

M.Sc. Birte Mull

**Investigation of an active air sampling strategy
for biocides, PCBs and PAHs
at low air change rates**

Die vorliegende Arbeit entstand an der BAM Bundesanstalt für Materialforschung und -prüfung.

Impressum

**Investigation of an active air sampling strategy
for biocides, PCBs and PAHs at low air change rates**

2013

Herausgeber:

BAM Bundesanstalt für Materialforschung und -prüfung
Unter den Eichen 87

12205 Berlin

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E-Mail: info@bam.de

Internet: www.bam.de

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Layout: BAM-Referat Z.8

ISSN 1613-4249

ISBN 978-3-9815748-3-8

Investigation of an active air sampling strategy for biocides, PCBs and PAHs at low air change rates

vorgelegt von
Master of Science
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von der Fakultät III – Prozesswissenschaften
der Technischen Universität Berlin
zur Erlangung des akademischen Grades

Doktor rerum naturalium
- Dr. rer. nat. -

genehmigte Dissertation

Promotionsausschuss:

Vorsitzender: Prof. Dr.-Ing. Martin Jekel

Berichter: Prof. Dr. rer. nat. Wolfgang Rotard

Berichter: Priv.-Doz. Dr. rer. nat. Oliver Hahn

Tag der wissenschaftlichen Aussprache: 27. Februar 2013

Berlin 2013

D 83

Veröffentlichungen

Ergebnisse dieser Arbeit wurden in folgenden Beiträgen veröffentlicht:

B. Mull (Vortragende), K. Wiegner, W. Horn, *Development of a Screening Method for Semi Volatile Organic Compounds in Museum Showcases*

Vortrag: Technart 2011, Berlin, Deutschland

B. Mull, K. Wiegner, W. Horn, *Development of a Screening Method for Semi Volatile Organic Compounds in Museum Showcases*

Tagungsband: Technart 2011, Berlin, Deutschland

B. Mull, K. Wiegner, W. Horn, *Analytik von Bioziden in Kunst- und Kulturgut*,

Poster: Exponatec 2011, Köln, Deutschland

B. Mull (Vortragende), K. Wiegner, W. Horn, *Development of a Screening Method for SVOC in the Micro-Chamber Air and Indoors*

Vortrag: Emissions and Odours from Material 2011, Brüssel, Belgien

M. Torge, D. Brödner, I. Feldmann, S. Krug, H. Mathies and B. Mull, *Determination of wood protective agents in a world heritage site church*

Poster: Indoor Air Quality 2012, London, England

B. Mull (Vortragende), *Comparison of different air sampling adsorbents for a screening method for SVOC*

Vortrag: Healthy Buildings 2012, Brisbane, Australien

B. Mull, K. Wiegner, W. Horn, *Comparison of different air sampling adsorbents for a screening method for SVOC*

Tagungsband: Healthy Buildings 2012, Brisbane, Australien

M. Torge, D. Brödner, I. Feldmann, S. Krug, H. Mathies and B. Mull, *Analytical methods to determine wood protective agents in a world heritage site church*

Poster: 6. N.i.Ke.-Workshop Segen und Fluch – Biozide: I. Verwendung, Analytik, Bewertung, 2012, Berlin, Deutschland

B. Mull (Vortragende), *Neue Verfahren zur Probenahme von ausgewählten SVOCs aus der Luft*

Vortrag: 6. N.i.Ke.-Workshop Segen und Fluch – Biozide: I. Verwendung, Analytik, Bewertung, 2012, Berlin, Deutschland

B. Mull, K. Wiegner and W. Horn, *A low-volume air sampling method for biocides and PCBs in a micro-chamber*, Fresenius Environmental Bulletin, 2013, 22: p. 675-680.

Danksagung

Die vorliegende Arbeit entstand in der Zeit von Dezember 2009 bis November 2012 bei der BAM Bundesanstalt für Materialforschung und -prüfung unter Leitung von Herrn Dr. Wolfgang Horn und Frau Dr. Katharina Wiegner, denen ich für die Themenstellung und die engagierte Betreuung herzlich danken möchte. Ferner möchte ich Herrn Dr. Oliver Jann dafür danken, dass ich die Arbeit im Fachbereich „Materialien und Luftschadstoffe“ anfertigen konnte.

Herrn Prof. Dr. Wolfgang Rotard und Herrn Priv.-Doz. Dr. Oliver Hahn danke ich für die Übernahme der gutachterlichen Tätigkeiten und die fachlichen Ratschläge zum erfolgreichen Gelingen der Arbeit.

Für die Bereitstellung der Vitrinen und einiger Proben danke ich der Firma Glasbau Hahn GmbH (Frankfurt am Main) und hier insbesondere Herrn Matthias Farke. Frau Dr. Ina Stephan danke ich für die Bereitstellung der zahlreichen Holzproben. Herrn Priv.-Doz. Dr. Oliver Hahn möchte ich außerdem für die Möglichkeit der Depotraummessungen danken. Ebenso danke ich Herrn Dr. Manfred Torge für die Möglichkeit an der Mitarbeit zur Untersuchung einer Weltkulturerbekirche in Świdnica (Polen).

Des Weiteren möchte ich mich bei allen Mitarbeitern des Fachbereichs 4.2 der BAM sehr herzlich für die sowohl fachlichen Diskussionen und Hilfestellungen als auch moralische Unterstützung zum Gelingen der Arbeit bedanken und nicht zuletzt auch für die gute Zusammenarbeit. Ein besonderes Dankeschön an Herrn Michael Nohr für das angenehme und unterhaltsame Büroklima der letzten zweieinhalb Jahre.

Frau Heather Dickens danke ich für die sprachliche Überarbeitung der Arbeit.

Zuletzt danke ich vor allem meinen Eltern und meinem Freund Konstantin Poelke für die besonders motivierende Unterstützung während meines gesamten Studiums und meiner Promotion.

Zusammenfassung

Das Ziel der vorliegenden Arbeit war die Entwicklung einer Luftprobenahmestrategie mit geringen Probenahmeverolumina für Biozide, polychlorierte Biphenyle (PCB) und polyzyklische aromatische Kohlenwasserstoffe (PAK) bei niedrigen Luftwechselraten. Zunächst wurde eine analytische Messmethode für ein GC-MS-MS System entwickelt, bevor in Elutionsversuchen mit Standardlösungen ein geeignetes Adsorbiermaterial für die Luftprobenahmen dieser Verbindungsklassen ausgewählt wurde. Die Anforderungen an das Adsorbiermaterial waren eine schnellere und leichtere Aufarbeitung mit einem geringeren Lösemittelverbrauch als es für den häufig verwendeten Polyurethanschaum (PU) und das XAD-Adsorbens der Fall ist. Die Luftprobenahmequalität des ausgewählten Adsorbiermaterials wurde in Versuchen in einer Mikro-Kammer (Micro-Chamber/Thermal Extractor™ (μ -CTE™, Markes International)), die ebenfalls mit Standardlösungen beladen wurde, mit der des PU-Schaums verglichen. Anschließend wurden der Einfluss der Temperatur, Luftbewegung, Luftwechselrate und relativer Luftfeuchtigkeit auf das Emissionsverhalten der Biozide, PCBs und PAKs in Versuchen mit geringen Probenahmeverolumina in der μ -CTE, in 23 L und 24 L Emissionsmesskammern und in Vitrinen mit einem Volumen von 27 L mit selbst getränkten Holzproben untersucht. Außerdem wurde eine aktive Probenahmestrategie für niedrige Luftwechselraten erfolgreich in einer 24 L Emissionsmesskammer getestet.

Mit der entwickelten Probenahmemethode wurden Volumina von 24-50 L gesammelt und Nachweisgrenzen von $1\text{-}27\ \mu\text{g m}^{-3}$ konnten damit erreicht werden. Ein Styroldivinylbenzol-Polymer wurde als geeignetes Adsorbiermaterial ausgewählt. Mit 200 mg dieses Adsorbiers können mindestens $100\ \text{ng}\ \mu\text{L}^{-1}$ der ausgewählten Biozide, PCBs und PAKs ohne Durchbrüche gesammelt werden, was einem Konzentrationsbereich von $3000\text{-}6250\ \mu\text{g m}^{-3}$ für die geringen verwendeten Probenahmeverolumina entspricht.

