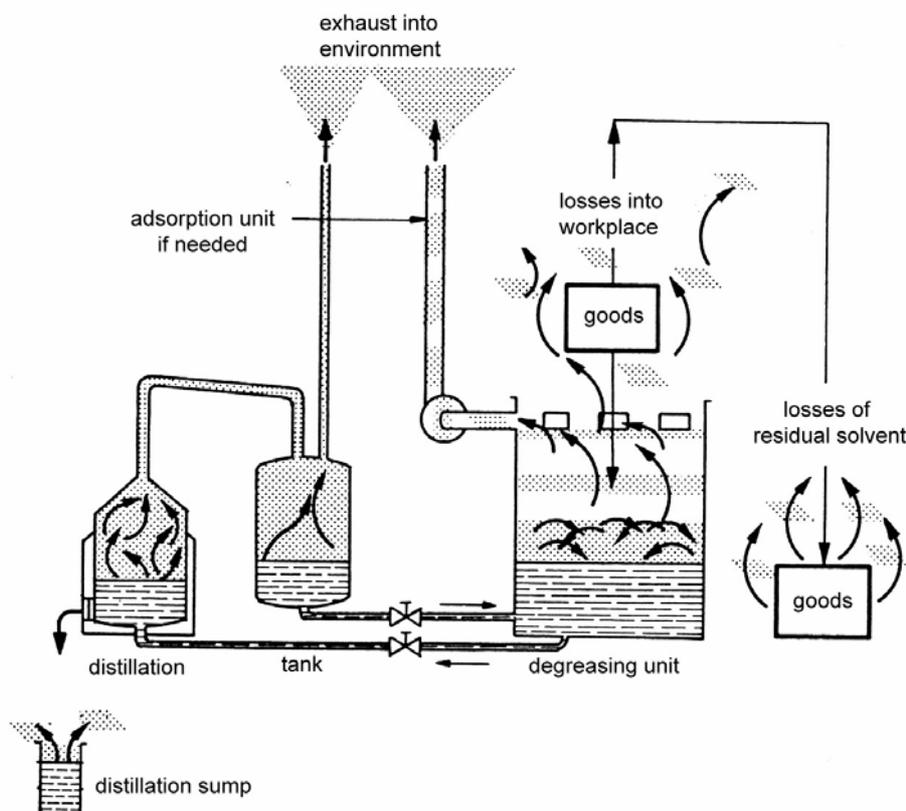


Figure 4.4: Schematic drawing showing the different emission sources of an open-top metal-degreasing machine (Mannheim et al., 1979).

Detailed lists of the different emission factors for each machine type and size are given in Appendix C.2.3. Note in advance that the emissions occurring at or shortly after loading and unloading contribute most to the overall emission. Validation of emission factors with measured data can be found in Chapter 4.3.6.

Continuous emission factor for diffuse emissions

In this case study, the diffuse emission factor \dot{E}_{c1} (g/h) describes a continuous discharge out of the metal-degreasing machine into box A. For open-top machines (type I and II), this corresponds to releases from open bath surfaces, which emit as long as the baths are heated. In fully emissive machines, the solvent vapor layer at the height of the air-cooler coils separates the vapor phase of the bath and the workplace air. Additionally, a rim exhauster directs the ascending hot vapor towards the side panel where the coolers are situated; the recirculation flow draws in fresh air from the workplace. In addition to the temperature of cooling and the capacity of the rim exhauster, the width of the baths and the freeboard rate, which is the ratio of freeboard height and bath width, also influence the emission mass flow (see schematic drawing in Figure 4.5).

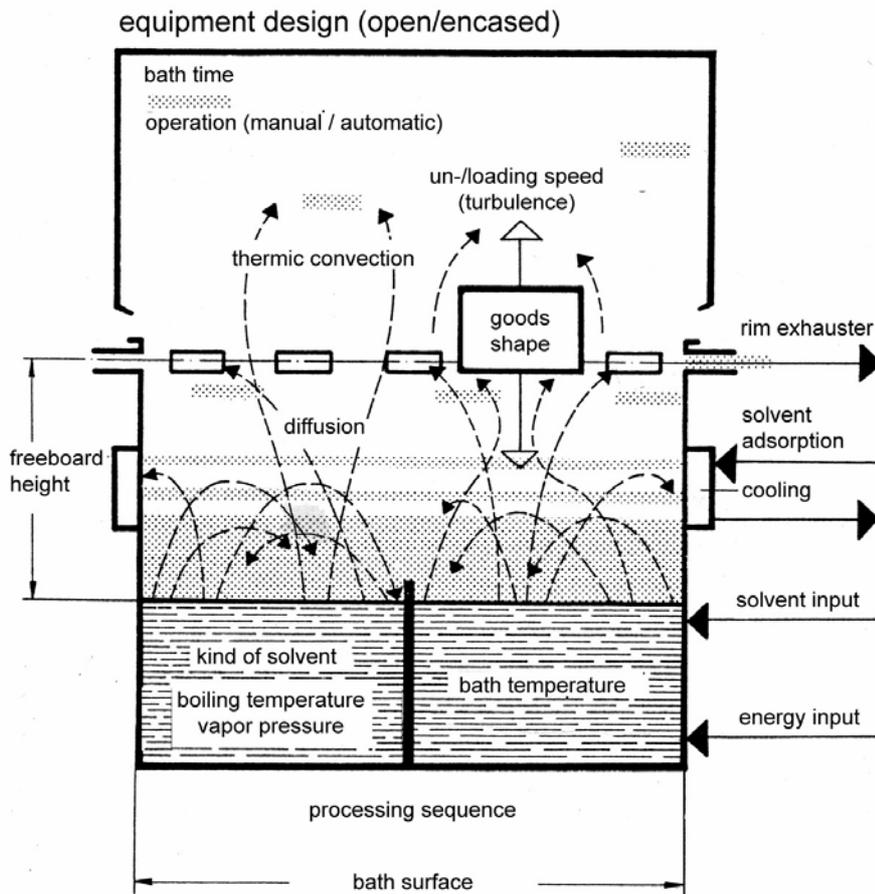


Figure 4.5: Schematic drawing of an open-top or encased metal-degreasing device (Mannheim et al., 1979).

Due to lack of adequate information on the volumetric flow rate and the dimensions and location of the exhauster inlet, an exact calculation of the emission mass flow is not feasible (Heinsohn, 1991). However, a simplified calculation makes it possible to determine reasonable estimates. The emissions from open bath surfaces are approximated with Fick's first diffusion law:

$$J_z = -D \frac{\Delta C}{\Delta h} \quad (4.1)$$

where J_z (g/(m²h)) is the diffusion mass flow in z direction, D (m²/h) the molecular diffusion coefficient, ΔC (g/m³) the concentration gradient between

the saturation concentration in the cooling zone and the air in box A, and Δh (m) the diffusion length. Δh was fitted so that the mass flow equals the results reported by CEFIC (1984b), which state that if common freeboard rates of 0.5 for open-top degreasers are increased to 0.75, solvent emissions can be reduced by 25% to 30%. As a cross-check, mass flows based on the fitted Δh were calculated for different cooling temperatures. The results agree with the finding that emissions can be reduced by 50% if the cooling temperature in open-top machines is reduced from 5°C to -30°C (CEFIC, 1984b). Multiplication of J_z by the bath surface results in the continuous emission factor \dot{E}_{c1} for metal degreasing. For encased type III machines, which consist of several baths (like types I and II), it was assumed that encasement reduces diffuse emissions by 80% relative to type II machines. For closed machines (type IV and V), \dot{E}_{c1} is taken as a leaking rate proportional to the solvent volume present in the machine (Cercl'Air, 1993) (\dot{E}_{c1} values for all types and subtypes are listed in Appendix C.2.3.1).

Continuous emission factor for cleaned metal parts

The cleaned parts taken out of the machine after washing and drying are sometimes not completely dry, especially if parts with cavities or cupped parts are cleaned. Emissions from cleaned parts depend on the drying time, the surface of the cleaned parts, and the existence of cavities and cupped areas (Scheff et al., 1992). In degreasing, metal parts vary very much in size, weight, and shape (e.g., from small needles to whole car bodies). Therefore, a range of standard metal parts is defined here with different amounts, sizes, and arrangements of plates and closely packed spheres. There are cavities between the closely packed spheres in which residual solvent can remain; the amount determines the emissions from cavities. Together with the amount dragged out by parts without cavities, this leads to the total amount of residual solvent E_{c2} (g). As an occupational worst-case scenario, it is assumed that all of the residual solvent will evaporate continuously over a certain period α (h), which lies between 0.5 and 1.5 times the batch time. The quotient of E_{c2} and α leads to the emission factor \dot{E}_{c2} (g/h) for metal degreasing.

For PERC, the residual solvent amounts on non-cupped cleaned parts dragged out of fully emissive open-top machines are assumed to be 3.9 to 4.3 g PERC per m² of metal surface after a solvent bath and 3.2 to 3.6 g/m² after vapor degreasing. The lower boiling point of TRIC and, therefore, the shorter interval until the metal parts have reached the boiling temperature explains why metal parts cleaned with TRIC drag out smaller amounts of residual solvent (1.2 to 1.3 g/m² after solvent bath and 1.0 to 1.1 g/m² after vapor degreasing). These figures correspond well with the reported amounts of solvent needed to refill open-top machines (Mannheim et al., 1979). For the closely packed spheres, it is assumed that there are cavities between the spheres that are not easily dried. It is assumed for type I to III machines that 2.5 to 5% of the sphere surface is cupped area, which drags out 32.5 g to 35.7 g PERC or 9.8 to 10.7 g TRIC per m² of sphere surface (Mannheim et al., 1979). Encased and closed type IV and V machines, which in contrast to the open-top machines are automated machines, have additional tilting devices for the baskets to make sure that cupped areas do not drag out solvent (Manufacturers, 1960-2001). The residual solvent amount of closed type IV and V machines is between 0.02 and 0.03g/m² for TRIC and between 0.05 and 0.1g/m² for PERC (all residual solvent amounts can be found in Appendix C.2.3.2). Validation data are given in Chapter 4.3.6.

Periodic emission factor for loading and unloading

Each time the machine is loaded or unloaded with a basket of metal parts, solvent-charged air from the chamber volume is exchanged with workplace air. This is described by the periodic emission factor E_p (g) for metal degreasing. For the open-top machines, the concentration in the working chamber can be calculated as the saturation concentration of the solvent at the height of the cooling device (values are given in Appendix C.2.3.3). During loading, only the vapor volume proportional to the volume of the metal parts is displaced; during unloading the basket volume minus the volume of the parts is dragged out (volume values are listed in Appendix C.2.2). The rim exhauster of the type I and II machines captured 50% of the solvent, whereas 90% could be kept back from evaporating into the workplace with type III and IV (Mannheim et al., 1979; Leisewitz and Schwarz, 1994; CEFIC, 1984b). In type V machines, the

cleaned parts are released only when the chamber concentration is below 1 g/m^3 (BlmSchV, 1990). The emission factor E_p is entered into the SceBRA calculations as intermittent emission occurring at the moment the door is opened.

4.2.3 Workplace parameters

Not only the degreasing equipment and the operation of the machine influence occupational exposure but also the workplace surroundings. The airborne concentration is dependent on the room volume and air exchange rates. Production hall volumes can vary from about 300 m^3 up to several thousand cubic meters. Here, relatively small volumes of 400 and 600 m^3 are assumed for the whole workplace (the fictitious near-field box has a constant volume of 100 m^3 ; see also Chapter 3.2). Typical air exchange rates in industrial facilities lie between 4 and 15 times per hour (Hayes, 1991; Recknagel et al., 2000). Wadden et al. reported an air exchange of 6 h^{-1} for metal degreasing with TRIC (Wadden et al., 1989) and 5.1 h^{-1} in an offset printing shop without local exhaust (Wadden et al., 1995). Workplaces for metal degreasing are equipped with local exhaust devices. Therefore, efficient and complete mixing for the near-field (box A) can be assumed. On the other hand, air exchange rates above 8 h^{-1} are not likely as they would produce an uncomfortable draught for the workers. Here, k_L values of 6 and 6.5 h^{-1} are used for open-top type I and II metal-degreasing machines, whereas for encased and closed machines values of 5.5 and 6 h^{-1} are employed. The air exchange rate between box A and box B, k_A , is assumed to be greater than the overall exchange rate k_L because older machines in particular are heat sources and create an upward flow of warm air (Bach et al., 1992; Heinsohn, 1991). Therefore, the k_A values are assumed to be 7 and 7.5 h^{-1} for open-top machines and 6 and 6.5 h^{-1} for type III to V machines. The model assumptions of workplace volumes and air exchange rates are summarized in Tables C.11 and C.12 in Appendix C.2.4.

4.2.4 Number of exposed workers

In addition to the risk quotient, SceBRA estimated the number of exposed workers. For this, a distinction between the different boxes with their different concentrations must be made. The number of exposed workers can be approximated from the number of machines in use in different years.

In Table C.13 of Appendix C.2.5, estimates of the numbers of metal-degreasing machines using TRIC and PERC are listed for the years 1985 (only former West German states, one year before the 2nd BImSchV of 1986) (Adams and Jeker, 1986), 1991 (only former West German states, during transitional regulation for 2nd BImSchV 1990) (Adams, 1993), 1996 (after the transition period of the 2nd BImSchV 1990) (Adams, 1997) and 1999 (Nader, 2001c; Nader, 2001a). The number of machines used in solvent cleaning and vapor degreasing decreased from approximately 4'900 for TRIC and 6'300 for PERC in 1985 (which were overestimations according to Adams (2002) see Appendix C.2.1 and C.2.5) to approximately 300 for TRIC and 1'400 for PERC in 1999 (only vapor degreasing).

It is assumed that between 1.5 and 3 workers (average of 2.25) were required to handle the mostly manually operated open-top type I and II machines. The encased and fully closed machines are automated and, therefore, need only 1–1.6 workers (average of 1.3) (Nader, 2001b). Furthermore, it is assumed that the workers operating the machines are present in the near-field during the whole 8 h working day.

The estimation of the number of workers in the far-field is more difficult. Because metal-degreasing machines are used all over in the metal-processing industries, workplaces can vary very much from small production halls with only a few workers to whole production lines. As the open-top machines were mostly used in times when the production processes were not automated, it is assumed that for type I and II machines 3–10 workers worked in the far-field, whereas for type III to V machines the number is set at 2–8 workers (in Appendix C.2.6, the assumptions about the number of exposed workers per machine are summarized in Table C.14).

4.3 Results of occupational exposure assessment in metal degreasing

The basic two-box model allows specification of the dynamic and long-term concentration of every single scenario. By combining all independent input parameters, up to 2'160 possible and plausible exposure scenarios can be obtained for each type of machine. From these, the maximum and minimum scenarios are selected for each size of machine. Thereby, the number of scenarios is reduced for each machine type to 20 (type I to III) or 40 (type IV and V), depending on whether subtypes are distinguishable. On this basis, the five types of machines can be compared, and characteristic differences between the two solvents can be depicted. Finally, for selected years, the number of exposed workers, N , is combined with the risk quotients, r , of the different types and sizes of machines. On this basis, the changes in the number of exposed workers and the magnitude of the risk quotient can be compared over a period of 15 years.

4.3.1 Dynamic concentrations

With one set of input parameters for a specific machine (machine parameters, emission factors, workplace parameters), the dynamic and long-term concentrations over an 8-h working day can be calculated for a single scenario. In Figure 4.6, an example of concentrations is shown for PERC used in an encased type III and size 5 metal-degreasing machine. In this scenario, metal plates are washed with a batch time, t_b , of 0.75 h.

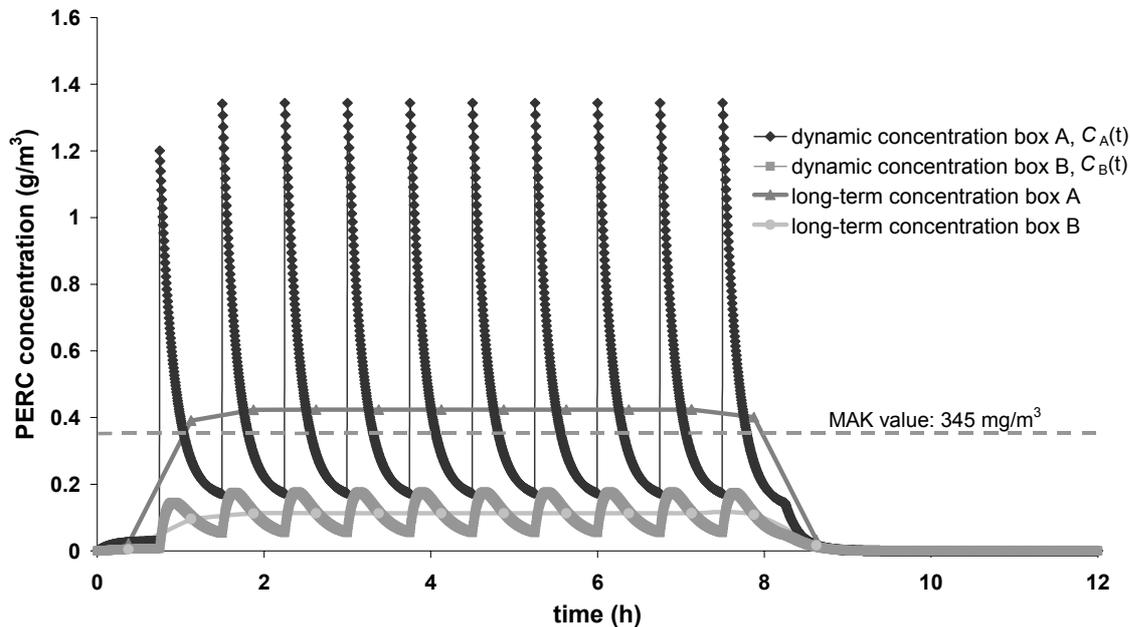


Figure 4.6: Dynamic concentration of PERC used in a type III size 5 metal-degreasing machine (E_p : 117 g, \dot{E}_{c1} : 17.2 g/h, \dot{E}_{c2} : 73.4 g/h, α : 0.75 h, t_b : 0.75 h, V : 400 m³, k_L : 5.5 h⁻¹, k_A : 6 h⁻¹).

Every time the basket with metal plates is unloaded, a peak concentration is observed. The long-term concentration is calculated as the integral of the concentration curve over one batch time, divided by t_b (see also Appendix B.3). After the second unloading (after 1.5 h), a steady state is reached; thereafter a regular pattern of subsequent peaks with a scenario-specific amplitude follows. After 8 h, operation of the metal-degreasing device stops and the ambient concentration decreases to the initial value. The long-term airborne concentration lies at 0.42 g/m³ in box A and at 0.11 g/m³ in box B, which means that for this specific scenario the long-term concentration in the near-field, the working area, is 1.2 times the MAK level of 345 mg/m³, whereas the far-field long-term concentration reaches only 32% of the MAK level.

4.3.2 Parameter combination

The systematic combination of all independent input parameters leads to up to 2'160 exposure scenarios for each machine type (for parameter combination see Figure C.4 in Appendix C.3). The resulting concentrations of all scenarios are indicated in Figure 4.7 as diamonds representing the long-term concentrations for both box A (Figure 4.7, diamonds in lighter gray) and box B (Figure 4.7, diamonds in darker gray). Here, results are given for a type II metal-degreasing machine using TRIC.

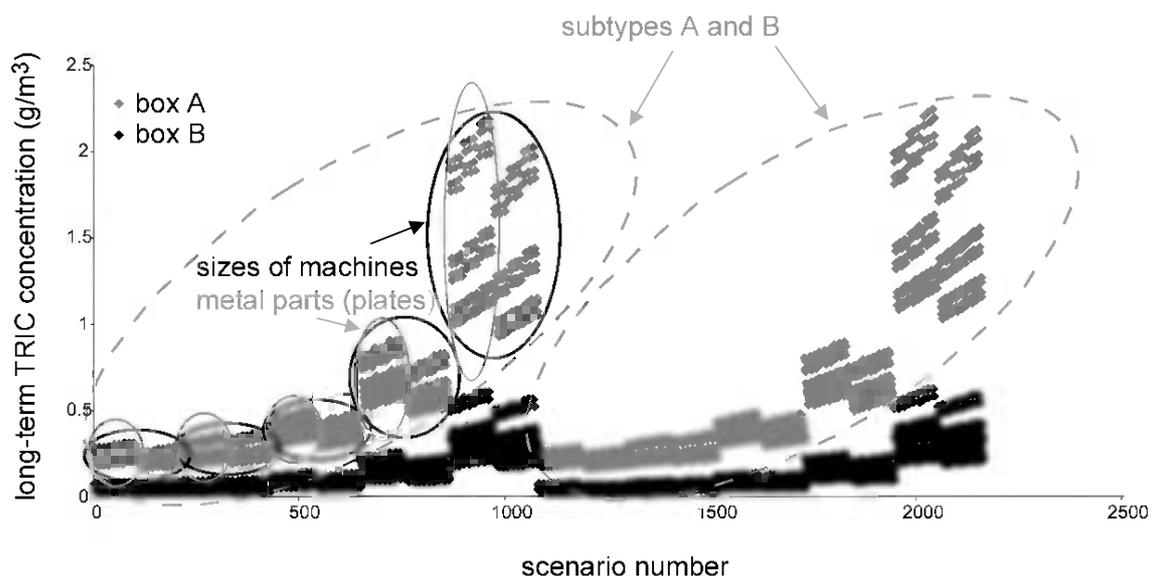


Figure 4.7: All exposure scenarios for an open-top type II metal-degreasing machine using TRIC with the different subtypes, sizes and metal parts indicated.

In Figure 4.7, different groups of marks can be made out. There are two principal groups indicating the different machine subtypes (Figure 4.7, dashed ellipses). For each subtype there are five groups indicating the different machine sizes (Figure 4.7, black ellipses, shown only for subtype A) and for each size there are two groups depicting the different metal parts being cleaned (Figure 4.7, gray ellipses in subtype A, indicating loads of plates). On the whole, within one machine type, the major impact on airborne concentration is determined by the size of the machine. The machine size influences the bath volumes and bath surfaces, the volumes of the baskets

and, therefore, the surfaces of the cleaned metal parts. It can be seen that within one machine size the scenario concentrations are not equally distributed but that there are several clusters of scenario.

In terms of long-term concentration, the two subtypes of type II machines cannot be distinguished from each other in Figure 4.7. Similar scenario combination plots can be obtained for all machine types for both solvents TRIC and PERC. By means of these plots, machines can be located for which it is useful to distinguish between subtypes for the exposure assessment with SceBRA. This is the case for types IV and type V machines; there, the different cooling temperatures (type IV) and the existence of a vacuum drying device (type V) have a significant effect on the ambient concentration in the near-field (see Figures C.5 to C.14 in Appendix C.3).

Next, the contribution of the different input parameters to the range of long-term airborne concentrations will be exemplified for a type II A, size 5 machine. The contribution of the different input parameters to the range of long-term near-field airborne concentrations is depicted in Figure 4.8.

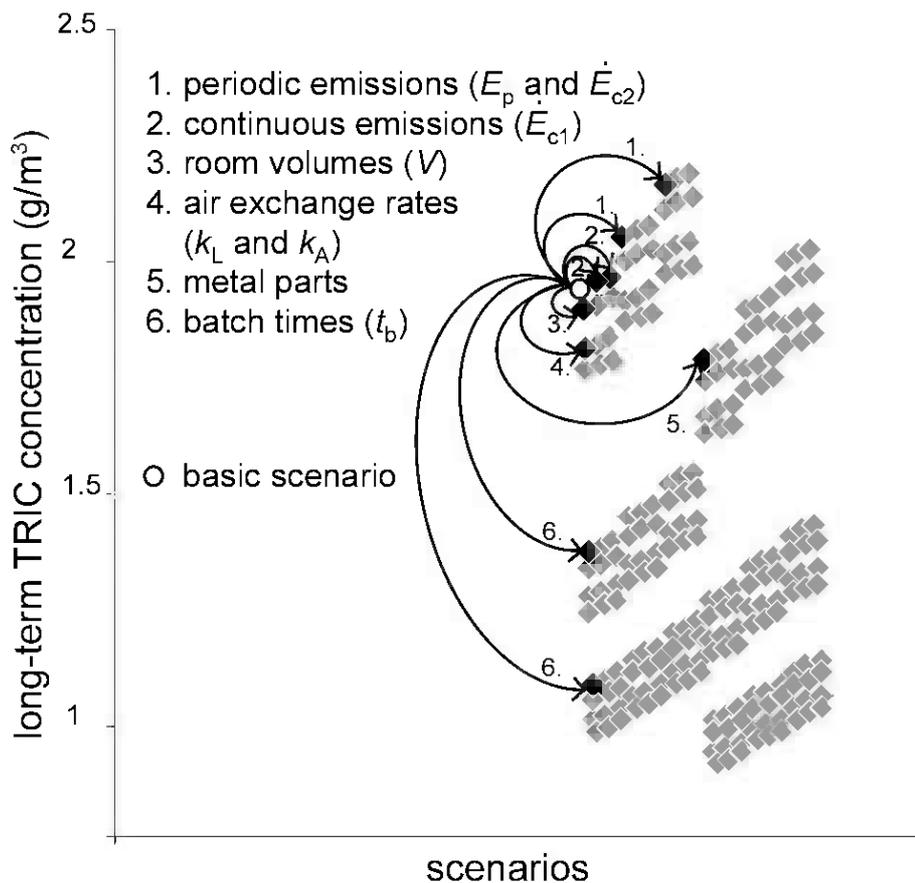


Figure 4.8: Contribution of changes in different input parameters to the long-term concentration in box A of a type IIA, size 5 metal-degreasing device using TRIC. Starting from a basic scenario (open circle), the different parameters are varied from their minimum to maximum values (arrows 3, 4, 5) or from their minimum to average to maximum values (arrows 1, 2, 6). For this machine, the minimum and the maximum long-term TRIC concentrations are 0.9 g/m^3 and 2.2 g/m^3 .

Numbered arrows starting from the basic scenario indicate concentration changes occurring when only a single parameter is changed. Changing more parameters results in the combination of individual effects; these scenarios are represented by gray marks. Parameters that vary scarcely between different scenarios have a relatively small influence on the long-term concentration. Such parameters are the continuous emission factor from open baths and leakage of closed machines (\dot{E}_{c1}) and the room volume (V) (Arrows 2 and 3 in Figure 4.8). This is because \dot{E}_{c1} represents emissions caused by machines in standby mode with only small fluctuations. The overall room volume has a

small effect on the airborne concentration in the near-field because it influences only the air exchange from box B to box A (k_B). The latter is dependent on the room volumes and the exchange rates k_A as the fictitious near-field box A is fixed at 100 m³.

Parameters that show stronger effects are:

- Batch time t_b (Arrow 6 in Figure 4.8): The length of t_b influences the long-term airborne concentration most strongly as it determines the spacing between the emission peaks.
- Kind of cleaned parts (Arrow 5 in Figure 4.8): The difference between the two kinds of metal parts is due to the different volume and surface ratio of plates and spheres.
- Coupled air exchange rates k_L and k_A (Arrow 4 in Figure 4.8): The air exchange rates k_L and k_A directly influence the removal of the pollutant. They are coupled because simultaneous high exchange rates in one box and low in the other are unlikely.
- Coupled periodic emissions E_p (g) and \dot{E}_{c2} (g/h) (Arrow 1 in Figure 4.8): The variations in E_p and \dot{E}_{c2} represent the variances in the work process; they depend on the saturation concentration in the machines, the geometry and volume of the metal parts, and the amount of solvent dragged out. The two emission factors are coupled as they are both dependent on the load (E_p : during loading the vapor volume proportional to the volume of the metal parts and during unloading the basket volume in C volume of the parts is exchanged; \dot{E}_{c2} : the residual amount is proportional to the parts surface).

4.3.3 Comparison of technologies

The different machine technologies can be compared by analyzing the range of the risk quotient, r , for each size of machine. In Figures 4.9 and 4.10, the minimum, maximum, and average logarithmic risk quotients, $\log r$, are given for the near-field of all five machine types and for the relevant subtypes (the according SceBRA exposure estimates are listed in Tables C.15 and C.16 in

Appendix C.3). $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value. It can be seen for both solvents that r decreases with decreasing machine size, and is reduced by more than two orders of magnitude from fully emissive open-top type I to closed-loop type V B machines with vacuum-drying devices.

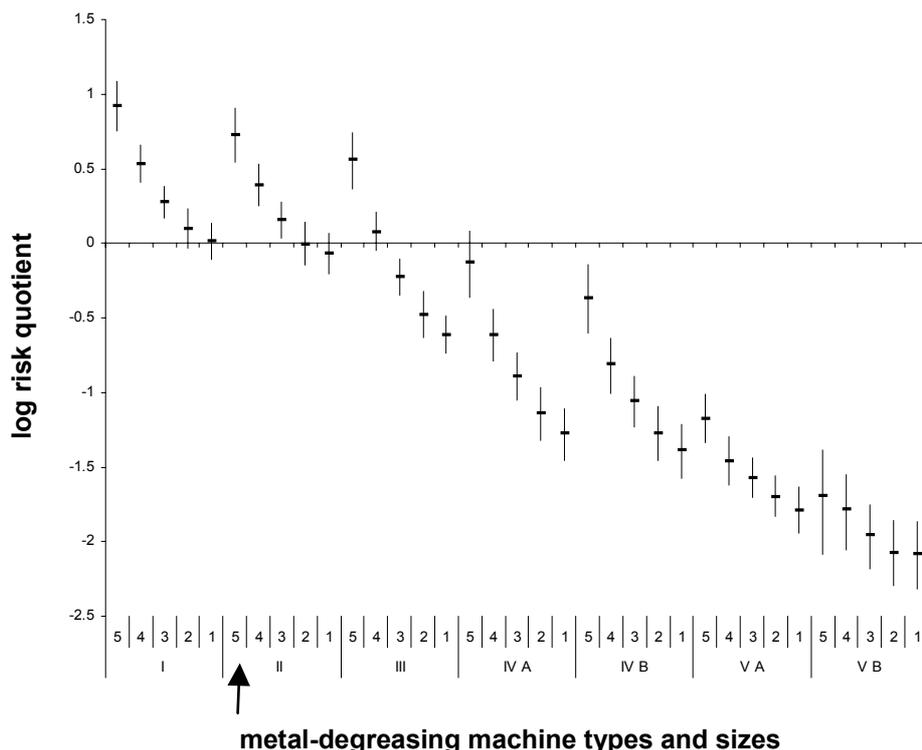


Figure 4.9: Comparison of the near-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the five types (and of relevant subtypes) subdivided into five sizes of metal-degreasing machines for TRIC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value. Arrow: machine characterized in Figure 4.8.

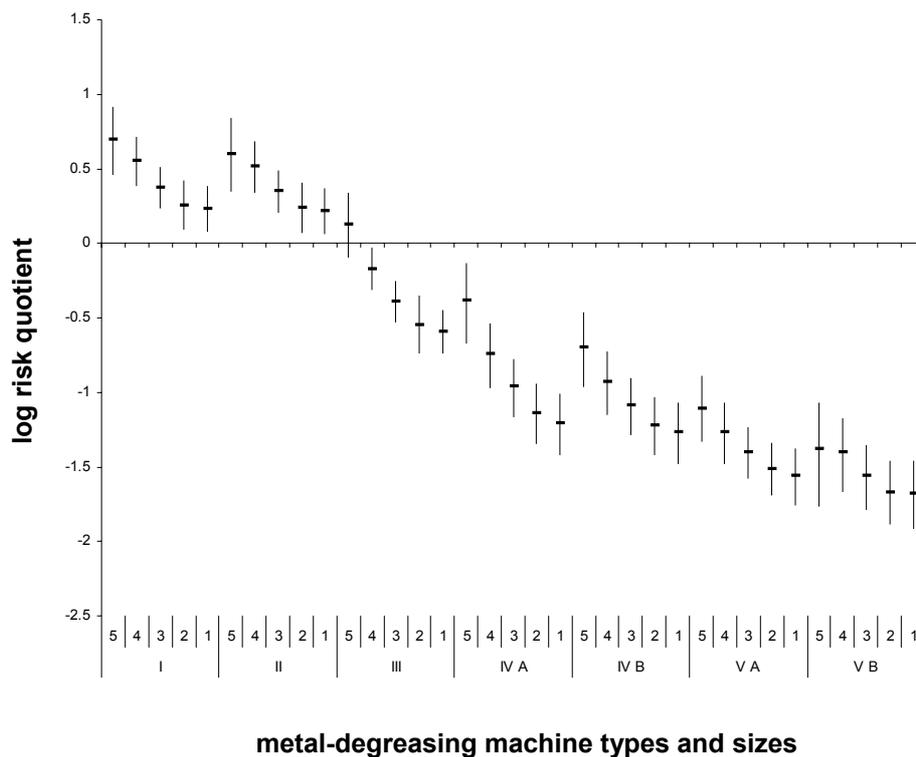


Figure 4.10: Comparison of the near-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the five types (and of relevant subtypes) subdivided into five sizes of metal-degreasing machines for PERC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value.

Fully emissive type I and II, and encased type III machines using TRIC show greater variation between the different sizes of machines than machines operated with PERC. This can be attributed to the fact that the vapor pressure of TRIC is higher for the temperature range in which these machines are used (see Figure C.3 in Appendix C.2.3.3). Therefore, higher concentrations are reached by increasing the bath surface and the volume of the basket from small size 1 to size 5 machines. According to the findings of this study, the MAK value is not exceeded for operators working in the near-field of type IV and V machines. For the most modern type V B machines, which have an integrated vacuum-drying system and which are required for TRIC in the amendment of the 2nd BImSchV 1990 (BImSchV, 2001), the long-term concentration lies below 2 ppm ($\log r -1.4$) for TRIC and below 4 ppm ($\log r -1.1$) for PERC, which is less than the 1/10 of the MAK value. A comparison of measured concentrations is given in Chapter 4.3.5.

The logarithmic risk quotients in the far-field of the different machine types and sizes are depicted in Figures 4.11 and 4.12 (the according SceBRA exposure estimates are listed in Tables C.17 and C.18 in Appendix C.3). From the SceBRA calculations, it can be seen that only the biggest size 5 open-top machines result in long-term airborne concentrations above the MAK value in the far-field. For the newest type V B machines, the calculated long-term airborne concentrations are below 0.5 ppm ($\log r -2$) for TRIC and below 1.2 ppm ($\log r -1.6$) for PERC.

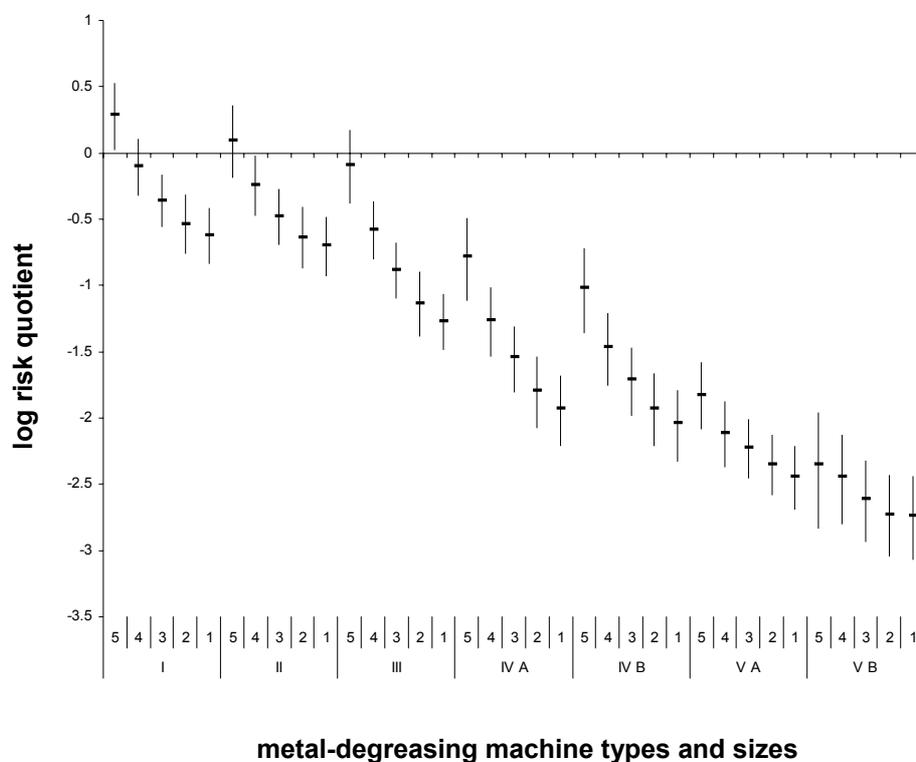


Figure 4.11: Comparison of the far-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the five types (and of relevant subtypes) subdivided into five sizes of metal-degreasing machines for TRIC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value.

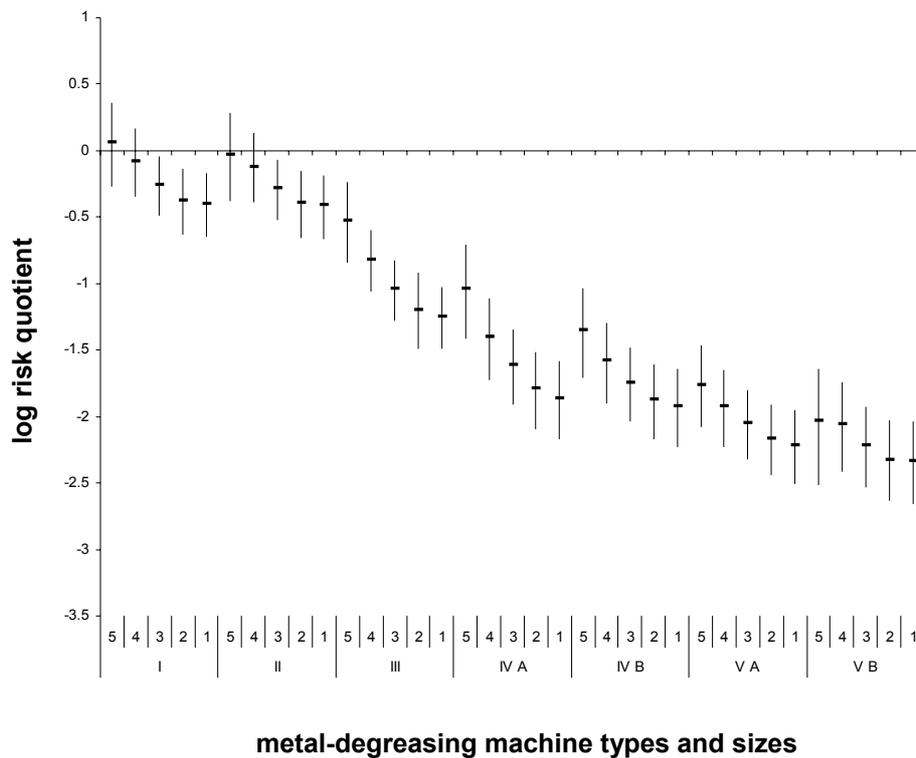


Figure 4.12: Comparison of the far-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the five types (and of relevant subtypes) subdivided into five sizes of metal-degreasing machines for PERC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value.

4.3.4 Cumulative risk

Finally, the average risk quotients of the different machine types and sizes in use at certain times in Germany are combined with the average number of workers exposed to TRIC and PERC in metal degreasing and compared for different years. Figure 4.13 shows a cumulative representation of the results for the near-field (box A) over 15 years.

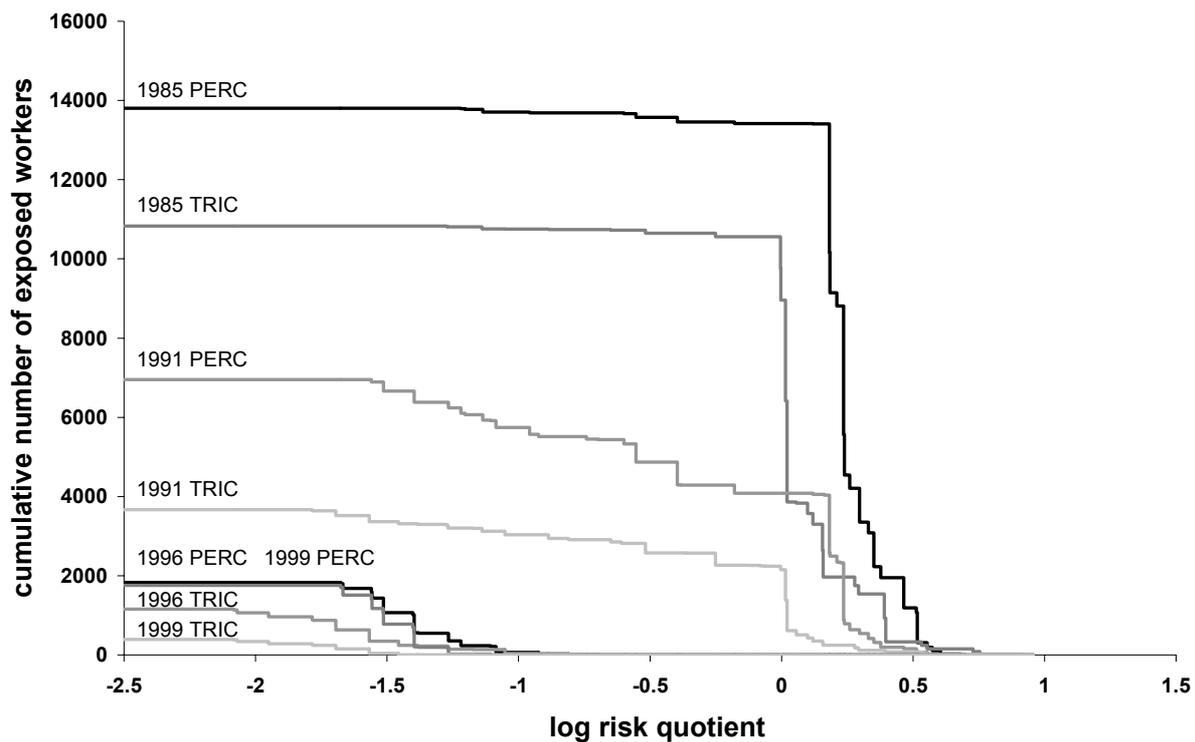


Figure 4.13: Cumulative N , $\log r$ -plot, of PERC and TRIC in the near-field for the years 1985*, 1991*, 1996, and 1999 in Germany (*only former Western Germany).

In the cumulative N , $\log r$ -plot, each point ($\log r$; N_{cum}) of the curve shows the total number of exposed workers, N_{cum} , with a risk quotient at least as high as indicated by $\log r$. This kind of plot combines the information from all scenarios of a solvent for a specified year in a single line and thus several years and both solvents can be compared in one plot. For each year, the total number of exposed workers and the number of exposed workers with a risk quotient above 1 (or any other particular value) can be derived from the plot. The total average number of exposed workers in the near-field in 1985 is 13'800 for PERC and 10'828 for TRIC, compared with 1'756 for PERC and 391 for TRIC in 1999 (see Chapter 4.2.4 and Appendix C.2.5 and C.2.6). If maximum or minimum numbers of exposed operators are taken instead of the average number, the values of N would be higher by a factor of 1.2 to 1.3 or lower by a factor of 0.7 to 0.8.

In Figure 4.14, the cumulative N , $\log r$ -plot is given for the far-field (box B). Here the risk quotients are combined with an average number of workers in the far-field.

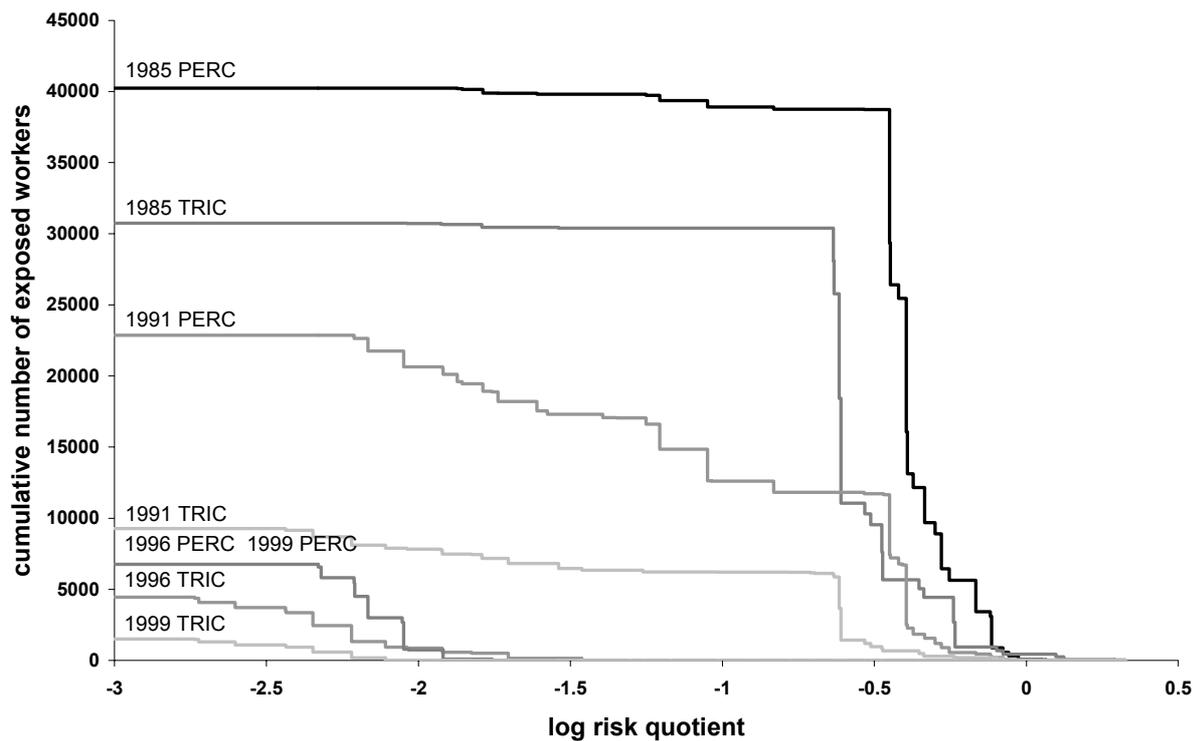


Figure 4.14: Cumulative N , $\log r$ -plot of PERC and TRIC in the far-field for the years 1985*, 1991*, 1996, and 1999 in Germany (*only former Western Germany).

Over all, it can be seen that almost no workers in the far-field were exposed to long-term concentrations above the MAK value. Here the total number of exposed workers in the far-field in 1985 is 40'244 for PERC and 30'733 for TRIC, compared with 6'755 for PERC and 1'505 for TRIC in 1999. Taking the maximum and minimum numbers of exposed workers in the far-field instead of the average, N would be a factor of 1.5 to 1.6 higher, or a factor of 0.4 to 0.5 lower, respectively. This reflects the large uncertainty about the number of exposed workers in the far-field.

In the comparison of the two cumulative N , $\log r$ -plots for the near-field and the far-field, the shapes of the curves are the same. This is because both plots are based on the same scenarios, but N is about four times higher and r significantly lower for the far-field.

In 1985, one year before the 2nd BImSchV was enacted, mainly open-top type I and II and encased type III machines were in use. In 1991, all machines had to fulfill the 2nd BImSchV of 1986. In 1996, after the transition period for the

amended regulations, and in 1999, all machines had to conform to the 2nd BImSchV of 1990, meaning that only closed-loop type V machines were allowed.

In 1985, 53'000 metric tons of PERC and 34'000 metric tons of TRIC were sold for different mostly open solvent applications (only former West German states), but in 2001 these figures had dropped to 4'400 metric tons of PERC and 4'400 metric tons of TRIC (Nader, 2002) (see Chapter 2.4). This is a reduction of 91.7% for PERC and 87% for TRIC. The reduction in the solvent amount used in metal degreasing is due to changes in environmental legislation, which led to: (i) technology changes (closed-loop machines with integrated recycling, where the solvent has a residence time in the machine of up to about 1 year (Nader, 1993) (for comparison: Mannheim et al. (1979) reported for open-top type I and II machines a total solvent loss of 0.9 kg/h for PERC and 0.7 kg/h for TRIC, which means that solvent had to be refilled once or twice a week in these machines); (ii) solvent substitution; and (iii) more efficient processing in metalworking industry with less greasing/degreasing and maximizing capacity utilization by suppressing machines not used to capacity. However, expert interviews showed that it is not possible to determine how much each factor (technology changes of metal-degreasing machines, solvent substitution, or more efficient metal-processing) contributed to the overall reduction. One of the reasons is that the earlier estimations of the number of machines are of poor quality (Adams, 2002) (see also Appendix C.2.1 and C.2.5).

4.3.5 Validation

In this section, estimated emission factors are first compared to measured data. In a second part, long-term near-field concentration outputs of the SceBRA exposure assessment are compared to published exposure measurements and to unpublished air measurements obtained by a needle manufacturer (Groz & Beckert). Validation of the long-term airborne concentration in box B cannot be carried out as there are no measurements published for the far-field; except for the biggest open-top machines, there was hardly ever the danger of exceeding the MAK value. Nevertheless, it can be

stated that the presently used two-box model provides realistic values for the far-field. This can be proved in the dry cleaning case study, where there are data to validate the far-field long-term concentrations (see Chapter 5.3.5).

Emission factors

From a discussion with an expert on the degreasing of needles with TRIC, residual solvent amounts for loads of 1000 needles for different machine types were obtained (Pehlke, 2002). To make these data comparable to the model estimates, they were converted into residual solvent amount per part surface (g/m^2). The conversion results in 1.6–8.8 g/m^2 for open-top machines and between 0.002 and 0.02 g/m^2 for type V B machines using TRIC. As needles include cavities, these data must be compared to the average residual amount dragged out by closely packed spheres, which is between 1.6 and 1.8 g/m^2 for a type I A or II A machine and approximately 0.002 g/m^2 for a type V A or V B machine (see Appendix C.2.3.2 Table C.7). The compared values are of the same order of magnitude.

Furthermore, Wadden et al. (1991) reported emission factors of 16.9 g TRIC/basket of parts for an open-top degreaser, where emissions from cleaned parts (\dot{E}_{c_2}) are not taken into consideration. The described machine is similar to a type II and size 3 machine. In the metal degreasing SceBRA calculations, the amount of E_p added to the amount of \dot{E}_{c_1} is 18.5–21.0 g/basket for a type II size 3 machine. This shows again good correspondence.

Near-field air measurements

Generally, TWA or long-term measurements are more appropriate for comparison with calculated long-term SceBRA concentrations than short-term measurements, which reflect only the momentary situation and where it is not indicated at which state of the batch cycle measurements were taken. Short-term measurements show a high variability with time (Boleij et al., 1995).

Published reports of TRIC and PERC exposure measurements in metal-degreasing facilities contain little information about the machines measured (see Tables C.19 and C.20 in Appendix C.4). Therefore, it is sometimes difficult to assign air measurements to machine types. Machine types, if not

described in the corresponding reference, were estimated according to information on the stage of technology development for different countries. Qualitatively good information with indicated number of samples, measurement range, and average concentration is available for type I, II, IV and V machines using TRIC and for type IV and V machines using PERC. In Figure 4.15 for TRIC and Figure 4.16 for PERC, the $\log r$ values of the published measurements (gray marks) are compared to the $\log r$ ranges of the SceBRA calculations for the five machine types (bars in black). Each gray mark depicts the average concentration of one series of measurements (see Tables C.19 and C.20 in Appendix C.4). Overall, a good correspondence can be seen between the measured data and the long-term near-field concentrations calculated with the two-box model.

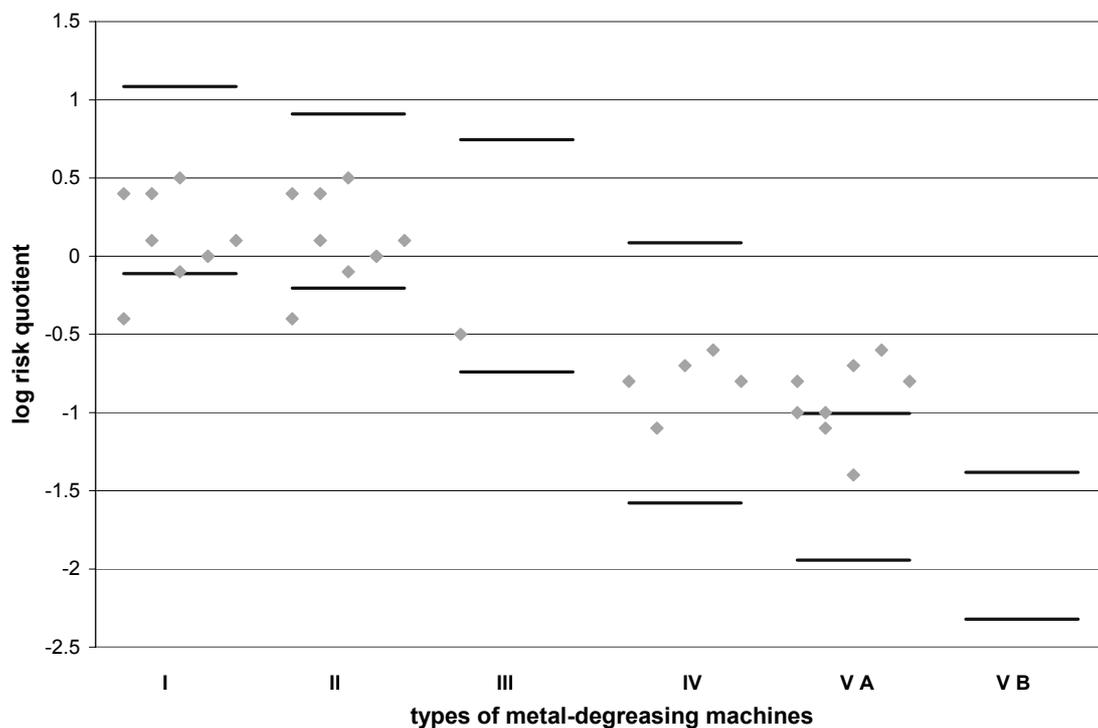


Figure 4.15: Comparison of risk quotients (logarithmic r values) of average near-field TRIC air measurements of published series of measurements in metal-degreasing facilities (gray marks) with the $\log r$ values of the SceBRA calculations (bars in black) (measurements listed in Table C.19).

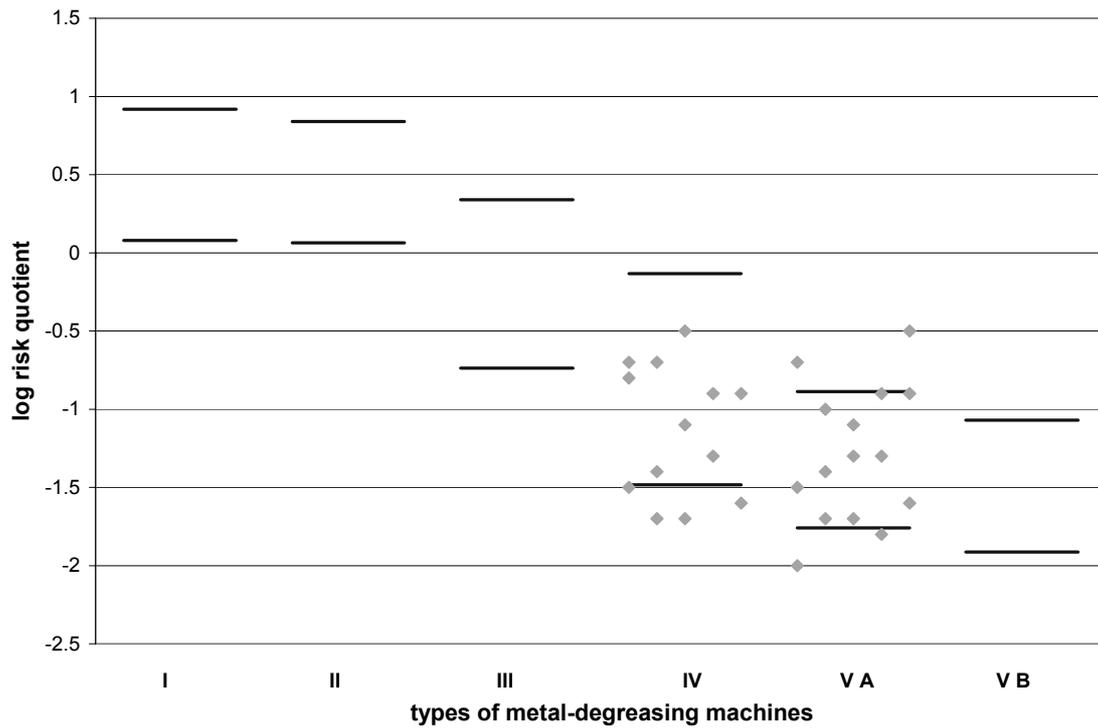


Figure 4.16: Comparison of $\log r$ values of average near-field PERC air measurements of published series of measurements in metal-degreasing facilities (gray marks) with the $\log r$ values of the SceBRA calculations (bars in black) (measurements listed in Table C.20).

In addition to the published TRIC and PERC exposure measurements in metal degreasing, unpublished TRIC and PERC exposure data were obtained at Groz & Beckert, a German high-tech needle manufacturer (Groz & Beckert, 2002) and were evaluated if feasible in terms of machine technology (see Tables C.21 and C.22 in Appendix C.4). The measurements are short-term and long-term routine measurements (long-term measurements over 3 to 4 h) carried out four times a year and measurements performed in cases of irregularities. Therefore, the measurements are not restricted to normal use, which has to be taken into consideration when comparing them to calculated long-term SceBRA concentrations.

Unfortunately, it was not possible to distinguish between measurements made during normal conditions and during machine irregularities. Apart from this, the Groz & Beckert data are good in quality, type of measurement, number of samples, and measurement range, and average concentrations are available for all measurements. The numerous TRIC data even allow distinction between subtypes of type V machines. With the amendment of the 2nd

BlmSchV in 2001 type V B machines will be required for all newly installed equipments, machines in use before 2001 have to be adapted until 2007 (BlmSchV, 2001) (see Chapter 2.5.3).

In Figure 4.17 for TRIC and Figure 4.18 for PERC, the $\log r$ value of the long-term measurements by Groz & Beckert (gray marks) are compared to the $\log r$ ranges of the SceBRA calculations for the five machine types (bars in black). Each gray mark depicts the average concentration of one series of measurements carried out in a specific year (measurements are listed in Tables C.21 and C.22 in Appendix C.4). Overall, a good correspondence can be seen between the measured data and the long-term near-field concentrations calculated with the two-box model.

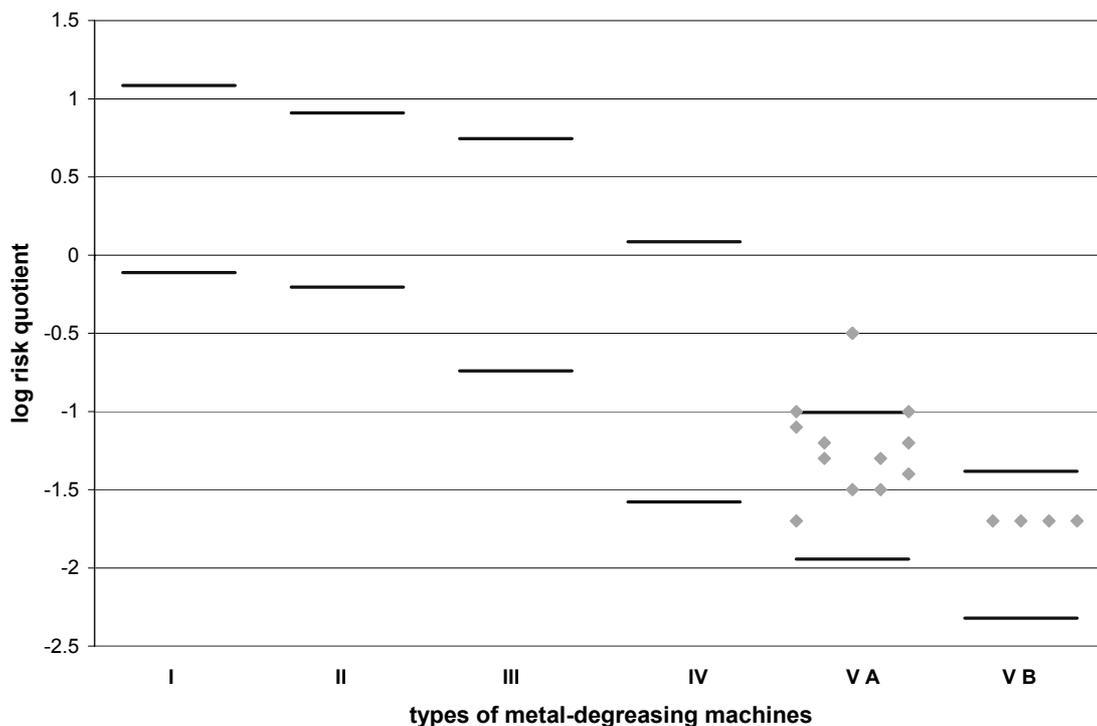


Figure 4.17: Comparison of average $\log r$ values of long-term air measurements of an unpublished series of measurements in the near-field of metal-degreasing machines using TRIC carried out in different years by Groz & Beckert (gray marks) with calculated near-field SceBRA $\log r$ values (bars in black) (measurements listed in Table C.21).

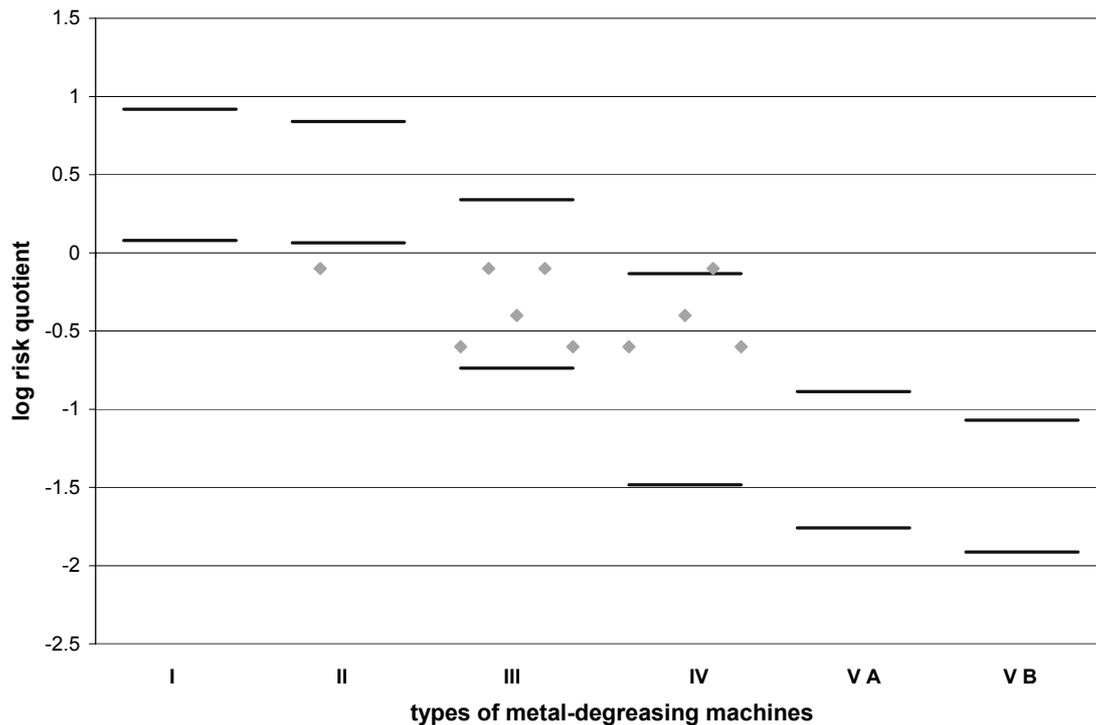


Figure 4.18: Comparison of average $\log r$ values of long-term air measurements of an unpublished series of measurements in the near-field of metal-degreasing machines using PERC carried out in different years by Groz & Beckert (gray marks) with calculated near-field SceBRA $\log r$ values (bars in black) (measurements listed in Table C.22).

4.3.6 Sensitivity analysis

In this section, results from a local sensitivity analysis are given for all uncertain input parameters. (Results of the global sensitivity analysis carried out in the dry cleaning case study are discussed in Chapter 5.4).

For one machine type, the size of the machine makes the major contribution to the risk quotient, r (see Figure 4.9 and 4.10). But the machine sizes are taken from sales brochures and are, hence, well-known distinct values of a discrete frequency distribution. Because the machine size is not an uncertain parameter, it is not included in the local sensitivity analysis.

The sensitivity, a , of the long-term airborne concentration of a type II A, size 3 metal-degreasing machine using TRIC, calculated according to Equation 3.8 in Chapter 3.5.4, is depicted in Figure 4.19 for the near-field (box A) and in Figure 4.20 for the far-field (box B). Each input parameter x_i was increased by 5%, while all other input parameters were kept constant.

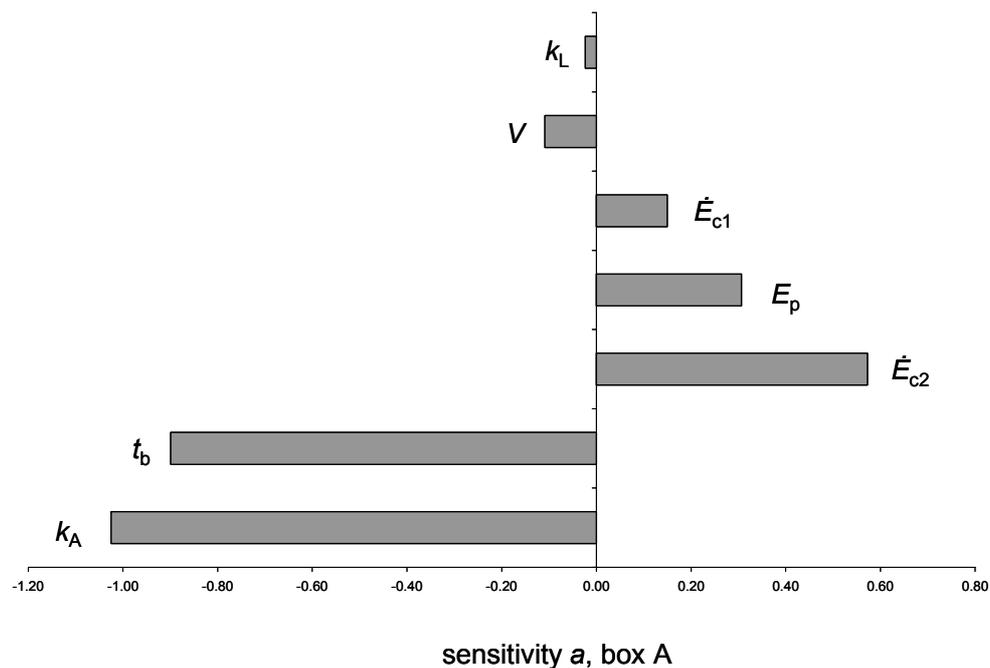


Figure 4.19: Local sensitivity analysis of the long-term airborne concentration in the near-field of a type II A, size 3 metal-degreasing machine using TRIC.

The local sensitivity analysis indicates that the batch time t_b and the air exchange rate k_A are the most influential parameters for the long-term ambient concentration in box A. The batch time depends on the loads of the machine, i.e. the weight, the material, and the shape of the parts. A specification of the parts and, therefore, more specific batch times would only make sense if the different parts cleaned in Germany could be described in more detail. As this is not possible in the context of a screening method, it is reasonable to use a realistic range of batch times derived from discussions with machine manufacturers of metal-degreasing devices.

The air exchange rate between boxes A and B is an assumption specifically made for the two-box model. More specific air exchange rates for certain workplaces could be estimated by tracer gas measurements (Sohn and Small, 1999). However, to estimate the concentrations for a broad range of industry facilities, it seems to be sufficient to take reasonable k_L values for rooms with local exhaust and to assume that for box A containing the machines, which

are relatively strong heat sources, the assumed k_A value is somewhat higher than k_L (see also Chapter 4.2.3).

Parameters with a medium influence are the emission factors \dot{E}_{c2} , E_p and \dot{E}_{c1} . Taken together, the three emission factors correspond well with reported total solvent losses (see Chapter 4.3.5). Better estimates could be achieved if emission factors were measured for different machine technologies; however, this is not feasible as only type V machines are in use in Germany today. Parameters with hardly any influence on the near-field long-term concentration are the total room volume, V , and k_L .

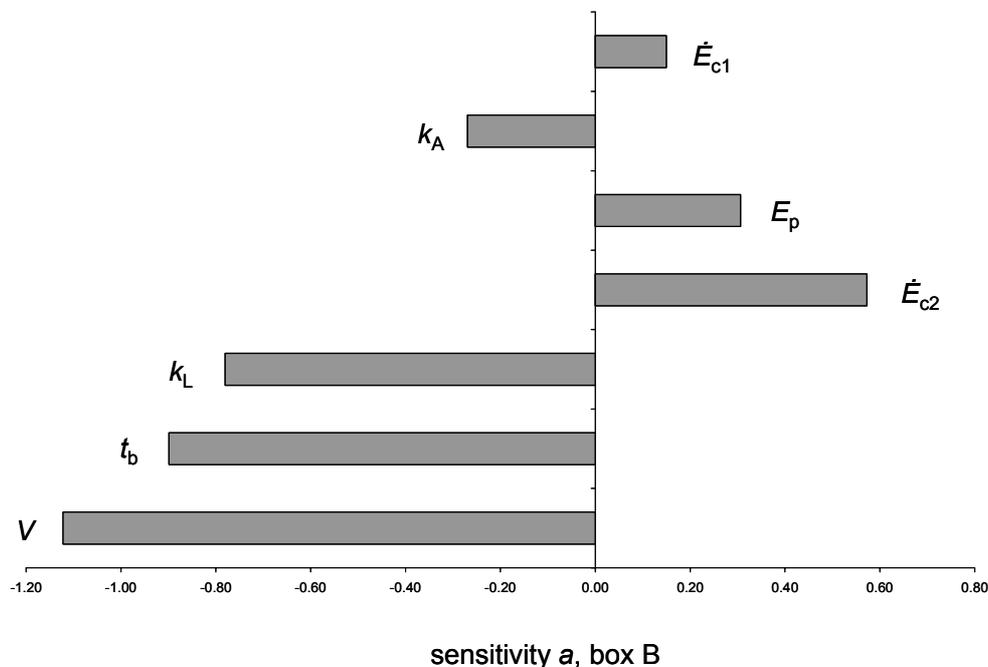


Figure 4.20: Local sensitivity analysis of the long-term airborne concentration in the far-field of a type II A, size 3 metal-degreasing machine using TRIC.

The results of the local sensitivity analysis of the far-field are very similar to those of the near-field, with the exception that here, logically, the total room volume, V , and the air exchange rate k_L have a strong influence on the long-term concentration in box B (note that the volume of box A is constant with 100m^3). A slightly negative a -value for an increase in air exchange rate k_A

occurs as long as the mass flow out of box B is higher than the mass flow into box B (i.e. the increase in k_A results in higher dynamic concentration amplitudes in box B). Note that for the SceBRA calculations, the air exchange rates k_A and k_L are coupled (see Chapter 4.3.2).

4.4 Conclusions

By using a broadly defined set of scenarios, it is possible to include the high variability of metal-degreasing facilities into a comprehensive exposure analysis. In the present application of the SceBRA method, this variability is described by clusters of parameter values, e.g., for machine size, type of cleaned parts, emission factor, air exchange rate, batch time and room volume, see Figures 4.7 and 4.8. Besides the machine size, which is a well-known discrete frequency distribution (see Chapter 4.3.6), the other input parameters, which include both variability and uncertainty, cannot be described with frequency distributions because of lack of data. For this reason, no probability density functions (PDF) of individual input parameters could be defined and, therefore, no detailed statistical exposure assessment could be carried out for this case study (see also Chapter 3.5.5). (Note that the set of scenarios can be seen as a discrete frequency distribution with identical frequencies for all model input parameter values.)

In contrast to metal degreasing, where not only the amount of cleaned metal parts but also their shape and arrangement in the basket affect the value of emissions, the dry cleaning case study deals with a much less heterogeneous functional unit (textiles). In this case, frequency distributions could be derived for the different model input parameters from series of measurements and questionnaires providing information on the parameters describing typical dry-cleaning facilities (see Chapter 5.4).

Note that, despite the few data on metal degreasing, all model parameters are based on empirical information and none of them has been adjusted in order to increase the correspondence of calculated and measured concentrations.

The core of the calculations with SceBRA presented in this case study is the long-term airborne concentrations obtained with the two-box model. As far as

a comparison with measured data is possible, these model results are in agreement with concentrations measured in metal-degreasing facilities, see Figures 4.15 and 4.16 for the comparison with published measurements and 4.17 and 4.18 for the comparison with unpublished data.

Overall, the long-term concentrations obtained with the scenarios correspond to the range of measured concentrations. This means that the scenarios cover a relevant range of exposure situations. A strategy for selecting a reasonable set of scenarios is first to define the scenarios “bottom up” by setting all reasonable parameter combinations (here a total of 2'160 scenarios for each machine size) and second to analyze which scenarios lead to very similar concentrations. On this basis, redundant scenarios can be omitted and those spanning the relevant long-term concentration range can be selected for further investigation.

In conclusion, the SceBRA method is suitable for characterizing the occupational risk of TRIC and PERC in metal degreasing. The numbers of exposed workers and the risk quotients in Figures 4.13 and 4.14 clearly indicate the combined effect of technological innovation and stricter legislation, leading to strongly reduced airborne concentrations and also to much lower numbers of exposed workers. The reduction in the number of workers is due to automatization and replacement of TRIC and PERC by non-chlorinated solvents. With the type V machines required today, the long-term near-field concentration according to the SceBRA calculations is below 5 ppm for TRIC and below 6.5 ppm for PERC in normal use of a type V A machine and below 2 ppm for TRIC and below 4 ppm for PERC in a type V B machine. The long-term far-field concentrations of below 2 ppm for both solvents in type V A and below 1.2 ppm for both solvents in type V B machines approach the limit of detection, which depends on the measurement device and is between 0.1 and 1 ppm. Consequently, it can be assumed that there is a low risk for operators and other employees in the far-field of metal-degreasing machines in Germany today. A similar assessment for the application of non-chlorinated solvents would be desirable.

A comparison of the metal degreasing and the dry cleaning case studies and further discussion of the advantages, abilities, and limits of the SceBRA method are given in Chapter 6.1.

Chapter 5

5 Case study: Dry cleaning

Dry cleaning is a process for removing spots and stains from fabrics that uses a non-aqueous organic solvent with added detergent in a special dry-cleaning machine. Dry cleaning is reported to have been discovered in 1826 when turpentine, used at that time for illumination, was accidentally spilled and found to cleanse fabric (Kirk and Othmer, 1950; Ullmann, 1975a). Several organic solvents have been used for dry cleaning. Appropriate solvents must have a high affinity for greases and oils but a low affinity for fabric dyes, must be chemically and thermally stable (hydrolysis and corrosion), must be sufficiently volatile so that the garments can be easily deodorized and must be suitable for purification by distillation. In the second half of the 19th century, kerosene, gasoline, benzene, and petroleum were used for dry cleaning. These substances gave good cleaning results but are inflammable and, in the 1890s, several explosions occurred in dry-cleaning facilities. Subsequently, a search for alternative non-flammable solvents began. Since the 1920s, the non-flammable chlorinated solvents TRIC, carbon tetrachloride, and PERC have been used. New more sensitive, artificial textile fibers prompted a search for less “aggressive” solvents. In the 1930s, CFCs such as R113 (1,1,2-trichlorotrifluoro ethane), and R11 (trichlorofluoro methane), and 1,1,1-trichloroethane were promoted for dry cleaning. After the Second World War, TRIC and carbon tetrachloride were withdrawn; TRIC because it dissolves some acetate dyes used for rayon, and carbon tetrachloride because of corrosion problems. In the 1950s, PERC gained market dominance; about 80% of garment dry cleaning was performed with PERC worldwide. Since the 2nd BImSchV of 1986, halogenated solvents for dry cleaning have been restricted

in Germany to PERC, dichloromethane, 1,1,1-trichloroethane, R-112 (1,1,2,2-tetrachloro-1,2-difluoro ethane), R-113, and R-11 (BlmSchV, 1986). The 2nd BlmSchV of 1990 only allows the use of PERC (BlmSchV, 1990). In the 1990s, new textiles and improved wet-cleaning machines (with a gentler action and running at lower temperature) required less dry cleaning and, therefore, organic solvent-based technologies were displaced to some extent. Besides improved PERC dry-cleaning machines, new hydrocarbon solvent machines were developed in the 1990s. At the “Expodetergo” in 1996 in Milan, a new dry-cleaning technology running with liquid carbon dioxide was introduced. In Germany today, dry cleaning is predominantly performed with PERC (78% in 2001) (DTV, 2002). About 1'500 metric tons of clothing were dry cleaned per day in 1994. This decreased to 825 metric tons per day in 2001, which is about 2.6 to 3.0 kg garments per capita and year (DTV, 2001; DTV, 2002).

The present case study will focus on the use of PERC in commercial and industrial dry-cleaning shops and facilities. Coin-operated machines will not be considered, as they are not common in Germany. The fact that dry-cleaning facilities are mostly placed in the heart of urban areas and that they were associated with very high emissions led to several revisions in the German legislation, starting with the 2nd BlmSchV of 1974, the 2nd BlmSchV of 1986, and the 2nd BlmSchV of 1990 (the amendment of the 2nd BlmSchV 1990 in 2001 is not relevant for dry cleaning, see Chapter 2.5). This case study will show how the changes in machine technology have influenced the occupational risk for machine operators and other employees such as garment pressers and sales personnel in dry-cleaning facilities. The number of workers exposed to long-term concentrations around the MAK value in the 1970s and the number in Germany today will be considered.

In Chapter 5.1, the dry-cleaning process is described and the five generations of dry-cleaning machines are introduced. In Chapter 5.2, the different model inputs describing the exposure scenarios are introduced (machine parameters, emission factors, workplace parameters, number of machines, and number of exposed workers). The results of the exposure assessment will be presented in Chapter 5.3. This is followed by a detailed statistical exposure assessment (Monte Carlo simulations) (Chapter 5.4). In Chapter 5.5, initial conclusions about the dry cleaning case study are drawn.

5.1 Technological development

Dry cleaning is a three-step process of washing, extracting, and drying. At the start of the washing process, clothes are manually loaded through the front door into the cylinder of the machine. After the door is closed and the machine is activated, PERC is automatically pumped into the cylinder. Water-based detergents are automatically injected into each load to aid in removing water-soluble stains. The contents of the machine cylinder are then agitated, which allows the solution to remove dirt and other offending materials. Following this, the clothes are spun at high speed to extract the solvent and the fabric is finally tumbled dry with heated air. The temperature of the air and the length of the drying cycle are determined by the garment fabric and by machine construction. Garments removed from the machine are pressed to remove wrinkles and to restore their original shape. Once the garments are pressed, they are put on hangers, wrapped in plastic, and stored to wait for customer pick-up. A schematic representation of a dry-cleaning machine is depicted in Figure 5.1.

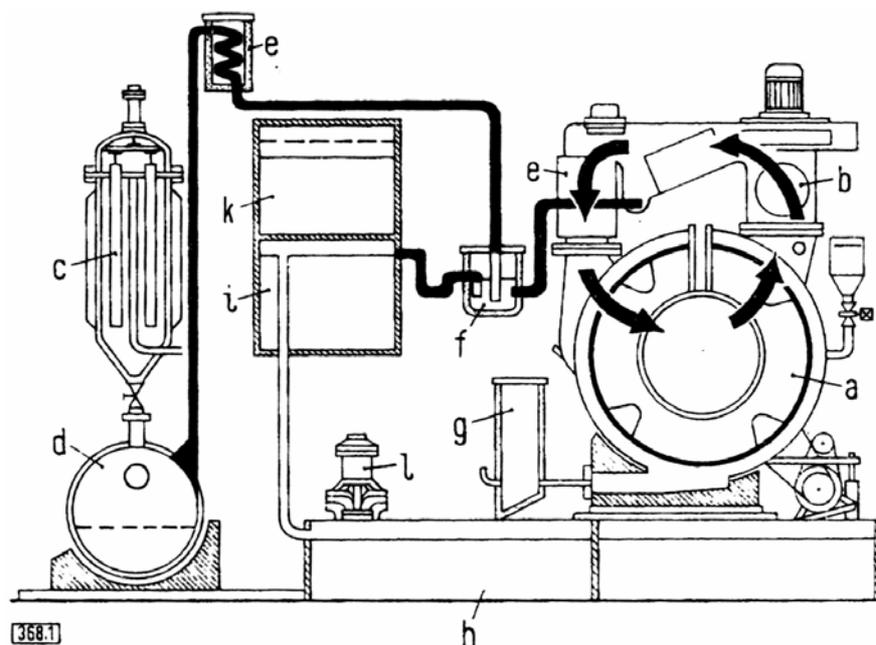


Figure 5.1: Schematic representation of a dry-cleaning machine with a: cylinder; b: air drying and recycling cycle; c: filter; d: distillation device; e: cooler; f: water separator; g: button trap; h: tank with cleaning solvent including detergents; i: tank with fresh solvent; k: tank for after treatment; l: solvent pump (Ullmann, 1975a).

The earliest dry-cleaning machines were transfer machines with separate washers and dryers. With these machines, manual transfer of solvent-laden clothing between the washer and dryer was required. The transfer activity involved high worker exposure to PERC. The total solvent consumption of transfer machines was about 300 to 500 g per kg clothing (total of all emissions, losses, and the solvent amount in the sump, which is disposed as waste) (Engels et al., 1975). According to Earnest (2002), transfer machines were used in the U.S.A. exclusively until the late 1960s. As there is very little information available about the use of such machines during the last 30 years in Germany, the focus here will be on dry-to-dry machines. These are used in a one-step process that eliminates garment transfer. The dry-to-dry machine generations range from vented devices with water-cooling to non-vented machines with closed-loop drying cycle. The technological development is commonly classified into dry-cleaning machine generations (Manufacturers, 1959-2002; Kurz and Klein, 1998; Earnest, 2002). The four generations at the focus of this case study are depicted in Figure 5.2. Information about machines is taken mainly from sales brochures (Manufacturers, 1959-2002).

2nd generation dry-to-dry vented machines have a water-cooled condenser at a temperature of about 15°C. During the drying cycle, the solvent charged air passes the water-cooling and is then blown out into the environment without passing through an activated carbon filter. At the end of the drying process, fresh air is drawn in through a trap and released outside of the building. At the face of the machine door, a fan is installed to prevent escape of PERC vapor during loading and unloading. The total solvent consumption is about 100 to 150 g solvent per kg textiles (Rentz et al., 1997; Riff, 1998; Merkhofer, 2001).

3rd generation vented dry-to-dry machines have a water-cooled (15°C) or a refrigeration-cooled unit (-15°C). At the end of the drying process, fresh air is drawn in through a trap, passes through the load to a single-pass carbon adsorber and is blown out into the environment. A small door vent prevents PERC vapor from escaping during loading and unloading. The total PERC consumption per kg textiles ranges from 40 to 80 g/kg (Rentz et al., 1997; Riff, 1998).

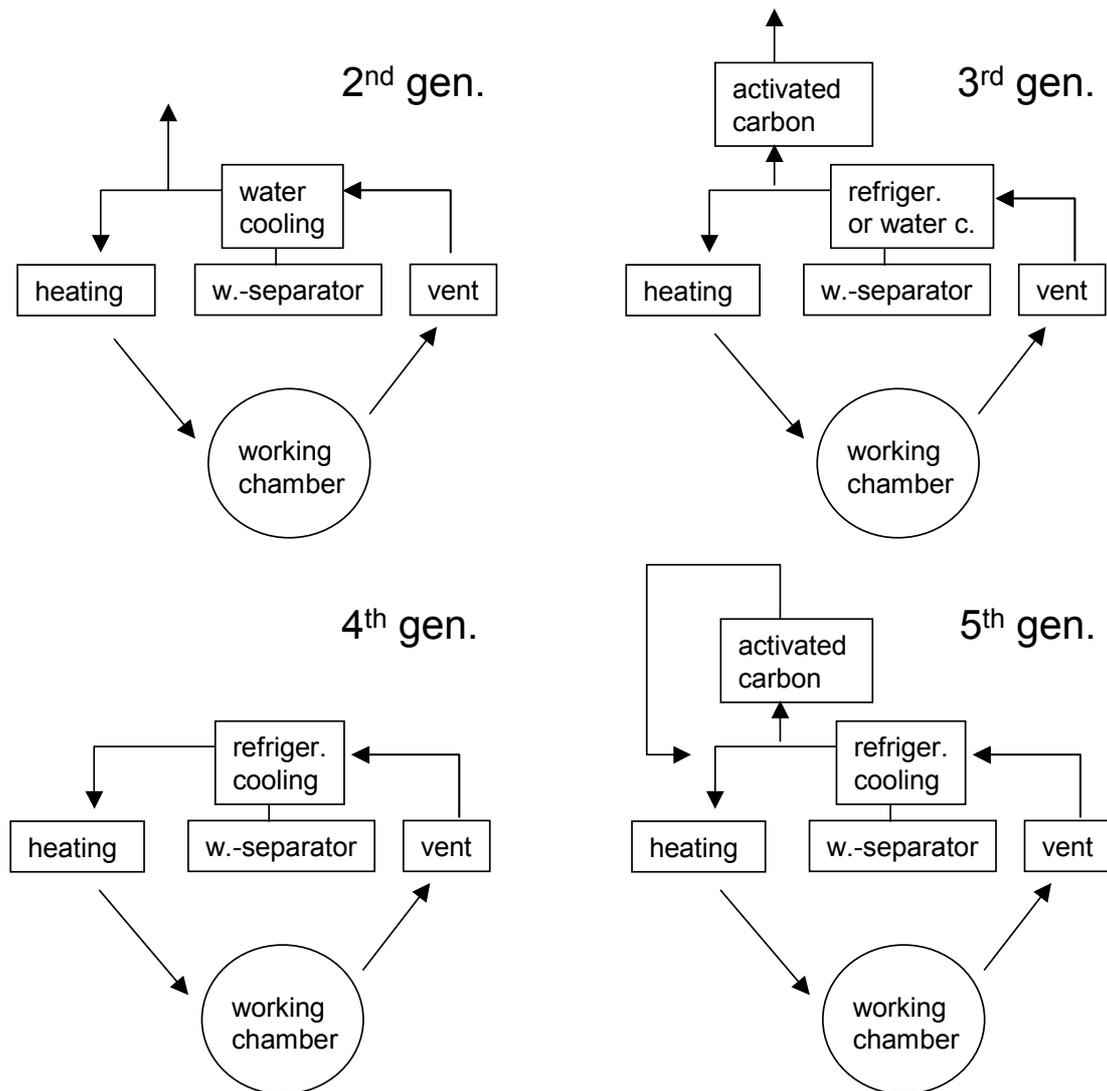


Figure 5.2: Technological progress of dry-cleaning machines represented by four machine generations (w: water; refriger.: refrigeration c.: cooling).