Die entwickelte Probenahmemethode wurde bereits erfolgreich in verschiedenen Projekten eingesetzt, in denen reale Holzproben in der μ -CTE untersucht wurden und ebenfalls Innenraumprobenahmen mit geringen Probenahmeverolumina durchgeführt wurden. In diesen Versuchen wurde die entwickelte Methode mit einer weiteren Methode verglichen, für die ein anderes Adsorbiermaterial verwendet wird.

Abstract

The aim of this study was to develop a low volume air sampling strategy for biocides, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) at low air change rates. Firstly a method of measurement for the GC-MS-MS system had to be created before an adsorbent for the air sampling of these compound classes was selected in elution experiments with target compound solutions. The key requirements for the adsorbent were that it had to engender a faster and easier work-up process while reducing solvent consumption, as it is not the case for the frequently used polyurethane foam (PUF) and XAD adsorbents. Using the selected adsorbent, air sampling quality was tested and compared with the one of PUF in experiments performed in a Micro-Chamber/Thermal Extractor™ (μ -CTE™, Markes International) with target compound solutions. To achieve air sampling under the aforementioned conditions the influences of temperature, air circulation, air change rate and relative humidity on the emission behavior of the selected biocides, PCBs and PAHs were investigated. This investigation was carried out with self soaked wood samples in low volume air sampling experiments in a μ -CTE, 23 l and 24 l emission test chambers and 27 l showcases. Furthermore, an active air sampling strategy for biocides, PCBs and PAHs at low air change rates was successfully tested in a 24 l emission test chamber.

Sampling volumes of 24-50 l were tested with the developed low volume air sampling strategy with limits of quantification between 1-27 $\mu\text{g m}^{-3}$. A styrene divinylbenzene polymer was selected as a suitable adsorbent and sampling of at least 100 $\text{ng } \mu\text{l}^{-1}$ of biocides, PCBs and PAHs without breakthroughs were possible with 200 mg of this polymer. This corresponds to a concentration range of 3000-6250 $\mu\text{g m}^{-3}$ for these low sampling volumes.

The low volume air sampling method developed in this study was successfully applied in projects investigating real wood samples in the μ -CTE as well as in low volume indoor air samples. In these experiments the applicability of the method was partly compared with a method using a different adsorbent.

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1 Introduction

Museum environments have created the need for an active air sampling strategy at air change rates close to zero, because of the occurrence of chemical pollutants in exhibits, which are stored mostly in showcases or storage equipments where barely any air change occurs. Organic and inorganic pollutants are present in the museum environment with different effects on the exhibits [1-3]; their relevant compounds are all named and described in detail in an overview given by Schieweck and Salthammer [1]. This study focuses on the analysis of organic pollutants in air, whereby only a few relevant biocides, polychlorinated biphenyls (PCB) and polycyclic aromatic hydrocarbons (PAH) were selected from the large group of organic contaminants. Biocides were purposely applied on organic exhibits, whereas PCBs, PAHs and other pollutants are emitted, for example by building materials, interior equipment or showcase equipment.

Biocides – the term originating from the Greek word *bios* (*life*) and from the Latin word *caedere* (*kill*) – are the predominately investigated compounds in this study. Designed with the aim to fight undesired organisms [4] biocides have been applied as active agents in wood preservatives, which, for example, have been used in the museum environment, in house construction and on interior equipment up to now. Because of their toxicity, they provide a particular threat to humans who have come in contact with contaminated air or materials justifying the need for appropriate measurement strategies and analytical methods for indoor air, emission test chambers and showcases with air change rates close to zero. Whereas active air sampling methods for biocides, PCBs and PAHs in ambient air already exist [5-9], active sampling at air change rates close to zero is up to now an unsolved problem. This study focuses on the development of an active air sampling strategy for low air change rates. Furthermore, a minimization of the air sampling volume from several m³ (according to ASTM D 6209-98 [7] and VDI 4301 part 2 [6]) to not more than hundred liters is preferable to shorten the sampling time. A further aim is to select an adsorbent with a lower work effort to minimize the solvent consumption and working time, because this is very high by using polyurethane foam (PUF) or XAD-2 according to ASTM D 4861-11[5], 4301 part 2 [6], ASTM D 6209-98 [7], VDI 3874 [8] and VDI 2464 [9].

Biocides were the main compounds investigated in this study including pentachlorophenol (PCP), lindane, dichlofluanid, tolyfluanid, isodrin, p,p'-dichlorodiphenyltrichloroethane (p,p'-DDT) and permethrin. Permethrin is a cis-trans isomer and in the following cis-Permethrin is called permethrin 1 and trans-permethrin is known as permethrin 2. Only PCB 28 and PCB 153 from the large group of PCBs were investigated and benzo[a]pyrene was the only investigated PAH, which is a particulate organic matter (POM).

Since organic compounds are divided into four categories according to their boiling points, enrichment in indoor compartments and exposure paths [10, 11], biocides, PCBs and the lower boiling PAHs belong to the semi volatile organic compounds (SVOC), whereas the higher boiling PAHs and other organic compounds are POMs. The classification of organic compounds was performed by the World Health Organization according to their boiling points and is presented in *Table 1.1*.

Table 1.1: Classification of organic compounds [10]

Description	Boiling point range [°C]
Very volatile organic compounds (VVOC)	< 0 to 50-100
Volatile organic compounds (VOC)	50-100 to 240-260
Semi volatile organic compounds (SVOC)	240-260 to 380-400
Particulate organic matter (POM)	> 380

2 Theoretical part

2.1 Compound information

According to the literature [1, 3] and to an oral reference [12] a few relevant SVOCs and one POM from the group of biocides, PCBs and PAHs, are selected for method development. A short description of all of the compounds involved is given below.

Pentachlorophenol (PCP)

Since 1936 PCP has been used as a wood preservative in the form of solvent-borne preservatives with a concentration of 4-6 % (see *Section 2.2*) [13]. Furthermore, it has been applied as a herbicide and fungicide, for example in wallpapers and paints [14]. In the beginning of the 1980s PCP started to be replaced by dichlofluanid and later tolylfuanid because of the contaminated internal air in treated buildings until the German PCP Prohibition Regulation completely prohibited the production, sale and use of PCP in 1989 [13-15]. PCP is still present on materials years after application because of its high stability and low vapor pressure and it is mainly detectable on all surfaces including dust [16].

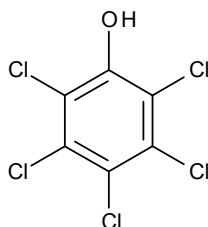


Figure 2.1: Structural formula of PCP

Table 2.1: Chemical and physical properties of PCP

Name	Pentachlorophenol
Molecular formula	C_6HCl_5O
CAS-RN	87-86-5
Molecular weight	$266.35 \text{ g mol}^{-1}$
Boiling point	$300 \text{ }^\circ\text{C}$ (decomposes) [13]
Vapor pressure	$2.3 \times 10^{-2} \text{ Pa}$ ($20 \text{ }^\circ\text{C}$) [13]

Lindane

Hexachlorocyclohexane has several isomers (α , β , γ , δ , ϵ) but only the γ -isomer is contained in wood preservatives available in Germany, whose insecticidal effect was discovered in 1933 by Bender [13, 14]. It was applied as an active agent in solvent-based wood preservatives mostly in combination with PCP or DDT, as in Hylotox[®] 59 and

Xylamon (see Section 2.2), in concentrations between 0.3-0.9 % [13]. It belongs to the group of components that have a higher tendency to be measurable in gaseous form in indoor air [16].

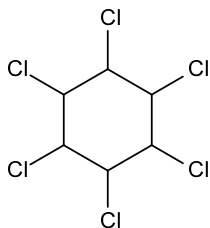


Figure 2.2: Structural formula of lindane

Table 2.2: Chemical and physical properties of lindane

Name	γ -1,2,3,4,5,6-Hexachlorocyclohexane
Molecular formula	$C_6H_6Cl_6$
CAS-RN	58-89-9
Molecular weight	$290.86 \text{ g mol}^{-1}$
Boiling point	$176 \text{ }^\circ\text{C}$ at 1.3 kPa [13]
Vapor pressure	$1.2 \times 10^{-3} \text{ Pa}$ ($20 \text{ }^\circ\text{C}$) [13]

Dichlofluamid

Dichlofluamid is a fungicide developed in 1965 by Bayer AG [17]. Solvent-based preservatives or emulsions contained dichlofluamid in concentrations between 0.2-2 % [13]. There are currently no dichlofluamid-containing preservatives admitted in Germany [17].

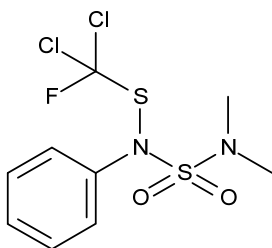


Figure 2.3: Structural formula of dichlofluamid

Table 2.3: Chemical and physical properties of dichlofluanid

Name	N,N-Dimethyl-N'-fourodichloromethylthio-N'-phenyl-sulfamide
Molecular formula	$C_9H_{11}Cl_2FN_2O_2S_2$
CAS-RN	1085-98-9
Molecular weight	$333.23 \text{ g mol}^{-1}$
Vapor pressure	$1.4 \times 10^{-6} \text{ Pa (20 } ^\circ\text{C)}$ [13]

Tolyfluanid

Tolyfluanid was introduced in 1973 by Bayer [18]. The concentration of tolyfluanid in solvent-based preservatives or emulsions is between 0.1-3 % [13].

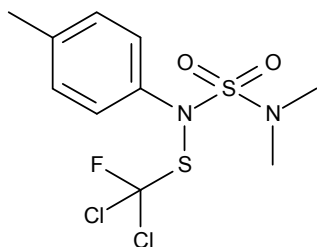


Figure 2.4: Structural formula of tolyfluanid

Table 2.4: Chemical and physical properties of tolyfluanid

Name	N-Dichlorofluoromethylthio-N',N'-dimethyl-N-p-tolylsulfamide
Molecular formula	$C_{10}H_{13}Cl_2FN_2O_2S_2$
CAS-RN	731-27-1
Molecular weight	$347.26 \text{ g mol}^{-1}$
Vapor pressure	$1.6 \times 10^{-4} \text{ Pa (20 } ^\circ\text{C)}$ [13]

Isodrin

Isodrin is a persistent insecticide from the group of the organochlorine insecticides. Hexachlorocyclopentadiene is the building block for several insecticides including isodrin and dieldrin, which are all prohibited in Germany [17].

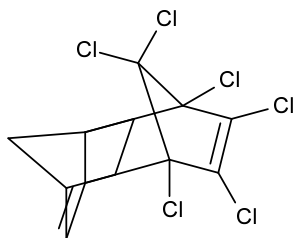


Figure 2.5: Structural formula of isodrin

Table 2.5: Chemical and physical properties of isodrin

Name	(1R,4S,5R,8S)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8 ^a -hexahydro-1,4:5,8-dimethanonaphthalene
Molecular formula	C ₁₂ H ₈ Cl ₆
CAS-RN	465-73-6
Molecular weight	364.91 g mol ⁻¹

Dichlorodiphenyltrichloroethane (DDT)

DDT is a worldwide known insecticide whose insecticidal effect was discovered in 1939. Technical DDT mixtures contain approximately 70 % p,p'-DDT, which is the isomer with the highest insecticidal effect, as well as o,p'-DDT and small amounts of technical contaminants e.g. o,p'-dichlorodiphenyldichloroethane (DDE) and p,p'-DDE [19]. The concentration range of p,p'-DDT in wood preservatives is about 2-3.5 % and it is one of the active agents in Hylotox[®] IP and 59 (see Section 2.2) [13]. Furthermore, because of its non-systemic character it was used for insect control in the agriculture as well as inside of houses and in the medical industry [17]. Like PCP it is mainly detectable on surfaces as well as in dust particles [16]. In 1972 it was banned by law in the Federal Republic of Germany because of its high persistence [13]. Nevertheless, DDT was used in the German Democratic Republic till 1989 [20].

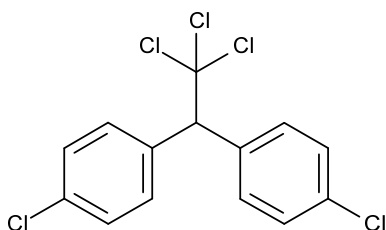


Figure 2.6: Structural formula of p,p'-DDT

Table 2.6: Chemical and physical properties of p,p'-DDT

Name	p,p'-Dichlorodiphenyltrichloroethane, 1,1,1-Trichloro-2,2-di(4-chlorophenyl)-ethane
Molecular formula	C ₁₄ H ₉ Cl ₅
CAS-RN	50-29-3
Molecular weight	354.49 g mol ⁻¹
Boiling point	260 °C [13]
Vapor pressure	2.5×10 ⁻⁵ Pa (20 °C) [13]

Permethrin

Permethrin is an insecticide belonging to the group of pyrethroids and was developed by the National Research Development Corp. [21]. 80-85 % of wood preservatives with insecticidal effects contain permethrin and due to its high efficiency it replaced Lindane in almost all fields of application [22]. In solvent systems it is contained in a concentration range between 0.01-2.5 % [13] but mostly in a range of 0.10-0.25 % [22].

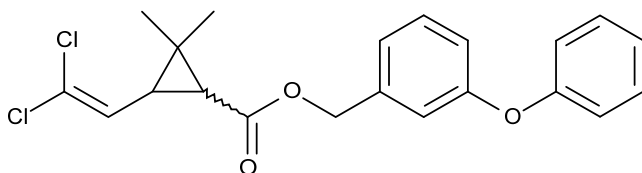


Figure 2.7: Structural formula of permethrin

Table 2.7: Chemical and physical properties of permethrin

Name	(1 <i>RS</i>)-cis,trans-3-(2,2-dichlorovinyl)- 2,2-dimethylcyclopropane-carboxylate
Molecular formula	C ₂₁ H ₂₀ Cl ₂ O ₃
CAS-RN	52645-53-1
Molecular weight	391.28 g mol ⁻¹
Boiling point	210-220 °C at 101.3 kPa [13]
Vapor pressure	1.0×10 ⁻⁴ Pa (20 °C) [13]

Benzo[a]pyrene

Because of the large number of PAHs (approximately 280) only a few are selected for the analytics to represent the whole substance group. Benzo[a]pyrene, which is a POM, is chosen to be the leading compound for the evaluation of PAHs. Furthermore, only a few PAHs were specifically synthesized for the production of biocides [23].

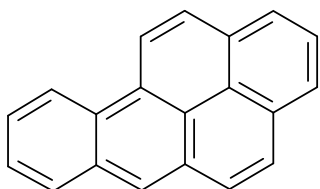


Figure 2.8: Structural formula of benzo[a]pyrene

Table 2.8: Chemical and physical properties of benzo[a]pyrene

Name	Benzpyren(3,4), Benzo(d,e,f)chrysen
Molecular formula	C ₂₀ H ₁₂
CAS-RN	50-32-8
Molecular weight	252.32 g mol ⁻¹
Boiling point	495.5 °C [24]

Polychlorinated Biphenyls

There are 209 possible PCB congeners but the toxicologically active PCBs are the ones with chlorine substitutions at both para (4,4') and at least two meta (3,3', 5,5') positions [25]. In 1980 Ballschmiter and Zell published a systematic numbering of all 209 PCB compounds, known as the Ballschmiter nomenclature [26]. The use of PCBs was very common because of their non-flammability, electrical-insulating properties and chemical and thermal stabilities. In 1966 it was found out that PCBs are environmental contaminants which are present in human breast milk and in Antarctic snow [27].