4th generation machines are non-vented dry-to-dry machines with a closed drying cycle. The air stream of the drying cycle passes repeatedly through the refrigeration-cooled condenser (-20°C), which vaporizes and recovers most of the residual solvent. While passing through the cooling coil, PERC vapor condenses and flows to the separator, where water is removed. Liquid PERC flows back into the machine tank. During the drying cycle, no exhaust air is released to the environment. The total consumption lies in the range of 20 to 40 g PERC per kg clothing (Zott, 1993; Adams, 1994; Rentz et al., 1997; Riff, 1998).

5th generation dry-to-dry machines are sealed, with a closed-loop drying cycle similar to 4th generation machines. In addition, a drying sensor measures the solvent flow between the refrigerated condenser and the water separator during the drying cycle. When condensation stops, this automatically switches the system to the cool-down/deodorize step, where air is cooled in the refrigerated condenser before passing through the carbon adsorber and returning to the drying drum. An interlock on the machine door ensures that the machine cannot be opened until the drying/vapor recovery process reaches completion, i.e., before the concentration in the drum is below the legal threshold of 2 g/m³ (BlmSchV, 1990). With this newest technology of dry-cleaning machines, the total PERC consumption is less than 10 g per kg garments (Zott, 1993; Adams, 1994; Rentz et al., 1997; Riff, 1998; Merkhofer, 2001).

In Germany, 2nd generation machines were built from the late 1950s and were used until the 2nd BlmSchV of 1986. In the late 1960s, 3rd generation machines were introduced. In the transitional period, they had to be adapted to the cylinder concentration requirements laid down in the 2nd BlmSchV of 1986 (see Chapter 2.5.1). In the early 1980s, 4th generation machines came on the market that were in agreement with the 2nd BlmSchV of 1986. The 2nd BlmSchV of 1990 requires non-vented 5th generation machines. These were developed in the late 1980s and came on the market in 1990. Figure 5.3 shows the chronology of dry-cleaning machine generations triggered by the German 2nd BlmSchV regulations.

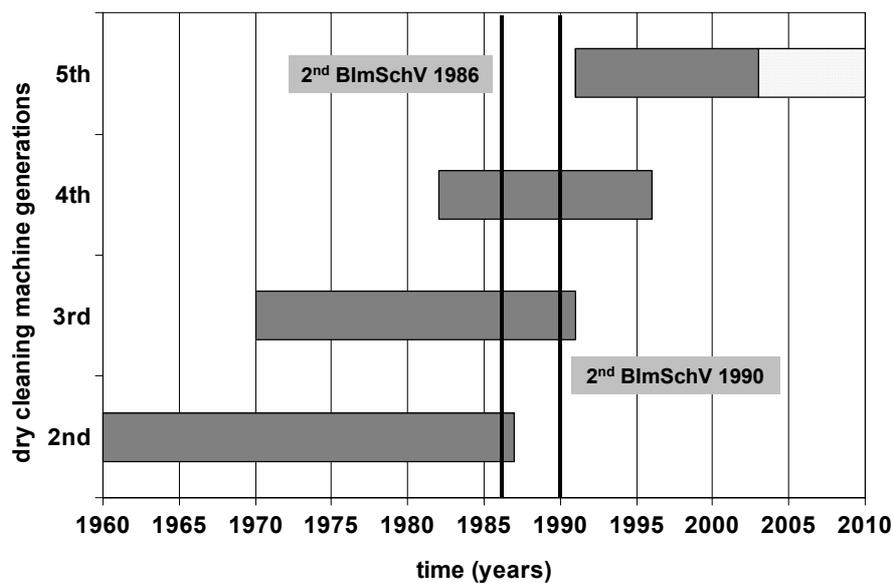


Figure 5.3: Chronology of dry-cleaning machine generations triggered by the German 2nd BImSchV regulations (the amendment in 2001 of the 2nd BImSchV 1990 is not relevant for dry cleaning).

5.2 Scenario definition

As mentioned by Earnest et al. (2002), factors other than machine design and capacity affect exposure, such as clothing fabric, number of loads per day, general ventilation, and work practices. To represent the different exposure situations in the dry cleaning case study, a range of possible and plausible use scenarios is defined. The different scenarios are described by: (i) machine parameters such as machine generation and machine capacity, (ii) emission factors, and (iii) workplace parameters such as room size and air exchange rates. Compared to the different sizes and shapes of metal parts, which strongly influence the solvent emissions (see Chapter 4.2 and 4.2.2), textiles are a relatively homogeneous commodity. Therefore, the functional unit can be defined as a textile load of 1 kg weight. Information on the different input parameters was mainly obtained from reports by the Hohenstein Research Institute (“Bekleidungsphysiologisches Institut Hohenstein”, which specializes in textiles), and from the German textile cleaning association (DTV: “Deutscher

Textilreinigungs-Verband”), from scientific publications and from a questionnaire sent to 248 German dry-cleaning shops in 2002 (level of return 23.8%) (see Appendix D.1.1). In the end, it was of interest to know how many machines of a certain technology were used and how many operators and other dry-cleaning employees were exposed in specific years in Germany.

5.2.1 Machine parameters

Reduction of emissions has been one of the main targets in the development of new machines. The four machine generations focused on in this study are described in Chapter 5.1. Each machine generation is manufactured in different sizes, to adjust capacity to the size and demand of dry-cleaning shops. For this study, the five most common machine capacities are chosen. Small size 1 machines have a capacity of 12 kg and large size 5 machine a capacity of 32 kg per load (see Table 5.1) (Manufacturers, 1959-2002). According to our dry-cleaner survey, size 2 machines with a share of 25.7% and size 3 with a share of 30% are the most commonly used machines.

Table 5.1: Characteristic cylinder volumes and capacities of the five machine sizes, and frequency of capacities used in Germany in 2002 according to dry-cleaner survey.

Size	Cylinder volume (m ³)	Capacity (kg)	Frequency of capacities* (%)
1	0.24	12	10.0
2	0.32	16	25.7
3	0.44	22	30.0
4	0.56	28	15.7
5	0.64	32	18.6

* according to dry cleaner survey in 2002

Given that good cleaning results can only be obtained when the machine is not overloaded, both in terms of weight and volume, garment loads are

weighed beforehand and the machines have a maximum level indicator. In the present study, a loading factor, f_L , is introduced to determine the degree of filling. An average value for f_L of 0.79 was derived in a survey carried out by Klein and Kurz in 1994. The duration of one washing cycle (batch time, t_b) is dependent on the machine generation and on the garment fabric, but mainly on the time needed for drying. Batch times lie between 40 to 55 minutes for vented 2nd generation machines and about 50 to 70 minutes for 5th generation machines (for more information, see Appendix D.1.2).

5.2.2 Emission factors

In this chapter, the three emission factors used for the SceBRA calculations of the dry cleaning case study are explained in detail. Summaries of the different emission factors for each machine generation and size are listed in Appendix D.1.3.

Continuous emission factor for diffuse emissions

In the dry cleaning case study, the diffuse emission factor \dot{E}_{c1} (g/h) describes a continuous discharge into box A. It is based on the leaking rate per functional unit (average textile load of 1 kg) E_{c1} (g/kg), including emissions from leakage of sealing, drum, button trap, and lint trap. In vented 2nd and 3rd generation machines, diffuse emissions account for 22.8% of total solvent losses to the air (Schmidt et al., 1995) (see Table D.2 in Appendix D.1.3.1). For generations for which no data about diffuse emissions could be acquired diffuse emissions are determined from the total consumption per functional unit: total consumption minus solvent amount in waste (g/kg) gives the total losses to air. From this amount, vented emissions (g/kg), emissions from maintenance operations and tank filling, continuous emissions from cleaned garments E_{c2} (g/kg), and periodic emissions during loading and unloading E_p (g/kg) are subtracted to give E_{c1} (g/kg) (see Table D.3 in Appendix D.1.3.1). By doing so, it is warranted that the total of all emissions together with the solvent amount in the waste equals the total solvent consumption. Furthermore, it is assumed that diffuse emissions are the same for vented 2nd

and 3rd generation machines. Multiplication of E_{c1} (g/kg) by the load and division by the batch time results in the emission factor \dot{E}_{c1} (g/h) over a batch time t_b (\dot{E}_{c1} values for all machine generations are listed in Table D.4 in Appendix D.1.3.1).

Continuous emission factor for cleaned textiles

The cleaned garments taken out of the cylinder after washing and drying are not absolutely dry but contain residual solvent in the fabric. The amount of residual solvent depends on the drying time and the garment fabric. Measured data can be found for “normal loads” and for “off-the-peg” clothing (i.e., suits and jackets with shoulder pads) (residual solvent amounts are listed in Table D.5 in Appendix D.1.3.2). A “normal load” includes approximately 40% wool, 20% cotton, 20% polyester, 10% polyacrylic fibers, and 10% other fabrics. 80% of the garments being dry cleaned in Germany can be classified as “normal loads” (Klein et al., 1991). The average residual solvent in “normal loads” is 0.38 g/kg for 3rd, 0.26 g/kg for 4th, and 0.12 g/kg for 5th generation machines (Klein et al., 1991). As no measured data are available for 2nd generation machines, the residual solvent amount is assumed to be 1.2 times the amount of 3rd generation machines. This corresponds to findings in the U.S.A. for 2nd or 3rd generations machines (Brodmann, 1975).

For “off-the-peg” clothing, Klein et al. (1991) measured values between 1.02 and 1.43 g/kg for 5th generation machines. These data correspond with findings collected in a semester work reporting 3.75 g/kg for 4th and 1.26 g/kg for 5th generation machines (Werner, 1996). As no “off-the-peg” residual data were available for vented 2nd and 3rd generation machines, it is assumed that the proportion of “normal load” to “off-the-peg” clothing is the same as for 4th generation machines.

As an occupational worst-case scenario, it is assumed that all of the residual solvent will evaporate continuously over a certain period, α (h), which lies between one-third and one-fourth of the batch time. This assumption is supported by the fact that residual solvent can be reduced considerably during ironing (Klein et al., 1991). Weber (1992) reports residual solvent amounts after ironing of 0.005 g/kg in garments cleaned in 5th generation machines.

Additionally, the evaporation times, α , are in agreement with findings from off-gassing experiments showing that after 5 minutes 90% and after 10 minutes 99% of the residual solvent evaporates from garments cleaned in 4th generation machines (Earnest, 1996; Earnest, 2002). A chart of a typical off-gassing experiment can be seen in Appendix D.1.3.2, Figure D.1.

The quotient of E_{c2} (g/kg) and α leads to the dry-cleaning emission factor \dot{E}_{c2} (g/h) for cleaned textiles. Minimum values of \dot{E}_{c2} represent “normal loads” and maximum values stand for emissions from “off-the-peg” loads. An average emission factor is derived from an average load consisting of 80% “normal” and 20% “off-the-peg” clothing. (Residual solvent amounts and values for \dot{E}_{c2} are listed in Table D.6 and D.7 in Appendix D.1.3.2 for all generations and sizes of dry-cleaning machines).

Periodic emission factor for loading and unloading

Each time the machine is loaded or unloaded, solvent-charged air from the cylinder is exchanged with workplace air. This is described by the periodic emission factor E_p (g).

In vented machines (2nd and 3rd generation), a fan is installed that draws in air as long as the front door is open to reduce emissions into the workplace. This retains 50% of the solvent-charged air. For non-vented machines (4th and 5th generation), it is assumed that the whole cylinder volume of solvent-charged air exchanges with the workplace. For 2nd generation machines, the cylinder concentration is between 150 and 240 g/m³ (Klein et al., 1991; Rentz et al., 1997). For 3rd to 5th generation machines, the maximum cylinder concentrations at the time the garments are taken out are fixed in the 2nd BImSchV regulations. For vented 3rd generation machines, the cylinder concentration must be below 42 g/m³, for non-vented 4th generation machines below 25 g/m³ (BImSchV, 1986) (see Chapter 2.5.1). In 5th generation machines, the door can only be opened if the cylinder concentration is below 2 g/m³ (BImSchV, 1990) (see Chapter 2.5.2). The emission factor is calculated as an intermittent emission that occurs at the moment the door is opened. (Tables with literature data, model inputs for minimum and maximum cylinder

concentrations, and periodic emission factors for all machine generations and sizes can be found in Appendix D.1.3.3).

5.2.3 Workplace parameters

Not only the dry-cleaning equipment and the operation of the machine influence occupational exposure but also the workplace surroundings. The airborne concentration in a dry-cleaning shop depends upon the room volume and the air exchange rates. According to the survey, volumes of dry-cleaning facilities vary from small shops of about 70 m³ to volumes of 3000 m³ (with a mean of 618m³, more details can be found in Appendix D.1.4 and D.4.1). A survey by the Hohenstein Research Institute determined volumes of 200 to 630 m³ with a mean of 362 m³ (Klein and Kurz, 1994). For the SceBRA calculations, volumes of 400 and 600 m³ are assumed for the whole workplace (the fictitious near-field box in which the machine is located has a constant volume of 100m³, see also Chapter 3.2).

Typical air exchange rates in dry-cleaning facilities lie between 5 and 19 times per hour (Engels et al., 1975; Fachgruppe Lufthygiene, 1996; Kurz and Klein, 1998). Recommended air exchange rates in laundries are between 10 and 15 h⁻¹ (Recknagel et al., 2000), whereas normal commercial air-conditioning systems have air exchange rates of 5 to 6 h⁻¹ (Hayes, 1991). In a survey carried out by the Hohenstein Research Institute in 1994, air exchange rates in German dry-cleaning facilities varied between 1 and 19 h⁻¹, with a mean of 8 h⁻¹ (Klein and Kurz, 1994). For the SceBRA calculations, k_L values of 6 and 10 h⁻¹ were employed. The air exchange rate between box A and box B, k_A , is assumed to be higher than the overall exchange rate k_L because dry-cleaning machines are heat sources that create an upward flow of warm air (Heinsohn, 1991; Klein et al., 1991; Bach et al., 1992). Vented 2nd and 3rd generation machines also have integrated fans drawing in workplace air, which increases the air exchange. For those reasons, k_A values are assumed to be 8 h⁻¹ (for a k_L of 6 h⁻¹) and 12 h⁻¹ (for a k_L of 8 h⁻¹). The model assumptions on workplace volumes and air exchange rates are listed in Tables D.11 and D.12 in Appendix D.1.4.

5.2.4 Number of exposed workers

In addition to the risk quotient, the number of exposed workers in the two boxes with their different concentrations is investigated with SceBRA. The number of exposed workers can be estimated from the number of machines used in certain years. Estimates of the numbers of dry-cleaning machines using PERC are listed in Table D.13 of Appendix D.1.5. Machine numbers in the former West German states are given for the years 1975, 1986 (in this year the 2nd BImSchV 1986 was enacted), 1989 (during transitional regulation of 2nd BImSchV 1986), and 1990 (year of enactment of the 2nd BImSchV 1990) (Engels et al., 1975; Klein et al., 1991; Rentz et al., 1997). Numbers for all German states are given for the years 1992, 1994, 1996 (after the transition regulation of the 2nd BImSchV 1990), 1998 and 2001 (Adams, 1994; Rentz et al., 1997; DTV, 2001; DTV, 2002). The number of dry-cleaning machines using PERC decreased from approximately 20'520 in 1975 to 4'700 in 2001.

It is assumed that between 1 and 1.5 operators (average of 1.25) are required to operate the dry-cleaning machines (Earnest, 2002). Furthermore, it is assumed that the operators are present in the near-field during the whole 8 h working day.

Estimation of the number of workers in the far-field is more difficult. Workplaces can vary very much from small shops performing only dry cleaning to large laundry facilities with both aqueous machines and dry-cleaning machines. Evaluation of our survey resulted in a mean of 7.8 employees (full-time and part-time employees) per shop. Other studies report 3 to 5 (Engels et al., 1975), 3 to 4 (Klein et al., 1991), and for the U.S. an average of 8.1 (Earnest, 2002) employees per shop.

For the dry cleaning case study, a total of between 5 and 6.5 exposed workers per machine is assumed. Of these, 4 to 5 workers (average of 4.5) are present in the far-field; these are mostly pressers and sales personnel. The assumptions about numbers of exposed operators and other workers are listed in Table D.14 in Appendix D.1.6. A comparison of the total number of exposed workers estimated in this case study with published numbers of employees for the whole dry-cleaning sector, including workers in "cold shops" (receiving offices, where no dry cleaning is performed), is made in Chapter 5.3.4.

5.3 Results of occupational exposure assessment in dry cleaning

The basic two-box model allows specification of the dynamic and the long-term concentrations of each scenario. By combining all independent input parameters, 180 possible and plausible exposure scenarios are obtained for each machine generation. From these, the maximum and minimum scenarios are selected for each size of machine. Thereby, the number of scenarios is reduced for each machine generation to 10 scenarios, i.e. to 5 sizes with two scenarios per size. On this basis, the four generations of machines can be compared and characteristic differences depicted. Finally, for selected years, the number of exposed workers, N , is combined with the risk quotients, r , of the different generations and sizes of machines. On this basis, the changes in the number of exposed workers and the magnitude of the risk quotient can be compared over a period of 26 years.

5.3.1 Dynamic concentrations

With one set of input parameters for a specific machine (machine parameters, emission factors, workplace parameters), the dynamic and long-term concentrations over an 8-h working day can be calculated for a single scenario. In Figure 5.4, these concentrations are shown in an example of a vented 3rd generation dry-cleaning machine of size 5. In this scenario, 25.3 kg garments are washed with a batch time, t_b , of 0.8 h.

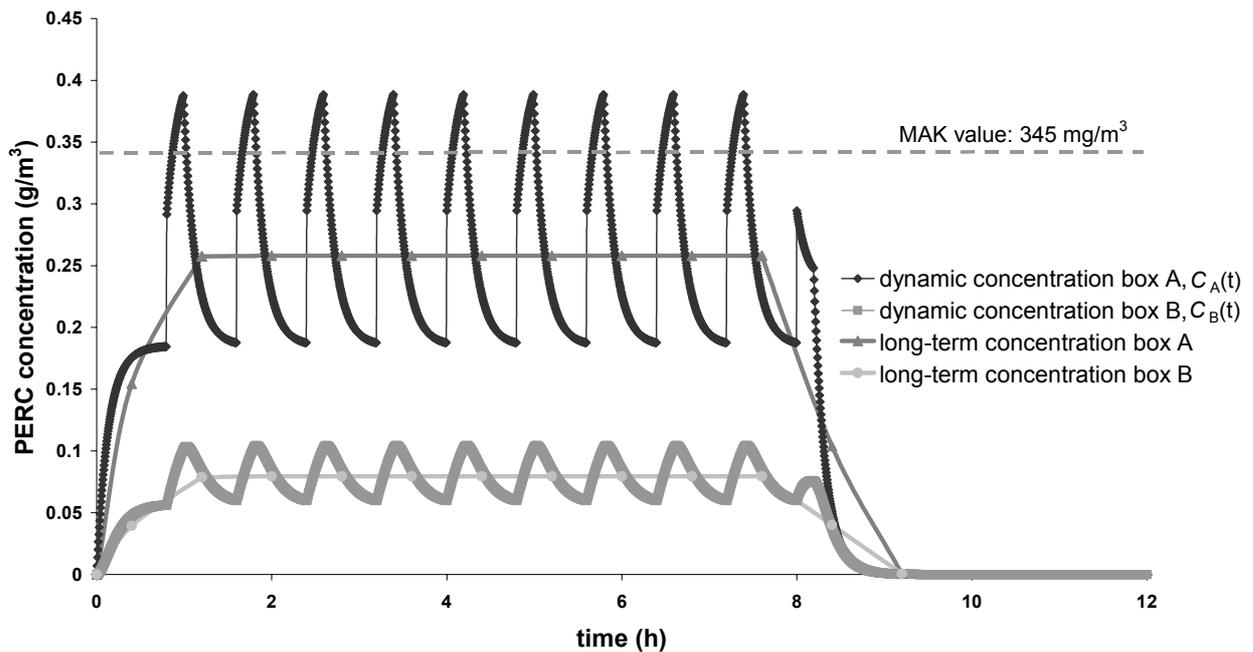


Figure 5.4: Dynamic PERC concentration of a vented 3rd generation size 5 dry-cleaning machine (E_p : 10.7 g, \dot{E}_{c1} : 143 g/h, \dot{E}_{c2} : 181 g/h, α : 0.2 h, t_b : 0.8 h, V : 400 m³, k_L : 6 h⁻¹, k_A : 8 h⁻¹).

Each time the machine is unloaded, a peak concentration is observed, followed by a further concentration increase until all residual solvent from the cleaned textiles is emitted. The long-term concentration is calculated as the integral of the concentration curve over one batch time, divided by t_b (see also Appendix B.3). Shortly after the first unloading (after approximately 1 h) a steady state is reached; thereafter a regular pattern of subsequent peaks with a scenario-specific amplitude follows. The shape of the dynamic concentration curve with the subsequent pattern of peaks during loading and unloading is typical of dry-cleaning facilities. This is confirmed by workplace measurements reported by Earnest (2002) and by peak exposure measurements listed in Table D.15 for the near-field and Table D.16 for the far-field of dry-cleaning machines (see Appendix D.3). After 8 hours, operation of the dry-cleaning machine is stopped and the airborne concentration decreases to the initial value. The long-term airborne concentration lies at 0.26 g/m³ in box A and at 0.08 g/m³ in box B. This means that for this specific scenario the long-term concentration in the near-field, i.e., the working area, reaches 75% of the MAK

level of 345 mg/m^3 , whereas the far-field long-term concentration reaches only 23% of the MAK value.

5.3.2 Parameter combination

The systematic combination of all independent input parameters leads to 180 exposure scenarios for each machine generation (for parameter combination see Figure D.2 in Appendix D.2). The resulting concentrations of all scenarios are indicated in Figure 5.5 as diamonds representing the long-term concentrations for both box A (Figure 5.5, diamonds in lighter gray) and box B (Figure 5.5, diamonds in black). Here, results are given for a vented 3rd generation dry-cleaning machine.

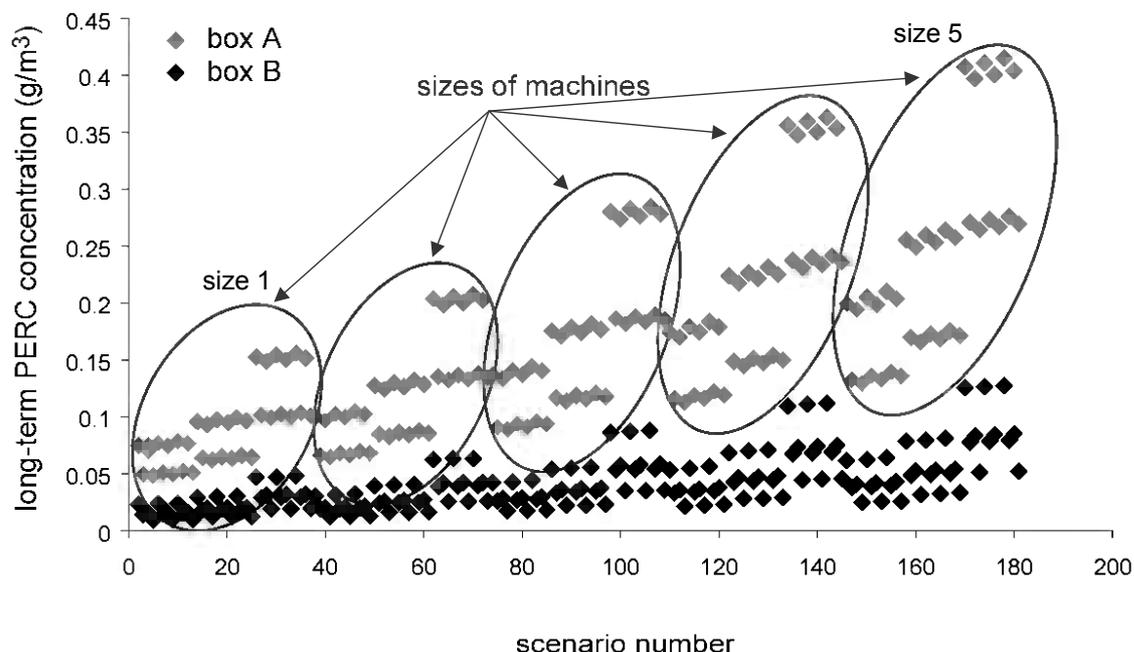


Figure 5.5: All exposure scenarios of a vented 3rd generation dry-cleaning machine with the different sizes of machines indicated.

In Figure 5.5, five different groups of marks indicating the different machine sizes can be made out (Figure 5.5, black ellipses). It can be seen that, within

one machine generation, the size of the machine has a major impact on the long-term airborne concentration, both for the near-field and the far-field. The size of the dry-cleaning machine has an influence on cylinder volume and, therefore, on periodic emissions, as well as on garment loads and, thus, also on continuous emissions from leakage and continuous emissions from cleaned textiles. It can be seen that within one machine size the scenario concentrations are not equally distributed but that there are several clusters of scenario.

Similar scenario combination plots can be obtained for all generations of dry-cleaning machines (see Figures D.3 to D.6 in Appendix D.2).

Next, the contribution of the different input parameters to the range of long-term ambient concentrations will be exemplified for a 3rd generation machine of size 5. The contribution of the different input parameters to the range of near-field long-term airborne concentrations is depicted in Figure 5.6.

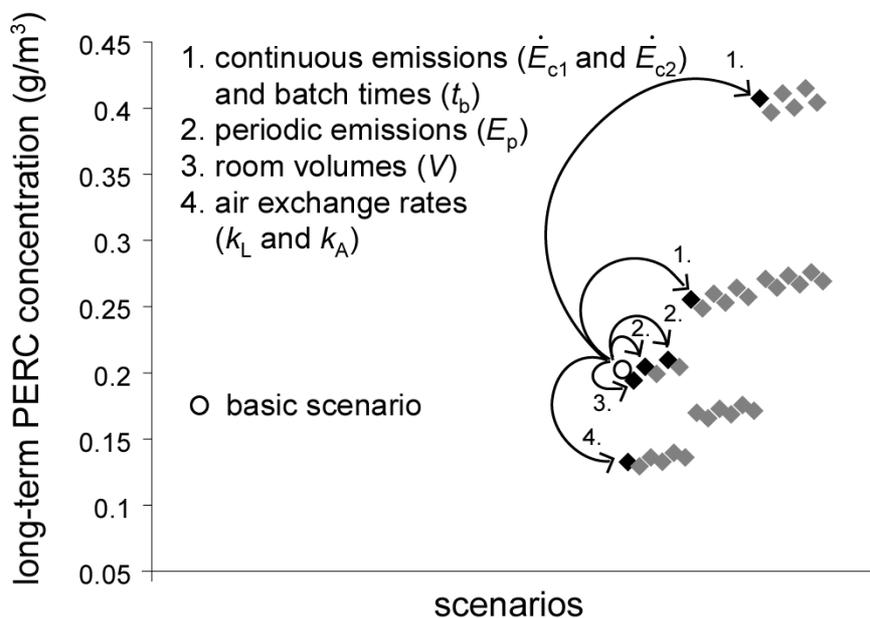


Figure 5.6: Contribution of changes in different input parameters to the long-term concentration in box A of a 3rd generation, size 5 dry-cleaning machine. Starting from a basic scenario (open circle), the different parameters are varied from their minimum to average to maximum values (arrows 1 and 2) or from their minimum to maximum values (arrows 3 and 4). For this machine, the minimum and the maximum near-field PERC long-term concentrations are 0.13 g/m³ and 0.42 g/m³.

Numbered arrows starting from the basic scenario indicate concentration changes occurring when only a single parameter is changed. Changing more parameters results in combination of the individual effects; these scenarios are represented by the gray marks. Parameters that vary little between different scenarios have a relatively small influence on the long-term concentration. Such parameters are the periodic emissions from loading and unloading (E_p) and the room volume (V) (Arrows 3 and 2 in Figure 5.6). During loading and unloading, solvent-laden air from the cylinder is released into the workplace. The cylinder has only a limited volume and emissions occur only every 40 to 70 minutes. This has a minor influence on the long-term airborne concentration.

The overall room volume has a small effect on the near-field long-term concentration because it influences only the air exchange from box B to box A (k_B), which is dependent on the room volume, V , and the exchange rate, k_A , as the fictitious near-field box A is fixed at 100m^3 .

Parameters that show more pronounced effects are:

- The continuous emission factors \dot{E}_{c1} (g/h) and \dot{E}_{c2} (g/h) and the batch time t_b , which are all coupled (Arrow 1 in Figure 5.6): The variations in \dot{E}_{c1} and \dot{E}_{c2} represent the variances in the cleaning process and the variance in the cleaned garments (“normal” or “off-the-peg” clothing). The continuous diffuse emissions \dot{E}_{c1} are emissions from leakage, which depend on the condition of the machine, and they include emissions out of the lint trap and the bottom trap, which are proportional to the cleaned textiles. \dot{E}_{c2} are emissions out of cleaned garments, which depend on the garments being dry cleaned and the amount of solvent dragged out per kg of textiles. The two emission factors are coupled with the batch time because in the literature they are both given as emissions per functional unit of 1 kg textiles. Therefore, they must be multiplied by the load and divided by the batch time to give rates of emissions (g/h). Additionally, t_b influences the long-term airborne concentration strongly because it determines the spacing between the emission peaks.

- Coupled air exchange rates k_L and k_A (Arrow 4 in Figure 5.6): The air exchange rates k_L and k_A directly influence the removal of the pollutant. They are coupled because simultaneous high exchange rates in one box and low in the other box are unlikely.

5.3.3 Comparison of technologies

The different machine generations and sizes can be compared by analyzing the range of the risk quotient, r , for all sizes of each machine generation. In Figure 5.7, the minimum, maximum, and average logarithmic risk quotients, $\log r$, for the near-field are given for all four machine generations (the according SceBRA exposure estimates are listed in Table D.15 in Appendix D.2). $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value. It can be seen that $\log r$ decreases with decreasing machine size and is reduced by more than one unit from venting 2nd to non-venting 5th generation machines that fulfill the 2nd BImSchV of 1990.

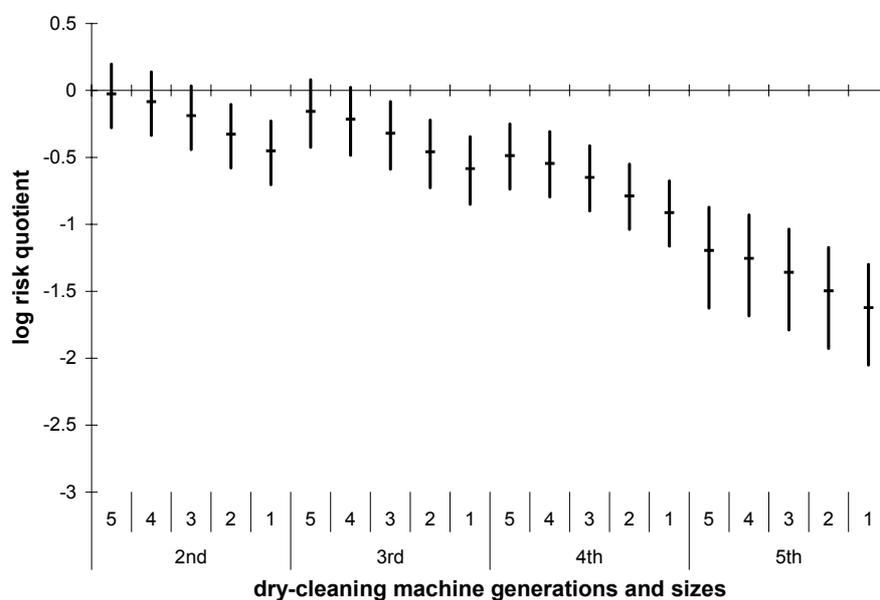


Figure 5.7: Comparison of the near-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the four machine generations subdivided into five sizes of dry-cleaning machines using PERC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value. Arrow: machine characterized in Figure 5.6.

It can be seen that 2nd and 3rd generation dry-cleaning machines have similar long-term concentration ranges for the near-field. The risk quotients are only slightly reduced for 3rd generation machines. Nevertheless, the two generations are distinguished as only 3rd generation machines fulfill the 2nd BImSchV of 1986. Hence, it can be seen that the 2nd BImSchV of 1986 focused mainly on reduction of solvent emissions into the environment and only in a second attempt on improvement of workplace conditions. The total solvent consumption for 2nd generation machines was between 100 to 150 g PERC per kg textiles, in comparison to 40 to 80 g/kg for 3rd generation machines (see Chapter 5.1). With 4th generation machines and especially with the 5th generation machines required by the 2nd BImSchV of 1990, a significant improvement in terms of lower workplace concentrations in the near-field can be seen.

According to SceBRA calculations, the MAK value is not exceeded for operators working in the near-field of properly operating size 1 to size 4 vented 2nd and 3rd generation machines and for all sizes of non-vented 4th and 5th generation machines. For 5th generation machines required by the 2nd BImSchV of 1990, the calculated long-term PERC concentrations in the near-field are below 8 ppm ($\log r - 0.8$), which is less than 16% of the MAK value. A comparison of SceBRA calculations with measured airborne PERC concentration data is shown in Chapter 5.3.5.

The logarithmic risk quotients in the far-field of the different machine generations and sizes are depicted in Figure 5.8 (the according SceBRA exposure estimates are listed in Table D.16 in Appendix D.2). From the SceBRA calculations, it can be seen that no machines cause long-term airborne concentrations above the MAK value in the far-field. For the newest 5th generation machines, the calculated long-term airborne concentrations are below 2 ppm PERC ($\log r - 1.4$), which is mostly below the limit of detection.

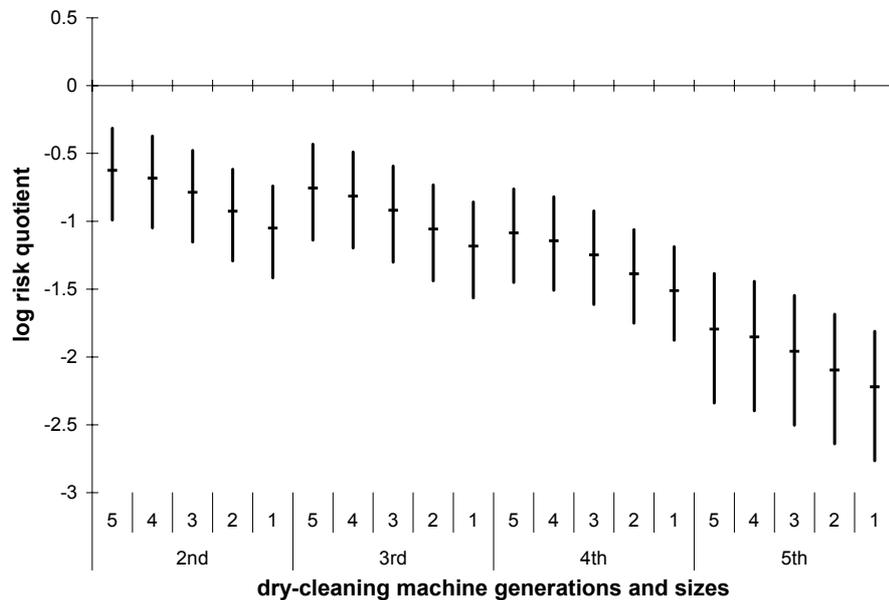


Figure 5.8: Comparison of the far-field risk quotients (logarithmic r values: minimum, maximum, and average $\log r$) of the four machine generations subdivided into five sizes of dry-cleaning machines for PERC. $\log r$ values greater than 0 indicate that the long-term concentration exceeds the MAK value.

5.3.4 Cumulative risk

Finally, the average risk quotients of the different machine generations and sizes in use at a certain time in Germany are combined with the average number of workers exposed to PERC in dry-cleaning facilities and compared for different years. Figure 5.9 shows a cumulative representation of the results for the machine operators in the near-field (box A) over 26 years.

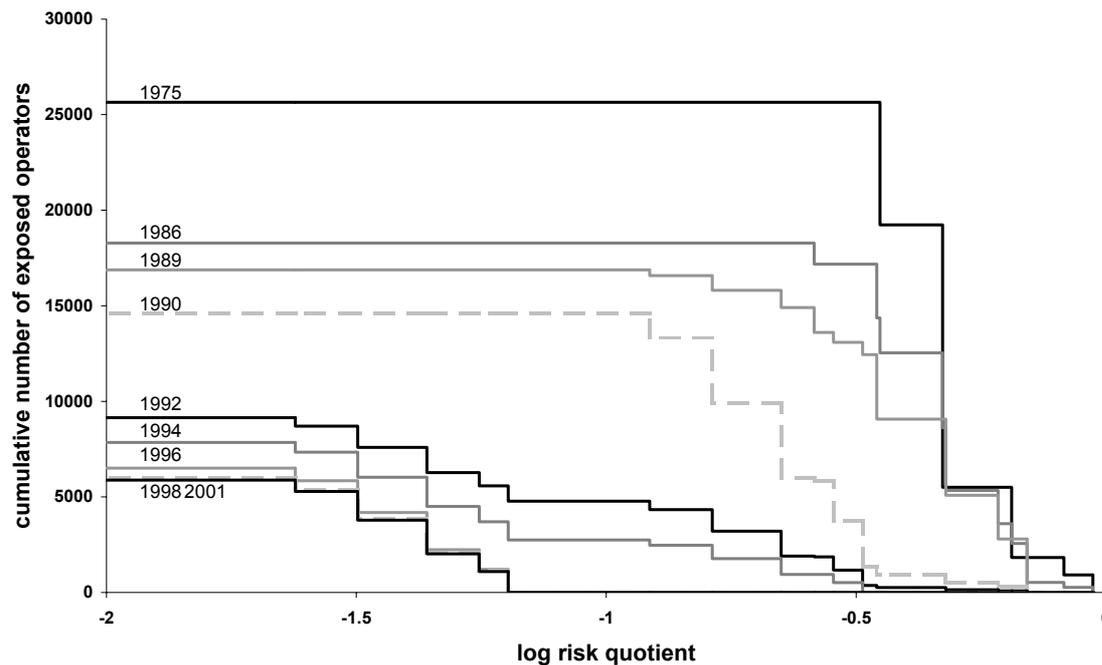


Figure 5.9: Cumulative N , $\log r$ -plot for machine operators in the near-field for the years 1975*, 1986*, 1988*, 1989*, 1990*, 1992, 1994, 1996, 1998, 2001 in Germany (* only former Western Germany).

In the cumulative N , $\log r$ -plot, each point $(\log r, N_{\text{cum}})$ of the curve shows the total number of exposed workers, N_{cum} , with a risk quotient at least as high as indicated by $\log r$. This kind of plot combines the information from all dry-cleaning scenarios for a specified year in a single line and thus several years can be compared in one plot. For each year, the total number of exposed workers and the number of exposed workers with a log risk quotient above -0.5 (or any other particular value) can be derived from the plot. The average for the total number of machine operators in 1975 is 25'650, compared with 5'875 in 2001. This is a reduction in exposed operators of 77%. N would be higher by a factor of 1.25 or lower by a factor of 0.83 if the maximum and minimum numbers, respectively, of exposed workers in the near-field were taken instead of the average number. The steeper curve for 1975 compared with 1992 is due to the fact that the total of 20'520 machines in use in 1975 were all 2nd generation machines, whereas the 7'313 machines in use in 1992 were 3rd, 4th, or 5th generation machines.

In Figure 5.10, the cumulative N , $\log r$ -plot is given for the far-field (box B). Here the risk quotients are combined with an average number of workers in the far-field.

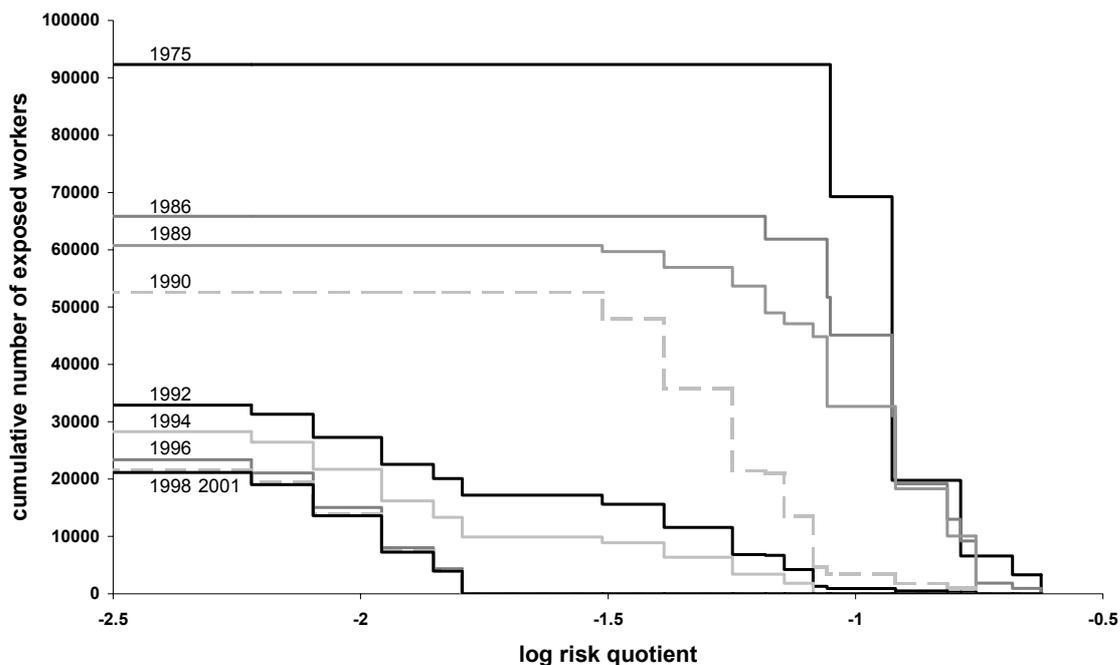


Figure 5.10: Cumulative N , $\log r$ -plot for workers in the far-field for the years 1975*, 1986*, 1988*, 1989*, 1990*, 1992, 1994, 1996, 1998, 2001 in Germany (* only former Western Germany).

For the far-field in all years, no workers were exposed to long-term concentrations above a $\log r$ value of -0.5 (16 ppm) during normal use. The total number of exposed workers in the far-field in 1975 was 92'340, compared with 21'150 in 2001. N would be higher by a factor of 1.13 and lower by a factor of 0.9, if the maximum and minimum numbers, respectively, of exposed workers in the far-field were taken instead of the average numbers. The reduction in exposed far-field workers is the same as for operators in the near-field, because it was assumed that the number of pressers and other dry-cleaning workers needed per machine has remained the same since 1975.

Comparing the two cumulative N , $\log r$ -plots for both the near-field and the far-field, the shape of the curves appears the same. This is because the two plots

are based on the same scenarios, although N is about 3.6 times higher and r significantly lower for the far-field.

In 1975, only 2nd generation machines were in use, whereas in 1986 (the year of enactment of the 2nd BImSchV 1986) about two-thirds of the machines were already 3rd generation machines. In 1989, only 3rd and 4th generation machines (complying with the 2nd BImSchV of 1986) were operating. By the time the 2nd BImSchV 1990 was enacted, 4th generation machines had already replaced the majority of the 3rd generation machines. In 1994, one year before the transition period of the amended regulations ended, only a little more than half the machines were still 4th generation. In the years 1996, 1998, and 2001, only 5th generation machines were in use.