PCB 28

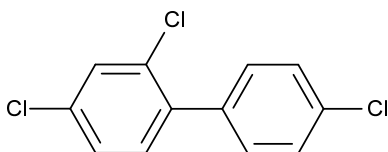


Figure 2.9: Structural formula of PCB 28

Table 2.9: Chemical and physical properties of PCB 28

Name	2,4,4'-Trichlorobiphenyl
Molecular formula	C ₁₂ H ₇ Cl ₃
CAS-RN	7012-37-5
Molecular weight	257.54 g mol ⁻¹

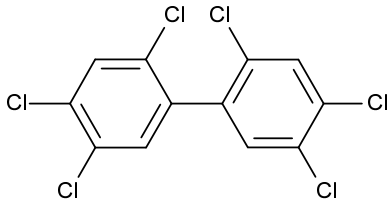
PCB 153

Figure 2.10: Structural formula of PCB 153

Table 2.10: Chemical and physical properties of PCB 153

Name	2,2',4,4',5,5'-Hexachlorobiphenyl
Molecular formula	C ₁₂ H ₄ Cl ₆
CAS-RN	35065-27-1
Molecular weight	360.88 g mol ⁻¹

2.2 Wood preservatives

The aim of wood preservatives is to mortify or to render insects or fungi harmless. They are divided into water soluble preservatives, solvent-based preservatives and coal oil or carbolineum. Water soluble preservatives consist of inorganic salts which are 80-100 % of the active ingredients. Only 0.2-5 % of organic compounds are contained as active ingredients in solvent-based preservatives due to their effective activity. Biocides are the organic compounds in solvent-based wood preservatives which give insecticidal or fungicidal effects. Coal oil and carbolineum are byproducts of coking and usually contain 100 % of the active ingredients [22]. This thesis focuses on the solvent-based wood preservatives containing biocides only. PCBs and PAHs are also present in some wood preservatives [28].

Predominantly PCP, lindane and DDT, later dichlofluamid and permethrin, were the active agents in solvent based wood preservatives. A lot of different combinations of these and other active agents were available, e.g. Hylotox[®] 59 (3.5 % DDT, 0.5 % lindane) and Hylotox[®] IP (3 % DDT, 5 % PCP), which were predominantly used in the German Democratic Republic and the preservative Xylamon (5 % PCP, 0.9 % lindane) was often used in the Federal Republic of Germany [13].

2.2.1 Application of wood preservatives

Solvent-based wood preservatives are not only used for interior equipments and wood or cloth protection but they can also be found in building construction and museum environments.

2.2.1.1 Wood preservatives in house construction

The use of wood preservatives in house construction and in interior equipment leads to the presence of biocides in indoor air [22]. During the second half of the 20th century organic based biocides – mainly containing PCP, lindane, DDT, dichlofluamid or permethrin – were applied in large quantities for pest control in buildings, which consist completely or partially of wood or wooden elements such as stairs, doors and walls [22].

Attics, predominately in the former German Democratic Republic, were also treated with wood preservatives and this subsequently became a problem when the attics were converted to modern apartments. Lindane concentrations of 5-120 ng m⁻³ and DDT concentrations of 10-40 ng m⁻³ could be measured in reconstructed attics – these concentrations were higher than in attics that had not been altered [29]. A reference value of 1 µg m⁻³ for lindane (and PCP) in the indoor air was set by the German Federal Public Health Department in 1990 [30], this has to be considered for a classification of these concentration values.

2.2.1.2 Organic pollutants in the museum environment

Wood preservatives with biocides as active agents have been applied in museums for insect protection on organic exhibits, especially in the 1950s and 1960s [16]. Since 1956 lindane and DDT (until its prohibition) were used for the treatment of artworks [13]. A summary of possible application periods of biocides in museum environments was published by Schieweck et al. [3]. According to them PCP, lindane and DDT belong to the most applied biocides, whereby lindane seems to still be in use as preventative active agent. During their studies in several German museums Schieweck et al. conducted several investigations of indoor air, dust and material analysis, not only for biocides but also for VOCs, further SVOCs and organic acids. Furthermore, elemental analysis and nuclear radiation experiments have also been performed [1-3, 16].

A survey made by Spiegel [31] shows that biocides occur predominately in storage rooms and not in exhibition rooms or showcases, because of their use for acute insecticidal- and preventive-control in storage rooms.

Damages of the exhibits surfaces might be a result of former treatment with biocides. For example, DDT can cause blooming on the surface. By exceeding the saturation concentration white blooming or coatings become visible on the exhibits surfaces before the crystals finally evaporate [32].

Because of the wide range of contaminated exhibits made of various materials, several decontamination options have been developed and published by Unger [32] and Klinzmann [33], who used a heated chamber to minimize the emissions of the toxic components by accelerating their emission processes. Temperatures between 52-55 °C are obtained in the middle of the contaminated materials for this decontamination technique.

Emissions of organic compounds from building products or from showcase materials can also damage exhibits [3]. Exhibits are stored in showcases to be shielded from outside influences, for example dust, contaminated air and touching by visitors [34].

Unfortunately, they are still exposed to polluted air, because the showcase equipment (sealing compounds, clothes, coatings, wood plates etc.) emit VOCs as well as SVOCs. On this account showcases made of low emission materials are developed and constructed as a further contribution to preventive conservation [35, 36]. Since the air change rate in a showcase is usually close to zero it is of great importance for the objects stored inside that the emissions from construction materials are very low to prevent them from being damaged further by emitted components. The same applies to cupboards or storage containers in the storage rooms.

According to Schieweck and Salthammer [1] several other compounds or compound classes are relevant for the air quality in museums and storage rooms. PCBs and PAHs may also be found in the internal air of museums and their analysis is important for human and cultural safety. Textile dyes, paints and fireproofing agents, among others, are PCB containing products. One of the main PCB sources from indoors are the polymeric sealing materials, containing 5-45 % technical PCB mixtures [27]. PAHs are ingredients in mineral oil, bitumen and tar and are produced by microorganisms, plants and animals. Anthropogenic sources for PAHs are from smoking and food preparation e.g. from barbecuing and cooking [23]. Hence, food preparation and smoking in and around the museum can spoil the cultural assets with PAH contaminated air [1].

2.3 Literature studies: Air sampling adsorbents, strategies and measurements for biocides, PCBs and PAHs

A large number of publications relating to air sampling and analysis of biocides, PCBs and PAHs have been published and different air sampling adsorbents and air sampling strategies are presented for these compounds. Furthermore, several guidelines were developed presenting air sampling methods and strategies for these compound classes (see below).

Organic Indoor Air Pollutants [37] contains work by Jann and Wilke [38], Ball and Salthammer [28] and Butte [39] on sampling, analysis and occurrence of biocides, PCBs and PAHs in test chambers or indoor air. Horn et al. published an article about the analysis of biocides in test chambers [40].

The application of different air sampling adsorbents was investigated by several authors. Roinestad et al. [41] determined pesticides (among others lindane and permethrin) in indoor air with Tenax[®] TA. Air sampling with PUF, silica gel and XAD were performed by Blessing and Derra [30] for the determination of PCP and lindane indoors. Kasel et al. [42] published the air sampling of dichlofluanid, PCP and lindane with Chromosorb[®] 102. The sampling of benzo[a]pyrene with PUF was published by Turner and Glotfelty [43]. Lewis published some important articles in the late 1970s and the early 1980s regarding the air sampling of pesticides, PCBs and other SVOCs with PUF and a combination of PUF and granular adsorbents [44-46]. Lewis and Jackson [46] performed air sampling experiments for some PCBs and semi volatile pesticides with PUF combined with granular adsorbents (Chromosorb[®] 102, Porapak[®] R, Amberlite XAD-2, Tenax[®] GC and Florisil[®] PR Grade) to improve the sampling efficiency. The efficiency with granular

adsorbents is higher than with PUF but they are more expensive and have a higher air flow resistance than PUF. PCB 153 and p,p'-DDT were measured among others in these experiments. With PUF/XAD-2 the best results for PCB 153 have been obtained and for p,p'-DDT with PUF/Porapak[®] R. Lewis and MacLeod [45] sampled pesticides, PCBs and other SVOCs in indoor air with a combination of PUF and Tenax[®] GC. With reference to all of the aforementioned publications, the air sampling volume ranged from several liters up to several hundred cubic meters.

The use of PUF as an air sampling adsorbent has several advantages: it is cheaper than most of the other applicable adsorbents, it can be cleaned after use, it is easy to handle in the field and it has a low air flow resistance [46, 47]. Nevertheless, PUF also has disadvantages compared to other adsorbents; its work-up and cleaning is very time and solvent-consuming. However, both parameters can be reduced by using different air sampling adsorbents with an easier and faster work-up process.

Some of the aforementioned publications for sampling biocides and PCBs are the basis for the development of guidelines. The work of Lewis and MacLeod [45] as well as the work of Lewis et al. [44] contributed to the preparation of ASTM D 4861-11 [5]. Important for the preparation of VDI 4300 part 4 [4] was the work of Blessing and Derra [30].

Several guidelines describing air sampling methods for biocides, PCBs and PAHs with GC-MS analysis have been published. ASTM D 4861-11 [5] concerns the sampling and analysis of pesticides and PCBs and ASTM D 6209-98 [7] the sampling of PAHs. Furthermore, the VDI 4300 and VDI 4301 series contain parts with measurement strategies and measurements of PCBs, PAHs, and the two biocides PCP and lindane [6, 14, 48]. Moreover, the VDI 2464 describes the measurement of some PCBs [9] and VDI 3874 the determination of PAHs [8]. *Table 2.11* gives an overview of the mentioned guidelines and adsorbents.

Table 2.11: Guidelines for air sampling and analysis of biocides, PCBs and PAHs and their corresponding adsorbents

Guideline	Compounds	Adsorbents
ASTM D 4861-11 [5]	Pesticides, PCBs	(Particle filter if desired) PUF or PUF with granular adsorbents (Tenax [®] GC, XAD-2)
ASTM D 6209-98 [7]	PAHs	Particulate filter and PUF or XAD-2
VDI 4301 part 2 [6]	Lindane, PCP	Glass fiber filter and PUF
VDI 2464 [9]	PCB (28, 52, 101, 138, 153, 180)	Glass fiber filter and PUF
VDI 3874 [8]	PAHs	XAD-2

In these guidelines PUF is the medium used for air sampling of biocides and PCBs, and XAD-2 is the adsorbent for PAHs. Here and in other studies published in the literature the

work-up of PUF is performed by Soxhlet extraction, whereas Schoknecht et al. [49] published the work-up of PUF by extraction in an ultrasonic bath, which minimizes the time and solvent exposure and does not affect the quality of the results.

2.4 Air sampling strategies: Active sampling and diffusive sampling

Active or diffusive samplings are possible air sampling strategies for biocides, PCBs and PAHs. These are described in detail in the sections below.

2.4.1 Active sampling

Active sampling is defined as an air sampling strategy realizable with a pump and a defined air flow rate to pump air through a filter, an adsorbent, or both, on which particular or gaseous phase compounds are trapped. A combination is also possible [50]. When sampling SVOCs, including pesticides, or if a high sensitivity is required, large sampling volumes are necessary [51, 52]. The determination of concentrations with active sampling is only possible over a short period of time. If concentrations over longer time periods are to be determined several samples have to be taken [50]. However, active sampling with small sampling volumes and short sampling times is useful to investigate dynamic processes (e.g. kinetic experiments in emission test chambers) [52]. Several active air sampling adsorbents are mentioned above (see *Section 2.3*).

Active sampling is easily realizable indoors or outdoors as well as in test chambers with a suitable air change rate. In contrast, with air change rates close to zero, which is common in museum showcases, active sampling is difficult. An option to still realize this is retransferring the pumped air back into the showcase or test chamber after it has passed the adsorbent and the pump. However, by doing so the equilibrium inside the showcase or test chamber would unfortunately be disturbed.

2.4.2 Diffusive sampling

An alternative sampling option for SVOCs is diffusive sampling. Diffusive samplers are described as follows [53]: “A diffusive sampler is a device which is capable of taking samples of gas or vapor pollutants from the atmosphere at a rate controlled by a physical process, such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler.” The diffusion and permeation processes are described by Fick’s first law of diffusion [53]. In molar units it is

$$J = -D \frac{dc}{dx} .$$

Equation 2.1 [54]

- D – Diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
- $\frac{dc}{dx}$ – Concentration gradient [mol m^{-4}]
- J – Diffusion flux [$\text{mol m}^{-2} \text{s}^{-1}$]

Fick's first law is the result of different connected proportionalities: $J \sim s$; $s \sim F$ and

$F \sim \frac{dc}{dx}$ with the consequence that J is proportional to $\frac{dc}{dx}$ [54].

- s – Drift velocity
- F – thermodynamic force

In contrast to the short sampling times of active sampling, diffusive sampling can last for several days, weeks, months or even years, due to the diffusion driven process. Firstly airborne compounds need to enter the sampler before they get trapped by the adsorbent [50, 52] and the adsorbents need to have a high retention capacity for the compounds they collect [51]. Long time or seasonal measurements of concentrations in air are easier to realize with diffusive samplers than with active samplers [50, 52].

Common diffusive samplers are semi-permeable membrane devices (SPMD), PUF disks, XAD-2, solid-phase microextraction (SPME) fibers and polymer-coated glass samplers (POG). SPMDs consist of a polyethylene membrane containing a thin film of triolein, a neutral synthetic lipid, and the compounds accumulate in the lipid phase. SPME fibers are made of fused silica coated with a thin layer of sorbent. The advantage of SPME is its one step combination of sampling and preconcentration [50]. POGs are made of a thin polymeric stationary phase (ethylene vinyl acetate) on a glass surface [51].

2.5 Emission test chambers

Emission test chambers are used to investigate the emission behavior of materials under standardized and extensively constant conditions. The definition of an emission test chamber by DIN EN ISO 16000-9 [55] is as follows: "Enclosure with controlled operational parameters for the determination of volatile organic compounds emitted from building products".

The determination of VOC and SVOC emissions from materials is predominantly performed in emission test chambers, which are available in different sizes from a few cm^3

to several m^3 [56]. Emission test chambers serve as simulations of interiors with several advantages; in contrast to interiors, the sink-effect¹ can be easily reduced to the chamber surface and the sample itself. Furthermore, the emission of just one material is measurable. Emission tests are carried out with certain adjustments of temperature T , relative humidity $r. h.$, air change rate n , air velocity and product loading factor L [56]. The area specific air flow rate q is a further parameter in emission test chamber measurements, which is calculated from the air change rate and product loading factor.

$$q = \frac{n}{L} \quad \text{Equation 2.2}$$

- q – Area specific air flow rate [$\text{m}^3 \text{m}^{-2}\text{h}^{-1}$]
- n – Air change rate [h^{-1}]
- L – Product loading factor [$\text{m}^2 \text{m}^{-3}$]

Using the area specific air flow rate from *Equation 2.2* and the measured concentration c the area specific emission rate SE_{R_a} can be calculated. The SE_{R_a} is useful to compare results of the same samples in different emission test chambers.

$$SE_{R_a} = c \cdot \frac{n}{L} = c \cdot q \quad \text{Equation 2.3}$$

- SE_{R_a} – Area specific emission rate [$\mu\text{g} \text{m}^{-2}\text{h}^{-1}$]
- c – Concentration [$\mu\text{g} \text{m}^{-3}$]

The necessary parameters for measurements in emission test chambers can be regulated by the user and are adjusted before the measurement starts. In accordance with DIN EN ISO 16000-9 the air velocity over the surface of the test specimen has to be between $0.1\text{-}0.3 \text{ m s}^{-1}$ [55]. The measurements of this thesis are realized in three different

¹ Sink-effect: The sink effect describes the ability of components, emitting from a material, to adsorb within the emission test chamber. This effect is influenced by the construction materials [56]. Furthermore, the samples in the emission test chambers also act as sinks [57] however, this behavior cannot be controlled [58].

emission test chamber types: Micro-Chamber/Thermal Extractor™ (μ -CTE™, Markes International), 23 l and 24 l emission test chambers and 27 l showcase. These chambers are described below.