The overall reduction in exposed workers both in the near-field and the far-field is mainly due to the reduced amount of textiles being dry cleaned in Germany (see introduction into Chapter 5). A second factor is that about 90% of the dry cleaning in Germany in 1989 was performed with PERC (Klein et al., 1991), but in 1992 it was around 85% (Nolte and Joas, 1992) and today it is about 80% (DTV, 2002). This is a reduction of about 11% due to solvent substitution between 1989 and 2001. The two factors together led to the closure of shops. Furthermore, shops in less-populated areas were united into large dry-cleaning facilities processing textiles from several “cold shops”. Thus, the number of dry-cleaning machines was reduced by 77%.

The amount of PERC used in Germany in different solvent applications, such as dry cleaning and metal degreasing, decreased by more than 93.2% between 1982, with 56'000 metric tons (only former West German states), and 2001, with 4'400 metric tons (Nader, 2002) (see Chapter 1.5). One reason is the reduction in amount of PERC used in dry cleaning due to changes in environmental legislation and the subsequent technology changes (non-vented machines with integrated recycling and longer solvent residence times). For the vented 2nd generation machines, solvent consumption was between 100 and 150 g PERC per kg textiles. This could be reduced to less than 10 g/kg in 5th generation machines (a reduction of more than 90%) (see

Chapter 5.1). Other reasons are the above-mentioned reduction in amount of dry-cleaning, because of novel fabrics that do not need to be dry cleaned, and partly the substitution of dry cleaning solvents.

5.3.5 Validation

In this section, near-field concentration outputs are first compared to published air measurements near the machine and to personal operator exposure measurements. In a second part, far-field concentration outputs are compared to published airborne concentrations further away from the dry-cleaning machines, for example at the counter, or personal measurements carried out on pressers. In a third part, the estimated numbers of exposed workers are compared with data for the whole dry-cleaning sector.

Published reports of PERC exposure measurements in dry-cleaning facilities do not always include information about the machine technology. In such cases, whenever possible, machine generations were assigned to the measurements according to knowledge of the stage of technology development for certain countries and years.

Generally, TWA or long-term measurements are more appropriate for comparison with calculated SceBRA concentrations than short-term measurements, which reflect only the momentary situation and where it is not indicated at which stage of the batch cycle the measurements were taken. Therefore, published measurements were divided into short-term and long-term measurements. Short-term peak exposure measurements are listed in Table D.17 for the near-field and in Table D.18 for the far-field (see Appendix D.3).

Near-field air measurements

Qualitatively good information with number of samples, measurement range, and average concentration is available for all machine generations (see Table D.19 in Appendix D.3). In Figure 5.11, the $\log r$ value of the published measured concentrations (gray marks) are compared to the $\log r$ ranges of the SceBRA calculations for the four machine generations (bars in black). Overall,

there is a good correspondence between the measured PERC data and the near-field concentrations calculated with the two-box model.

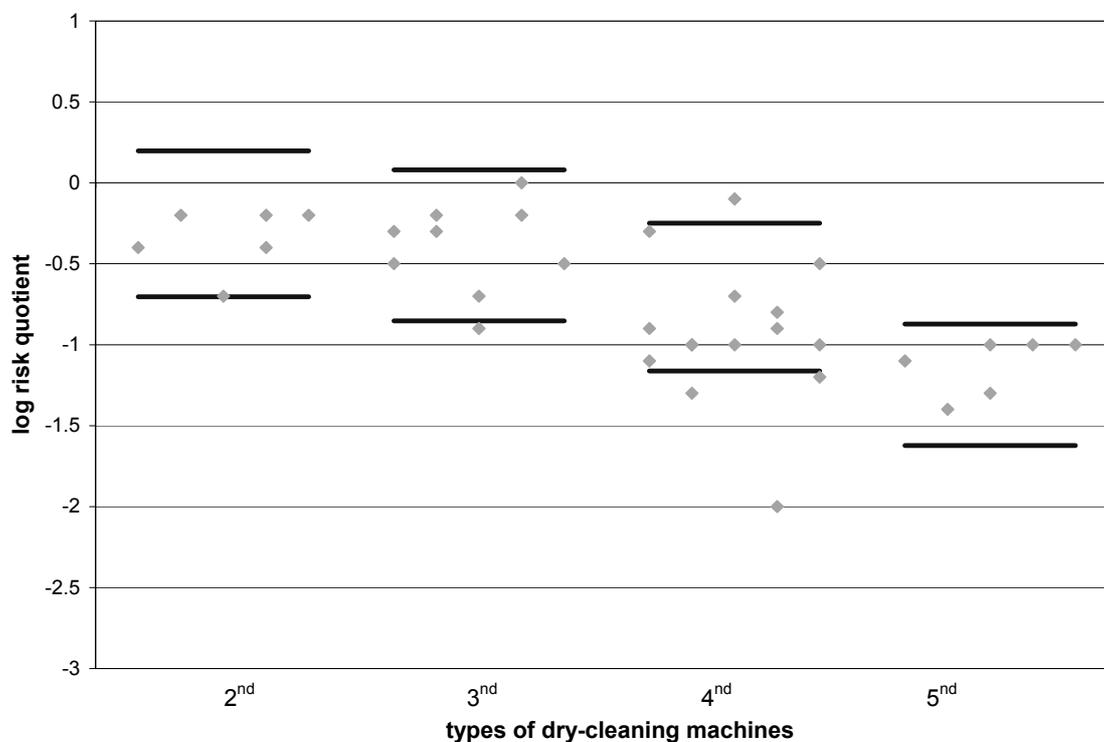


Figure 5.11: Comparison of risk quotients for PERC (logarithmic r values) of average near-field air measurements and personal operator exposure measurements of published series of measurements in dry-cleaning shops (gray marks) with the $\log r$ ranges of the ScE BRA calculations (bars in black) (measurements listed in Table D.19).

Far-field air measurements

Fewer measurements have been published for occupational exposure in the far-field of dry-cleaning devices. Nevertheless, qualitatively good information with number of samples, measurement range, and average concentration is available for all machine generations (see Table D.20 in Appendix D.3). For 5th generation machines, the value lies below the limit of detection of 0.12 ppm ($\log r < -2.6$). Overall, a good correspondence can be seen between the measured PERC data (gray marks) and the far-field concentrations calculated with the ScE BRA method (bars in black); see Figure 5.12.

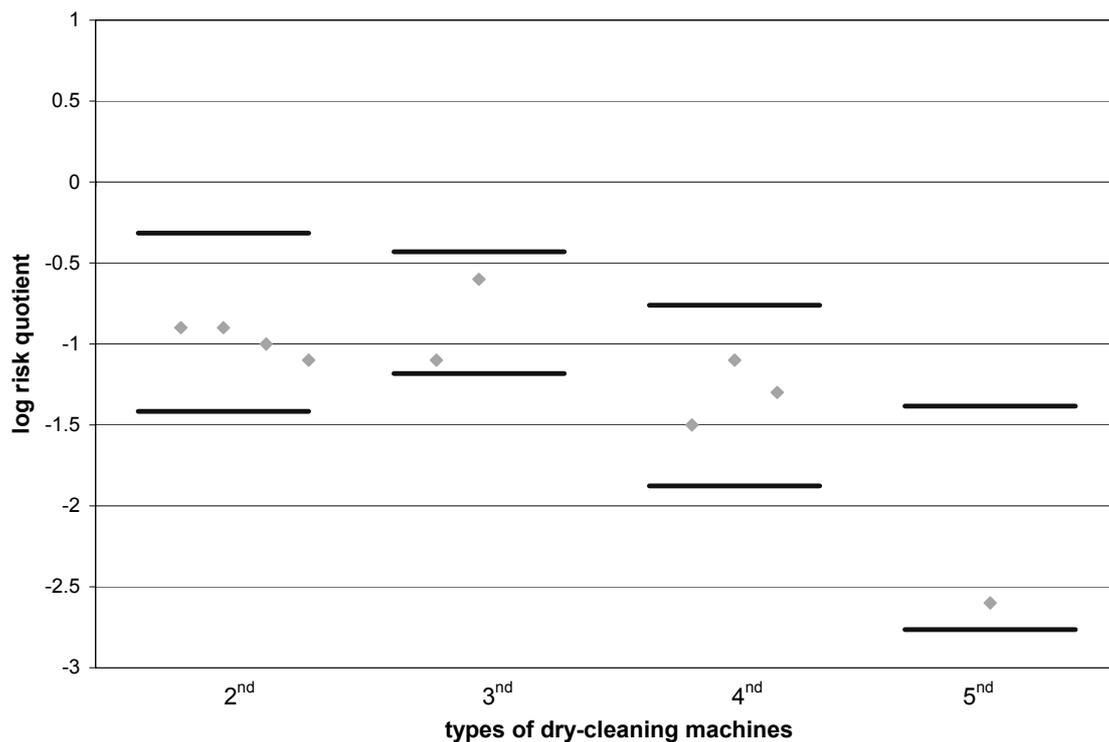


Figure 5.12: Comparison of $\log r$ values for PERC of published far-field PERC air measurements and personal presser exposure measurements in dry-cleaning shops (gray marks) with $\log r$ ranges of the SceBRA calculations (bars in black) (measurements listed in Table D.20).

Number of exposed workers

DTV mentions for the whole dry-cleaning sector in 1997/98 a total of 37'000 employees. This means approximately 29'600 workers dry cleaning with PERC (about 80% of the dry cleaning volume). This number includes people working in the "cold shops" supplying the PERC facilities with dirty garments. With the SceBRA method, the total number of workers exposed to PERC is estimated to range from 24'400 to 31'900, with an expected value of 27'600 for 1998.

5.4 Statistical exposure assessment and sensitivity analysis (Monte Carlo)

In the first part of this section, results from the SceBRA method are compared to results from a statistical exposure assessment. In the second part, results from a global sensitivity analysis of the Monte Carlo simulations are discussed, based on the example of a 5th generation, size 2 machine.

When performing a risk assessment with the SceBRA method for the use of a certain chemical in a specific application, in this case occupational exposure to PERC in dry cleaning in Germany, it is necessary to define the possible and plausible exposure scenarios that reproduce the situation in the specified country based on expert knowledge. The SceBRA method is especially designed for risk assessment of chemicals used in a wide range of heterogeneous applications and, therefore, includes great variability.

At the beginning of an exposure assessment, the existence of specific exposure data and exact knowledge of factors influencing the occupational exposure is generally very poor; low data quality often prevents a statistical exposure assessment. During the exposure assessment, the collected data may turn out to be of good quality and suitable for statistical evaluation. It is then possible to determine the exposure risk with statistics techniques. This is the case for the use of PERC in dry cleaning. The advantage of a statistical approach in comparison to a scenario-based approach is that information on the *frequency* of certain output ranges is obtained. In this thesis, a statistical exposure analysis was carried out to compare the scenario-based and the statistical approaches. Note, that for both approaches the underlying data are the same. From these data, plausible scenarios are selected for the SceBRA calculations and probability density functions (PDF) defined for the Monte Carlo simulations.

Within one generation of dry-cleaning machines, the size of the machine has the strongest influence on the long-term concentration and, therefore, on the risk quotient, r (see Figure 5.5). But as the machine sizes are taken from sales brochures and were confirmed by the dry-cleaner survey, they are hence well-

known, distinct values of a discrete frequency distribution. The statistical calculations are, therefore, carried out for each of the five sizes of one machine generation (see also discussion in Chapter 3.5.3).

The procedure of the statistical exposure analysis will be exemplified with 5th generation machines still in use in Germany today, for which qualitatively the best data are available, in terms of measurements and evaluated questionnaires. In a first step, PDFs must be defined for all input parameters of 5th generation machines. (The PDFs for the other machine generations are obtained from the data and sources described in Appendix D.2, in cases where only very limited data are available, the data is taken as 5th and 95th percentile boundaries for the corresponding PDFs).

In a second step, dependencies (correlations) among parameters must be determined. In the statistical approach and the SceBRA calculations, the same correlations between parameters (except for k_A and k_L) are integrated (for parameter correlation see Chapter 5.3.2). The exception arises from the fact that the other correlations can be integrated into the exposure calculations for which the Monte Carlo simulations are performed. In the case of k_A and k_L , correlation on the basis of the PDFs would have been needed. In a third step, parameter variability, which plays a major role (see also the discussion in Chapter 3.5.3), and parameter uncertainty are propagated through the model. Whenever possible, PDFs were fitted to data series obtained in our survey or taken from studies and surveys carried out by the Hohenstein Research Institute. Goodness-of-fit tests were used to examine how well a sample of data agrees with a given distribution. There are four common tests used to measure goodness-of-fit: (i) the Chi-Square test for discrete or continuous distribution functions, (ii) the Kolmogorov-Smirnov test only for continuous distributions (an empirical distribution test), and (iii) the Anderson-Darling test for continuous distributions (similar to Kolmogorov-Smirnov test but with more emphasis on tail values), and (iv) graphical tests using probability plots (comparison graph, difference graph, probability-probability graph plots, and quantile-quantile graph plots) (Morgan and Henrion, 1990; Palisade, 2002). The best distributions are selected with the help of these goodness-of-fit tests. The fitting of distributions to large data sets was possible for the two machine parameters: loading factor f_L (Klein and Kurz, 1994) and batch time t_b (dry-

cleaner survey), for the emission factor E_p , which is based on the cylinder concentration (measurements published by Kurz and Klein (1995)), and for the two workplace parameters: volume of workplace V (dry-cleaner survey) and air exchange rate k_L (Klein and Kurz, 1994). The fitted distributions are listed in Appendix D.4. For input parameters with less than 10 data points, normal distributions are assumed for published arithmetic means and standard deviations. Truncation criteria were integrated for all fitted and constructed distributions based on expert knowledge (e.g., air exchange rates k_L cannot be smaller than 0.1 h^{-1} and are never higher than 25 h^{-1}). The values outside the truncation limits are not sampled during the simulation. All distributions with indicated truncation limits are listed in Tables D.21, D.22, D.23 in Appendix D.4.

In a next step, mathematical techniques are required to propagate the uncertainties according to the functional relationships among the component variables. To this end, @Risk (Palisade, 2002), a commercially available simulation software, is used to perform the Monte Carlo simulation (see also Chapter 3.5.5). To assure accurate and stable results, the number of iterations is not limited and iterations are performed until all output distribution statistics change less than an entered convergence threshold, here 1.5%. In the present study, normally between 800 and 1900 iterations were needed until convergence was achieved.

Plots of concentration output distributions for 5th generation size 2 machines for both the near-field and the far-field are depicted in Figures D.12 and D.13 in Appendix D.4. The concentration distribution describes a distribution over all German dry-cleaning shops using 5th generation size 2 machines and is, therefore, not a probabilistic distribution of a single value (Suter, 1998). The long-term ambient concentration outputs are approximately lognormal distributions. This corresponds with the fact that series of measurements of TWA concentrations are usually lognormal distributions (Boleij et al., 1995).

The SceBRA results and the results of the statistical exposure analysis are depicted in one plot, in Figure 5.13 for the near-field and in Figure 5.14 for the far-field. The black bars specify the SceBRA ranges and the gray “box plots” the results of the statistical exposure analysis. The statistical box plots indicate the 5th percentile (lower end of the bar), 25th percentile (lower end of the gray

box), mean (white line), 75th percentile (upper end of the gray box), and 95th percentile (upper end of the bar).

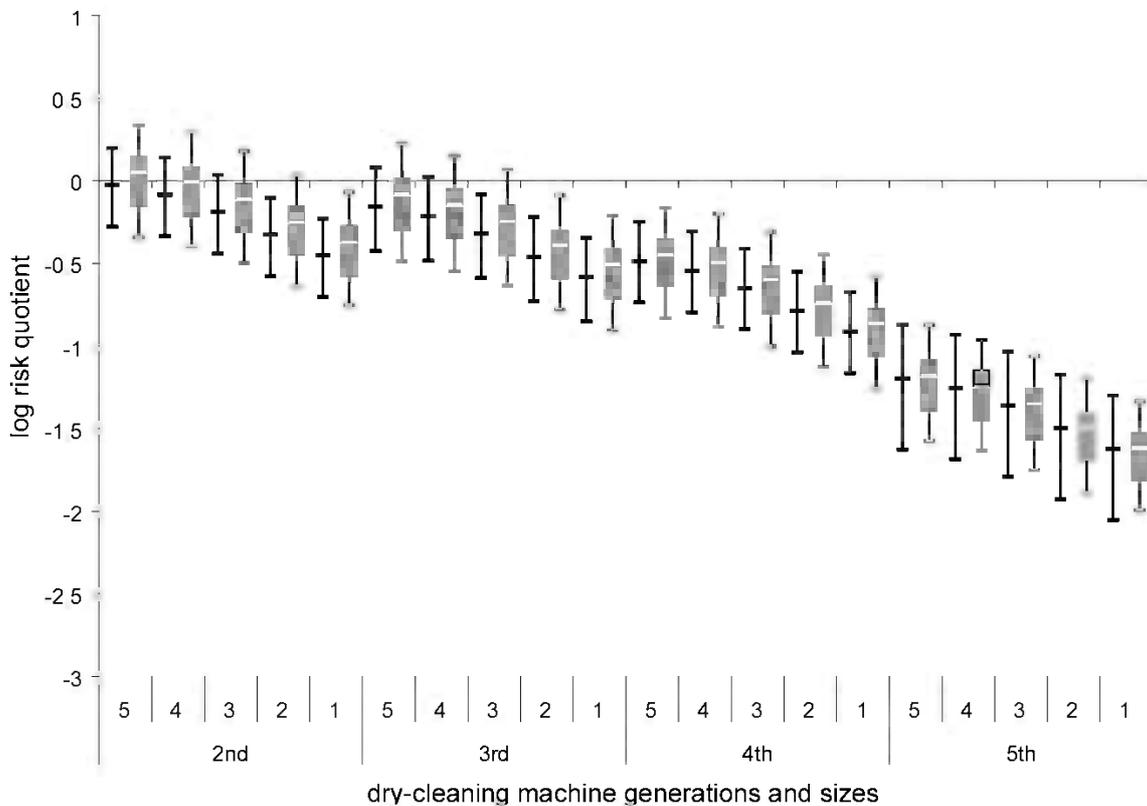


Figure 5.13: Comparison of the near-field $\log r$ ranges from SceBRA calculations (black bars) with the gray “box plots” of $\log r$ from Monte Carlo simulations (5th percentile (lower end of the bar), 25th percentile (lower end of the gray box), mean (white line), 75th percentile (upper end of the gray box), and 95th percentile (upper end of the bar)) for all four generations and five sizes of dry-cleaning machines.

The range of $\log r$ indicates in the first instance not uncertainty but mainly variability, as there is not a single true concentration value for a specific machine generation being used in Germany (Boleij et al., 1995). Besides machine technology and size, operator exposure depends strongly on the amount of textiles being dry cleaned and on the workplace conditions, which are not uncertain but variable when an exposure assessment for a whole country is performed. In the statistical approach, in comparison to the SceBRA calculations, k_A and k_L are not correlated. A correlation of k_A and k_L would

probably lead to somewhat narrower output distributions. In general, the SceBRA ranges correspond well with the ranges indicated by the statistical approach. It can be seen for 2nd to 3rd generation machines that the variability depicted by the statistical approach is higher than the variability depicted by the scenario-based approach. This is true for cases where only very limited data are available for the different input parameters because of lack of precise studies (as mentioned before the data are taken as 5th and 95th percentile boundaries in these cases).

Further on, the selected SceBRA scenarios for 5th generation machines, which are based on qualitatively good data, depict a greater range than the 90% most likely cases indicated by the “box plots” (range of 5th percentile to 95th percentile). From this it can be seen that the SceBRA scenarios, which are based on expert knowledge, tend to overestimate the range of most likely occupational exposure where many data are available. This reflects the fact that experts cannot assess the likelihood of a certain scenario; the assignment of certain scenarios is based on plausibility checks.

Except for 2nd and 3rd generation machines, for which the log r ranges are indistinguishable (see discussion in Chapter 5.3.3), the other machine generations can be clearly differentiated. For the five sizes of machines, differentiation is not that clear but it can be concluded that smaller machine sizes generate at worst the same exposure as machines one size larger. Nevertheless, average PERC exposure for the operator is reduced.

The greater variability for 5th generation machines than for older machines can be attributed, for both the SceBRA and the statistical approaches, to two facts. First, more data are available for 5th generation machines and this, therefore, reflects greater variability of exposure situations in Germany. Second, measured concentrations and solvent amounts of 5th generation input parameters are much lower than for 2nd generation machines (i.e., residual solvent amount in cleaned textiles; see Table D.5 in Appendix D.1.3.2). These results are often near the limit of detection and, therefore, measurement uncertainty is greater.

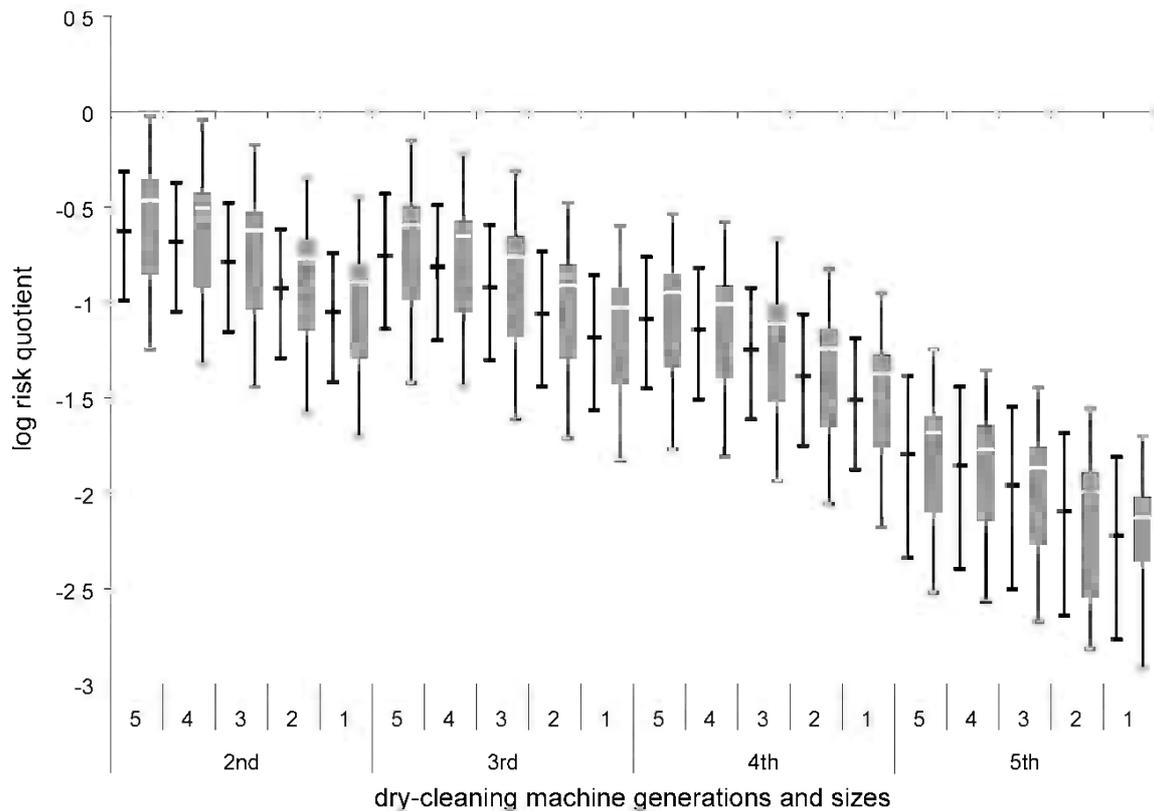


Figure 5.14: Comparison of the far-field $\log r$ ranges from SceBRA calculations (black bars) with the gray “box plots” of $\log r$ from Monte Carlo simulations (5th percentile (lower end of the bar), 25th percentile (lower end of the gray box), mean (white line), 75th percentile (upper end of the gray box), and 95th percentile (upper end of the bar)) for all four generations and five sizes of dry-cleaning machines.

In the comparison of far-field exposures, the points to be mentioned are generally those arising from the comparison of near-field exposures, with the exception that the SceBRA method, especially for 2nd, 3rd, and 4th generation machines, does not describe the whole variability of occupational far-field exposure. This is because the SceBRA method was constructed to depict in particular the occupational situation of highly exposed workers in the near-field. Thus, the selected scenarios fall short in reflecting the entire variability of factors strongly influencing the far-field exposure. Such factors are the room volume, V , and the air exchange rate, k_L (see also Figure 5.16 about global sensitivity analysis for the far-field). Based on plausibility considerations and expert knowledge, only two distinct parameter values are taken for each of these two parameters. For the room volume, values of 400 m³ and 600 m³ are

taken out of the range of 200 to almost 3000 m³ evaluated by the dry-cleaner survey. Two distinct k_L values are selected out of a similarly broad range of 1 to 19 air exchanges per hour measured by Klein and Kurz (1994) (selected k_L values can be found in Chapter 5.2.3). The variability of the air exchange rate in the near-field of the machine is also much lower than for the far-field, for two reasons. First, the machines are heat sources and, second, local exhaust systems are present; low air exchange rates are, therefore, less likely. The selection of only two distinct values for V and k_L has only a minor effect on the range of near-field ambient concentration (see Figure 5.15).

As the aim of the SceBRA calculations is to depict in particular the occupational situation of the highly exposed workers in the near-field, it is sufficient to know the magnitudes of occupational far-field exposure, as those workers are hardly ever exposed to critical long-term concentrations. The statistical calculations are, therefore, more appropriate to depict the variability of far-field exposure.

Sensitivity analysis

In this section, results from a global sensitivity analysis performed during the Monte Carlo simulations are discussed (a general introduction into sensitivity analysis is given in Chapter 3.5.4). To this end, sampled input parameter values (variation in the input parameters over their entire range of values) are regressed in @Risk in a multivariate stepwise regression analysis against the two output values (near-field and far-field long-term ambient concentrations), leading to a measurement of sensitivity by input parameter (Palisade, 2002). Results of a local sensitivity analysis carried out in the metal degreasing case study are discussed in Chapter 4.3.6.

The sensitivity of the long-term airborne PERC concentration of a 5th generation size 2 dry-cleaning machine is depicted in “tornado” plots in Figure 5.15 for the near-field (box A) and in Figure 5.16 for the far-field (box B).

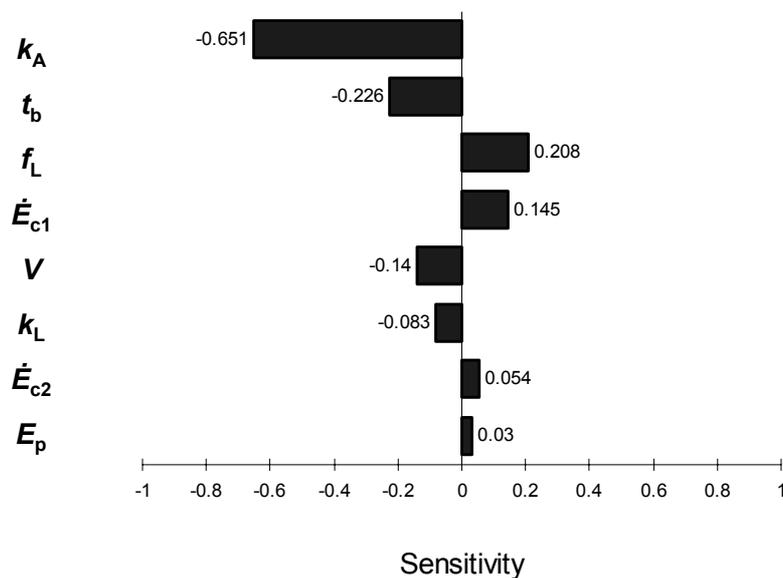


Figure 5.15: Global sensitivity analysis of the long-term airborne PERC concentration in the near-field of a 5th generation size 2 dry-cleaning machine.

The global sensitivity analysis indicates that the air exchange rate k_A is the most influential parameter for the long-term airborne concentration in box A, followed by the batch time t_b and the loading factor f_L . The air exchange rate between boxes A and B has a major effect on the near-field concentration, because it is the only factor by which the airborne concentration in box A is reduced. The air exchange rate between boxes A and B is an assumption specifically made for the two-box model. More specific air exchange rates for certain workplaces could be estimated by tracer gas measurements (Sohn and Small, 1999). Here, the PDF of k_A was estimated based on the PDF for k_L , for which the PDF was fitted to data from a study carried out by Kurz and Klein (1994) (see also Chapter 5.2.3). In the SceBRA calculations, values of k_A and k_L are coupled, as it does not make sense to have at the same time a high air exchange rate in one box and a low rate in the other. As mentioned before, the two parameters were not entered as correlated inputs into the

present statistical exposure assessment; therefore, the variability ranges are almost certainly broader.

The batch time, which depends on the machine load, i.e. the fabrics being dry cleaned, determines the spacing between the emission peaks and has, therefore, a strong influence on the long-term near-field concentration. The same is true of the loading factor f_L , which defines the quantity of textiles that are dry cleaned at the same time in the machine.

Parameters with a medium influence are the emission factor \dot{E}_{cl} , the room volume V , and the air exchange rate k_L . From the three emission factors, the diffuse emission factor \dot{E}_{cl} is the most uncertain, as it is estimated from the total solvent consumption minus all known emissions and losses. V and k_L are responsible for the concentration decline in box A by dilution or discharge into the environment over the exhaust air in box B.

Parameters with little influence on the near-field concentration are the emission factors \dot{E}_{cl} and E_p . Both factors are very well defined, with narrow distributions and low variability, especially for 5th generation machines (see Appendix D.4).

Parameters not directly connected to the dry-cleaning process that depict the variability of the workplace environment rather than the dry-cleaning process are k_L , k_A , and V .

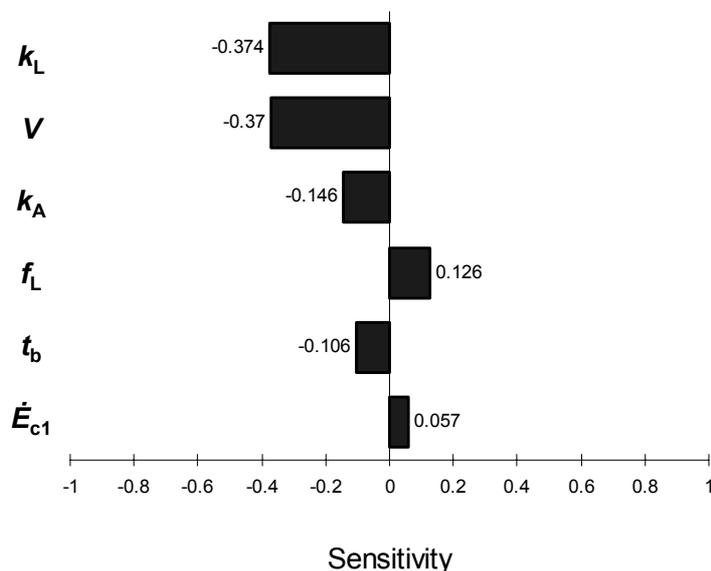


Figure 5.16: Global sensitivity analysis of the long-term airborne PERC concentration in the far-field of a 5th generation size 2 dry-cleaning machine.

For the global sensitivity analysis of the far-field, parameters of medium influence are the air exchange rate k_L and the room volume, V . V and k_L are responsible for the concentration decline in box B by dilution or by discharge into the environment over the exhaust. All other input parameters have only a minor influence on the long-term concentration in the far-field. A slightly negative sensitivity value for an increase in air exchange rate k_A occurs as long as the mass flow out of box B is higher than the mass flow into box B (i.e., increase in k_A results in higher dynamic concentration amplitudes in box B) (see also Figure 4.20 in Chapter 4.3.6).

Input parameters such as the two emission factors \dot{E}_{c2} and E_p have such a small influence on far-field concentration that they do not show up in Figure 5.16.

5.5 Conclusions

Using a broadly defined set of scenarios, it is possible to include the high variability of German dry-cleaning facilities into a comprehensive exposure analysis. In the present application of the SceBRA method, clusters of parameter values describe this variability, e.g., for machine size, emission factors, air exchange rates, batch times, and room volumes, see Figure 5.5 and 5.6.

The core of the SceBRA calculations presented in this case study is the long-term airborne concentrations obtained with the two-box model. All model parameters are based on empirical information and none was adjusted to increase the correspondence of calculated and measured concentrations. Comparison of the model results with measured data, both for the near-field and far-field of dry-cleaning facilities, shows good agreement (see Figures 5.11 and 5.12).

The machine generations and machine sizes, which are well-known discrete frequency distributions with low uncertainty (see Chapter 5.4), define distinct “cases” of exposure, namely occupational exposure to a machine of a certain technology type and size. It is pointless to include these parameters describing machine technology and size into the statistical exposure assessment, as this would involve a loss of information. For all other input parameters, which can be described with continuous distributions, a statistical exposure assessment was carried out to compare the scenario-based and the statistical approach. In this evaluation, $\log r$ ranges are compared to $\log r$ output frequency distributions from the Monte Carlo simulations, which indicate not only uncertainty but mainly variability (see Figure 5.13 and 5.14). It can be seen that the SceBRA ranges correspond well with the ranges indicated by the statistical approach, which means that the scenarios cover relevant exposure situations. But the effective exposure variability in the far-field in Germany is still to some extent higher than the variability depicted by the scenario approach. This is because the SceBRA method is constructed to depict in particular the occupational situation of the highly exposed workers in the near-field and, therefore, the selected scenarios fall short when reflecting

the entire variability of factors that strongly influence the far-field but only weakly the near-field exposure. Such factors are the room volume, V , and the air exchange rate, k_L . For these parameters only two distinct most probable values are selected as SceBRA inputs out of the large variability of possible values.

In conclusion, the SceBRA method is suitable for characterizing occupational risk of exposure to PERC in dry cleaning. The numbers of exposed operators and other dry-cleaning workers and the risk quotients in Figures 5.9 and 5.10 clearly indicate the combined effects of technological innovation and stricter legislation, leading to markedly reduced airborne concentrations and much lower numbers of exposed workers. According to the SceBRA calculations for normal use of the present-day 5th generation machines, the long-term near-field concentration is below 8 ppm and that of the far-field below 2 ppm, which is near the limit of detection. Consequently, it can be assumed today that there is low risk for operators and other dry-cleaning employees in Germany. The reduction in the number of workers has arisen by drastic reduction in the amount of dry-cleaned textiles through the use of efficient wet-cleaning machines and new textiles that do not require dry cleaning.

Where data quality and availability permits construction of *reliable* PDFs for all input parameters, as was the case for the dry cleaning case study, the effective variability of the occupational risk of a chemical used in different applications is displayed better by a statistical risk assessment than by the SceBRA method.

A comparison of the metal degreasing and the dry cleaning case studies together with further discussion of the advantages, abilities and limitations of scenario-based risk assessment are presented in Chapter 6.1.

Chapter 6

6 Conclusions and outlook

In the first section of this chapter, the capacity and limitations of the SceBRA method are shown for the two case studies of metal degreasing and dry cleaning. The most important results from both case studies are summarized and recommendations are made about when and how the SceBRA method should be implemented in an exposure assessment. In a second part, ideas for further applications of the SceBRA method and further research needs are discussed.

6.1 Conclusions

The aim of this study was to develop a method capable of representing, for an entire country, the risk of occupational exposure to chemicals used in different applications by integrating the complexity of activity patterns of workers and temporal and spatial variability of machine technology and workplace conditions. To this end, the enhanced “Scenario-based risk assessment” (SceBRA) method was used. In SceBRA, based on expert knowledge, a set of possible and plausible exposure scenarios is defined which reflect the real situation in a given country for a given year. The occupational risk is depicted for each scenario or cluster of scenarios by the risk quotient, i.e. the ratio of airborne concentrations and an effect level, and the number of exposed workers. The usefulness and value of this method could be demonstrated by applying it to two case studies, the use of TRIC and PERC in metal degreasing and the use of PERC in dry cleaning.

Both case studies deal with the industrial application of TRIC and/or PERC in different degreasing and cleaning tasks in Germany. Private use of these chemicals is not allowed. Metal degreasing and dry cleaning are performed in highly variable settings, for metal parts of different size and shape and for garments of different textile fibers, and with machines of different capacities and technological standards. In Germany, the same legislation, namely the 2nd BImSchV, regulates the use of TRIC and PERC in both metal degreasing and dry cleaning. In both cases, the 2nd BImSchV triggered a similar chronological development of machine technology. The two case studies differ significantly in the way in which the goods being degreased or cleaned can be characterized. For dry cleaning, all emission factors can be related to the functional unit of 1 kg garments, because textiles are a relatively homogeneous commodity. This is not the case for metal degreasing. There, the amount, the surface area and the shape of the metal parts, and the arrangement of the metal parts in the baskets are crucial for the degree of emission.

Furthermore, the amount and quality of data needed for the exposure assessment (machine parameters, emission factors, workplace parameters etc.) are different for the two case studies. In contrast to the metal degreasing case study, a lot more information is available on dry cleaning. The main reason for this is that dry cleaning is an independent service sector, whereas metal degreasing is only one intermediate stage in the metal-processing industry. For the dry cleaning case study, data was obtained from the textile cleaning association (DTV), from the Hohenstein Research Institute, an independent scientific organization performing studies on processing and cleaning of textiles, and by conducting a survey of dry cleaners.

In the application of the SceBRA method to the two case studies, variability is described by clusters of parameter values, e.g., for machine size, types of cleaned parts (only metal degreasing), emission factors, air exchange rates, batch times and room volumes; see Figures 4.7 and 4.8 for metal degreasing and Figures 5.5 and 5.6 for dry cleaning. Note that despite the few data on metal degreasing, for both case studies all model input parameters are based

on empirical information and none were adjusted to increase the correspondence of calculated and measured concentrations.

The core of the SceBRA calculations is the long-term airborne concentration obtained with the two-box model. As far as a comparison with measured data is possible, these model results are in agreement with near-field concentrations measured in metal-degreasing facilities (see Figures 4.15, 4.16, 4.17, and 4.18) and with both near-field and far-field measurements in dry-cleaning shops (see Figures 5.11 and 5.12). Overall, for both case studies, the long-term concentrations obtained for the scenarios correspond to the range of measured concentrations, meaning that the selected scenarios cover a relevant range of exposure situations.

The number of exposed workers and the risk quotients for different years, depicted in Figures 4.13 and 4.14 for metal degreasing and in Figures 5.9 and 5.10 for dry cleaning, clearly indicate the combined effect of technological innovation and stricter legislation, leading to markedly reduced airborne concentrations and much lower numbers of exposed workers.

With the type V metal-degreasing machines required today, the long-term near-field concentration for normal use is, according to the SceBRA calculations, below 5 ppm for TRIC and 6.5 ppm for PERC in type V A machines and below 2 ppm for TRIC and 4 ppm for PERC in type V B machines. The long-term far-field concentrations of below 2 ppm for both solvents in type V A and below 1.2 ppm for both solvents in type V B machines are near the limit of detection. For dry cleaning, the long-term near-field and far-field concentrations for the required 5th generation machines are below 8 ppm and below 2 ppm. For both applications, it can be seen that there is a low risk for operators and other employees in the far-field of metal-degreasing and dry-cleaning machines in Germany today.

For metal degreasing, the reduction in the number of exposed workers has been due to automatization and replacement of TRIC and PERC by non-chlorinated solvents. In dry cleaning, however, this effect is due to a drastic reduction in the amount of dry-cleaned textiles following the appearance of new textiles that require no dry cleaning, and better wet-cleaning machines.

For Germany, environmental legislation in the form of the 2nd BImSchV of 1986, the 2nd BImSchV of 1990, and the amendment of the 2nd BImSchV 1990

in 2001 brought about the technology changes. These led to emission reductions both in the environment and the workplace and, therefore, to improved occupational situations. The 2nd BImSchV of 1986 mainly focused on reduction of solvent emissions into the environment and only in a second phase on the improvement of workplace conditions. This becomes apparent when the results of the 2nd and 3rd generation dry-cleaning machines are compared (see Figures 5.7 and 5.8). Even though only the 3rd generation machines fulfill the 2nd BImSchV of 1986, the two machine generations differ only slightly in their ranges of long-term exposure concentrations. The 2nd BImSchV of 1990, however, focuses more on reduction of emissions into the workplace. This resulted in clearly reduced long-term concentrations with type 5 metal-degreasing and 5th generation dry-cleaning machines, compared with former machine types and generations (see Figures 4.9, 4.10, 4.11 and 4.12 for metal degreasing and Figures 5.7 and 5.8 for dry cleaning).

Because of lack of data, a statistical exposure assessment could not be carried out for the metal degreasing case study but only for the dry cleaning case study. In the latter, it was possible to define frequency distributions for all relevant model input parameters. As the machine generations and sizes can be described by well-known discrete frequency distributions with low uncertainty, they define distinct “classes” of exposure. Therefore, a Monte Carlo simulation was performed for each “class”, i.e., for all machine generations and sizes.

The range of the risk quotient of the statistical exposure assessment indicates not uncertainty but mainly variability, as there is not one single value for a specific machine generation being used in Germany. Besides machine technology and size, occupational exposure depends strongly on the amount of textiles being dry cleaned and on the workplace conditions, which are not uncertain but variable when carrying out a risk assessment for a whole country. Therefore, a variability analysis and not an uncertainty analysis was performed, here called a statistical exposure assessment.

A comparison of the results from the scenario-based and the statistical exposure assessment is depicted in Figures 5.13 and 5.14. It can be seen that the SceBRA ranges correspond well with the variability ranges obtained from the statistical exposure assessment. Thus, the SceBRA scenarios cover a

relevant range of exposure situations, but the effective variability in Germany, especially for the far-field of dry-cleaning facilities, is still to some extent higher than the variability depicted by the SceBRA approach. This arises because the SceBRA method is constructed to depict in particular the occupational situation of highly exposed workers in the near-field. Therefore, the selected scenarios fall short of reflecting the entire variability of factors that strongly influence the far-field but only weakly the near-field exposure. Such factors are the room volume V and the air exchange rate k_L (see Figures 5.15 and 5.16 of the global sensitivity analysis). For these parameters, only two distinct most probable values were selected as SceBRA inputs out of the large variability range of possible values.

It can be concluded in this specific case study that statistical calculations are more appropriate for depicting the variability of far-field exposure because the SceBRA calculations are aimed at occupational situations of highly exposed workers in the near-field and for the far-field only the magnitude of occupational exposure is depicted as those workers are hardly ever exposed to critical long-term concentrations.

The advantage of the SceBRA method over other exposure assessment methods for highly or maximally exposed individuals is that it is appropriate for questions dealing with the exposure risk in an entire country to a certain chemical used in different applications and under varying conditions. In the scenario definition stage, a first impression about the variety can be obtained by defining possible and plausible exposure scenarios. But the full extent of variability is not obvious even to experts. Therefore, it is useful to perform, in a second step, a statistical analysis of parts or of the entire exposure assessment. At this point, it is very important to verify that parameters that build up “classes” of scenarios or parameters with discrete frequency distributions are not integrated into one single Monte Carlo simulation. This would result in a loss of information and in broad variability ranges of unknown origin. In such cases, it is advantageous to carry out a Monte Carlo simulation for each of the defined classes. In the present study, such “classes” are machine generations and machine sizes. If the machine sizes and capacities from the dry-cleaning survey had been integrated in the Monte Carlo

simulations, then only a single variability range would have resulted instead of the five ranges depicted in Figures 5.13 and 5.14 in Chapter 5.4.

Generally, a statistical approach to an exposure assessment of chemicals used in different applications only makes sense if data amount and data quality permit the definition of high quality frequency distributions for all input parameters. If this is not the case, the scenario-based approach is preferred to the statistical approach, as more or less known variability would be clouded by poorly defined uncertainty. Additionally, it could not be guaranteed that the whole magnitude of exposure is depicted. In the scenario-based approach on the other hand, experts define a set of realistic scenarios intended to represent reality. Another benefit of first conducting a scenario-based exposure assessment is that it reveals which parameters are highly influential on the outcome. This information is useful for setting up additional surveys or measurements to gather missing or insufficient data.