2.5.1 Micro-chamber (μ -CTE)

The μ -CTE (*Figure 2.11* and *Figure 2.12*) has been developed for rapid analysis of VOCs and SVOCs emitting from materials. It consists of six cylindrical stainless steel chambers in a heating block with a volume of 44 ml. The temperature range is from ambient to 120 °C [59]. The chambers are supplied with a controlled flow of synthetic air, adjusted via a controller, through the chamber lid. Before the synthetic air enters the chamber it is preheated to the adjusted chamber temperature. At the sampling port (*Figure 2.13*) in the lid, the air exits the chamber with a definite air flow and for that reason passive air sampling is done.

The idea of the μ -CTE is to reduce the chamber volume and consequently the testing time [56]. Fast and meaningful analysis of materials are possible in μ -CTE tests, these are less time-consuming and more economically viable in contrast to conventional emission test chamber tests. However, the results of μ -CTE tests are supposed to correlate with the results obtained by using conventional emission test chambers [60]. Schripp et al. performed several test experiments with the μ -CTE including the computational calculation of the fluid dynamics [60].



Figure 2.11: μ -CTE



Figure 2.12: μ -CTE inside view

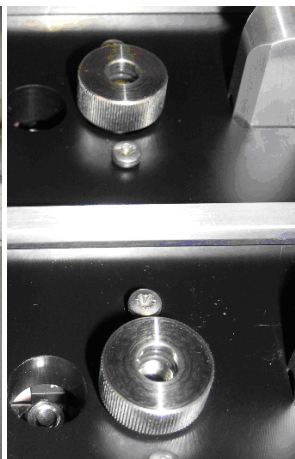


Figure 2.13: μ -CTE sampling port

2.5.2 23 l and 24 l Emission test chambers

24 l emission test chambers (*Figure 2.14*) have been successfully used in the past to determine biocide emissions from materials [38, 40]. The chamber volume can be

increased from 23 l to 24 l by introducing a stainless steel ring, equipped with further air sampling ports, between the chamber pot and lid. Ventilators are part of these emission test chambers to guarantee air circulation. Purified air is used for the air supply of these chambers and the humidity is regulated by mixing wet and dry air.

Flow patterns describing the influence of ventilators and samples on the air circulation were published by Müller et al. [61]. *Figure 2.15* to *Figure 2.17* present the corresponding flow patterns of the chamber top, center and bottom. Strong turbulences are present in the top and center of the chambers, whereas only low turbulences exist in the bottom. This might be a result of the samples standing on the chamber's bottom like shown in *Figure 2.18*.



Figure 2.14: 24 l Emission test chamber

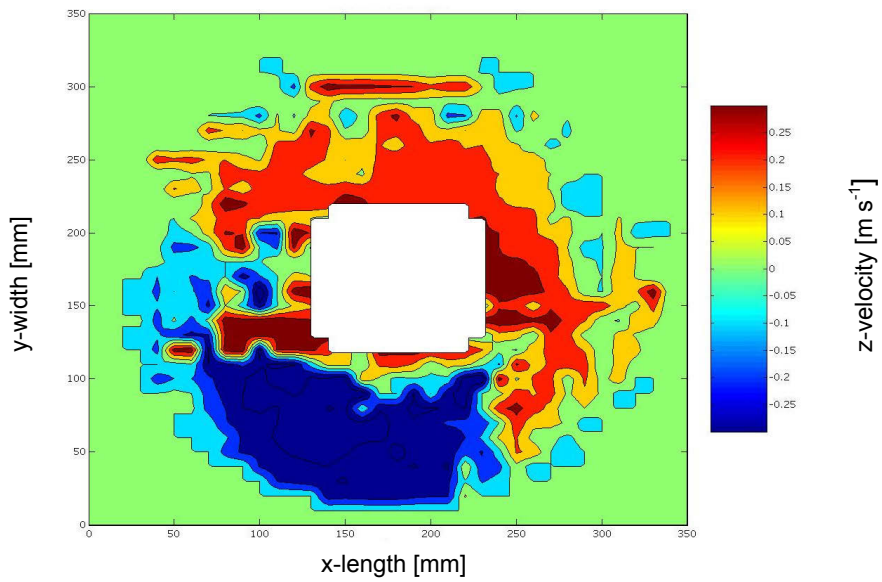


Figure 2.15: Flow pattern of the chamber's top [61]

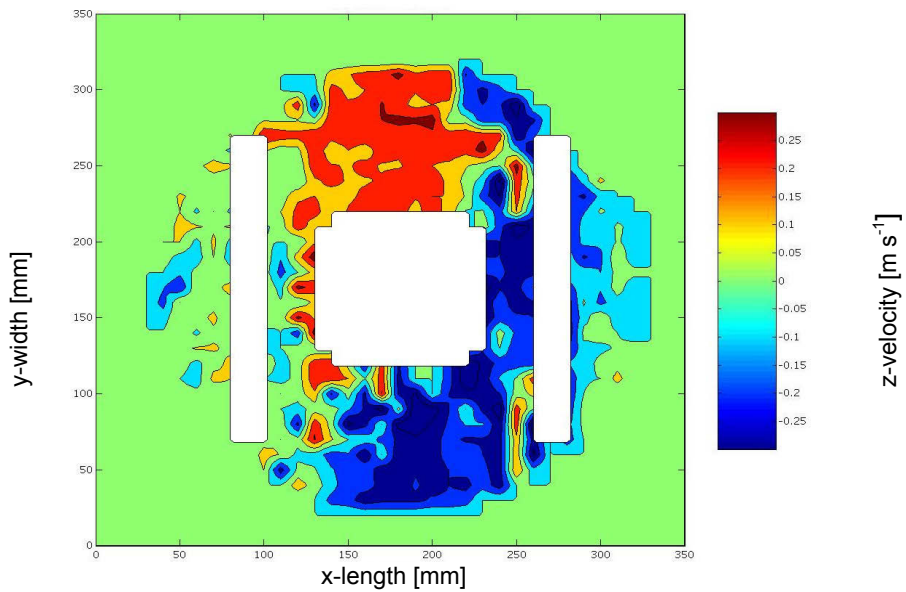


Figure 2.16: Flow pattern of the chamber's center [61]

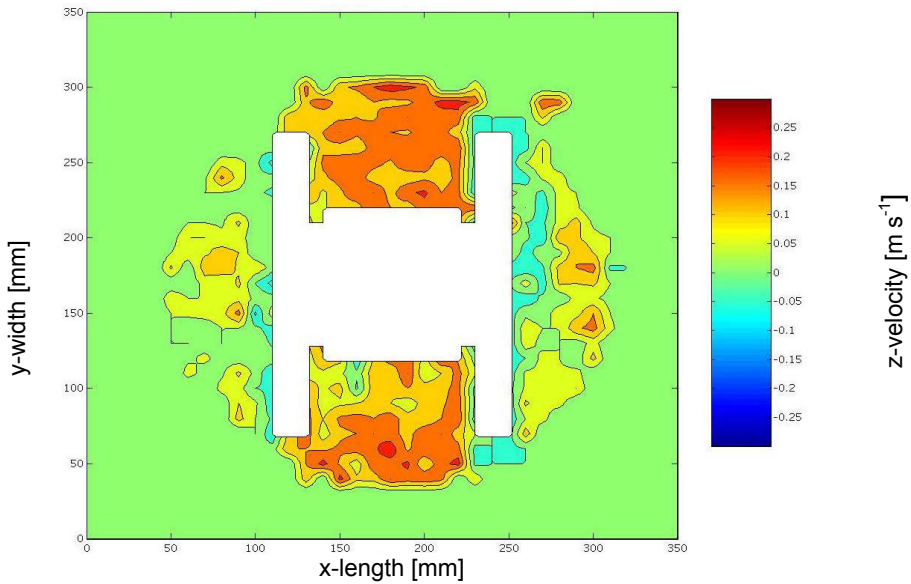


Figure 2.17: Flow pattern of the chamber's bottom [61]