In conclusion, SceBRA is a powerful method for achieving a first evaluation of the occupational exposure to widely spread chemicals used in different applications and under varying conditions. SceBRA can provide information on where action is needed without expensive and time-consuming measurements and surveys.

6.2 Outlook

In a next step, the SceBRA method, the qualities and limits of which are demonstrated in this thesis, should be applied to other countries, other chemicals, and other applications. The selected scenarios could be applied directly to other countries (e.g.; comparison of European Union countries) or, without extensive changes, to non-chlorinated solvents used in metal degreasing. Today, metal degreasing with hydrocarbons is mainly done in open systems. It would be of common interest to show the effect of the implementation of closed systems, which can be easily adapted for hydrocarbons, on occupational exposure.

The SceBRA method can also be applied to evaluate the effect on occupational exposure risks of new machine technologies that are still in the

development stage. Further on, SceBRA should be applied to other industrial solvent applications with suspected high occupational exposure, for example, spray painting with high-pressure spray guns, and as a first evaluation to applications for which the compilation of data is difficult.

Another potential application of the scenario-based exposure assessment is in the regulatory sector. With the help of this method, the legislator can evaluate the efficiency of a new hypothetical regulation (such as a new threshold limit value or regulations similar to the 2nd BImSchV specifying machine technology) in terms of occupational risk reduction. Based on the experiences in this study, specifying machine technology is more powerful in terms of risk reduction than stipulating emission or concentration thresholds, if only because machine technology is easier to control. Compliance to threshold values must be controlled repeatedly and it is, therefore, more difficult to detect non-compliance. Furthermore, there is a need for regulations focusing on the occupational situation. The leading principle of the European Union Directive (89/391/EEC) (Directive on the introduction of measures to encourage improvements in the safety and health of workers at work) about work-related hazards is that: "All measures have to be taken in a systematic approach and on the basis of the best available technology" (EEC, 1989). In the example of hydrocarbons being used in emissive metal-degreasing machines, it is clear that this requirement is not yet being observed.

Another point noticed during the exposure assessment is that data often lack descriptions of the duration and type of measurements, and almost never of the machine technology, machine size, workplace situation, or working process. Consequently, it is difficult to integrate concentration measurements into exposure assessments (Northage and Marquat, 2001; Money and Margary, 2002) or to compare them to estimates from exposure models. In the present study, it was not possible to validate the exposure ranges of different machine sizes. In general, it would be useful to set up standards for the measurement of airborne concentrations in industrial facilities and buildings in a "code of good monitoring practice", to ensure that the context of the measurement is clear.

For the validation of concentration outputs of *single* scenarios, measurements are required that indicate, besides machine technology and size, other factors with a significant influence on the occupational situation, such as air exchange rate, batch time, loading factor, and workplace volume (see local and global sensitivity analysis in Chapters 4.3.6 and 5.4).

Furthermore, scenarios could be integrated to reflect “bad working practice” and there is a considerable need for a similar research method focusing on the exposure risk to end users of different consumption products who may be exposed to suspect chemicals.

With the new REACH system (**R**egistration, **E**valuation, and **A**uthorization of **C**hemicals) proposed in the European “White Paper on the Strategy for a future Chemicals Policy”, more exposure assessment will be required in the future. The White Paper states: “Exposure estimates or, if appropriate, analytical determination of the exposure should be obligatory for manufacturers and downstream users (formulators and industrial users) of chemicals” (COM, 2001). In the course of this, the registration of chemical substances will take a first step towards the registration of *chemicals for different applications*. This means that not only the intrinsic properties of a chemical but also the exposure risk during a specific use pattern will be instrumental in deciding whether use of a substance should be allowed, restricted, or banned.

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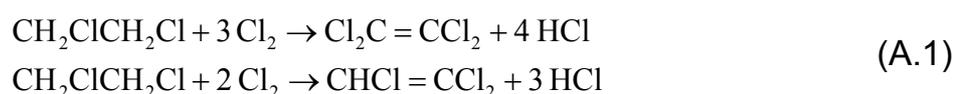
Appendix A

A. Chlorinated solvents TRIC and PERC

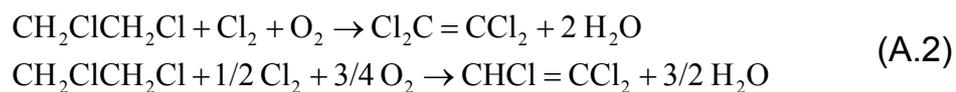
A.1. Production of TRIC and PERC

The following production processes for TRIC and PERC are commonly used today (Ullmann, 1986b; Ullmann, 1986a; Hickman, 1993; Mertens, 1993).

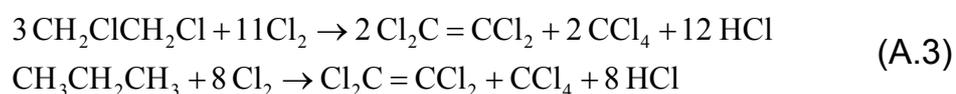
Chlorination of ethylene dichloride: TRIC and PERC can be produced by the noncatalytic chlorination of ethylene dichloride (EDC) or two-carbon (C2) chlorinated hydrocarbons. Product ratios of TRIC and PERC are controlled by adjusting the Cl₂:EDC ratio to the reactor. Partially chlorinated by-products are recycled to the chlorinator. The primary reactions are:



Oxychlorination of chlorinated C2 hydrocarbons: TRIC and PERC can be produced by reaction of EDC (or two-carbon (C2) chlorinated hydrocarbons) with chlorine or HCl and oxygen in the presence of a catalyst. When hydrochloric acid is used, additional oxygen is required. Product distribution is varied by controlling reactant ratios. This process is advantageous as no by-product HCl is produced, and it can be integrated with other processes as a net HCl consumer. The reactions may be represented as follows:

**Chlorination of C1-C3 hydrocarbons or partially chlorinated derivatives:**

In this process PERC and carbon tetrachloride are produced with or without a catalyst at high temperatures (550–700°C) from light hydrocarbon feedstocks or their partially chlorinated derivatives. This is one of the most versatile processes, allowing for a wide range of mixed chlorinated hydrocarbon wastes from other processes to be used as feedstocks. However, the large quantities of HCl produced require integration with other HCl-consuming processes. As with the previous processes, product distribution is controlled by controlling feedstock ratios, and partially chlorinated by-products are recycled to the chlorinator. As examples, reaction of EDC or propane are shown in the following:



Appendix B

B. Exposure Models

B.1. Solutions of differential equation systems

The solution of Equation (3.4) (in Chapter 3.3.2), two coupled linear inhomogeneous differential equations, is given for initial values $C_A(0) = 0$ and $C_B(0) = 0$ as (Braun, 1993):

$$\begin{aligned} C_A(t) &= C_A^\infty + A_{11} \cdot e^{\lambda_1 t} + A_{12} \cdot e^{\lambda_2 t} \\ C_B(t) &= C_B^\infty + A_{21} \cdot e^{\lambda_1 t} + A_{22} \cdot e^{\lambda_2 t} \end{aligned} \quad (\text{B.1})$$

where C_A and C_B (g/m^3) are the concentrations in box A and B. The new overall rate constants λ_1 and λ_2 , which are called “eigenvalues”, determine the time needed for the system to approach steady state. A_{jk} are the corresponding integration constants (j and k standing for 1 or 2). The concentrations at steady state are given as:

$$\begin{aligned} C_A^\infty &= \frac{k_B + k_L \cdot \frac{\dot{E}_A}{V_A}}{k_A \cdot (k_B + k_L) - k_A \cdot k_B} \\ C_B^\infty &= \frac{k_B \cdot \frac{\dot{E}_A}{V_A}}{k_A \cdot (k_B + k_L) - k_A \cdot k_B} \end{aligned} \quad (\text{B.2})$$

the eigenvalues λ_1 and λ_2 are given as:

$$\begin{aligned}\lambda_1 &= \frac{1}{2} \cdot \left[(-k_A - k_B - k_L) + \left((-k_A + k_B + k_L)^2 + (4 \cdot k_A \cdot k_B) \right)^{\frac{1}{2}} \right] \\ \lambda_2 &= \frac{1}{2} \cdot \left[(-k_A - k_B - k_L) - \left((-k_A + k_B + k_L)^2 + (4 \cdot k_A \cdot k_B) \right)^{\frac{1}{2}} \right]\end{aligned}\quad (\text{B.3})$$

the integrations A_{ij} constants are defined by:

$$\begin{aligned}A_{11} &= q \cdot \left[(-k_A - \lambda_2) \cdot (C_A^0 - C_A^\infty) + k_A \cdot (C_B^0 - C_B^\infty) \right] \\ A_{12} &= -q \cdot \left[(-k_A - \lambda_1) \cdot (C_A^0 - C_A^\infty) + k_A \cdot (C_B^0 - C_B^\infty) \right] \\ A_{21} &= q \cdot \left[(k_B \cdot (C_A^0 - C_A^\infty) - (k_B + k_L + \lambda_2)) \cdot (C_B^0 - C_B^\infty) \right] \\ A_{22} &= -q \cdot \left[(k_B \cdot (C_A^0 - C_A^\infty) - (k_B + k_L + \lambda_1)) \cdot (C_B^0 - C_B^\infty) \right] \\ q &= (\lambda_1 - \lambda_2)^{-1}\end{aligned}\quad (\text{B.4})$$

where C_A^0 and C_B^0 (g/m^3) are the background concentrations in box A and B at time $t = 0$.

The solution of the two coupled linear homogeneous differential equations (Equation 3.5 in Chapter 3.3.2) is a simplification of the inhomogeneous case, where the emission term \dot{E}_A (g/h) is zero, and where C_A^0 is replaced by $C_{A,i+1}^0$, the new background concentration after each pulse i (see Equation 3.6 in Chapter 3.3.2).

B.2. Dynamic concentration

In order to calculate the time-dependent dynamic concentration for one specific scenario according to the summation in Equation 3.7 (see Chapter 3.4) one needs to specify how the three emission factors interrelate with each other over the considered time period. The continuous emission factor \dot{E}_{c1} is constant over the whole working day. Consequently, the mass balance

equations can be solved once to give the according addends $C_{c1,A}(t)$ for box A and $C_{c1,B}(t)$ for box B for an arbitrary time t . This is not the case for the continuous emission factor \dot{E}_{c2} , which is only emitting over a limited duration α (h), and the intermittent emission factor E_p . Here the differential equation systems have to be solved at the beginning of each new emission phase or pulse, and for E_p additionally after the ending of α , because then the new background concentration $C_{p,A,i+\alpha}^0$ is:

$$C_{p,A,i+\alpha}^0 = C_{p,A}(t = i \cdot t_{\text{pulse}} + \alpha) + C_{c2,A}(t = i \cdot t_{\text{pulse}} + \alpha) \quad (\text{B.5})$$

Three cases can be distinguished: in the first case the duration α of the continuous emission factor \dot{E}_{c2} is as long as the batch time, t_b . In this case the differential equation systems describing the emission factors \dot{E}_{c2} and E_p have to be solved only at the beginning of each batch time. In the second case α is shorter than t_b . There, the differential equation systems of \dot{E}_{c2} and E_p have to be solved at the beginning of each batch and once more only for E_p at the very moment when α ends. And in the third case α is longer than one batch time but shorter than two times t_b . Therefore, continuous emissions \dot{E}_{c2} from two different batches overlap each other. In this case the differential equation systems of the two \dot{E}_{c2} have to be solved at their beginning and for E_p the differential equation system has to be solved at the beginning of one batch and when α of a former \dot{E}_{c2} is ending. The particularities of the three cases: (i) $\alpha = t_b$, (ii) $\alpha < t_b$, and (iii) $t_b < \alpha < 2 \cdot t_b$ are visualized in Figure B.1 (for $\alpha > 2 \cdot t_b$ the emissions of additional batches would overlap, this is not relevant for the two case studies as the evaporation times are not that long; see section, PER, Chemischreinigungen,

B.3. Long-term concentration

For the calculation of the risk quotient, r , (see Equation 3.1 in Chapter 3.2) the long-term concentrations over an 8h working day are needed for the two boxes. The averages are obtained by the summation of the time-weighted areas below the concentration function for box A and box B for each batch time. The concentration function is as described in Equation 3.4 (Chapter 3.3.2) the sum of the solutions of the differential equation systems describing the three emission factors \dot{E}_{c1} , \dot{E}_{c2} , and E_p . The three different cases of interrelation between the emission factors are described in Chapter B.2. The integrals of the composing functions are computed and subsequently the weighted sum is built.

Appendix C

C. Metal degreasing

C.1. Metal degreasing process

In Figure C.1 and Figure C.2, the metal degreasing process for a closed one-chamber type V A machine is represented in a schematic drawing.

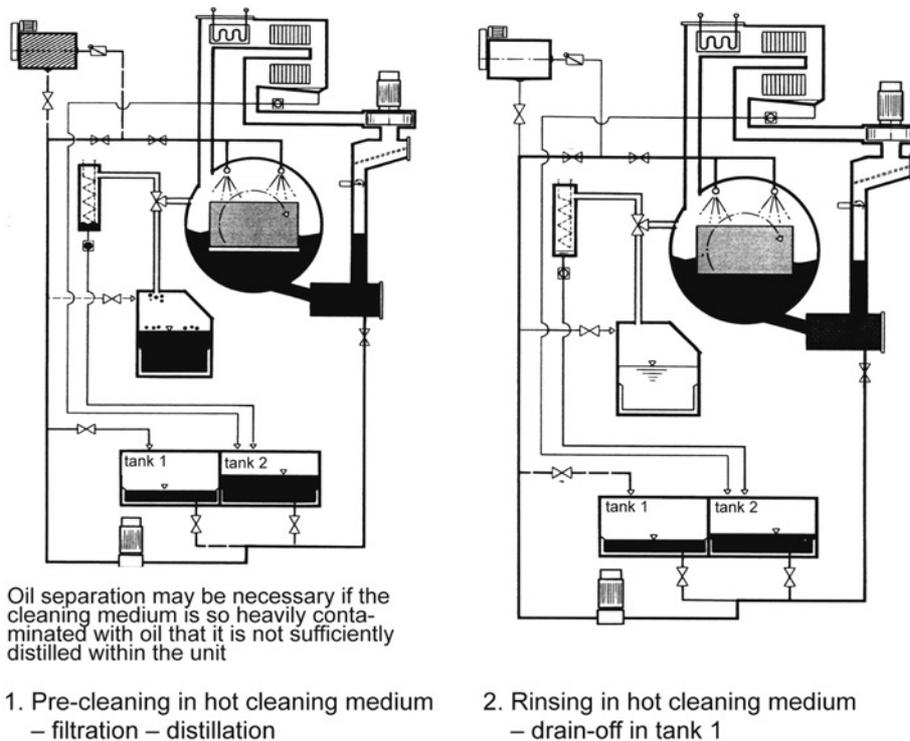


Figure C.1: First step of the metal degreasing process in a closed one-chamber type V A machine: Two solvent baths for pre-cleaning and cleaning (MULTIMATIC, 1996).

The first step of the process includes two solvent baths for pre-cleaning, and cleaning (Figure C.1) and in the second step the metal parts are vapor degreased and dried (Figure C.2) (see also Chapter 4.1).

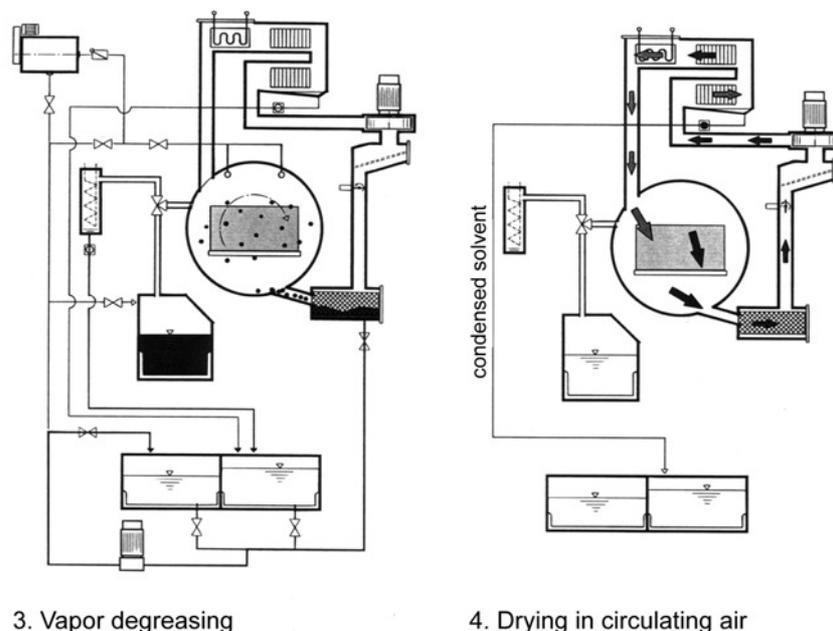


Figure C.2: Second step of the metal degreasing process in a closed one-chamber type V A machine: Vapor degreasing and drying (MULTIMATIC, 1996).

C.2. Metal degreasing input data

C.2.1. Method for metal degreasing data collection

As there are very few publications in scientific journals about metal degreasing, data was collected mainly from different reports, sales brochures of manufacturers, and expert interviews with both scientists and experts from industry. There are some general reports about the substances TRIC and PERC by BUA (1993, 1994, 1999) and ECETOC (1990, 1994, 1999); reports focusing on metal degreasing such as Mannheim et al. (1979), CEFIC (1984), Circl'Air (1993) and Leisewitz and Schwarz (1994); and many reports from solvent producers, manufacturers and metal degreasers. All model parameters

such as machine parameters, emission factors, workplace parameters, number of machines and number of exposed workers are based on empirical information from the above-mentioned sources.

Generally, the data availability were good for machine technology, machine parameters such as size, load and batch time, for emission factors and number of machines of recent machine technologies, and for the overall air exchange rates in industrial facilities. Data availability was medium for the number of exposed machine operators (near-field), and for some emission factors (total emissions and emissions from unloading) and the number of machines of older machine technologies.

The numbers of older machines estimated by industrial representatives tended to be overestimations according to a personal communication with N.H. Adams from Dow Europe S.A (2002). Only very general information was available on the volumes of the workplaces and the number of exposed workers in the far-field. No published data were available for diffusion out of open-top degreasers and for typical air exchange rates in the near-field. Therefore, those parameters were estimated based on information from expert interviews.

C.2.2. Machine parameters

The different types and subtypes of metal degreasing machines are described in Chapter 4.1 and the five different sizes are introduced in Chapter 4.2.1. For the open-top type I and II and the encased type III metal degreasing machines, the dimensions of the baskets and baths can be seen for the five machine sizes in Table C.1.

Table C.1: Dimensions of open-top type I and II and encased type III metal-degreasing machines (Manufacturers, 1960-2001).

Size	Dimensions of baskets				
	Length (mm)	Breadth (mm)	Height (mm)	Volume (m ³)	Load (kg)
1	370	220	200	0.016	40-50
2	530	320	200	0.034	50-60
3	660	480	300	0.095	120-150
4	1200	850	500	0.510	approx. 600
5	3000	1000	1000	3.000	approx. 1000

Size	Dimension of baths				
	Length of one bath (mm)	Breadth of one bath (mm)	Surface of one bath (m ²)	Total bath surface subtype A (m ²)	Total bath surface of subtype B (m ²)
1	796	253	0.20	0.40	0.60
2	1140	368	0.42	0.84	1.26
3	1419	552	0.78	1.57	2.35
4	2580	978	2.52	5.04	7.57
5	6450	1150	7.42	14.84	22.25

The closed type IV and V machines are one-cleaning chamber machines in which the solvent is brought to the metal parts and not vice versa. The dimensions of the cleaning chambers can be found in Table C.2 for each machine size.

Table C.2: Dimensions of closed type IV and V metal-degreasing machines (Manufacturers, 1960-2001).

Size	Dimensions of baskets				
	Length (mm)	Breadth (mm)	Height (mm)	Volume (m ³)	Load (kg)
1	370	220	200	0.016	40-50
2	530	320	200	0.034	50-60
3	660	480	300	0.095	120-150
4	1200	850	500	0.510	approx. 600
5	3000	1000	1000	3.000	approx. 1000

Size	Dimension of cleaning chamber		
	Diameter of chamber (mm)	Length of chamber (mm)	Volume of chamber (m ³)
1	446	555	0.09
2	566	795	0.20
3	849	990	0.56
4	1479	1800	3.09
5	2121	4500	15.90

The batch times, t_b , which are dependent on the loads, are specified in Table 4.2 (see Chapter 4.2.1).

To account for different metal parts being cleaned, in this study the hypothetical baskets are filled with plates (placed vertically) or closely packed spheres (further information in Chapter 4.2.2). The dimension of the different loads, such as surface, weight and percentage of basket volume, which is not filled with parts, is indicated in Table C.3 and C.4.

Table C.3: Dimensions of the load for baskets filled with metal plates.

Machine size	Thickness of one plate (mm)	Number of plates (-)	Surface of one plate (m ²)	Surface of all plates (m ²)	Volume of one plate (m ³)
1	1.0	73	0.13	9.9	6.3E-05
2	1.2	64	0.19	12.3	1.1E-04
3	1.4	60	0.36	21.6	2.4E-04
4	2.0	71	1.09	77.1	1.0E-03
5	2.0	25	5.43	135.7	5.1E-03

Machine size	Volume of all plates (m ³)	Density of metal (kg/m ³)	Weight of one plate (kg)	Weight of all plates (kg)	Free basket volume (%)
1	4.7E-03	7870	0.5	37	71.4
2	7.0E-03	7870	0.9	55	79.4
3	1.4E-02	7870	1.9	112	85.0
4	7.3E-02	7870	8.1	574	85.7
5	1.3E-01	7870	40.5	1012	95.7

Table C.4: Dimensions of the load for baskets filled with closely packed spheres.

Machine size	Diameter of one sphere (mm)	Number of spheres (-)	Surface of one sphere (m ²)	Surface of all spheres (m ²)	Volume of one sphere (m ³)
1	4.0	127260	5.0E-05	6.4	3.4E-08
2	5.0	121800	7.9E-05	9.6	6.5E-08
3	6.0	125280	1.1E-04	14.2	1.1E-07
4	9.0	180456	2.5E-04	45.9	3.8E-07
5	12.0	149604	4.5E-04	67.7	9.0E-07

Machine size	Volume of all spheres (m ³)	Density of metal (kg/m ³)	Weight of one sphere (kg)	Weight of all spheres (kg)	Free basket volume (%)
1	4.3E-03	7870	2.6E-04	34	73.8
2	8.0E-03	7870	5.2E-04	63	76.5
3	1.4E-02	7870	8.9E-04	112	85.1
4	6.9E-02	7870	3.0E-03	542	86.5
5	1.4E-01	7870	7.1E-03	1065	95.5

For baskets filled with plates or with closely packed spheres the average free basket volume is 83.5% for all machine sizes.

The volume of the average load and the free basket volume are needed to determine the volumes of saturated solvent air, which are replaced during loading and unloading. The surface areas are required to calculate the amount of residual solvent E_{c2} (g) for the different loads, including emissions from cavities (more details can be found in Chapter 4.2.2).

C.2.3. Emission factors

In this section, the calculations of the different emission factors are described in detail where this has not already been done in Chapter 4.2.2. Additionally, upper and lower values are given for all types, subtypes and sizes. The average values, which are also included in the SceBRA calculations, are the arithmetic means of the upper and lower values.

C.2.3.1 Continuous emission factor for diffuse emissions

The approach of estimating the diffuse emissions out of open-top type I and II machines with Fick's first diffusion law is described in Chapter 4.2.2. For encased type III machines it was assumed that with the encasement 80% of the diffuse emissions of type II machines can be kept back. For the closed machines (type IV and V), \dot{E}_{c1} is taken as a leaking rate proportional to the solvent volume present in the machine. For encased and closed machines, \dot{E}_{c1} is taken as a leaking rate proportional to the solvent volume present in the machine. The values for the closed machines, which can be seen in Table C.5, correspond with data suggest by Leisewitz and Schwarz (1994).

Table C.5: Diffuse emission factors \dot{E}_{cl} for all machine types, subtypes and sizes using TRIC or PERC.

Diffuse emission factor for TRIC						
\dot{E}_{cl} (g/h)						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A	min	3.73E+01	5.34E+01	6.65E+01	1.21E+02	3.02E+02
	max	4.10E+01	5.87E+01	7.31E+01	1.33E+02	3.32E+02
I B	min	5.59E+01	8.01E+01	9.97E+01	1.81E+02	4.53E+02
	max	6.15E+01	8.81E+01	1.10E+02	1.99E+02	4.99E+02
II A	min	2.14E+01	3.06E+01	3.81E+01	6.92E+01	1.73E+02
	max	2.35E+01	3.36E+01	4.19E+01	7.62E+01	1.90E+02
II B	min	3.20E+01	4.59E+01	5.71E+01	1.04E+02	2.60E+02
	max	3.52E+01	5.05E+01	6.28E+01	1.14E+02	2.86E+02
III	min	6.41E+00	9.18E+00	1.14E+01	2.08E+01	5.19E+01
	max	7.05E+00	1.01E+01	1.26E+01	2.29E+01	5.71E+01
IV A or B	min	1.50E+00	2.17E+00	2.92E+00	3.33E+00	8.33E+00
	max	2.40E+00	3.47E+00	4.67E+00	5.33E+00	1.33E+01
V A	min	1.14E+00	1.65E+00	2.22E+00	2.53E+00	6.33E+00
	max	1.50E+00	2.17E+00	2.92E+00	3.33E+00	8.33E+00
V B	min	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	max	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

Diffuse emission factor for PERC						
\dot{E}_{cl} (g/h)						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A	min	1.27E+01	1.82E+01	2.26E+01	4.12E+01	1.03E+02
	max	1.40E+01	2.00E+01	2.49E+01	4.53E+01	1.13E+02
I B	min	1.90E+01	2.73E+01	3.40E+01	6.17E+01	1.54E+02
	max	2.09E+01	3.00E+01	3.74E+01	6.79E+01	1.70E+02
II A	min	7.05E+00	1.01E+01	1.26E+01	2.29E+01	5.72E+01
	max	7.76E+00	1.11E+01	1.38E+01	2.52E+01	6.29E+01
II B	min	1.06E+01	1.52E+01	1.89E+01	3.43E+01	8.58E+01
	max	1.16E+01	1.67E+01	2.08E+01	3.77E+01	9.43E+01
III	min	2.12E+00	3.03E+00	3.77E+00	6.86E+00	1.72E+01
	max	2.33E+00	3.33E+00	4.15E+00	7.55E+00	1.89E+01
IV A or B	min	1.50E+00	2.17E+00	2.92E+00	3.33E+00	8.33E+00
	max	2.40E+00	3.47E+00	4.67E+00	5.33E+00	1.33E+01
V A	min	1.14E+00	1.65E+00	2.22E+00	2.53E+00	6.33E+00
	max	1.50E+00	2.17E+00	2.92E+00	3.33E+00	8.33E+00
V B	min	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	max	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

If \dot{E}_{cl} (g/h) of type I and II machines is divided by the bath surface the diffusion mass flow in z direction, J_z (g/(m²h)), can be obtained. Type I B and II B

consists of three baths in comparison to two baths in the subtypes A and, therefore, diffuse emissions are higher. For the subtypes IV A and IV B, the diffuse emission factors are the same, as changes in cooling temperature do not affect the diffuse emissions. For type V B machines the diffuse emissions into the workplace can be neglected as the machines are operated under vacuum.

C.2.3.2 Continuous emission factor for cleaned metal parts

The residual solvent amount in g/m^2 together with the surface area of the cleaned parts is needed to calculate the amount of residual solvent E_{c2} (g) for each load. For parts with cupped areas the amount of cupped surface is also needed (5% for closely packed spheres in open-top type I and II machines and 2.5% for encased machines, the definition of cleaned parts can be found in Appendix C.2.2). In Table C.7 the residual solvent amounts (g/m^2) are summarized for the different machine types.

Table C.7: Residual solvent amount in g/m^2 of part surface for different machine types.

Residual solvent amount in g/m^2 for non-cupped areas										
Type	I A or II A		I B or II B		III		IV A or IV B		V A or V B	
	min	max	min	max	min	max	min	max	min	max
TRIC	1.17E+00	1.29E+00	9.77E-01	1.07E+00	1.22E-01	1.34E-01	3.05E-02	3.36E-02	1.53E-02	1.68E-02
PERC	3.90E+00	4.28E+00	3.25E+00	3.57E+00	4.06E-01	4.46E-01	1.01E-01	1.12E-01	5.07E-02	5.58E-02

Residual solvent amount in g/m^2 for cupped areas				
Type	I A/B or II A/B		III	
	min	max	min	max
TRIC	9.77E+00	1.07E+01	3.26E+00	3.58E+00
PERC	3.25E+01	3.57E+01	1.08E+01	1.19E+01

The difference between open-top IA and IIA to IB and IIB machines is due to the fact that metal parts drag out more residual solvent from solvent baths than from vapor baths. The reduction from open-top machines to encased type III machines can be associated with the fact that encased machines, in contrast to open-top machines, are automated and, therefore, the parts remain longer in the drying zone. In machines with improved drying systems and

tilting devices (type IV and V), the residual solvent amount on the metal parts could be reduced further and the amount of solvent dragged out by cupped areas could be reduced to almost 0.

The division of the total amount of residual solvent E_{c_2} (g) dragged out by a load by the time α (h) needed for evaporation (released metal parts are still warm therefore evaporation times are relatively short) results in the continuous emission factor \dot{E}_{c_2} (g/h) for metal degreasing.

Table C.7: Continuous emission factors \dot{E}_{c_2} (g/h) for emissions from cleaned plates for all machine types, subtypes and sizes using TRIC or PERC. Emissions described by \dot{E}_{c_2} occur for a period of length α .

TRIC emission factor from cleaned plates						
\dot{E}_{c_2} (g/h) for period α						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or II A	min	9.64E+01	9.65E+01	1.20E+02	1.83E+02	2.12E+02
	max	3.18E+02	3.18E+02	3.98E+02	6.03E+02	7.00E+02
I B or II B	min	8.03E+01	8.04E+01	1.00E+02	1.52E+02	1.77E+02
	max	2.65E+02	2.65E+02	3.31E+02	5.02E+02	5.83E+02
III	min	1.00E+01	1.00E+01	1.26E+01	1.90E+01	2.21E+01
	max	3.31E+01	3.32E+01	4.14E+01	6.28E+01	7.29E+01
IV A or B	min	2.51E+00	2.51E+00	3.14E+00	4.76E+00	5.52E+00
	max	8.28E+00	8.29E+00	1.04E+01	1.57E+01	1.82E+01
V A or B	min	1.26E+00	1.26E+00	1.57E+00	2.38E+00	2.76E+00
	max	4.14E+00	4.15E+00	5.18E+00	7.85E+00	9.11E+00

PERC emission factor from cleaned plates						
\dot{E}_{c_2} (g/h) for period α						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or II A	min	3.20E+02	3.21E+02	4.00E+02	6.07E+02	7.05E+02
	max	1.06E+03	1.06E+03	1.32E+03	2.00E+03	2.33E+03
I B or II B	min	2.67E+02	2.67E+02	3.34E+02	5.06E+02	5.87E+02
	max	8.81E+02	8.82E+02	1.10E+03	1.67E+03	1.94E+03
III	min	3.34E+01	3.34E+01	4.17E+01	6.32E+01	7.34E+01
	max	1.10E+02	1.10E+02	1.38E+02	2.09E+02	2.42E+02
IV A or B	min	8.34E+00	8.35E+00	1.04E+01	1.58E+01	1.84E+01
	max	2.75E+01	2.76E+01	3.44E+01	5.22E+01	6.06E+01
V A or B	min	4.17E+00	4.17E+00	5.21E+00	7.90E+00	9.18E+00
	max	1.38E+01	1.38E+01	1.72E+01	2.61E+01	3.03E+01

Table C.8: Continuous emission factors \dot{E}_{c_2} (g/h) for emissions from cleaned closely packed spheres for all machine types, subtypes and sizes using TRIC or PERC. Emission described by \dot{E}_{c_2} occur for a period of length α .

TRIC emission factor from cleaned spheres						
\dot{E}_{c_2} (g/h) for period α						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or II A	min	8.54E+01	1.02E+02	1.08E+02	1.49E+02	1.45E+02
	max	2.82E+02	3.37E+02	3.57E+02	4.90E+02	4.77E+02
I B or II B	min	7.55E+01	9.03E+01	9.55E+01	1.31E+02	1.28E+02
	max	2.49E+02	2.98E+02	3.15E+02	4.34E+02	4.22E+02
III	min	1.07E+01	1.28E+01	1.35E+01	1.86E+01	1.81E+01
	max	3.53E+01	4.22E+01	4.46E+01	6.14E+01	5.97E+01
IV A or B	min	2.51E+00	2.51E+00	3.14E+00	4.76E+00	5.52E+00
	max	8.28E+00	8.29E+00	1.04E+01	1.57E+01	1.82E+01
V A or B	min	8.13E-01	9.73E-01	1.03E+00	1.42E+00	1.38E+00
	max	2.68E+00	3.21E+00	3.40E+00	4.67E+00	4.54E+00

PERC emission factor from cleaned spheres						
\dot{E}_{c_2} (g/h) for period α						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or II A	min	2.84E+02	3.39E+02	3.59E+02	4.94E+02	4.80E+02
	max	9.36E+02	1.12E+03	1.19E+03	1.63E+03	1.59E+03
I B or II B	min	2.51E+02	3.00E+02	3.18E+02	4.37E+02	4.25E+02
	max	8.28E+02	9.91E+02	1.05E+03	1.44E+03	1.40E+03
III	min	3.55E+01	4.25E+01	4.49E+01	6.18E+01	6.01E+01
	max	1.17E+02	1.40E+02	1.48E+02	2.04E+02	1.98E+02
IV A or B	min	5.41E+00	6.47E+00	6.84E+00	9.41E+00	9.15E+00
	max	1.78E+01	2.13E+01	2.26E+01	3.11E+01	3.02E+01
V A or B	min	2.70E+00	3.23E+00	3.42E+00	4.71E+00	4.58E+00
	max	8.92E+00	1.07E+01	1.13E+01	1.55E+01	1.51E+01

C.2.3.3 Periodic emission factor for loading and unloading

In Table C.9 the saturation concentrations of the solvent-charged air exchanged with the workplace environment during loading and unloading are listed.

Table C.9: Concentrations of solvent-charged air that is exchanged with workplace air (Manufacturers, 1960-2001).

Concentration at the height of the cooling device (g/m^3)							
Type	I A or B		II A or B		III		
	min	max	min	max	min	max	
TRIC	480	515	275	315	260	300	
PERC	180	220	100	130	90	115	

Chamber concentration (type IV and V) (g/m^3)								
Type	IV A		IV B		V A		V B	
	min	max	min	max	min	max	min	max
TRIC	50	65	25	35	0.5	1	0.3	0.75
PERC	25	40	7	10	0.5	1	0.3	0.75

The concentration differences between TRIC and PERC for the older machines are due to the different saturation concentrations for a given temperature in the cooling zone (see Figure C.3).

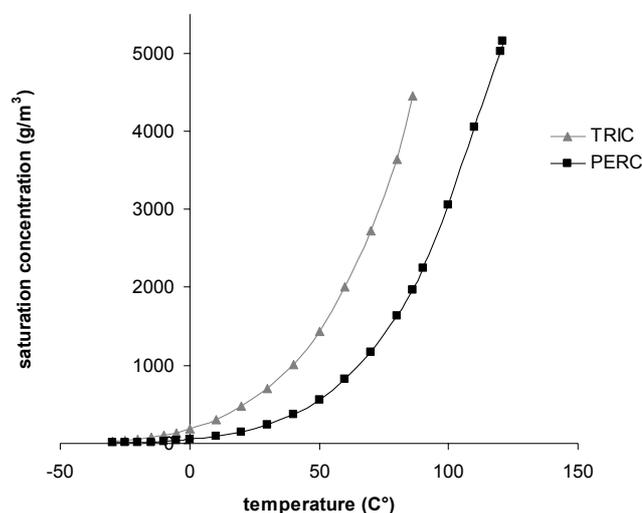


Figure C.3: Saturation concentrations curve fitted through concentration measurements for TRIC and PERC in air (measurements done by Wacker-Chemie GmbH, 1990).

To define the periodic emissions E_p , the volume of the average load, the free basket volume and the efficiency of the rim exhausters are needed to determine the volumes of saturated solvent air replaced during loading and

unloading (the volumes are listed in Table C.3 and C.4 in Appendix C.2, and the efficiencies are described in Chapter 4.2.2.).

Table C.10: Periodic emission factors E_p for all machine types, subtypes and sizes using TRIC or PERC.

Periodic TRIC emission factor from chamber air						
E_p (g)						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or B	min	3.91E+00	8.14E+00	2.28E+01	1.22E+02	7.20E+02
	max	4.19E+00	8.73E+00	2.45E+01	1.31E+02	7.73E+02
II A or B	min	2.24E+00	4.66E+00	1.31E+01	7.01E+01	4.13E+02
	max	2.56E+00	5.34E+00	1.50E+01	8.03E+01	4.73E+02
III	min	1.84E+00	3.83E+00	1.07E+01	5.75E+01	3.38E+02
	max	2.12E+00	4.41E+00	1.24E+01	6.64E+01	3.90E+02
IV A	min	3.53E-01	7.36E-01	2.06E+00	1.11E+01	6.51E+01
	max	4.59E-01	9.56E-01	2.68E+00	1.44E+01	8.46E+01
IV B	min	1.77E-01	3.68E-01	1.03E+00	5.53E+00	3.25E+01
	max	2.47E-01	5.15E-01	1.44E+00	7.74E+00	4.56E+01
V A	min	3.53E-03	7.36E-03	2.06E-02	1.11E-01	6.51E-01
	max	7.06E-03	1.47E-02	4.12E-02	2.21E-01	1.30E+00
V B	min	2.12E-03	4.41E-03	1.24E-02	6.64E-02	3.90E-01
	max	5.30E-03	1.10E-02	3.09E-02	1.66E-01	9.76E-01

Periodic PERC emission factor from chamber air						
E_p (g)						
Type		Size 1	Size 2	Size 3	Size 4	Size 5
I A or B	min	1.47E+00	3.05E+00	8.55E+00	4.59E+01	2.70E+02
	max	1.79E+00	3.73E+00	1.05E+01	5.61E+01	3.30E+02
II A or B	min	8.14E-01	1.70E+00	4.75E+00	2.55E+01	1.50E+02
	max	1.06E+00	2.20E+00	6.18E+00	3.32E+01	1.95E+02
III	min	6.36E-01	1.32E+00	3.71E+00	1.99E+01	1.17E+02
	max	8.12E-01	1.69E+00	4.74E+00	2.54E+01	1.50E+02
IV A	min	1.77E-01	3.68E-01	1.03E+00	5.53E+00	3.25E+01
	max	2.82E-01	5.89E-01	1.65E+00	8.85E+00	5.21E+01
IV B	min	4.94E-02	1.03E-01	2.89E-01	1.55E+00	9.11E+00
	max	7.06E-02	1.47E-01	4.12E-01	2.21E+00	1.30E+01
V A	min	3.53E-03	7.36E-03	2.06E-02	1.11E-01	6.51E-01
	max	7.06E-03	1.47E-02	4.12E-02	2.21E-01	1.30E+00
V B	min	2.12E-03	4.41E-03	1.24E-02	6.64E-02	3.90E-01
	max	5.30E-03	1.10E-02	3.09E-02	1.66E-01	9.76E-01

C.2.4. Workplace parameters

The different workplace volumes, V , as well as the air exchange rates k_A and k_L for open-top machines (type I and II) and for closed machines (type III to V) as described in Chapter 4.2.3 are summarized in Table C.11 and Table C.12.

Table C.11: Workplace volumes for metal-degreasing facilities.

Workplace volume for all types of machines V (m ³)		
Entire workplace	min	400
	max	600

Table C.12: Air exchange rates k_A and k_B for metal-degreasing facilities.

Air exchange rates		Type I - II	Type III - V
k_A (1/h)	min	7	6
	max	7.5	6.5
k_L (1/h)	min	6	5.5
	max	6.5	6

C.2.5. Number of machines

The estimated numbers of metal-degreasing machines in Germany both machines using TRIC and those using PERC are given in Table C.13. For the year 1985 (only former West German states), the numbers of metal-degreasing machines subdivided into different types and sizes are given as cumulated numbers for chlorinated hydrocarbons (Adams and Jeker, 1986). From the solvent proportions, which are given in the same report, the number of machines using TRIC and the number of machines using PERC can be estimated, assuming that the solvent proportions are the same for all machine sizes. For the year 1991 (only former West German states), almost the same information is available (Adams, 1993), the only difference being that in this

report the numbers are not subdivided into different sizes. Therefore, it was assumed that the fractions of machines remained the same as in 1985. Where no distinction between subtypes was made in the previous reports (type I and II), it was assumed that both subtypes exist in equal shares. For the year 1996, Adams (1997) reports the number of machines using TRIC and those using PERC cumulated in one number. For 1999, the data for TRIC and PERC can be found in the reports of Nader (2001a, 2001b). For the years 1996 and 1999, partitioning into sizes was done according to type III in Adams and Jeker (1986). In a personal communication by F.W. Nader from VCI (2001b), this separation was affirmed.

Table C.13: Estimates of the number of metal-degreasing machines using TRIC and PERC in Germany for the years 1985, 1991, 1996 and 1999 (1985, 1991: only former West German states). Sources: a: (Adams and Jeker, 1986), b: (Adams, 1993), c: (Adams, 1997), d: (Nader, 2001c), e: (Nader, 2001a).

Machine type	Year Sizes	TRIC				PERC			
		1985* (a)	1991* (b)	1996 (c)	1999 (d)	1985* (a)	1991* (b)	1996 (c)	1999 (e)
IA	1	1133	342			1444	648		
	2	117	35			149	67		
	3	96	29			122	55		
	4	39	12			50	22		
	5	5	2			6	3		
IB	1	1133	343			1444	649		
	2	117	35			149	67		
	3	95	29			122	55		
	4	38	12			49	22		
	5	4	1			5	2		
IIA	1	0	5			0	9		
	2	354	19			452	35		
	3	298	23			379	44		
	4	268	8			341	16		
	5	30	1			38	2		
IIB	1	0	5			0	9		
	2	354	19			451	35		
	3	297	23			379	44		
	4	268	8			341	16		
	5	29	1			38	2		
III	1	14	46			18	88		
	2	57	188			72	353		
	3	71	234			90	442		
	4	25	82			32	157		
	5	3	10			4	20		
IVA	1	10	14			13	27		
	2	41	56			52	106		
	3	10	70			13	133		
	4	0	25			0	47		
	5	0	3			0	6		
IVB	1	1	14	15		1	27	24	
	2	5	56	59		6	106	94	
	3	1	70	74		1	133	118	
	4	0	25	26		0	47	42	
	5	0	3	3		0	6	5	
VA	1		23	45	17		44	70	75
	2		93	179	67		177	282	300
	3		117	223	83		221	352	375
	4		41	79	30		79	125	133
	5		5	10	4		10	16	17
VB	1		0	15	8			23	38
	2		0	59	33			94	150
	3		0	74	42			117	188
	4		0	26	15			42	67
	5		0	3	2			5	8
<i>total</i>		4913	2127	890	301	6261	4028	1408	1351
<i>vapor degreasing only</i>		2573	1651	890	301	3280	3127	1408	1351

* only former West German states

According to a personal communication by N. Adams from Dow Europe S.A., the industrial estimates for the years 1985 and 1991 are rather high (at those times industry knew very little about the exact numbers), whereas data quality for the years 1996 and 1999 is supposed to be very good (Adams, 2002).