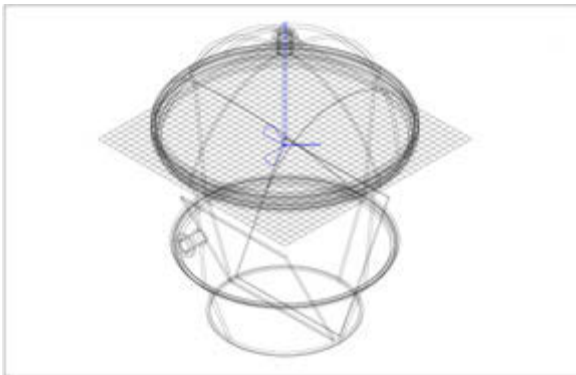


Figure 2.18: Emission test chamber with samples inside [61]

2.5.3 Showcases

The aim of museum showcases is the long-term protection of cultural assets and artifacts from external damages and influences. Many different showcase constructions and sizes are available and they can be made of one or more materials (e.g. glass, wood, clothes and concrete). Simple quadratic glass construction showcases (Figure 2.19) with a

volume of 27 l stuck together with a siloxane containing glue are used in this thesis. The advantage of these glass showcases is that the only emitting source is the siloxane containing sealant but not the construction material itself. A clean air- and humidity-instrument is available to control the humidification of the showcase air. Each showcase is equipped with four ports in the lid used for air supply, air sampling, a humidification sensor and a control sensor. The air, used for humidification, is sucked in via a filter into an air washer in a water tank (Figure 2.20). The water is necessary to humidify the air, which is then transferred to the clean air- and humidity-instrument. From here the air passes a flow regulator and a controlled air flow is introduced into the showcase. In later experiments the showcases are equipped with a ventilator (Figure 2.21) to provide air circulation as in the emission test chamber.

As mentioned above the main task of a showcase is to prevent the objects stored inside from external influences, including the protection from external pollutants. Air change rates close to zero are essential to guarantee the protection of cultural assets but since pollutants can be emitted by the objects or the showcase materials themselves, these low air change rates are a problem for the objects inside. When air change does not occur the objects are continually exposed to the pollutants, which is why they can easily become damaged (see Section 2.2.1.2). A further disadvantage of low air change rates is the impossible performance of active air sampling up to now.

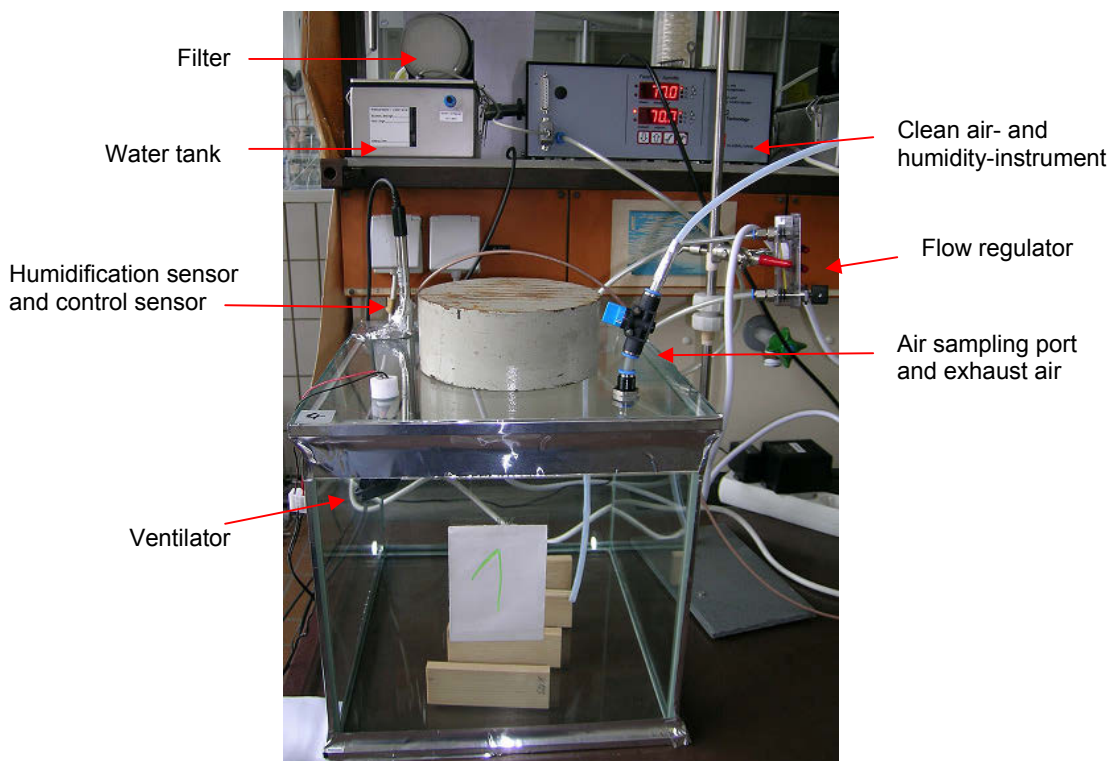


Figure 2.19: A showcase and its equipment

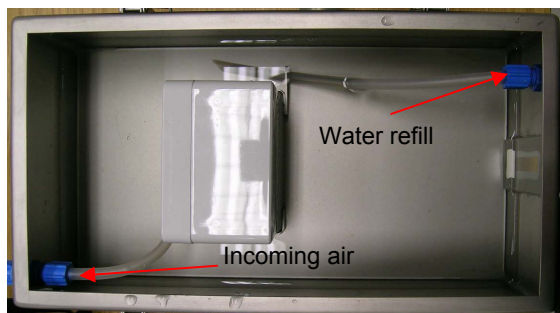


Figure 2.20: Air washer in the water tank



Figure 2.21: Ventilator

2.5.4 Comparison of the chamber types

A comparison of the three chamber types is given in *Table 2.12*.

Table 2.12: Comparison of the μ -CTE, emission test chamber and 27 l showcase

μ -CTE	23 l and 24 l emission test chamber	27 l showcase
<ul style="list-style-type: none"> - Cylindrical shape - Temperatures up to 120 °C are possible - Air flow is adjustable - Synthetic air for air supply - Relative humidity is neglected 	<ul style="list-style-type: none"> - Cylindrical shape - Ventilator for air circulation - Heating of the chamber is possible - Air flow is adjustable - Air supply with purified and humidified air - Relative humidity is adjustable 	<ul style="list-style-type: none"> - Quadratic shape - Commonly no ventilator - Sealant is a further sink - Heating is impossible, sealant components would emit - Air change rate is mostly ≈ 0 in museums - Air change occurs with the ambient (contaminated) air - Relative humidity is adjustable

The lack of a ventilator in the showcase affects the inner air circulation. μ -CTE cells also miss a ventilator but the cell size is lower and the air flow through each cell is mostly higher, which leads to air circulation. When adequate air circulation does not occur the emitted compounds from exhibits in a showcase might stick to their surfaces instead of adsorbing at the showcase surface. This and the missing air change in showcases can cause additional influence on the exhibit lifetime. Therefore an air change rate > 0 is useful to avoid damages on the exhibits.