C.2.6. Number of exposed workers

In Table C.14 the assumptions on the number of exposed workers per machine are summarized as described in Chapter 4.2.4. The only available information on the number of exposed workers in the near-field is from a report stating that in Germany the newer machines are operated by an average of 1.25 workers (Nader, 2001c) and from a paper reporting for Sweden an average of 1.6 workers per machine (Ulander et al., 1992). This second value was taken as a maximum value, whereas the minimum value is 1 machine operator. No data sources could be found for the number of operators for older machines and for the number of exposed workers in the far-field.

Table C.14: Estimations of the number of exposed workers per machine for different machine types, with separate indication for the near-field and the far-field.

Number of exposed workers per machine	Near-field			Far-field		
	min	max	average	min	max	average
type I and II	1.5	3	2.25	3	10	6.5
type III to V	1	1.6	1.3	2	8	5

C.3. Metal degreasing results

The systematic combination of all independent input parameters leads to up to 2'160 exposure scenarios for each machine type. The parameter combination is visualized in Figure C.4.

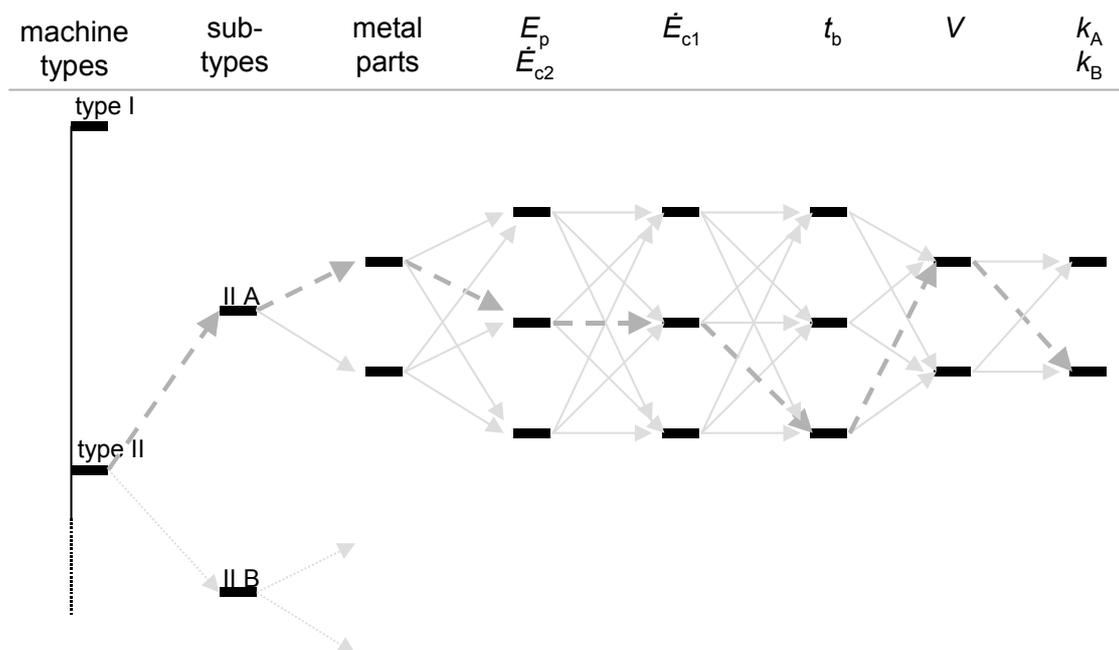


Figure C.4: Parameter combination of all independent input parameters shown for a type II A machine.

In the following, scenario plots similar to the representation in Figure 4.7 (see Chapter 4.3.2) are shown for all five machine types using TRIC and PERC. With the help of these plots, it may be decided whether the distinction between subtypes is relevant in terms of long-term near-field concentration. Note that the scaling of the y-axis (long-term TRIC or PERC concentration (g/m^3)) is different for all plots.

From the scenario plots, it can be seen that for types IV and V machines it is useful to distinguish between subtypes for the exposure assessment. These differences between the subtypes occur because of different cooling temperatures of type IV A and IV B machines and because of the existence of a vacuum drying device in type V B machines. This has an effect on the long-term airborne concentration in the near-field (box A).

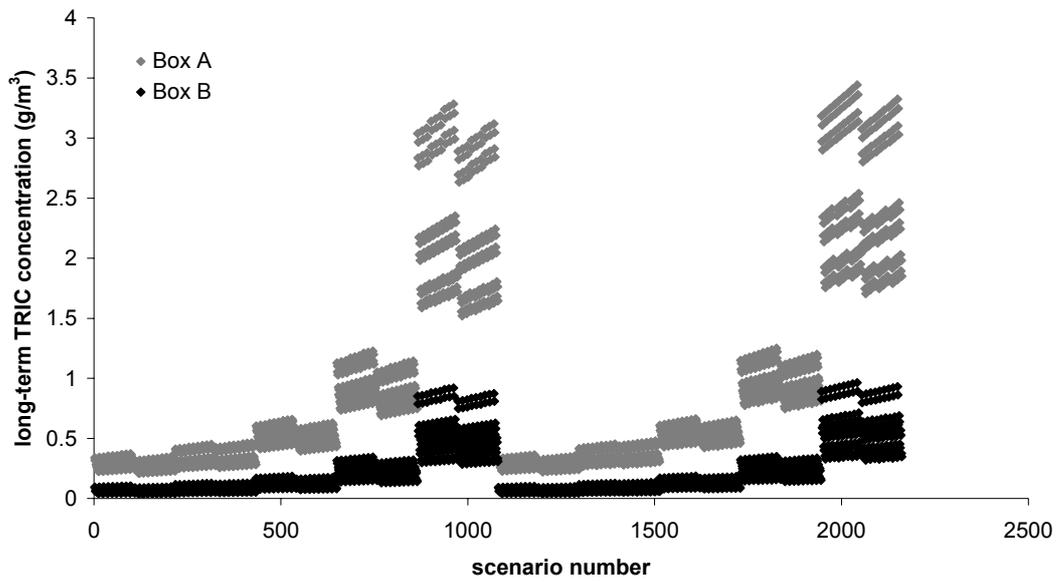


Figure C.5: Scenario plot for an open-top type I machine using TRIC.

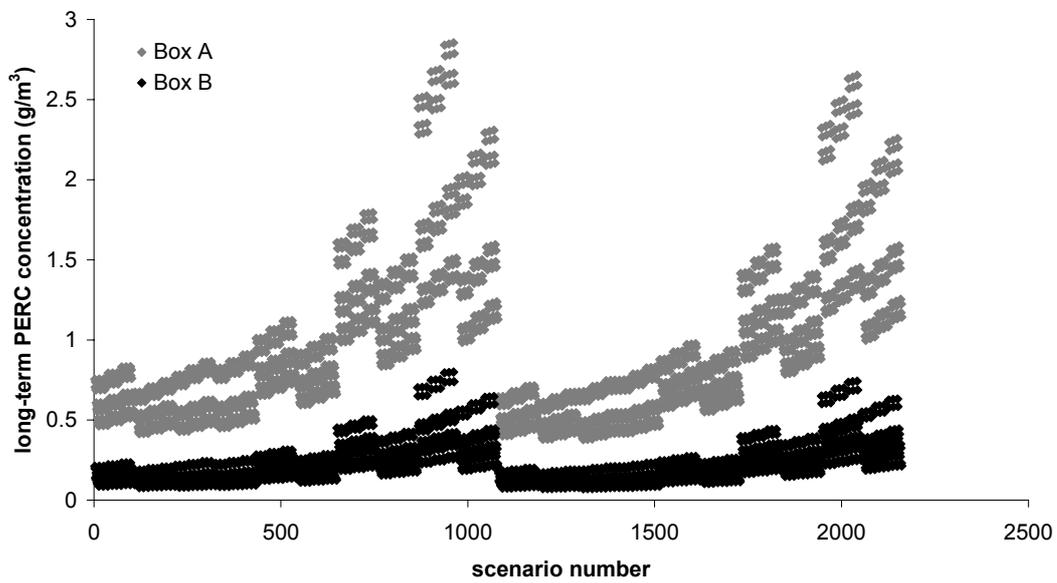


Figure C.6: Scenario plot for an open-top type I machine using PERC.

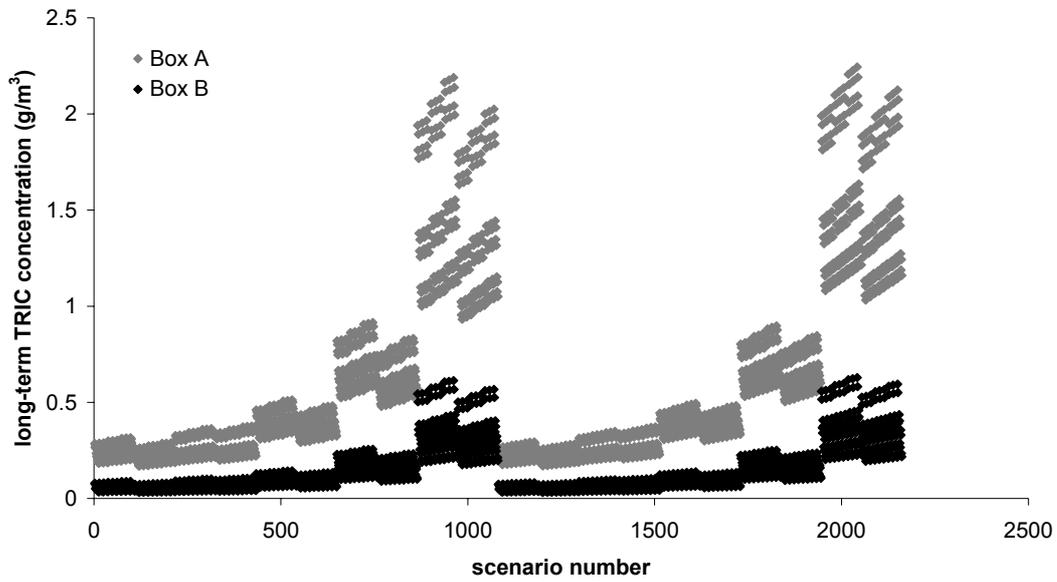


Figure C.7: Scenario plot for an open-top type II machine using TRIC.

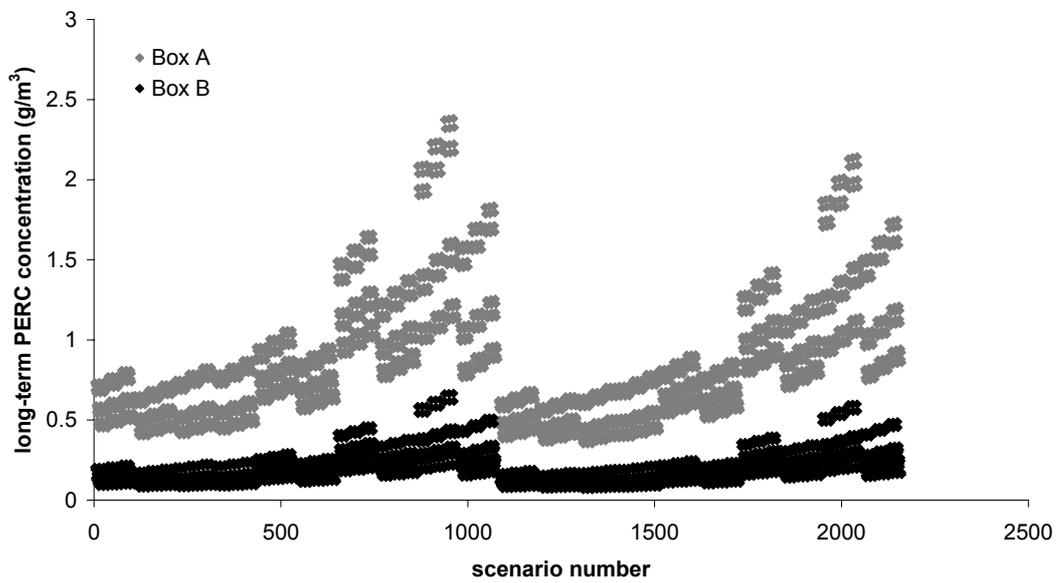


Figure C.8: Scenario plot for an open-top type II machine using PERC.

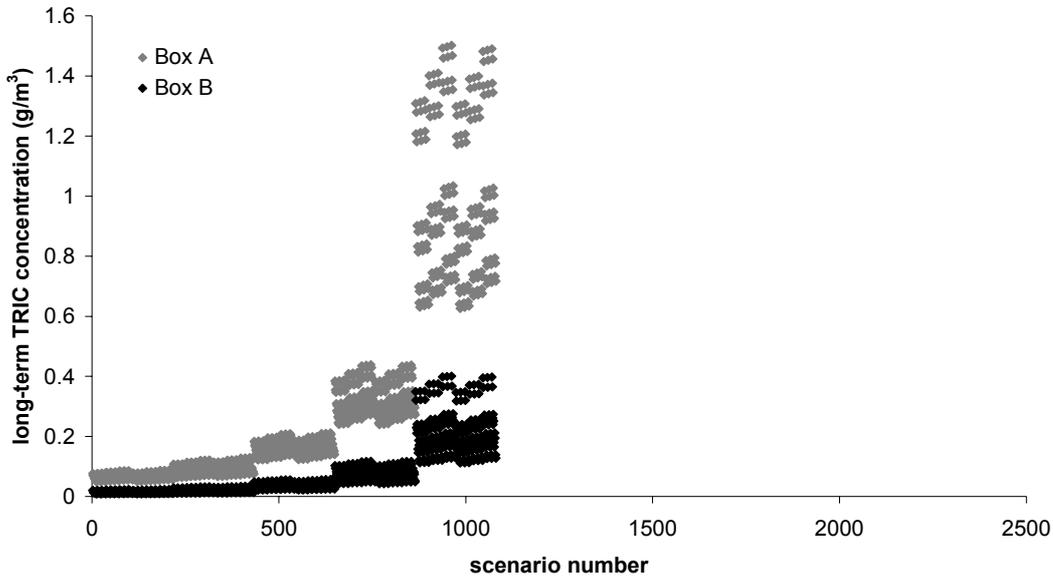


Figure C.9: Scenario plot for an encased type III machine using TRIC.

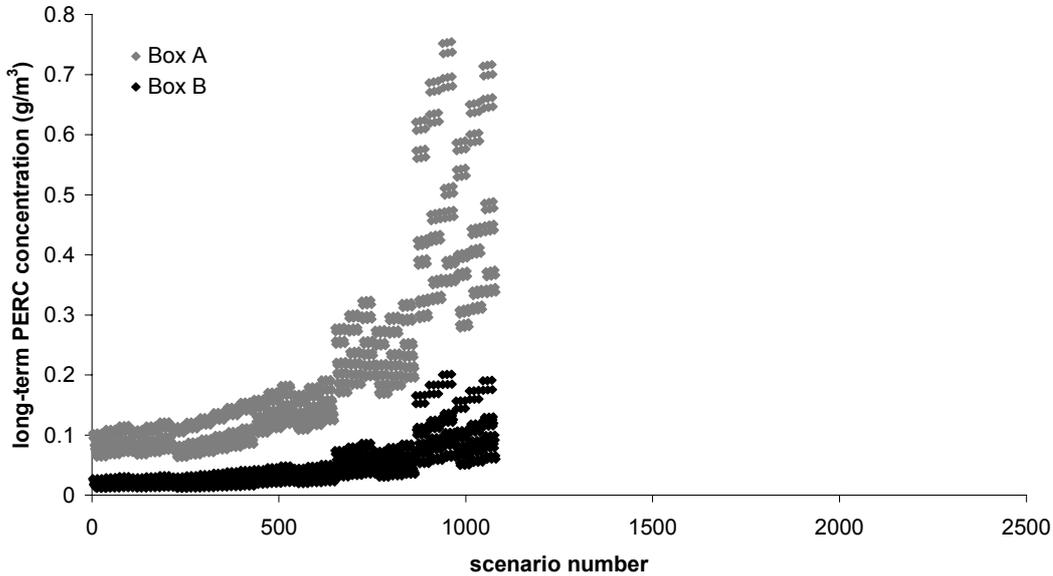


Figure C.10: Scenario plot for an encased type III machine using PERC.

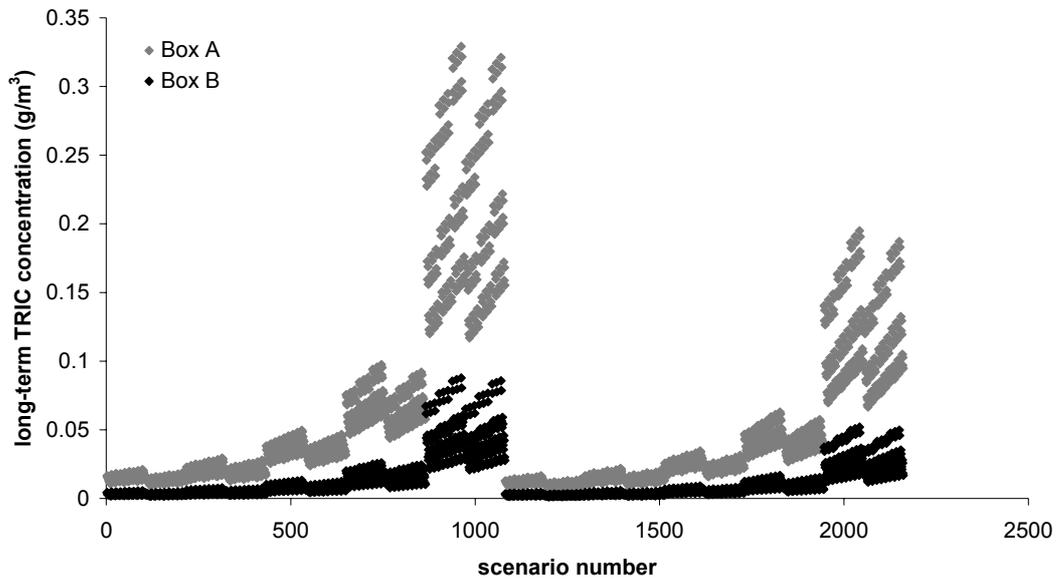


Figure C.11: Scenario plot for a closed one-chamber type IV machine using TRIC.

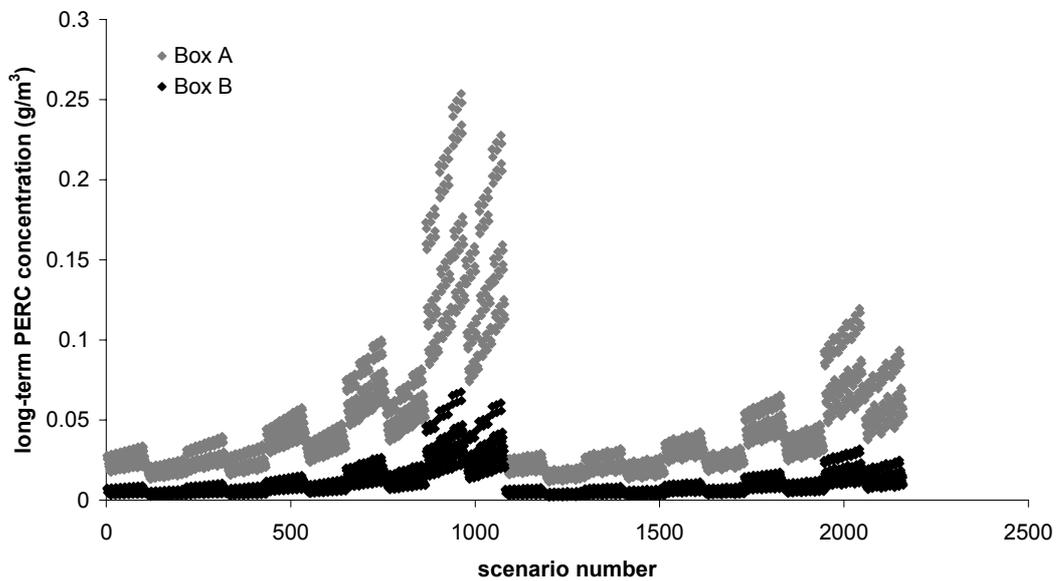


Figure C.12: Scenario plot for a closed one-chamber type IV machine using PERC.

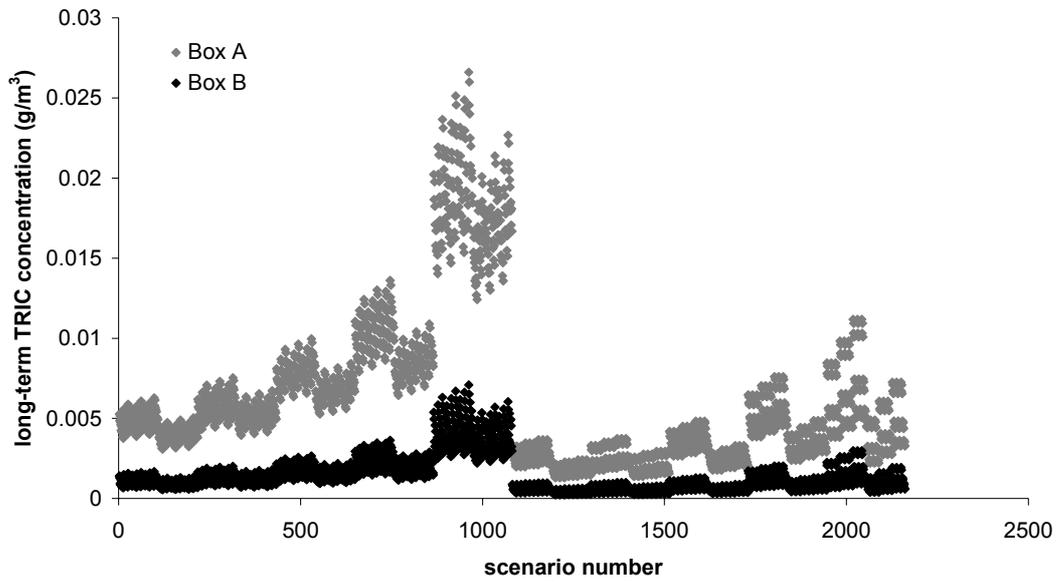


Figure C.13: Scenario plot for a closed-loop one-chamber type V machine using TRIC.

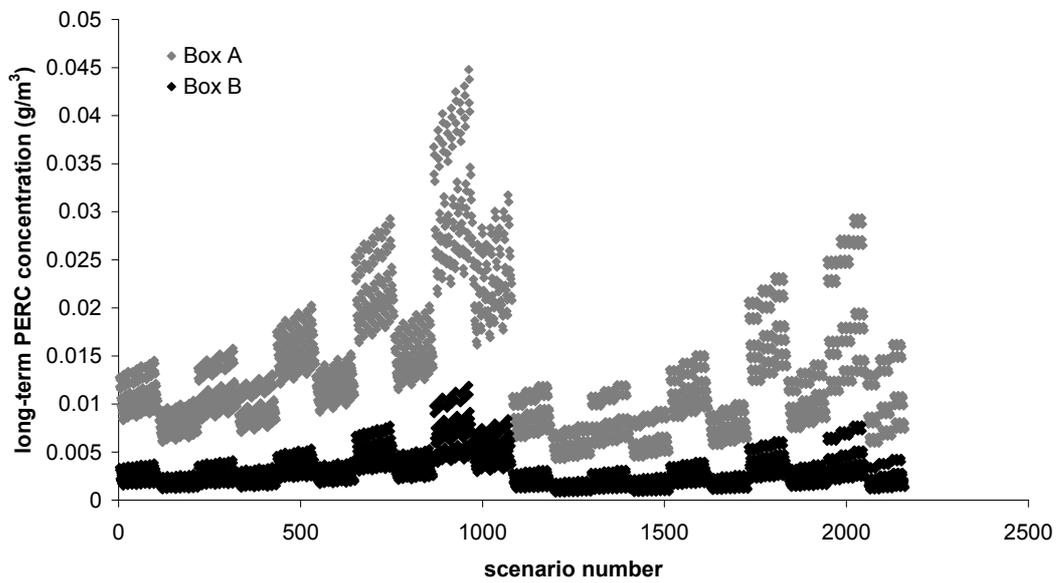


Figure C.14: Scenario plot for a closed-loop one-chamber type V machine using PERC.

In the following, the SceBRA exposure estimates are given as near-field and far-field long-term concentrations for all machine types and sizes using TRIC or PERC (see Tables C.15 to C.18).

Table C.15: Long-term TRIC exposure concentrations, calculated with SceBRA, for the near-field of all machine types and sizes.

Type	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
I	5	3284	1519	2250	608.1	281.3	416.8
	4	1227	689	920	227.2	127.6	170.3
	3	659	395	512	122.0	73.1	94.7
	2	464	250	339	85.9	46.4	62.8
	1	372	209	279	68.9	38.6	51.8
II	5	2190	932	1442	405.6	172.7	267.0
	4	916	479	664	169.5	88.7	122.9
	3	512	291	388	94.9	54.0	71.9
	2	377	192	268	69.8	35.6	49.7
	1	316	168	232	58.6	31.2	43.0
III	5	1502	626	986	278.1	115.9	182.5
	4	439	239	325	81.2	44.3	60.2
	3	212	121	161	39.2	22.4	29.8
	2	129	63	90	23.9	11.6	16.6
	1	88	49	66	16.3	9.1	12.2
IV A	5	329	117	202	60.9	21.7	37.4
	4	97	44	66	18.1	8.1	12.3
	3	50	24	35	9.2	4.4	6.5
	2	29	13	20	5.5	2.4	3.6
	1	21	9	14	3.9	1.7	2.7
IV B	5	195	67	117	36.1	12.3	21.7
	4	63	27	42	11.7	4.9	7.7
	3	35	16	24	6.4	2.9	4.4
	2	22	9	15	4.1	1.7	2.7
	1	17	7	11	3.1	1.3	2.1
V A	5	27	12	18	4.9	2.3	3.4
	4	14	6	9	2.5	1.2	1.7
	3	10	5	7	1.8	1.0	1.4
	2	8	4	5	1.4	0.7	1.0
	1	6	3	4	1.2	0.6	0.8
V B	5	11	2	5	2.1	0.4	1.0
	4	8	2	4	1.4	0.4	0.8
	3	5	2	3	0.9	0.3	0.6
	2	4	1	2	0.7	0.3	0.4
	1	4	1	2	0.7	0.2	0.4

Table C.16: Long-term PERC exposure concentrations, calculated with SceBRA, for the near-field of all machine types and sizes.

Type	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
I	5	2855	985	1712	413.8	142.8	248.1
	4	1794	835	1234	260.0	121.1	178.8
	3	1121	595	823	162.5	86.2	119.2
	2	910	429	625	131.9	62.1	90.6
	1	833	415	593	120.7	60.1	86.0
II	5	2383	762	1385	345.3	110.5	200.7
	4	1662	756	1131	240.9	109.6	163.9
	3	1060	555	773	153.6	80.5	112.1
	2	875	407	598	126.8	59.0	86.7
	1	810	400	575	117.4	57.9	83.3
III	5	755	278	468	109.4	40.3	67.8
	4	325	167	234	47.0	24.2	34.0
	3	193	102	142	27.9	14.8	20.5
	2	155	62	99	22.5	9.0	14.3
	1	122	63	89	17.7	9.2	12.8
IV A	5	254	74	143	36.8	10.7	20.7
	4	100	37	63	14.5	5.3	9.1
	3	58	24	38	8.4	3.4	5.5
	2	40	16	25	5.8	2.3	3.7
	1	34	13	22	4.9	1.9	3.1
IV B	5	120	38	69	17.3	5.5	10.0
	4	65	24	41	9.5	3.5	6.0
	3	43	18	28	6.2	2.6	4.1
	2	32	13	21	4.7	1.9	3.0
	1	29	11	19	4.2	1.6	2.7
V A	5	45	16	27	6.5	2.3	3.9
	4	29	11	19	4.2	1.7	2.7
	3	20	9	14	2.9	1.3	2.0
	2	16	7	11	2.3	1.0	1.5
	1	15	6	10	2.1	0.9	1.4
V B	5	29	6	14	4.3	0.9	2.1
	4	23	7	14	3.4	1.1	2.0
	3	15	6	10	2.2	0.8	1.4
	2	12	4	7	1.7	0.6	1.1
	1	12	4	7	1.7	0.6	1.1

Table C.17: Long-term TRIC exposure concentrations, calculated with SceBRA, for the far-field of all machine types and sizes.

Type	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
I	5	919	285	527	170.3	52.7	97.6
	4	344	129	215	63.6	23.9	39.9
	3	184	74	120	34.1	13.7	22.2
	2	130	47	79	24.0	8.7	14.7
	1	104	39	65	19.3	7.2	12.1
II	5	613	175	338	113.6	32.4	62.5
	4	256	90	155	47.5	16.6	28.8
	3	143	55	91	26.6	10.1	16.8
	2	106	36	63	19.5	6.7	11.6
	1	89	32	54	16.4	5.8	10.1
III	5	400	111	220	74.2	20.6	40.7
	4	117	43	72	21.7	7.9	13.4
	3	56	22	36	10.4	4.0	6.6
	2	34	11	20	6.4	2.1	3.7
	1	23	9	15	4.3	1.6	2.7
IV A	5	88	21	45	16.3	3.9	8.3
	4	26	8	15	4.8	1.4	2.7
	3	13	4	8	2.5	0.8	1.4
	2	8	2	4	1.5	0.4	0.8
	1	6	2	3	1.0	0.3	0.6
IV B	5	52	12	26	9.6	2.2	4.8
	4	17	5	9	3.1	0.9	1.7
	3	9	3	5	1.7	0.5	1.0
	2	6	2	3	1.1	0.3	0.6
	1	4	1	2	0.8	0.2	0.5
V A	5	7	2	4	1.3	0.4	0.7
	4	4	1	2	0.7	0.2	0.4
	3	3	1	2	0.5	0.2	0.3
	2	2	1	1	0.4	0.1	0.2
	1	2	1	1	0.3	0.1	0.2
V B	5	3	0	1	0.6	0.1	0.2
	4	2	0	1	0.4	0.1	0.2
	3	1	0	1	0.2	0.1	0.1
	2	1	0	1	0.2	0.0	0.1
	1	1	0	0	0.2	0.0	0.1

Table C.18: Long-term PERC exposure concentrations, calculated with SceBRA, for the far-field of all machine types and sizes.

Type	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
I	5	799	185	401	115.9	26.8	58.1
	4	502	157	289	72.8	22.7	41.9
	3	314	111	193	45.5	16.2	27.9
	2	255	80	146	36.9	11.6	21.2
	1	233	78	139	33.8	11.3	20.1
II	5	667	143	324	96.7	20.7	47.0
	4	465	142	265	67.4	20.5	38.4
	3	297	104	181	43.0	15.1	26.3
	2	245	76	140	35.5	11.1	20.3
	1	227	75	135	32.9	10.9	19.5
III	5	201	49	104	29.2	7.2	15.1
	4	87	30	52	12.5	4.3	7.6
	3	51	18	32	7.4	2.6	4.6
	2	41	11	22	6.0	1.6	3.2
	1	33	11	20	4.7	1.6	2.9
IV A	5	68	13	32	9.8	1.9	4.6
	4	27	7	14	3.9	0.9	2.0
	3	15	4	8	2.2	0.6	1.2
	2	11	3	6	1.5	0.4	0.8
	1	9	2	5	1.3	0.3	0.7
IV B	5	32	7	15	4.6	1.0	2.2
	4	17	4	9	2.5	0.6	1.3
	3	11	3	6	1.6	0.5	0.9
	2	9	2	5	1.2	0.3	0.7
	1	8	2	4	1.1	0.3	0.6
V A	5	12	3	6	1.7	0.4	0.9
	4	8	2	4	1.1	0.3	0.6
	3	5	2	3	0.8	0.2	0.4
	2	4	1	2	0.6	0.2	0.3
	1	4	1	2	0.6	0.2	0.3
V B	5	8	1	3	1.1	0.2	0.5
	4	6	1	3	0.9	0.2	0.4
	3	4	1	2	0.6	0.1	0.3
	2	3	1	2	0.5	0.1	0.2
	1	3	1	2	0.5	0.1	0.2

C.4. Concentration measurements in metal-degreasing facilities

In the following, published airborne concentration measurements are listed for TRIC in Table C.19 and for PERC in Table C.20. In Chapter 4.3.5, the measured values are compared to long-term airborne concentrations

calculated with the two-box model in Figure 4.15 for PERC and Figure 4.16 for TRIC.

Table C.19: Published exposure measurements of TRIC used in metal degreasing (log r = log (concentration/50 ppm)) (measurements depicted in Figure 4.15 in Chapter 4.3.5).

Year	Country	Machine type	Maschine description	Measurement	Sample	Number of machines	Number of samples	Range (ppm)	log r of range	Average (ppm)	log r of average	References
1942	USA	I	n.d.	during normal operation	personal	108	n.d.	n.d.	n.d.	128.9	0.4	Morse and Goldberg (1943)
1947-59	Denmark	I	n.d.	n.d.	air	n.d.	200	n.d.	n.d.	120.9	0.4	Raaschou-Nielsen et al. (2002)
1952-57	USA	I	n.d.	n.d.	air	323	n.d.	50%-pct. 49.8	50%-pct. 0.0	n.d.	n.d.	Hargarten et al. (1961)
1956	n.d.	I	n.d.	n.d.	air	n.d.	n.d.	5.0 to 600.0	-1.0 to 1.1	n.d.	n.d.	Bardodej and Vyskocil (1956)
1955*	Switzerland	I and II	mostly open-top degreasers	5-10 min samples	air	n.d.	84	n.d.	n.d.	49.8	0.0	Grandjean et al. (1955)
1950s	Sweden	I and II	mostly open-top degreasers	TWA	personal	18	n.d.	n.d.	n.d.	37.8	-0.1	Ahlmark et al. (1964)
1960-96	Denmark	I or II	n.d.	n.d.	air	n.d.	50	n.d.	n.d.	59.6	0.1	Raaschou-Nielsen et al. (2002)
1972*	Japan	n.d.	automatic metal degreasing	n.d.	air	5	> 25	n.d.	n.d.	34.8	-0.2	Ikeda et al. (1972)
1972	Germany	I or II	vapor degreasing with exhaust	n.d.	personal	1	n.d.	22.0 to 47.0	-0.4 to 0.0	n.d.	n.d.	Nicklin (1972)
1972	Germany	I or II	vapor degreasing without exhaust	n.d.	personal	1	n.d.	65.0 to 165.0	0.1 to 0.5	n.d.	n.d.	Nicklin (1972)
1973	GB	I or II	2/3 of open-top machines with rim exhaust	TWA	personal	21	71	75%-pct. 100.0	75%-pct. 0.3	n.d.	n.d.	Kay (1973)
1970-79	Denmark	I or II	n.d.	n.d.	air and personal	n.d.	116	n.d.	n.d.	55.9	0.0	Raaschou-Nielsen et al. (2002)
1984*	France	I and II	n.d.	n.d.	n.d.	64	n.d.	50%-pct. 149.3	50%-pct. 0.5	n.d.	n.d.	Barret et al. (1984)
1984	Western Europe	I and II	open-top equipment	n.d.	air	n.d.	n.d.	90%-pct. 100.0 75%-pct. 50.0	90%-pct. 0.3 75%-pct. 0.0	n.d.	n.d.	CEFIC (1984)
1980-89	Denmark	II and III	n.d.	n.d.	air and personal	n.d.	371	n.d.	n.d.	13.0	-0.6	Raaschou-Nielsen et al. (2002)
1985-91	Germany	III and IV	n.d.	TWA and range measurements	n.d.	267	748	90%-pct. 101.3	90%-pct. 0.3	15.4	-0.5	BK-Report (1999)
1988-89	Sweden	n.d.	vapor degreasing	TWA	personal	19	29	0.6 to 26.7	-2 to -0.3	5.0	-1.0	Ulander, Selden and Ahlborg (1992)
1990-95	Germany	IV and V	manually operated	TWA	personal	7	14	90%-pct. 56.3 95%-pct. 109.6	90%-pct. 0.0 95%-pct. 0.3	7.6	-0.8	Bock et al. (1999)
1990-95	Germany	IV and V	automatic without exhaust	TWA	personal	18	23	90%-pct. 52.2 95%-pct. 104.8	90%-pct. 0 95%-pct. 0.3	4.1	-1.1	Bock et al. (1999)
1990-95	Germany	IV and V	automatic with exhaust	TWA	personal	74	159	90%-pct. 44.3 95%-pct. 67.4	90%-pct. -0.1 95%-pct. 0.1	10.0	-0.7	Bock et al. (1999)
1990-95	Germany	IV and V	n.d.	<1h	personal	22	30	50%-pct. 44.6 90%-pct. 131.7	50%-pct. 0.0 90%-pct. 0.4	n.d.	n.d.	Bock et al. (1999)
1992-97	Germany	IV and V	n.d.	TWA and only for 1992 range measurements	n.d.	97	179	90%-pct. 52.4	90%-pct. 0.0	11.3	-0.6	BK-Report (1999)
1997*	Australia	IV and V	n.d.	TWA	personal	n.d.	5	n.d.	n.d.	8.9	-0.8	Neghab et al. (1997)
1993*	Germany	V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< -1	Staudinger (1993)
2000	Germany	V	n.d.	information from manufacturers	air	n.d.	n.d.	2.0 to 5.0	-1.4 to -1	n.d.	n.d.	Manufacturers (1960-2001)

n.d. not defined; * no year of measurement given, year of publication used; pct. percentile

Table C.20: Published exposure measurements of PERC used in metal degreasing ($\log r = \log(\text{concentration}/50 \text{ ppm})$) (measurements depicted in Figure 4.16 in Chapter 4.3.5).

Year	Country	Machine type	Maschine description	Measurement	Sample	Number of machines	Number of samples	Range (ppm)	$\log r$ of range	Average (ppm)	$\log r$ of average	References
1982-85	Finland	n.d.	n.d.	n.d.	air	3	n.d.	1.8 to 5.0	-1.4 to -1	3.0	-1.2	Rantala, Riiginen and Anttila (1992)
1985	Germany	n.d.	n.d.	n.d.	air	n.d.	n.d.	12.5 to 20.0	-0.6 to -0.4	n.d.	n.d.	Niemann (1995)
1988	Germany	IV	n.d.	n.d.	air	n.d.	n.d.	7.2 to 10.0	-0.8 to -0.7	n.d.	n.d.	Niemann (1995)
1988	Germany	IV	n.d.	TWA	personal	n.d.	n.d.	n.d.	n.d.	8.4	-0.8	Niemann (1995)
1991	Germany	IV and V	n.d.	n.d.	air	n.d.	n.d.	1.3 to 6.2	-1.6 to -0.9	n.d.	n.d.	Niemann (1995)
1991	Germany	IV and V	n.d.	TWA	personal	n.d.	n.d.	1.4 to 2.0	-1.5 to -1.4	n.d.	n.d.	Niemann (1995)
1990-95	Germany	IV and V	manually operated	TWA	personal	8	12	90%-pct. 92.3 95%-pct. 116.4	90%-pct. 0.3 95%-pct. 10.4	1.0	-1.7	Bock et al. (1999)
1990-95	Germany	IV and V	automatic without exhaust	TWA	personal	19	31	90%-pct. 46.7 95%-pct. 73.2	90%-pct. 0.0 95%-pct. 0.2	2.6	-1.3	Bock et al. (1999)
1990-95	Germany	IV and V	automatic with exhaust	TWA	personal	135	279	90%-pct. 48.0 95%-pct. 78.8	90%-pct. 0.0 95%-pct. 1.0	5.9	-0.9	Bock et al. (1999)
1990-95	Germany	IV and V	n.d.	<1h	personal	22	30	50%-pct. 5.1 90%-pct. 39.6 95%-pct. 46.2	50%-pct. -1.0 90%-pct. -0.1 95%-pct. 0.0	n.d.	n.d.	Bock et al. (1999)
1996	Finland	IV and V	n.d.	n.d.	air	1	n.d.	1.0 to 10.0	-1.7 to -0.7	5.2	-1.0	OECD (1996)
1996	Finland	IV and V	n.d.	n.d.	air	1	n.d.	3.8 to 16.4	-1.1 to -0.5	10.1	-0.7	OECD (1996)
1993	Germany	V	n.d.	n.d.	air	n.d.	n.d.	< 0.7	< -1.8	n.d.	n.d.	Niemann (1995)
1993	Germany	V	n.d.	TWA	personal	n.d.	n.d.	n.d.	n.d.	2.8	-1.3	Niemann (1995)
1993*	Germany	V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 5	< -1	Staudinger (1993)
1998	Germany	V	n.d.	control of TWA according to 2 nd BImSchV 1990	air	9	52	95%-pct. 10.1	95%-pct. -0.7	0.5	-2.0	Thoulass (1998)

n.d. not defined; * no year of measurement given, year of publication used; pct. percentile

In Tables C.21 and C.22, the unpublished Groz & Beckert air measurements are listed for TRIC and for PERC. In Chapter 4.3.5, the measured long-term values are compared to long-term airborne concentrations calculated with the SceBRA method for PERC in Figure 4.17 and for TRIC Figure in 4.18.

Table: C.21: Unpublished exposure measurements for the use of TRIC in metal degreasing machines of different technology in Germany ($\log r = \log (\text{concentration}/50 \text{ ppm})$) (Groz&Beckert, 2002) (long-term measurements depicted in Figure 4.17).

Year	Machine type	Measurement	Sample	Number of samples	Range (ppm)	$\log r$ of range	Arithmetic mean (ppm)	$\log r$ of arithm. mean
1984-86	II or III	short-term	air	7	<1 to 100 50%-percentile 20.0 70%-percentile 21.0 90%-percentile 55.0	< -1.7 to 0.3 50%-percentile -0.4 70%-percentile -0.4 90%-percentile 0.0	24.3	-0.3
1987	II or III	short-term	air	20	<1 to 35 50%-percentile 10.0 70%-percentile 21.5 90%-percentile 30.0	< -1.7 to -0.2 50%-percentile -0.7 70%-percentile -0.4 90%-percentile -0.2	12.5	-0.6
1988	III or IV	short-term	air	23	<1 to 18 50%-percentile 6.0 70%-percentile 8.8 90%-percentile 15.0	< -1.7 to -0.4 50%-percentile -0.9 70%-percentile -0.8 90%-percentile -0.5	7.3	-0.8
1989	III or IV	short-term	air	23	<1 to 30 50%-percentile 10.0 70%-percentile 14.4 90%-percentile 20.0	< -1.7 to -0.2 50%-percentile -0.7 70%-percentile -0.5 90%-percentile -0.4	11.3	-0.6
1992	V A	long-term (approx. 3 to 4h)	air	26	<1 to 27 50%-percentile 1.5 70%-percentile 5.5 90%-percentile 11.5	< -1.7 to -0.3 50%-percentile -1.5 70%-percentile -1.0 90%-percentile -0.6	4.5	-1.0
1992	V A	short-term	air	6	<1 to 3 50%-percentile <1 70%-percentile 1.0 90%-percentile 2.5	< -1.7 to 50%-percentile < -1.7 70%-percentile -1.7 90%-percentile -1.3	0.8	-1.8
1993	V A	long-term (approx. 3 to 4h)	air	12	<1 to 47 50%-percentile 7.5 70%-percentile 22.5 90%-percentile 40.2	< -1.7 to 0 50%-percentile -0.8 70%-percentile -0.3 90%-percentile -0.1	14.7	-0.5
1993	V A	short-term	air	40	<1 to 120 50%-percentile 2.0 70%-percentile 5.0 90%-percentile 21.0	< -1.7 to 0.4 50%-percentile -1.4 70%-percentile -1 90%-percentile -0.4	9.9	-0.7
1994	V A	long-term (approx. 3 to 4h)	air	36	1 to 11 50%-percentile 2.0 70%-percentile 3.0 90%-percentile 7.4	-1.7 to -0.7 50%-percentile -1.4 70%-percentile -1.3 90%-percentile -0.8	2.9	-1.2
1994	V A	short-term	air	7	1 to 10 50%-percentile 2.0 70%-percentile 3.4 90%-percentile 7.0	-1.7 to -0.7 50%-percentile -1.4 70%-percentile -1.2 90%-percentile -0.9	3.6	-1.1
1995	V A	long-term (approx. 3 to 4h)	air	31	<1 to 13 50%-percentile 2.0 70%-percentile 3.0 90%-percentile 8.0	< -1.7 to -0.6 50%-percentile -1.4 70%-percentile -1.3 90%-percentile -0.8	3.5	-1.2
1996	V A	short-term	air	40	<1 to 7 50%-percentile 2.5 70%-percentile 3.3 90%-percentile 5.0	< -1.7 to -0.9 50%-percentile -1.3 70%-percentile -1.2 90%-percentile -1.0	2.5	-1.3
1996	V A	long-term (approx. 3 to 4h)	air	8	1 to 4 50%-percentile 2.0 70%-percentile 3.8 90%-percentile 4.0	-1.7 to -1.1 50%-percentile -1.4 70%-percentile -1.1 90%-percentile -1.1	2.6	-1.3
1997	V A	long-term (approx. 3 to 4h)	air	31	<1 to 32 50%-percentile 3.0 70%-percentile 4.0 90%-percentile 11.0	< -1.7 to -0.2 50%-percentile -1.3 70%-percentile -1.1 90%-percentile -0.7	5.3	-1.0

Table C.21, continued

Year	Machine type	Measurement	Sample	Number of samples	Range (ppm)	log r of range	Arithmetic mean (ppm)	log r of arithm. mean
1998	V A	long-term (approx. 3 to 4h)	air	14	2 to 64 50%-percentile 6.0 70%-percentile 11.4 90%-percentile 46.7	-1.4 to 0.1 50%-percentile -0.9 70%-percentile -0.6 90%-percentile 0.0	15.6	-0.5
1998	V A	long-term (approx. 3 to 4h)	air	39	<1 to 24 50%-percentile 2.0 70%-percentile 3.0 90%-percentile 10.0	< -1.7 to -0.3 50%-percentile -1.4 70%-percentile -1.3 90%-percentile -0.7	3.9	-1.1
1999	V A	long-term (approx. 3 to 4h)	air	28	<1 to 9 50%-percentile 1.0 70%-percentile 1.0 90%-percentile 2.6	< -1.7 to -0.7 50%-percentile -1.7 70%-percentile -1.7 90%-percentile -1.3	1.5	-1.5
2000	V A	long-term (approx. 3 to 4h)	air	38	<1 to 17 50%-percentile 1.0 70%-percentile 2.0 90%-percentile 5.0	< -1.7 to -0.5 50%-percentile -1.7 70%-percentile -1.4 90%-percentile -1.0	2.1	-1.4
2000	V B with vacuum size 2	long-term (approx. 3 to 4h)	air	9	<1 to 3 50%-percentile <1 70%-percentile <1 90%-percentile 1.6	< -1.7 to -1.2 50%-percentile < -1.7 70%-percentile < 1.7 90%-percentile -1.5	<1	< -1.7
2001	V A	long-term (approx. 3 to 4h)	air	26	<1 to 4 50%-percentile 1.0 70%-percentile 1.0 90%-percentile 2.5	< -1.7 to -1.1 50%-percentile -1.7 70%-percentile -1.7 90%-percentile -1.3	1.0	-1.7
2001	V B with vacuum size 2	long-term (approx. 3 to 4h)	air	10	<1 to 4 50%-percentile <1 70%-percentile 1.0 90%-percentile 2.2	< -1.7 to -1.1 50%-percentile < -1.7 70%-percentile -1.7 90%-percentile -1.4	<1	< -1.7
2002	V A	long-term (approx. 3 to 4h)	air	16	1 to 6 50%-percentile 1.0 70%-percentile 2.0 90%-percentile 4.0	-1.7 to -0.9 50%-percentile -1.7 70%-percentile -1.4 90%-percentile -1.1	1.7	-1.5
2002	V A	short-term	air	14	<1 to 2 50%-percentile <1 70%-percentile <1 90%-percentile 1.7	< -1.7 to -1.4 50%-percentile < -1.7 70%-percentile < -1.7 90%-percentile -1.5	<1	< -1.7
2002	V B with vacuum size 2	long-term (approx. 3 to 4h)	air	6	<1 to 2 50%-percentile <1 70%-percentile <1 90%-percentile 1.5	< -1.7 to -1.4 50%-percentile < -1.7 70%-percentile < -1.7 90%-percentile -1.5	<1	< -1.7
2002	V B with vacuum size 2	short-term	air	6	<1 50%-percentile <1 70%-percentile <1 90%-percentile <1	< -1.7 50%-percentile < -1.7 70%-percentile < -1.7 90%-percentile < -1.7	<1	< -1.7

Table: C.22: Unpublished exposure measurement for the use of PERC in metal degreasing machines of different technology in Germany ($\log r = \log (\text{concentration}/50 \text{ ppm})$) (Groz&Beckert, 2002) (long-term measurements depicted in Figure 4.18).

Year	Machine type	Measurement	Sample	Number of samples	Range (ppm)	$\log r$ of range	Arithmetic mean (ppm)	$\log r$ of arithm. mean
1986	II or III	short-term	air	14	10 to 120	-0.7 to 0.4	55.7	0.0
					50%-percentile 40.0	50%-percentile -0.1		
					70%-percentile 46.0	70%-percentile 0.0		
					90%-percentile 100.0	90%-percentile 0.3		
1987	II or III	long-term (approx. 3 to 4h)	air	4	24 to 58	-0.3 to 0.0	35.5	-0.1
					50%-percentile 30.0	50%-percentile -0.2		
					70%-percentile 32.8	70%-percentile -0.2		
					90%-percentile 49.6	90%-percentile 0.0		
1987	II or III	short-term	air	12	3 to 150	-0.2 to 0.5	42.3	-0.1
					50%-percentile 30.0	50%-percentile -0.2		
					70%-percentile 47.0	70%-percentile 0.0		
					90%-percentile 79.0	90%-percentile 0.2		
1988	II or III	short-term	air	35	3 to 180	-0.2 to 0.6	33.2	-0.2
					50%-percentile 20.0	50%-percentile -0.4		
					70%-percentile 46.0	70%-percentile 0.0		
					90%-percentile 80.0	90%-percentile 0.2		
1989	III or IV	long-term (approx. 3 to 4h)	air	61	12 to 106	-0.6 to 0.3	36.1	-0.1
					50%-percentile 33.0	50%-percentile -0.2		
					70%-percentile 38.0	70%-percentile -0.1		
					90%-percentile 58.0	90%-percentile 0.0		
1989	III or IV	short-term	air	147	2 to 130	-1.4 to 0.4	27.6	-0.3
					50%-percentile 25.0	50%-percentile -0.3		
					70%-percentile 40.0	70%-percentile -0.1		
					90%-percentile 50.0	90%-percentile 0.0		
1990	III or IV	long-term (approx. 3 to 4h)	air	14	7 to 33	-0.9 to -0.2	13.9	-0.6
					50%-percentile 10.5	50%-percentile -0.7		
					70%-percentile 14.3	70%-percentile -0.5		
					90%-percentile 25.7	90%-percentile -0.3		
1990	III or IV	short-term	air	58	<1 to 70	< -1.7 to 0.1	14.9	-0.5
					50%-percentile 10.0	50%-percentile -0.7		
					70%-percentile 18.0	70%-percentile -0.4		
					90%-percentile 31.0	90%-percentile -0.2		
1991	III or IV	long-term (approx. 3 to 4h)	air	7	3 to 57	-1.2 to 0.0	18.6	-0.4
					50%-percentile 12.0	50%-percentile -0.6		
					70%-percentile 22.6	70%-percentile -0.3		
					90%-percentile 37.8	90%-percentile -0.1		
1991	III or IV	short-term	air	33	<1 to 20	< -1.7 to -0.4	3.4	-1.2
					50%-percentile 1.0	50%-percentile -1.7		
					70%-percentile 3.4	70%-percentile -1.2		
					90%-percentile 11.0	90%-percentile -0.7		
1992	III or IV	long-term (approx. 3 to 4h)	air	7	4 to 23	-1.1 to -0.3	13.0	-0.6
					50%-percentile 13.0	50%-percentile -0.6		
					70%-percentile 14.0	70%-percentile -0.6		
					90%-percentile 20.0	90%-percentile -0.4		
1992	III or IV	short-term	air	20	<1 to 20	< -1.7 to -0.4	2.6	-1.3
					50%-percentile <1	50%-percentile -1.7		
					70%-percentile 2.0	70%-percentile -1.4		
					90%-percentile 5.7	90%-percentile -0.9		
1992	IV	short-term	air	4	<1 to 2	< -1.7 to -1.4	<1	< -1.7
					50%-percentile <1	50%-percentile < -1.7		
					70%-percentile <1	70%-percentile < -1.7		
					90%-percentile 1.4	90%-percentile -1.5		
2001	V B with vacuum size 2	short-term	air	2	<1	< -1.7	<1	< -1.7
					50%-percentile <1	50%-percentile < -1.7		
					70%-percentile <1	70%-percentile < -1.7		
					90%-percentile <1	90%-percentile < -1.7		

Appendix D

D. Dry cleaning

D.1. Dry cleaning input data

D.1.1. Method for dry cleaning data collection

In comparison to the metal degreasing case study, a lot more information is available for the dry cleaning case study. The main reason is that dry cleaning is a separate service sector, whereas metal degreasing is only one interstage in the metal-processing industry. General information on dry cleaning as well as specific input data for the SceBRA calculations were obtained from publications in scientific journals, different reports, sales brochures of manufacturers, interviews with both scientists and experts from industry, and from a survey sent to 248 dry-cleaning shops all over in Germany in 2002.

All model parameters are based on empirical information from the above-mentioned sources. Extensive information of high quality on machine parameters, emission factors, workplace parameters, and number of machines is available in reports from the research institute Hohenstein (Bekleidungsphysiologisches Institut Hohenstein, specialized on textiles) (Klein et al., 1991; Klein and Kurz, 1994; Kurz, 1995; Kurz and Klein, 1995; Kurz and Klein, 1998). Whenever information was available from these reports, they were favored over other references. Additional information on the number of machines and the total number of employees in the dry-cleaning sector, which include workers in “cold shops” (receiving offices, where no dry cleaning is performed), was obtained from reports of the German textile

cleaning association DTV (Deutscher Textilreinigungs-Verband) (DTV, 2001; DTV, 2002).

For our dry-cleaner survey, DTV provided us with addresses of dry-cleaning shops using PERC, equally distributed all over Germany. Information on how to structure, perform, and evaluate a survey mailing was obtained from the literature (Bortz and Döring, 1995; Grote, 1995; Moser, 1997; Schumann, 1997). In spring 2002, the survey, which contained 8 pages of questions about the catchment area, the dry-cleaning machines, the dry-cleaning process, the employed persons, and the working hours, was sent to 248 dry-cleaning shops. With 23.8%, a very high rate of return was achieved. From the evaluation of the survey, qualitatively good information on numbers and capacities of dry-cleaning machines, batch times, numbers of batches, room volumes, and numbers of employees were obtained. The collected data about the batch times, t_b , and the room volumes, V , made the definition of frequency distributions for the Monte Carlo uncertainty analysis possible (see Chapter 5.3.6 and Appendix D.4).

D.1.2. Machine parameters

The different generations of dry-cleaning machines are described in Chapter 5.1 and the five machine sizes with their capacities and cylinder volumes are introduced in Chapter 5.2.1. Information on the machine parameters of the different generations is taken from Hohenstein reports (Klein et al., 1991; Klein and Kurz, 1994; Kurz and Klein, 1995) and from sales brochures provided by European manufacturers such as BÖWE, FRIMAIR, MULTIMATIC, ILSA, UNION, AMA UNIVERSAL, RENZACCI, LINDUS, REALSTAR (Manufacturers, 1959-2002). In Table D.1, machine characteristics and batch times are listed for all machine generations.

Table D.1: Machine characteristics and batch times for different machine generations (Klein et al., 1991; Kurz and Klein, 1995; Merkhofer, 2001).

Generation	Characteristics	Batch time (min)
2 nd	vented, water-cooling	40 – 55
3 rd	vented, water or electro-cooling, according to 2 nd BImSchV 86	40 – 55
4 th	electro cooling, closed drying cycle, according to 2 nd BImSchV 86	45 – 65
5 th	closed drying cycle with activated carbon and door lock, according to 2 nd BImSchV 90	50 – 70

D.1.3. Emission factors

In the following, additional information is given for the definitions of the different emission factors being introduced in Chapter 5.2.2. To this end, the amount of textiles cleaned during one batch and the composition of the garments are needed to determine emissions per functional unit of 1 kg garments (more details can be found in Chapter 5.2.1 and 5.2.2). The upper and lower emission factors are given for all generations and sizes of machines. In the SceBRA calculations average emission factors are included in addition to upper and lower values; these are, if not specified explicitly, the arithmetic means.

D.1.3.1 Continuous emission factor for diffuse emissions

Very little is published about the magnitude of diffuse emissions (i.e., emissions into the workplace air resulting from leakage of sealing, and emissions out of drum, button trap, and lint trap). In Table D.2, some literature, data about losses and emissions are listed.

Table D.2: Literature data about losses and emissions of dry-cleaning machine generations (a: Rentz et al., 1997; b: Riff, 1998; c: Merkhofer, 2001; d: Adams, 1994; e: Zott, 1993; f: Schmidt et al., 1995; g: Werner, 1996; h: BlmSchV, 1990; i: Klein et al., 1991; j: Flückiger, 1999).

Generation	Losses and emissions (g/kg)			
	2 nd	3 rd	4 th	5 th
Total consumption	100 - 150 ^{a-c}	40 - 80 ^a 50 - 80 ^b	20 - 40 ^{a,b,d} 20 - 30 ^e	<10 ^{a-e}
Losses to air	50 ^f	63 ⁱ 15 - 25 ^f	27 ^g 15.6 - 17.5 ^g	1.7 ^{f,g,j}
Losses to workplace air	n.d.	n.d.	15 - 25 ^f 10 - 15 ^d	n.d.
Solvent to waste	n.d.	n.d.	11.6 - 11.8 ^g	8.3 ^g
Maintenance operation and tank filling losses	n.d.	n.d.	0.36 ^g	0.04 ^g
Vented emission	n.d.	8.7% of losses to air ^f	10.7 ^g	0 ^h
Diffuse emissions	n.d.	22.8% of losses to air ^f	n.d.	n.d.

n.d.: not defined

Where no literature data is available E_{c1} (g/kg) is estimated based on total consumption with the following contributions subtracted: (i) solvent amount in waste, (ii) vented emissions, (iii) emissions from maintenance operations and tank filling, (iv) continuous emissions from cleaned garments, E_{c2} , and periodic emissions during loading and unloading, E_p . This guarantees that all emissions and losses add up to the total solvent consumption. For 2nd generation machines, it is assumed that the diffuse emissions are the same as for 3rd generation machines. In Table D.3, maximum and minimum values of the diffuse emissions can be found in g PERC per kg of garments.

Table D.3: Diffuse emissions in g PERC per kg garments for all machine generations.

Generation	Diffuse emissions (g/kg)			
	2 nd	3 rd	4 th	5 th
min	3.4	3.4	1.7	0.2
max	5.7	5.7	2.1	0.4

Together with the machine loads and batch times, the emission factors \dot{E}_{c1} (g/h) can be derived; values are listed in Table D.4.

Table D.4: Diffuse emission factors \dot{E}_{c1} for all machine generations and sizes.

Generation		Diffuse emission factor \dot{E}_{c1} (g/h)				
		Size 1	Size 2	Size 3	Size 4	Size 5
2 nd	min	4.79E+01	6.39E+01	8.79E+01	1.12E+02	1.28E+02
	max	5.85E+01	7.80E+01	1.07E+02	1.37E+02	1.56E+02
3 rd	min	4.79E+01	6.39E+01	8.79E+01	1.12E+02	1.28E+02
	max	5.85E+01	7.80E+01	1.07E+02	1.37E+02	1.56E+02
4 th	min	2.08E+01	2.77E+01	3.81E+01	4.85E+01	5.54E+01
	max	1.79E+01	2.39E+01	3.29E+01	4.18E+01	4.78E+01
5 th	min	1.99E+00	2.66E+00	3.65E+00	4.65E+00	5.31E+00
	max	2.83E+00	3.77E+00	5.18E+00	6.59E+00	7.53E+00

D.1.3.2 Continuous emission factor for cleaned textiles

The garment temperature at taking out is above 30°C for 2nd to 4th generation machines and must be above 35°C for 5th generation machines (BlmSchV, 1990). A broad spectrum of literature values is reported on the amount of residual solvent in cleaned textiles, E_{c2} (g/kg) (see Table D.5).

Table D.5: Literature data on residual solvent amount in cleaned textiles (g/kg) (a: Kawauchi and Nishiyama, 1989; b: Brodmann, 1975; c: Earnest, 1996; d: Earnest, 2002; e: Werner, 1996; f: Kurz, 1995; g: Klein and Kurz, 1994; h: Klein et al., 1991; i: Weber, 1992).

Residual solvent in cleaned textiles (g/kg)				
Generation	2 nd	3 rd	4 th	5 th
				0.001 ^d
"normal load"	up to 0.8 ^b	up to 0.8 ^b	0.03 ^{c,d}	0.12 ^h
	1.6 ^a	0.38 ^h	0.26 ^h	0.3 to 0.5 ⁱ
		1.6 ^a		0.2 to 0.9 ^f
"off-the-peg load"			3.75 ^e	1.0 ^g
				1.26 ^e
				1.02 to 1.43 ^h

The values from Klein et al. (1991) originate from a study carried out by Hohenstein Institute on behalf of the UBA (German Federal Environmental Office). This study declares the composition of the loads and as it is specifically done for Germany the model inputs are based on it. Further information about the estimation of missing data can be found in Chapter 5.2.2. The model input data of residual solvent in cleaned textiles are listed in Table D.6.

Table D.6: Residual solvent amount in cleaned textiles for different machine generations (Klein et al., 1991; Werner, 1996).

Residual solvent in cleaned textiles (g/kg)				
Generation	2 nd	3 rd	4 th	5 th
"normal load"	0.46	0.38	0.26	0.12
"off-the-peg load"	6.58	5.48	3.75	1.26

Multiplication of E_{c2} (g/kg) with machine loads and division by evaporation times, α , result in the emission factors \dot{E}_{c2} (g/h). The values for the "normal" loads (minimum values), the "off-the-peg" loads (maximum values) and the

average loads for Germany (average values) consisting of 80% “normal” and 20% “off-the-peg” clothing, are listed in Table D.7.

Table D.7: Continuous emission factors \dot{E}_{c_2} (g/h) over time α for emissions from cleaned garments for all machine generations and sizes (min: “normal clothing”; max: “off-the-peg” clothing; average: 80% “normal” and 20% “off-the-peg” clothing).

Emission factor from cleaned textiles						
\dot{E}_{c_2} (g/h) for period α						
Generation		Size 1	Size 2	Size 3	Size 4	Size 5
2 nd	min	1.95E+01	2.60E+01	3.57E+01	4.55E+01	5.19E+01
	average	8.17E+01	1.09E+02	1.50E+02	1.91E+02	2.18E+02
	max	3.71E+02	4.94E+02	6.80E+02	8.65E+02	9.89E+02
3 rd	min	1.62E+01	2.16E+01	2.98E+01	3.79E+01	4.33E+01
	average	6.81E+01	9.07E+01	1.25E+02	1.59E+02	1.81E+02
	max	3.09E+02	4.12E+02	5.67E+02	7.21E+02	8.24E+02
4 th	min	9.92E+00	1.32E+01	1.82E+01	2.32E+01	2.65E+01
	average	4.16E+01	5.55E+01	7.63E+01	9.71E+01	1.11E+02
	max	1.89E+02	2.52E+02	3.46E+02	4.41E+02	5.04E+02
5 th	min	4.14E+00	5.52E+00	7.59E+00	9.65E+00	1.10E+01
	average	1.37E+01	1.82E+01	2.50E+01	3.19E+01	3.64E+01
	max	5.74E+01	7.65E+01	1.05E+02	1.34E+02	1.53E+02

A significant decline can be seen from 3rd to 4th generation machines; in the latter PERC is condensed at -20°C in a closed loop drying cycle. A further reduction by approximately a factor of 2 in comparison to 4th generation machines is achieved by including a carbon adsorber at the end of the drying cycle, as done in 5th generation machines.

The assumed evaporation times α (h) of between one-third and one-fourth of a batch time are in agreement with findings from Earnest 1996 and 2002. Results from an off-gassing test comparing swatches from 4th and 5th generation machines are shown in Figure D.1.

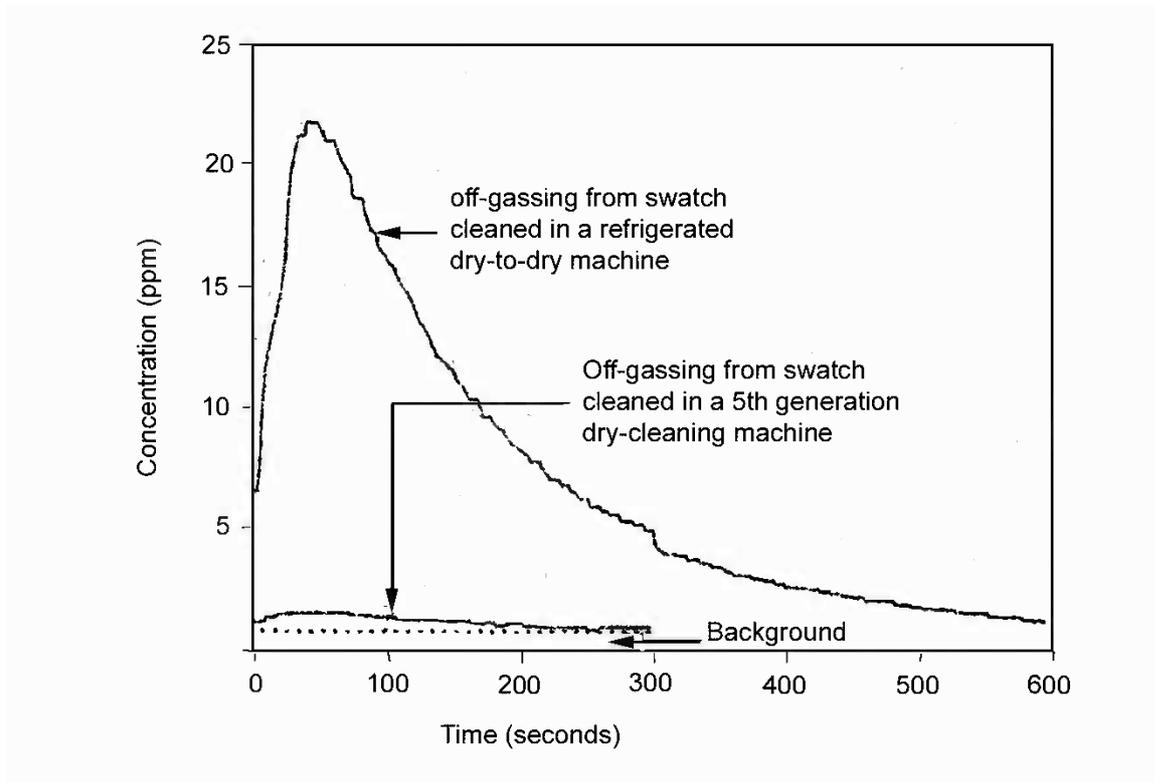


Figure D.1: A comparison of typical swatch off-gassing from an approximately 3rd generation machine versus a 5th generation machine. The total amount of off-gassed PERC is approximately 31.8 mg/kg cloth for the 3rd and 1.34 mg PERC/kg cloth for the 5th generation machine (Earnest, 2002).

D.1.3.3 Periodic emission factor for loading and unloading

The cylinder concentration is dependent on cooling device, drying time, and amount of cleaned clothes (Klein et al., 1991). In Table D.8, literature data on cylinder concentrations can be found for all machine generations.

Table D.8: Literature data on cylinder concentrations for all machine generations.

Generation	Cylinder concentration before unloading (g/m ³)				Ref.
	2 nd	3 rd	4 th	5 th	
150 – 240	25 – 42	13 – 25			Klein et al. 1991
130					Schmidt et al. 1995
				1 – 2	Kurz and Klein 1995
150	25 – 42	13 – 25		0.5 – 2	Rentz et al. 1997
150 - 240					Riff 1998
	25 – 42	13 – 25		< 2	Kurz and Klein 1998
207					Ewers et al. 2002

From the above data, maximum and minimum concentrations based on the studies from Hohenstein Research Institute are taken as model input, see Table D.9.

Table D.9: Maximum and minimum cylinder concentrations before unloading for all machine generations (Klein et al., 1991; Kurz and Klein, 1995; Kurz and Klein, 1998).

Generation	Cylinder concentration before unloading (g/m ³)			
	2 nd	3 rd	4 th	5 th
min	150	25	13	1
max	240	42	25	2

In vented 2nd and 3rd generation machines, 50% of the solvent charged cylinder volume and for non-vented 4th and 5th generation machines the whole cylinder volume exchanges with the workplace (details see Chapter 6.2.2). The emission factor is calculated as intermittent emissions that occur at the moment the door is opened, values for E_p are listed in Table D.10.

Table D.10: Periodic emission factors E_p for all machine generations and sizes.

Periodic emission factor from cylinder air						
E_p (g)						
Generation		Size 1	Size 2	Size 3	Size 4	Size 5
2 nd	min	1.80E+01	2.40E+01	3.30E+01	4.20E+01	4.80E+01
	max	2.88E+01	3.84E+01	5.28E+01	6.72E+01	7.68E+01
3 rd	min	3.00E+00	4.00E+00	5.50E+00	7.00E+00	8.00E+00
	max	5.04E+00	6.72E+00	9.24E+00	1.18E+01	1.34E+01
4 th	min	3.12E+00	4.16E+00	5.72E+00	7.28E+00	8.32E+00
	max	6.00E+00	8.00E+00	1.10E+01	1.40E+01	1.60E+01
5 th	min	2.40E-01	3.20E-01	4.40E-01	5.60E-01	6.40E-01
	max	4.80E-01	6.40E-01	8.80E-01	1.12E+00	1.28E+00

The higher emission factor for non-vented 4th generation machines in comparison to vented 3rd generation machines is based on the assumption that the whole cylinder volume, and not only 50% as for vented machines with door fans, exchanges with the workplace air during loading and unloading (more information is found in Chapter 5.2.2).

D.1.4. Workplace parameters

The different workplace volumes, V , as well as the air exchange rates k_A and k_L implemented in the SceBRA calculations as described in Chapter 5.2.3 are listed Table D.11 and Table D.12.

Table D.11: Summary of workplace volumes for dry-cleaning facilities.

Workplace volume for all machine generations		
V (m ³)		
Entire workplace	min	400
	max	600

Table D.12: Summary of air exchange rates k_A and k_L (h^{-1}) for dry-cleaning facilities.

Air exchange rates (1/h)		
for all generations		
k_A	min	8
	max	12
k_L	min	6
	max	10

D.1.5. Number of machines

The estimated numbers of dry-cleaning machines in Germany can be seen in Table D.13. For the year 1975 (only former West German states), the total number of dry-cleaning machines is given. In those days, 95% of dry cleaning was performed with PERC and this mainly with 2nd generation machines (Engels et al., 1975). Therefore, it is assumed that 90% were 2nd generation machines and 10% transfer machines; the latter are not investigated in this case study. For the years 1986, 1990, 1992, 1994, and 1996, the total number of machines is derived from the total number of dry-cleaning facilities, the percentage of dry-cleaning machines using PERC and the average number of machines in one shop. For the years 1989, 1998, and 2001, the number of machines is indicated explicitly in the corresponding references.

The subdivision of the total number of 2nd generation machines into the five sizes is done according to findings from a Hohenstein survey performed in 1994, indicating that 25% are size 1, 54% size 2, 14% size 3, 4% size 4 and 4% size 5 machines. For all other generations, frequencies determined in our survey (2002) are taken (for frequencies see Table 5.1 in Chapter 5.2.1). This differentiation is done to account for the fact that small sizes were more frequent in machines, which did not fulfill the 2nd BImSchV of 1986 (Engels et al., 1975).

Table D.13: Estimates of the number of dry-cleaning machines in Germany for the years 1975, 1986, 1989, and 1990 (only former West German states); and for the years 1992, 1994, 1996, 1998, and 2001 (a: Engels et al., 1975; b: Rentz et al., 1997; c: Klein et al., 1991; d: DTV, 2001; e: Adams, 1994; f: DTV, 2002)

Machine generation	Year Sizes	Number of dry cleaning machines								
		1975* (a)	1986* (b)	1989* (c)	1990* (b)	1992 (b)	1994 (d,e)	1996 (b)	1998 (d)	2001 (f)
2nd	1	5130	1463							
	2	10993	3134							
	3	2931	836							
	4	733	209							
	5	733	209							
3rd	1		880	1040	117	32				
	2		2252	2703	300	83				
	3		2632	3188	351	96				
	4		1381	1832	184	51				
	5		1631	2239	217	60				
4th	1			236	1056	351	221			
	2			614	2702	897	564			
	3			725	3158	1048	659			
	4			416	1657	550	346			
	5			509	1957	650	409			
5th	1					351	410	522	482	471
	2					897	1048	1334	1232	1206
	3					1048	1225	1559	1439	1410
	4					550	643	818	755	739
	5					650	759	966	892	873
<i>Total</i>		20520	14625	13500	11700	7313	6283	5200	4800	4700

* only former West German states

D.1.6. Number of exposed workers

In Table D.14 the assumptions about the number of exposed workers per machine are listed as described in Chapter 5.2.4.

Table D.14: Assumptions about the number of exposed workers per machine indicated for the near-field and the far-field.

	Near-field			Far-field		
	min	max	average	min	max	average
Number of exposed workers per machine	1	1.5	1.25	4	5	4.5

D.2. Dry cleaning results

The systematic combination of all independent input parameters leads to 180 exposure scenarios for each machine generation. The parameter combination is visualized in Figure C.2.

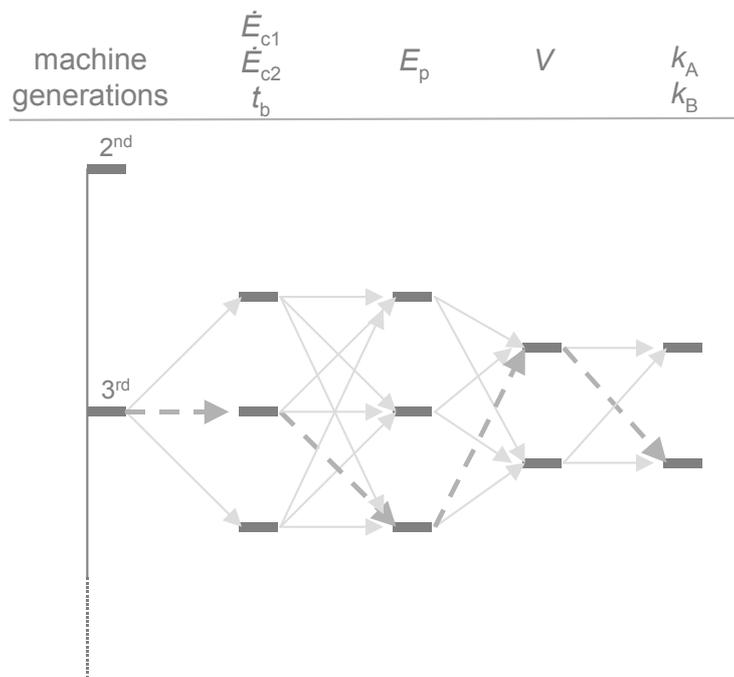


Figure C.2: Parameter combination of all independent input parameters shown for a 3rd generation machine.

In the following, scenario plots similar to that in Figure 5.5 (see Chapter 5.3.2) are shown for all four machine generations. Note that the scaling of the y-axis (long-term PERC concentration (g/m³)) is different for all plots.

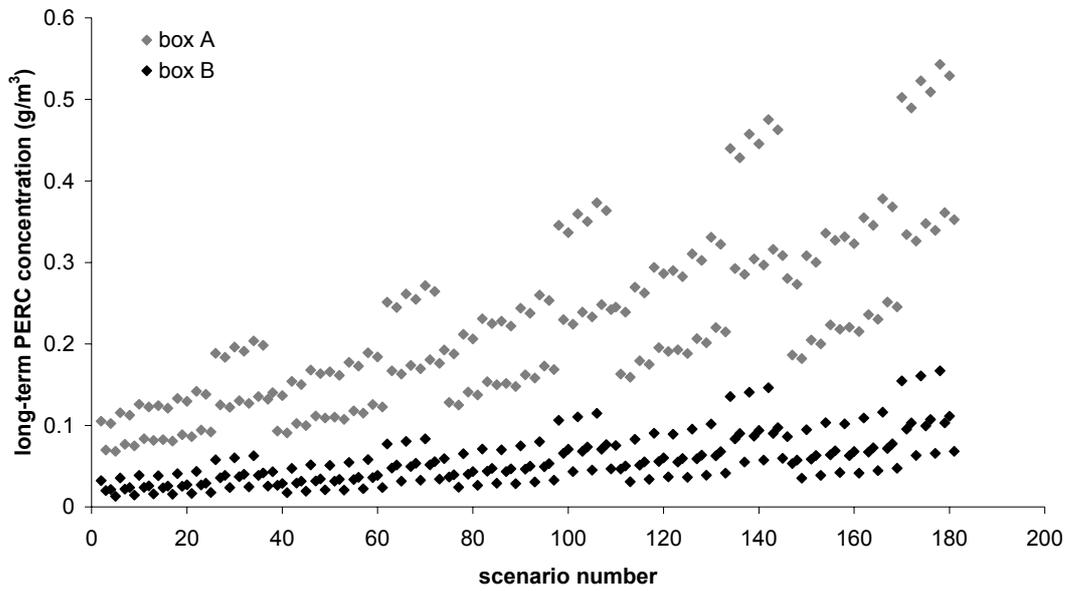


Figure D.3: Scenario plot for a 2nd generation dry-cleaning machine.

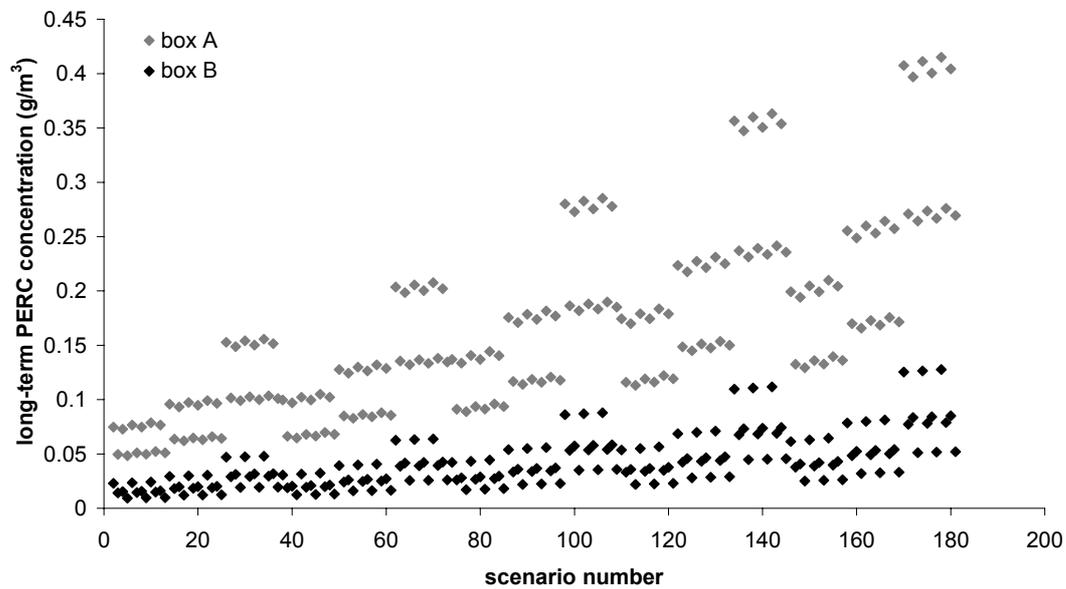


Figure D.4: Scenario plot for a 3rd generation dry-cleaning machine.

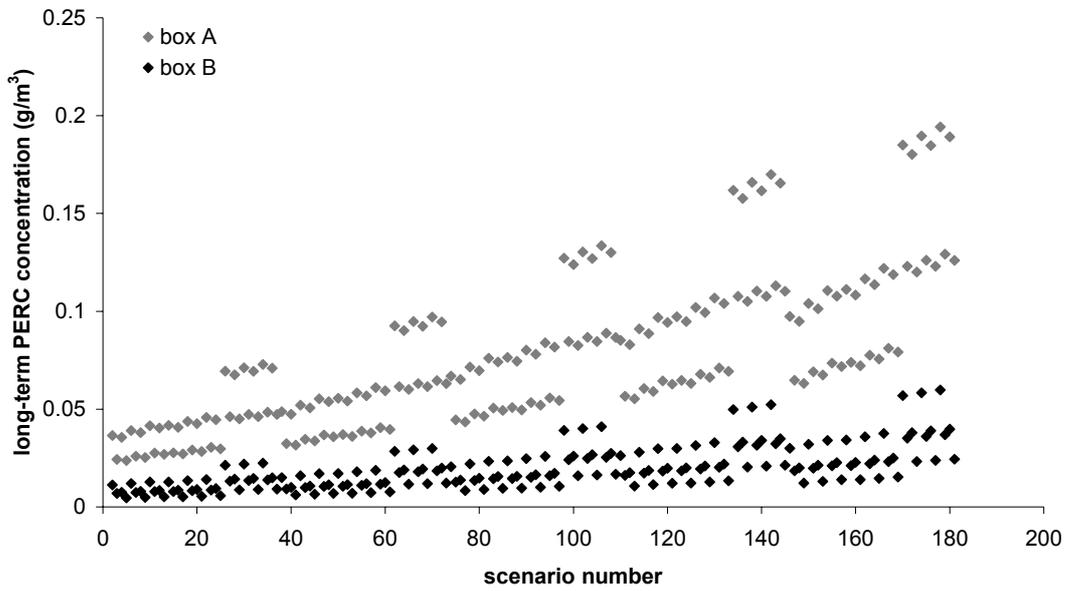


Figure D.5: Scenario plot for a 4th generation dry-cleaning machine.

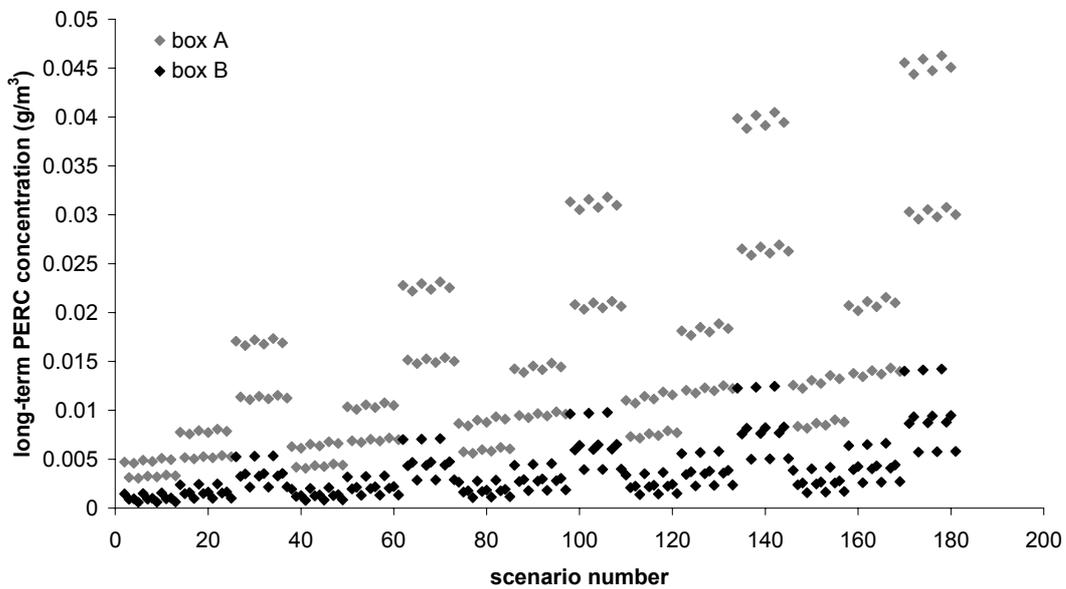


Figure D.6: Scenario plot for a 5th generation dry-cleaning machine.

In the following, the SceBRA exposure estimates are given as near-field and far-field long-term PERC concentrations for all machine generations and sizes (see Tables C.15 to C.18).

Table D.15: Long-term PERC exposure concentrations, calculated with SceBRA, for the near-field of all machine generations and sizes.

Generation	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
2 nd	5	543	182	325	78.7	26.4	47.1
	4	475	159	284	68.9	23.1	41.2
	3	373	125	223	54.1	18.1	32.4
	2	272	91	162	39.3	13.2	23.5
	1	204	68	122	29.5	9.9	17.7
3 rd	5	415	129	240	60.2	18.7	34.8
	4	363	113	210	52.6	16.4	30.4
	3	285	89	165	41.4	12.9	23.9
	2	208	65	120	30.1	9.4	17.4
	1	156	49	90	22.6	7.0	13.0
4 th	5	194	63	112	28.1	9.2	16.3
	4	170	55	98	24.6	8.0	14.3
	3	134	43	77	19.4	6.3	11.2
	2	97	32	56	14.1	4.6	8.1
	1	73	24	42	10.6	3.4	6.1
5 th	5	46	8	22	6.7	1.2	3.2
	4	40	7	19	5.9	1.0	2.8
	3	32	6	15	4.6	0.8	2.2
	2	23	4	11	3.4	0.6	1.6
	1	17	3	8	2.5	0.4	1.2

Table D.16: Long-term PERC exposure concentrations, calculated with SceBRA, for the far-field of all machine generations and sizes.

Generation	Size	Max. (mg/m ³)	Min. (mg/m ³)	Average (mg/m ³)	Max. (ppm)	Min. (ppm)	Average (ppm)
2 nd	5	167	35	82	24.2	5.1	11.9
	4	146	31	72	21.2	4.5	10.4
	3	115	24	56	16.6	3.5	8.2
	2	84	18	41	12.1	2.6	5.9
	1	63	13	31	9.1	1.9	4.4
3 rd	5	128	25	60	18.5	3.6	8.8
	4	112	22	53	16.2	3.2	7.7
	3	88	17	42	12.7	2.5	6.0
	2	64	13	30	9.3	1.8	4.4
	1	48	9	23	6.9	1.4	3.3
4 th	5	60	12	28	8.7	1.8	4.1
	4	52	11	25	7.6	1.6	3.6
	3	41	8	19	6.0	1.2	2.8
	2	30	6	14	4.3	0.9	2.1
	1	22	5	11	3.2	0.7	1.5
5 th	5	14	2	6	2.1	0.2	0.8
	4	12	1	5	1.8	0.2	0.7
	3	10	1	4	1.4	0.2	0.6
	2	7	1	3	1.0	0.1	0.4
	1	5	1	2	0.8	0.1	0.3

D.3. Dry cleaning validation data

In Tables D.17 and D.18, published PERC peak exposure measurements are listed for the near-field and the far-field of dry-cleaning shops.

Table D.17: Published near-field peak exposure measurements in dry-cleaning facilities using PERC (log r = log (concentration/50 ppm)).

Year	Country	Machine generation	Machine description	Measurement	Sample	Number of shops	Number of samples	Peak values (ppm)	log r of peak values	References
1975*	Germany	transfer	n.d.	peak exposure operator	personal	6	37	4.0 to 40.0	-1.1 to -0.1	Engels, Schütz and Wolf (1975)
1982	USA	transfer	without or with inadequate local exhaust	peak exposure	personal	14	n.d.	peak exposure during transfer 31.2 to 302.7	peak exposure during transfer -0.2 to 0.8	Materna (1985)
1982	USA	transfer	with adequate local exhaust	peak exposure	personal	3	n.d.	peak exposure during transfer 28.5 to 184.0	peak exposure during transfer -0.2 to 0.6	Materna (1985)
n.d.	USA	transfer	n.d.	peak exposure	personal	n.d.	n.d.	peak exposure during transfer 500 to 1500	peak exposure during transfer 1 to 1.5	Earnest (2002)
1983*	USA	transfer and 2nd	80% transfer	5 min peak operator	personal	39	134	un-/loading dryer 1000 to 4000 76	un-/loading dryer 1.3 to 1.9 0.2	Ludwig et al. (1983)
1983*	USA	transfer and 2nd	80% transfer	15 min peak operator	personal	30	49	55	0.2	Ludwig et al. (1983)
1975*	Germany	2nd	n.d.	peak exposure operator	personal	5	24	9.0 to 125.0	-0.7 to 0.4	Engels, Schütz and Wolf (1975)
n.d.	USA	2nd and 3rd	n.d.	peak exposure	personal	n.d.	n.d.	peak exposure: 1000 to 4000	peak exposure: 1.3 to 1.9	Earnest (2002)
n.d.	USA	3rd	n.d.	peak exposure	personal	n.d.	n.d.	peak exposure: 1000 to 4000	peak exposure: 1.3 to 1.9	Earnest (2002)
n.d.	USA	3rd	13.6kg	peak exposure un-/loading (60sec)	personal	1	14	peak exposure: un-/loading up to 1950.0 mean: 1139.3	peak exposure: un-/loading up to 1.6 mean: 1.4	Earnest et al. (2002)
1982	Germany	approx. 3rd	n.d.	peak exposure at 1m from machine	personal	2	n.d.	loading: 99.9 to 146.8	0.3 to 0.5	Buchter et al. (1984)
n.d.	USA	3rd retrofit to 4th	13.6kg	peak exposure un-/loading (60sec)	personal	1	19	peak exposure: un-/loading up to 1011.0 mean: 456.4	peak exposure: un-/loading up to 1.3 1.0	Earnest et al. (2002)
n.d.	USA	4th	20.4kg	peak exposure un-/loading (60sec)	personal	1	14	peak exposure: un-/loading up to 647.6 mean: 352.9	peak exposure: un-/loading up to 1.1 mean: 0.8	Earnest et al. (2002)
n.d.	USA	4th	n.d.	peak exposure	personal	n.d.	n.d.	< 290	< 0.8	Earnest (2002)
n.d.	USA	4th	24.9kg	peak exposure operator	personal	1	7	peak exposure: loading 846 unloading 271	peak exposure: loading 1.2 unloading 0.7	Earnest (1996)
1992-93	Italy	n.d.	n.d.	peak exposure	air	28	196	up to 44.6	up to 0.0	Aggazzotti et al. (1994)
n.d.	USA	retrofit to 5th	20.4kg	peak exposure un-/loading (60sec)	personal	1	15	un-/loading up to 69.2 mean: 29.4	un-/loading up to 0.1 mean: -0.2	Earnest et al. (2002)
1995	Germany	5th	25kg Multimatic Phoenix 500 X2	peak exposure	personal	1	4	peak exposure: un-/loading 18.0 to 25.0 mean: 17.0	peak exposure: un-/loading -0.4 to -0.3 mean: -0.5	Kurz and Klein (1995)

n.d. not defined; * no year of measurement given, year of publication used; pct. percentile

Table D.17: continued

Year	Country	Machine generation	Machine description	Measurement	Sample	Number of shops	Number of samples	Peak values (ppm)	log <i>r</i> of peak values	References
1995	Germany	5th	50kg Multimatic Phoenix 1000 X2	peak exposure	personal	1	13	peak exposure: 13.0 to 93.0 un-/loading 39.0	peak exposure: un-/loading -0.6 to 0.3 -0.1	Kurz and Klein (1995)
1995	Germany	5th	32kg Böwe-Passat P564	peak exposure	personal	1	3	peak exposure: 46.0 to 60.0 un-/loading mean: 49.0	peak exposure: un-/loading 0.0 to 0.1 mean: 0.0	Kurz and Klein (1995)
n.d.	USA	5th	n.d.	peak exposure	personal	n.d.	n.d.	< 290	< 0.8	Earnest (2002)
n.d.	USA	5th	16kg Boewe 536	peak exposure un-/loading	air	1	n.d.	peak exposure: loading 58.7 unloading 45.9	peak exposure: loading 0.1 unloading 0.0	Earnest (2002)
n.d.	USA	5th	21kg Boewe 546	peak exposure un-/loading	air	1	n.d.	peak exposure: loading 20.2 unloading 35.4	peak exposure: loading -0.4 unloading -0.1	Earnest (2002)

n.d. not defined; * no year of measurement given, year of publication used; pct. percentile

Table D.18: Published far-field peak exposure measurements in dry-cleaning facilities using PERC (log *r* = log (concentration/50 ppm)).

Year	Country	Machine generation	Machine description	Measurement	Sample	Number of shops	Number of samples	Peak values (ppm)	log <i>r</i> of peak values	References
1975*	Germany	transfer	n.d.	(1h) "far-field"	air	6	18	0.1 to 6.0	-2.7 to -0.9	Engels, Schütz and Wolf (1975)
1975*	Germany	2nd	n.d.	(1h) "far-field"	air	5	28	0.1 to 20.3	-2.7 to -0.4	Engels, Schütz and Wolf (1975)

n.d. not defined; * no year of measurement given, year of publication used; pct. percentile

In Table D.19 and Table D.20, published airborne concentration measurements are listed for the near-field and the far-field of dry-cleaning facilities using PERC. In Figure 5.11 and Figure 5.12 in Chapter 5.3.5, these near-field and far-field measurements are compared to average values obtained by the two-box model.

Table D.19: Published near-field exposure measurements of PERC used in dry cleaning (log r = log (concentration/50 ppm)) (measurements depicted in Figure 5.11 in Chapter 5.3.5).

Year	Country	Machine generation	Machine description	Measurement	Sample	No. of shops	No. of samples	Range of average con. (ppm)	log r of range	Average concentration (ppm)	log r of average conc.	References
before 1976	USA	n.d.	n.d.	TWA	air	n.d.	n.d.	up to 178	up to 0.6	n.d.	n.d.	Howard et al. (1990)
1975*	Germany	transfer	n.d.	TWA above machine door	air	6	n.d.	6.8 to 16.1	-0.9 to -0.5	9.9	-0.7	Engels, Schütz and Wolf (1975)
1975*	Germany	transfer	n.d.	(1h) operator	pers.	6	37	5.7 to 23.6	-0.9 to -0.3	14.5	-0.5	Engels, Schütz and Wolf (1975)
1982	USA	transfer	without or with inadequate local exhaust	TWA	pers.	14	n.d.	n.d.	n.d.	88.2	0.2	Materna (1985)
1982	USA	transfer	with adequate local exhaust	TWA	pers.	3	n.d.	n.d.	n.d.	80.8	0.2	Materna (1985)
n.d.	USA	transfer	n.d.	TWA	pers.	n.d.	n.d.	40 to 60	-0.1 to 0.1	n.d.	n.d.	Earnest (2002)
1986-87	USA	transfer	n.d.	TWA operator	personal	n.d.	8	n.d.	n.d.	58.4	0.1	Solet, Robins, and Sampaio (1990)
1983*	USA	transfer and 2nd	80% transfer	TWA operator	pers. and air	44	54	4.0 to 149.0	-1.1 to 0.5	31.0	-0.2	Ludwig et al. (1983)
1983*	USA	transfer and 2nd	80% transfer	TWA operator	pers.	39	134	3.3 to 366.0	-1.2 to 0.9	n.d.	n.d.	Ludwig et al. (1983)
1983*	USA	transfer and 2nd	80% transfer	TWA operator	pers.	30	49	1.0 to 269	-1.7 to 0.7	n.d.	n.d.	Ludwig et al. (1983)
1975*	Germany	2nd	n.d.	TWA above machine door	air	5	n.d.	2.9 to 36.0	-1.2 to -0.2	20.2	-0.4	Engels, Schütz and Wolf (1975)
1975*	Germany	2nd	n.d.	(1h) operator	pers.	5	24	11.0 to 45.3	-0.7 to 0.0	33.5	-0.2	Engels, Schütz and Wolf (1975)
1986-87	USA	2nd or 3rd	n.d.	TWA operator	pers.	n.d.	3	n.d.	n.d.	10.7	-0.7	Solet, Robins, and Sampaio (1990)
n.d.	USA	2nd and 3rd	n.d.	TWA	pers.	n.d.	n.d.	20 to 30	-0.4 to -0.2	n.d.	n.d.	Earnest (2002)
1982	USA	2nd and 3rd	with adequate local exhaust	TWA	pers.	3	n.d.	3.0 to 75.9	-1.22 to 0.2	28.2	-0.2	Materna (1985)
n.d.	USA	3rd	n.d.	TWA	pers.	n.d.	n.d.	15 to 25	-0.5 to -0.3	n.d.	n.d.	Earnest (2002)
n.d.	USA	3rd	13.6kg	TWA operator	pers.	1	11	26.2 to 31.3	-0.3 to -0.2	n.d.	n.d.	Earnest et al. (2002)
n.d.	USA	3rd	13.6kg	TWA above machine door	air	1	5	n.d.	n.d.	45.9	0.0	Earnest et al. (2002)
1982	Germany	approx. 3rd	n.d.	TWA	pers.	2	n.d.	9.0 to 42.9	-0.7 to -0.1	17.0	-0.5	Buchter et al. (1984)
1986*	Germany	approx. 3rd	n.d.	end of week	pers.	n.d.	55	2.3 to 97.4	-1.3 to 0.3	9.0	-0.7	Pannier, Hübner and Schultz (1986)
1987*	Germany	approx. 3rd	n.d.	TWA	pers.	1	n.d.	0.1 to 30.9	-2.7 to -0.2	7.0	-0.9	Schaller and Triebig (1987)
1989*	Germany	approx. 3rd	n.d.	TWA	pers.	n.d.	101	n.d.	n.d.	30.0	-0.2	Seeber (1989)
1987-89	Germany	3rd	coin-operated machines	n.d.	air	15	75	67%-pct. < 100 91%-pct. < 200	67%-pct. < 0.3 91%-pct. < 0.6	n.d.	n.d.	Gulyas and Hemmerling (1990)
n.d.	USA	3rd retrofit to 4th	13.6kg	TWA operator	pers.	1	4	n.d.	n.d.	22.6	-0.3	Earnest et al. (2002)
n.d.	USA	3rd retrofit to 4th	13.6kg	TWA above machine door	air	1	4	n.d.	n.d.	35.9	-0.1	Earnest et al. (2002)
1989*	Germany	approx. 4th	n.d.	n.d.	n.d.	39	n.d.	up to 36.7	up to -0.1	6.7	-0.9	Beier and Kohlert (1989)

No. number; n.d. not defined; pers. personal; * no year of measurement given, year of publication used; pct. percentile

Table 19: continued

Year	Country	Machine generation	Machine description	Measurement	Sample	No. of shops	No. of samples	Range of average con. (ppm)	log <i>r</i> of range	Average concentration (ppm)	log <i>r</i> of average conc.	References
n.d.	USA	4th	20.4kg	TWA operator	pers.	1	8	2.8 to 3.4	-1.3 to -1.2	n.d.	n.d.	Earnest et al. (2002)
n.d.	USA	4th	20.4kg	TWA presser	pers.	1	7	n.d.	n.d.	1.7	-1.5	Earnest et al. (2002)
n.d.	USA	4th	20.4kg	TWA above machine door	air	1	5	n.d.	n.d.	4.9	-1.0	Earnest et al. (2002)
n.d.	USA	4th	n.d.	TWA	pers.	n.d.	n.d.	n.d.	n.d.	< 10	< -0.7	Earnest (2002)
1990-94	Germany	4th	suspected higher exposure; with exhaust	n.d.	air	186	216	90%-pct. 22.9	90%-pct. -0.3	7.4	-0.8	Bock (1999)
n.d.	USA	4th	24.9kg	TWA operator	pers.	1	7	13.2 to 18.6	-0.6 to -0.4	15.8	-0.5	Earnest (1996)
n.d.	USA	4th	24.9kg	TWA near machine	air	1	28	1.9 to 23.0	-1.4 to -0.3	7.0	-0.9	Earnest (1996)
n.d.	USA	n.d.	nonvented machine without activated carbon	n.d.	air	6	46	1.7 to 52.3	-1.5 to 0.0	5.0 to 16.5	-1.0 to -0.5	Moschandreas (1995)
1990-91	Germany	n.d.	n.d.	worst case measurements	air	196	n.d.	90%-pct. 3.6	90%-pct. -1.1	n.d.	n.d.	Klein, Tagge and Kurz (1991)
1992-93	Italy	n.d.	n.d.	4h spot sampling	air	28	196	0.1 to 10.9	-2.8 to -0.7	3.1	-1.2	Aggazzotti et al. (1994)
1990-92	Germany	4th and 5th	n.d.	self-monitoring at worst case workplace	air	545	n.d.	90%-pct. 20	90%-pct. -0.4	< 5.0	< -1.0	Kurz and Klein (1998)
1990-94	Germany	4th and 5th	suspected higher exposure; without exhaust	TWA	air	127	147	90%-pct. 16.1	90%-pct. -0.5	4.9	-1.0	Bock (1999)
1993-94	Germany	4th and 5th	n.d.	at worst case workplace	air	21	n.d.	0.5 to 4.0	-2 to -1.1	n.d.	n.d.	Kurz and Klein (1998)
1993-97	Germany	4th and 5th	n.d.	self-monitoring at worst case workplace	air	442	n.d.	90%-pct. < 5	90%-pct. < -1	< 5.0	< -1.0	Kurz and Klein (1998)
n.d.	USA	retrofit to 5th	20.4kg	TWA operator	pers.	1	3	n.d.	n.d.	3.6	-1.1	Earnest et al. (2002)
n.d.	USA	retrofit to 5th	20.4kg	TWA above machine door	air	1	3	n.d.	n.d.	2.8	-1.3	Earnest et al. (2002)
1990-94	Germany	5th	suspected higher exposure	TWA	pers.	127	147	90%-pct. 16.1	90%-pct. -0.5	4.9	-1.0	Bock (1999)
1995	Germany	5th	n.d.	TWA	pers.	n.d.	n.d.	up to 5.1	up to -1	n.d.	n.d.	Bock (1999)
n.d.	USA	5th	16kg and 21kg Boewe 536 and 546	TWA operator	pers.	1	15	0.3 to 4.9	-2.2 to -1	1.8	-1.4	Earnest (2002)
n.d.	USA	5th	n.d.	TWA	pers.	n.d.	n.d.	n.d.	n.d.	< 5	< -1.0	Earnest (2002)

No. number; n.d. not defined; pers. personal; * no year of measurement given, year of publication used; pct. percentile

Table D.20: Published far-field exposure measurements of PERC used in dry cleaning ($\log r = \log(\text{concentration}/50 \text{ ppm})$) (measurements depicted in Figure 5.12 in Chapter 5.3.5).

Year	Country	Machine generation	Machine description	Measurement	Sample	No. of shops	No. of samples	Range of average con. (ppm)	$\log r$ of range	Average concentration (ppm)	$\log r$ of average conc.	References
1975*	Germany	transfer	n.d.	(1h) "far-field"	air	6	18	1.3 to 5.4	-1.6 to -1.0	3.5	-1.2	Engels, Schütz and Wolf (1975)
1986-87	USA	transfer	n.d.	TWA presser	pers.	n.d.	8	n.d.	n.d.	19.5	-0.4	Solet, Robins, and Sampaio (1990)
1983*	USA	transfer and 2nd	80% transfer	TWA presser	pers. and air	35	52	0.1 to 37.0	-2.7 to -0.1	5.7	-0.9	Ludwig et al. (1983)
1983*	USA	transfer and 2nd	80% transfer	TWA counter area (1h) "far-field"	pers. and air	31	31	0.3 to 26	-2.2 to -0.3	5.9	-0.9	Ludwig et al. (1983)
1975*	Germany	2nd	n.d.	(1h) "far-field"	air	5	28	3.3 to 5.6	-1.2 to -1.0	4.7	-1.0	Engels, Schütz and Wolf (1975)
1986-87	USA	2nd or 3rd	n.d.	TWA presser	pers.	n.d.	4	n.d.	n.d.	5.5	-1.1	Solet, Robins, and Sampaio (1990)
n.d.	USA	3rd	13.6kg	TWA presser	pers.	1	6	n.d.	n.d.	12.2	-0.6	Earnest et al. (2002)
n.d.	USA	4th	20.4kg	TWA presser	pers.	1	7	n.d.	n.d.	1.7	-1.5	Earnest et al. (2002)
n.d.	USA	4th	20.4kg	TWA presser	pers.	1	7	n.d.	n.d.	1.7	-1.5	Earnest et al. (2002)
n.d.	USA	4th	24.9kg	TWA at the reception	air	1	28	1.0 to 4.5	-1.7 to -1.0	2.3	-1.3	Earnest (1996)
n.d.	USA	5th	16kg and 21kg Boewe 536 and 546	TWA presser	pers.	1	15	n.d.	n.d.	< 0.12 (Limit of Detection)	< -2.6 (Limit of Detection)	Earnest (2002)

No. number; n.d. not defined; pers. personal; * no year of measurement given, year of publication used; pct. percentile

D.4. Statistical exposure assessment for dry cleaning

D.4.1. Probability density functions (PDF) of input parameters

In the following, the probabilistic density functions (PDF) are listed for all input parameters of 5th generation machines. Whenever possible, PDFs are obtained through data fitting (see Chapter 5.4). The PDFs for 2nd to 4th machine generations are obtained in a similar way from the data and sources described in Appendix D.2. In cases where only very limited data are available, it is taken as 5th and 95th percentile boundaries for the according PDFs.

When a physical property is measured in a given system, the frequency distribution is dominated by the measurement error and depicts, therefore, the uncertainty of the measurement. This is not the case for the model input parameters in this study. These parameters do not have a single true value

because they have to reproduce the situation in all German dry-cleaning shops. Consequently, the PDFs of the machine parameters, emission factors and workplace parameters depict primarily the variability of possible values and not the uncertainty of a single measurement.

In Table D.21, the PDFs of input parameters with normally distributed functions are listed. The fitted distributions for the air exchange rate k_L and for the loading factor f_L are depicted in Figure D.7 and Figure D.8. From the k_L values measured by Klein and Kurz (1994), it can be seen that this workplace parameter has great variability. If dry-cleaning machines are placed in rooms together with washing machines (wet cleaning), air exchange rates are much higher than in rooms in which only dry cleaning is performed. Typical air exchange rates in laundries are, because of the high humidity, between 10 and 15 h⁻¹ (Recknagel et al., 2000).

Table D.21: PDFs for input parameters of 5th generation machines (normal and lognormal distribution functions).

Input parameter	Mean	Standard deviation	Truncation min.	Truncation max.	Distribution function	Fitted to data (goodness-of-fit test)	Data source
Displacement factor (-) (displaced cylinder volume during loading and unloading)	1	0.05	0.1	1.2	Normal		Estimation (see Chapter 5.2.2 and Appendix D.1.3.3)
E_{c1} (g/kg)	0.26	0.05	0	2	Normal		Estimation (see Chapter 5.2.2 and Appendix D.1.3.1)
E_{c2} (g/kg) "normal" load	1.26	0.06	n.d.	n.d.	Normal		Werner 1996
E_{c2} (g/kg) "off-the-peg" load	0.12	0.01	n.d.	n.d.	Normal		Klein et al. 1991
E_{c2} (g/kg) (for average load: 80% "normal" and 20% "off-the-peg")	0.34	0.02	0	2	Normal		80% "normal" and 20% "off-the-peg" (see Chapter 5.2.2 and Appendix D.1.3.2)
k_L (1/h)	7.79	4.7	0.1	25	Lognorm	X (Chi-Sq)	Klein and Kurz 1994
k_A (1/h)	9.79	4.6	0.1	25	Lognorm		Estimation (see Chapter 5.2.3 and Appendix D.1.4)
f_L (-)	0.79	0.08	0.2	1.2	Lognorm	X (A-D)	Klein and Kurz 1994

goodness-of-fit tests: Chi-Sq: Chi-Square; K-S: Kolmogorov-Smirnov; A-D: Anderson-Darling

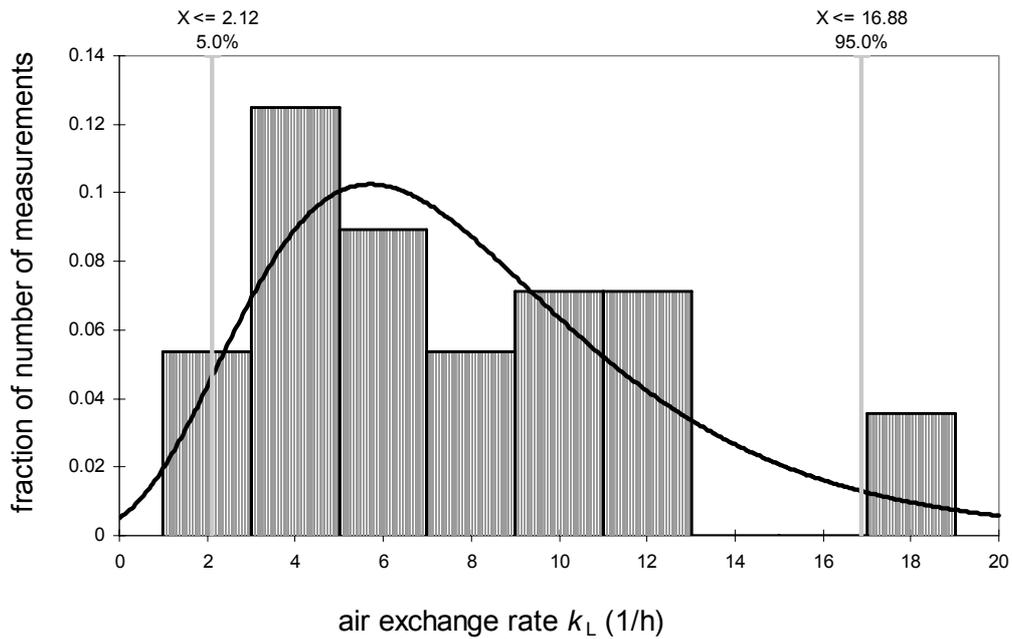


Figure D.7: Frequency distribution of air exchange rate k_L fitted to measured data reported by Klein and Kurz (1994).

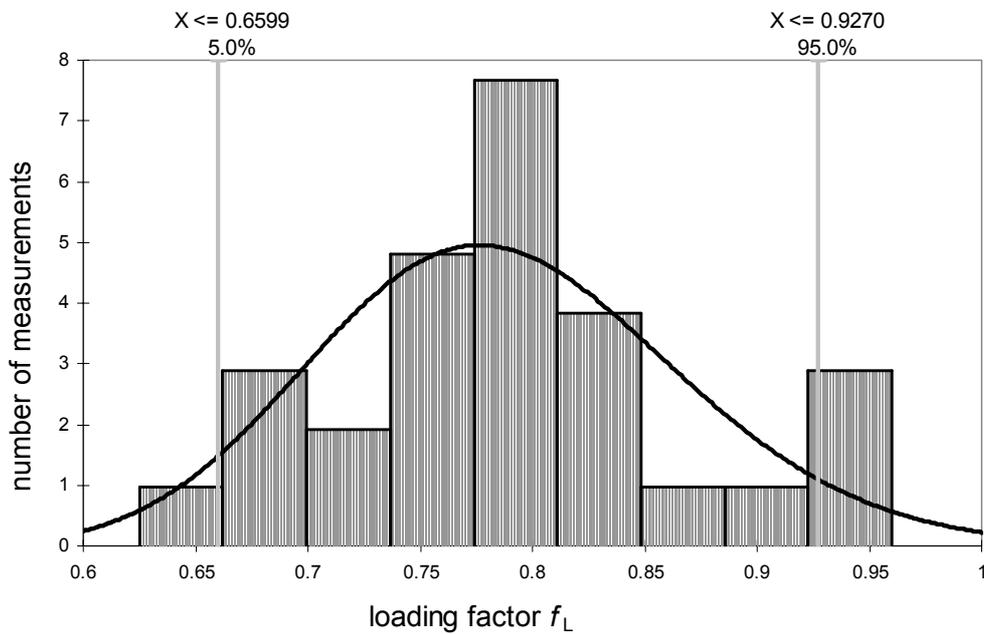


Figure D.8: Frequency distribution of loading factor, f_L , fitted to measured data reported by Klein and Kurz (1994).

In Table D.22, PDFs of the fitted distributions for the cylinder concentration and batch time are listed. The fitted distributions are depicted in Figure D.9 and Figure D.10.

Table D.22: PDFs for input parameters of 5th generation machines with extreme value (or Gumbel) distribution functions (extvalue distribution functions) (Palisade, 2002).

Input parameter	Expected value	Location parameter x	Scale parameter y	Truncation min.	Truncation max.	Distribution function	Fitted to data (goodness-of-fit test)	Data source
Cylinder concentration (g/m ³)	1.29	1.13	0.29	0	3	Extvalue	X (Chi-Sq/A-D)	Kurz and Klein 1995
t _b (min)	61.0	57.1	7.6	30	90	Extvalue	X (K-S)	Dry cleaner survey

goodness-of-fit tests: Chi-Sq: Chi-Square; K-S: Kolmogorov-Smirnov; A-D: Anderson-Darling

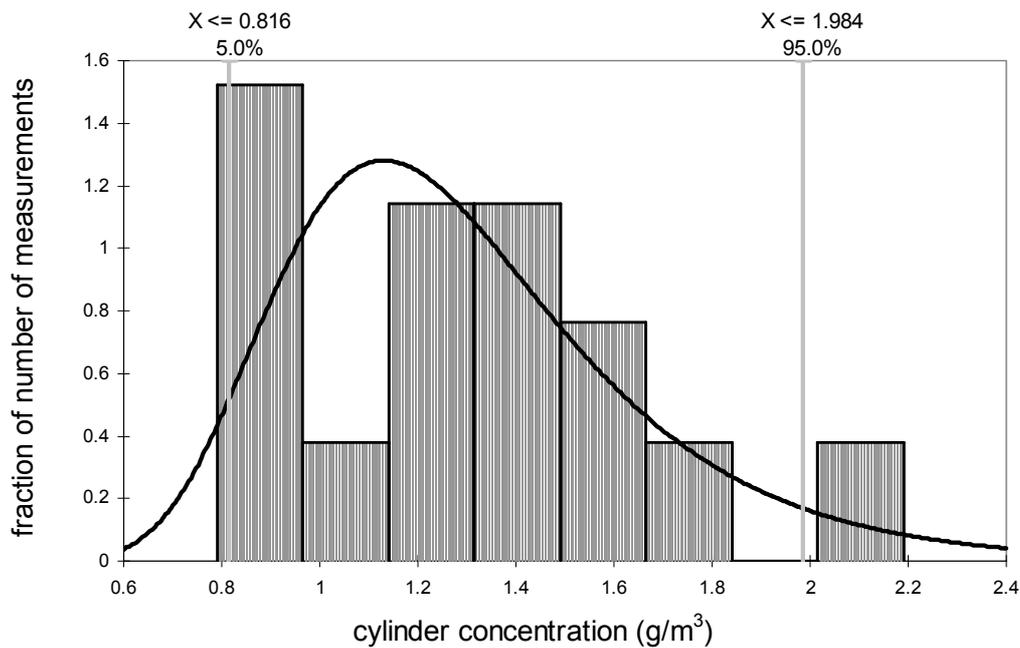


Figure D.9: Frequency distribution of cylinder concentration fitted to measured data reported by Kurz and Klein (1995).

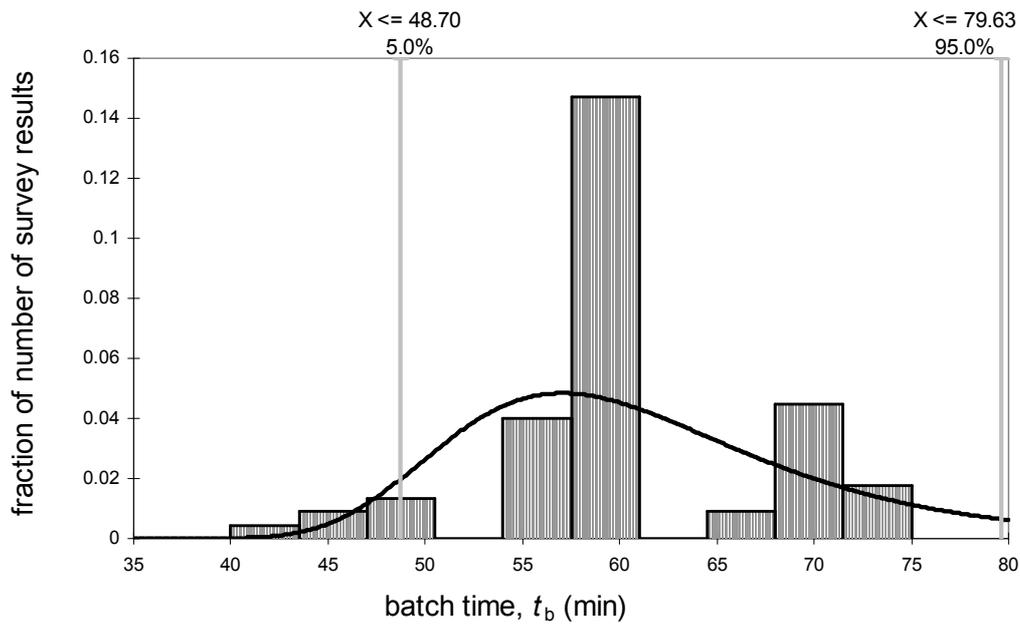


Figure D.10: Frequency distribution of batch time, t_b , fitted to data from dry cleaner survey.

In Table D.23 the PDF of the fitted workplace volume, V , is listed. The fitted distribution is depicted in Figure D.11.

Table D.23: PDF of workplace volume, V , of 5th generation machines (loglogistic distribution function).

Input parameter	Expected value	Alpha	Beta	Gamma	Truncation min.	Truncation max.	Distribution function	Fitted to data (goodness-of-fit test)	Data source
V (m^3)	618	55.9	281	1.62	200	3500	Loglogistic	X (Chi-Sq)	Dry cleaner survey

goodness-of-fit tests: Chi-Sq: Chi-Square

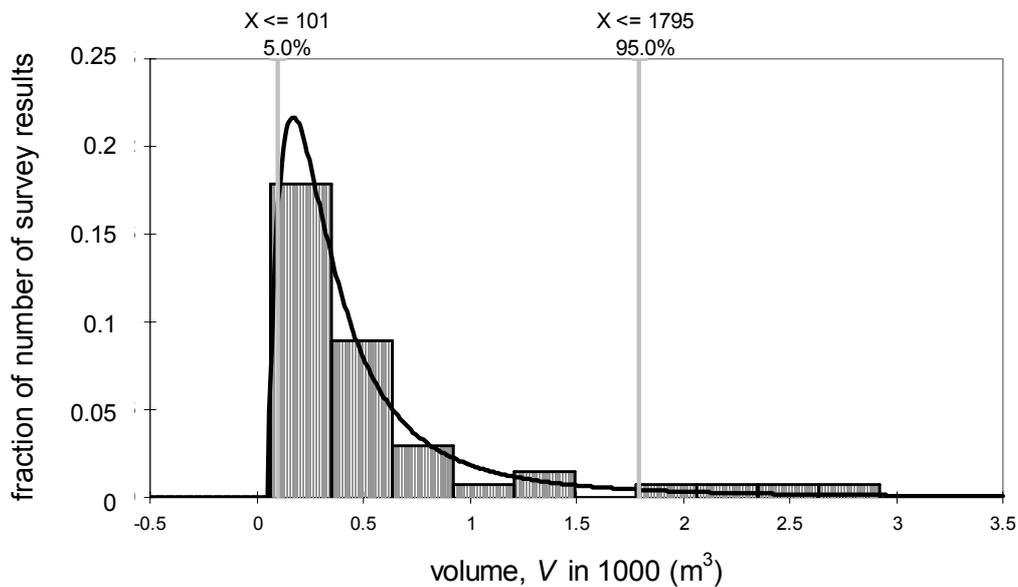


Figure D.11: Frequency distribution of total volume, V , fitted to data from dry cleaner survey.

D.4.2. Output distributions

In Figure D.12 and D.13, output distributions of the long-term concentration for the near-field and the far-field are given for a 5th generation size 2 machine as an example. The concentration distribution describes a distribution over all German dry-cleaning shops using 5th generation size 2 machines and is, therefore, not a probabilistic distribution of a single value (Suter, 1998).

The comparison of all frequency output ranges with the ranges of the SceBRA calculations can be seen in Figures 5.13 and 5.14 in Chapter 5.

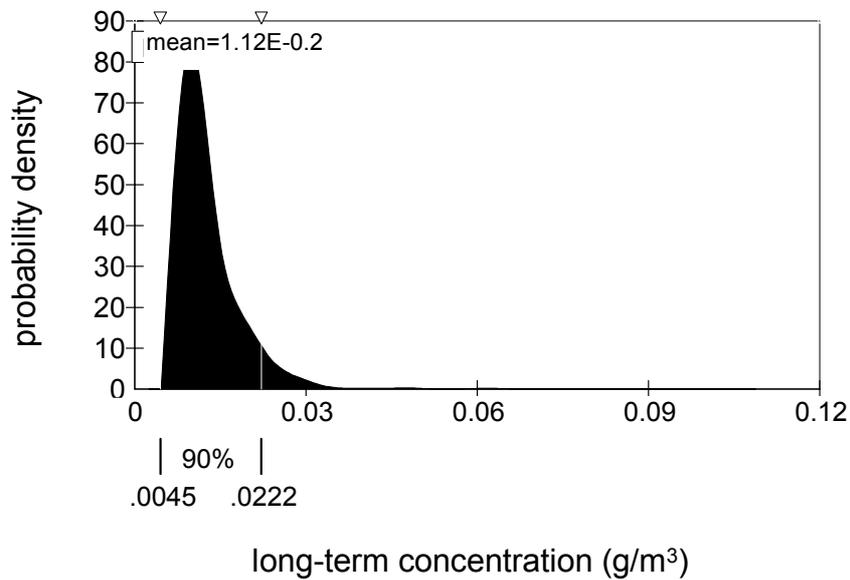


Figure D.12: Probability density distribution of near-field long-term concentration output for a 5th generation, size 2 dry-cleaning machine (with indication of 5th percentile, mean, and 95th percentile).

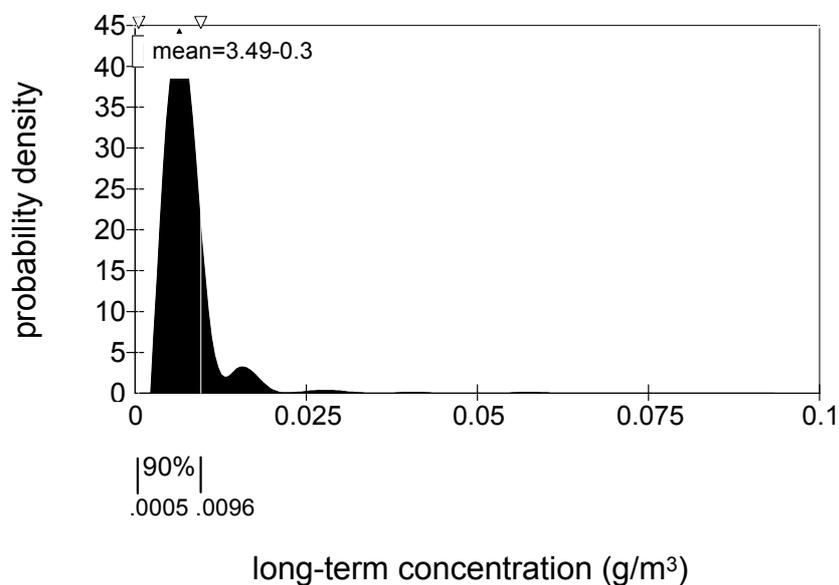


Figure D.13: Probability density distribution of far-field long-term concentration output for a 5th generation, size 2 dry-cleaning machine (with indication of 5th percentile, mean, and 95th percentile).

Appendix E

E. Symbols

E.1. Abbreviations

AGS	Committee for hazardous chemicals (“Ausschuss für Gefahrstoffe“)
AlCl ₃	Aluminum chloride
2 nd BImSchV	German 2 nd Federal Immission Protection Directive (“2. Bundes-Immissionsschutzverordnung“)
BImSchG	German Federal Clean Air Act (“Bundes-Immissionsschutzgesetz“)
BUA	Advisory Committee for Environmentally Hazardous Chemicals (“Beratergremium für umweltrelevante Altstoffe“)
Cancer cat. 1	Substance known to be carcinogenic
Cancer cat. 2	Suspected of having carcinogenic potential to humans
Cancer cat. 3	Possible carcinogenic effect to humans
CAS no.	Chemicals abstracts service number
CEFIC	European Chemical Industry Council (“Conseil Européen de l’Industrie Chimique“)
CFCs	Chlorofluorocarbons
Cl ₂	Chlorine
CRAHP	Committee on Risk Assessment of Hazardous Air Pollutants
DFG	Commission of the German Research Association
commission	(“Senatskommission der Deutschen Forschungsgemeinschaft“)
DTV	German textile cleaning association (“Deutscher Textilreinigungs-Verband“)

EASE	Estimation and Assessment of Substance Exposure model
ECETOC	European Center for Ecotoxicology and Toxicology of Chemicals
EDC	Ethylene dichloride
EU	European Union
EPA	U.S. Environmental Protection Agency
H ₂ O	Water
HCl	Hydrogen chloride
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer
LC ₅₀	Lethal concentration where 50% of the species die
LD ₅₀	Lethal dose where 50% of the species die
LOEL	Lowest Observed Effect Level
MAK	Maximum workplace concentration (“Maximale Arbeitsplatz Konzentration“)
min.	Minutes
n.d.	Not defined
NCI	U.S. National Cancer Institute
No.	Number
NOEL	No-observed effect level
NRC	National Research Council
pct.	Percentile
PDF	Probability density function
PERC	Perchloroethylene
ppm	Part per million
R-11	Trichlorofluoro methane
R-112	1,1,2,2-tetrachloro-1,2-difluoro ethane
R-113	1,1,2-trichlorotrifluoro ethane
R40	R-sentence: Limited evidence of carcinogenic effect
R45	R-sentence: May cause cancer
REACH	Registration, Evaluation and Authorization
SceBRA	Scenario-Based Risk Assessment
TCA	Trichloroacetic acid
TGD	Technical Guidance Document

TLV	Threshold limit value
TRGS	Technical regulations for dangerous substances (“Technische Regeln für Gefahrenstoffe“)
TRIC	Trichloroethylene
TWA	Time-weighted average concentration over a 8h working period
U.S.	United States of America
UBA	German Federal Environmental Office (“Umwelt Bundes Amt”)
VCI	German Chemical Industry Association (“Verband der Chemischen Industrie“)
Xn	Harmful to health

E.2. Model parameters

a	Sensitivity	[-]
A_{jk}	Integration constants (j and k standing for 1 or 2)	[g/m ³]
α	Duration of continuous emission factor \dot{E}_{c2}	[h]
$C(0)$	Concentration at time $t = 0$	[g/m ³]
$C(t)$	Concentration at time t	[g/m ³]
C^0	Background concentration at time $t = 0$	[g/m ³]
C_A	Concentration in box A	[g/m ³]
C_{air}	Background concentration of fresh air	[g/m ³]
C_B	Concentration in box B	[g/m ³]
C^∞	Steady state concentration	[g/m ³]
$C_{A,i+1}^0$	Background concentration of homogeneous differential system at time $t = i \cdot t_{pulse}$	[g/m ³]
$C_{p,A,i+\alpha}^0$	Background concentration for E_p at time $t = i \cdot t_{pulse} + \alpha$	[g/m ³]
D	Molecular diffusion coefficient	[m ² /h]
ΔC	Concentration gradient	[g/m ³]
Δh	Diffusion length	[m]
\dot{E}	Emission rate	[g/h]
\dot{E}_A	Emission rate into box A	[g/h]

\dot{E}_{c1}	Continuous emission factor for diffuse emissions from open bath surfaces or from leakage of sealing	[g/h]
E_{c1}	Continuous emissions for diffuse emissions from open bath surfaces or from leakage of sealing	[g/kg]
\dot{E}_{c2}	Continuous emission factor for emissions from cleaned metal parts and parts with cavities or cleaned textiles	[g/h]
E_{c2}	Continuous emissions for emissions from cleaned metal parts and parts with cavities or cleaned textiles	[g/kg]
E_p	Periodic factor for repetitive emissions from chamber air during loading and unloading	[g]
f_L	Loading factor, determines the degree of filling	[-]
i	Variable counting number of pulses/batches	[-]
J_z	Diffusion mass flow in z direction	[g/(m ² h)]
k	Loss rate constant	[h ⁻¹]
k_A	Air exchange rate of box A with box B	[h ⁻¹]
k_B	Air exchange rate of box B with box A	[h ⁻¹]
k_L	Air exchange rate of box B with environment	[h ⁻¹]
λ_j	Eigenvalues (j standing for 1 or 2)	[h ⁻¹]
MAK	Maximum workplace concentration ("Maximale Arbeitsplatz Konzentration")	[g/m ³]
N	Number of exposed Workers	[persons]
N_{cum}	Cumulate number of exposed Workers	[persons]
q	Ambiguous letter: $q = (\lambda_1 - \lambda_2)^{-1}$	[h ⁻¹]
r	Risk quotient	[-]
t	Time	[h]
t_b	Batch time	[h]
t_{pulse}	Time between two pulse emissions	[h]
V	Total room volume ($V = V_A + V_B$)	[m ³]
V_A	Volume of box A	[m ³]
V_B	Volume of box B	[m ³]

x	Location parameter for extvalue distribution functions	[-]
y	Scale parameter for extvalue distribution functions	[-]
x_i	Input parameter i , for sensitivity analysis	[-]
y_i	Output parameter i , for sensitivity analysis	[-]

Curriculum Vitae

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Education

1981 – 1990 Elementary school, Oberhofen, Switzerland
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1994 – 1998 Master of Science in chemistry, main subjects: organic, bioorganic, and environmental chemistry, University of Bern, Switzerland
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Professional Experience

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