2.6 Measurement: Multiple reaction monitoring

Measurements in the multiple reaction monitoring (MRM) mode are possible with triple quadrupole MS-MS systems, where both quadrupoles work in the selected ion monitoring (SIM) mode. The main advantages of the MRM-mode in contrast to the scan- and SIM-mode of single quadrupole and triple quadrupole systems are lower limits of detection due to higher selectivity. The methods of the MRM- and SIM-mode are similar: Only selected fragments reach the detector but in the MRM-mode the ions are fragmented twice, which improves the selectivity compared to the SIM-mode. The selection of suited precursor and product ions is necessary for MRM-measurements as well as the correct collision energies (CE), which improve the quality of the measurements.

The MRM-technique can be described as follows: Ions with determined mass-to-charge ratios pass the first quadrupole. These precursor ions enter the second quadrupole (collision cell) where they are fragmented due to collisions with neutral gas molecules (N_2 molecules), this is collision induced dissociation. These collisions result in a compound specific fragmentation – the so called product ions, which pass the third quadrupole and are detected in the detector [62]. See *Figure 2.22* for a schematic diagram of the MRM-mode.

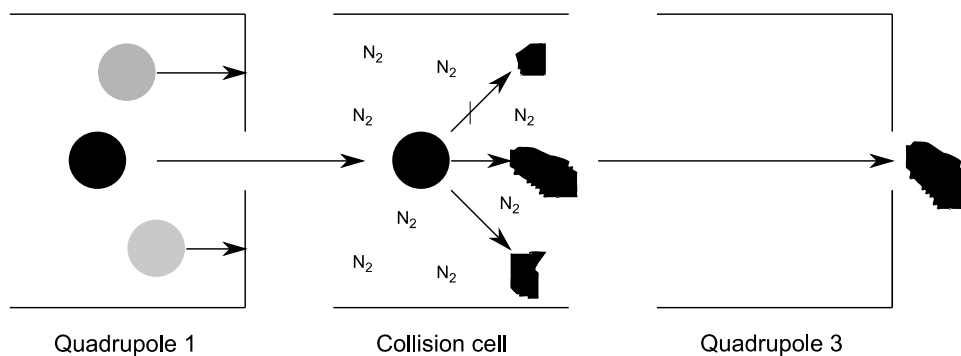


Figure 2.22: A schematic diagram of the MRM-mode

3 Materials and methods

3.1 Instrumentation

The measurements were carried out on a GC-MS-MS system from Agilent Technologies (GC: 7890 A; MS-MS: 7000 A) with a linear quadrupole unit and a linear hexapole collision cell. It was equipped with a cooled injection system (CIS) from Gerstel for liquid injection, and nitrogen was the collision gas for the MS-MS system. The chromatographic separation of the SVOCs was realized on a HP-5MS (5 % phenyl, 95 % dimethylpolysiloxane) column (30 m × 0.25 mm × 0.25 μm). The software for the GC-MS-MS system was Mass Hunter B.05.00 and for the injection system Gerstel Maestro 1.3.20.41.

3.2 Quantification and identification

Quantification and identification was performed in accordance with internal standards (ISTD) and calibration curves, which consisted of seven or eight calibration levels in different concentration ranges, all in ng μl⁻¹. ISTD 4-(4-chlorobenzoyl) pyridine and dieldrin were used and both were selected as they have been used previously (see Schoknecht et al. [63] and Jann et al. [64]). 4-(4-Chlorobenzoyl) pyridine was the ISTD for PCP and lindane, dieldrin was the ISTD for PCB 28, dichlofluanid, isodrin, tolyfluanid, PCB 153, p,p'-DDT, permethrin and benzo[a]pyrene.

4 Method development

The aim of the study is to find an air sampling strategy for selected SVOCs and POMs at low air change rates, while simultaneously determining as many compounds as possible and preferably with as few adsorbents as possible. The best outcome would be with only one. The idea is to use cartridges equipped with the suitable polymer, which requires a wet chemical work-up process. Because the selected compounds are from different compound groups (biocides, PCBs and PAHs) and classes (SVOC and POM), their physico-chemical properties such as boiling points and vapor pressures, differ partially strongly from each other (see *Section 2.1*), which needs to be taken into account when selecting the adsorbent.

The method development itself is divided into two parts: Firstly an analytical method for the GC-MS-MS system is required, including temperature programs for the GC oven and CIS and the selection of precursor ions, product ions and CEs of each compound for MRM measurements. The second part is the selection of an appropriate adsorbent and strategy for low volume air sampling of the selected biocides, PCBs and PAHs, which is then tested in several pre-tests in the μ -CTE with target compound solutions before further measurements with self soaked wood samples in the μ -CTE, emission test chambers (23 l and 24 l) and showcases (27 l) are performed. As air sampling at low air change rates should be realized a suitable strategy needs to be developed, which takes active sampling and active sampling with retransfer of the sampled air back into the test chamber into account. These options are tested in 23 l and 24 l emission test chambers and showcases. Retransfer of the sampled air back into the test chamber is necessary, because the air flow of the sampled air volume is higher than the air flow of the air supply.

Unfortunately the development of the temperature programs and the adsorbent selection had to be done without PCP and p,p'-DDT, because both compounds were not available at the time.

4.1 GC-MS-MS method

The development of the GC-MS-MS measurement method includes the selection of suitable GC oven and CIS temperature programs and the determination of a proper injection volume. A large number of oven temperature programs are published in the literature for these compounds and the used column type and a few of them were tested for the selected compounds (see [65-69]) and optimized for the utilized system. Several temperatures and heating rates were also tested and optimized for the CIS temperature program. The developed temperature programs and the injection volume are as follows:

- CIS temperature program: 60 °C for 0.01 min, 12 °C s⁻¹ to 280 °C for 3 min
- GC oven temperature program: splitless, 60 °C for 2 min, 40 °C min⁻¹ to 100 °C, 15 °C min⁻¹ to 300 °C for 5 min (run time 21.33 min)
- Injection volume: 1 μ l until changes at the injection system were made, injection volume was then reduced to 0.4 μ l

4.1.1 Multiple reaction monitoring measurements

MRM-measurements were selected for the analysis of this study because of their higher selectivity in contrast to scan- or SIM-measurements with triple or single quadrupole mass spectrometers. Since low sampling volumes are targeted it is necessary to use an analytical procedure with a very high selectivity and sensitivity, which is also relevant especially for real samples with a higher signal to noise ratio due to matrix effects.

The development of a MRM-method includes the selection of precursor ions, product ions and CEs for the fragmentation of the precursor ions in the hexapole. MRM-measurement details (including CEs, precursor and product ions) of a large number of biocides published by Walorczyk [65] were used as initial values for the selection of proper CEs, precursor and product ions. In *Table 4.1* the transitions for quantification and identification and the corresponding CEs of the compounds necessary for MRM-measurements are listed.

Table 4.1: MS-MS transitions for quantification and identification and CEs for MRM-measurements

Compound	Quantification			Identification		
	Precursor ion	Product ion	CE [eV]	Precursor ion	Product ion	CE [eV]
(derivatized) PCP	266	> 167	35	165	> 130	35
Lindane	181	> 145	15	219	> 183	10
¹³ C ₆ Lindane	225	> 189	5	153	> 117	5
4-(4-Chlorobenzoyl)pyridine	217	> 139	20	111	> 51	20
PCB 28	255	> 186	30	185	> 151	30
Dichlofluanid	224	> 123	20	123	> 96	20
Isodrin	192	> 123	25	66	> 51	25
Tolyfluanid	137	> 91	25	238	> 137	25
Dieldrin	79	> 51	35	262	> 193	35
PCB 153	359	> 289	25	289	> 218	25
p,p'-DDT	235	> 165	30	165	> 115	30
Permethrin 1	163	> 91	10	182	> 153	10
Permethrin 2	163	> 91	10	182	> 153	10
Benzo[a]pyrene	126	> 113	5	251	> 223	5

Figure 4.1 shows a MRM-chromatogram of all compounds from a calibration solution measured with the parameters presented in *Table 4.1*.

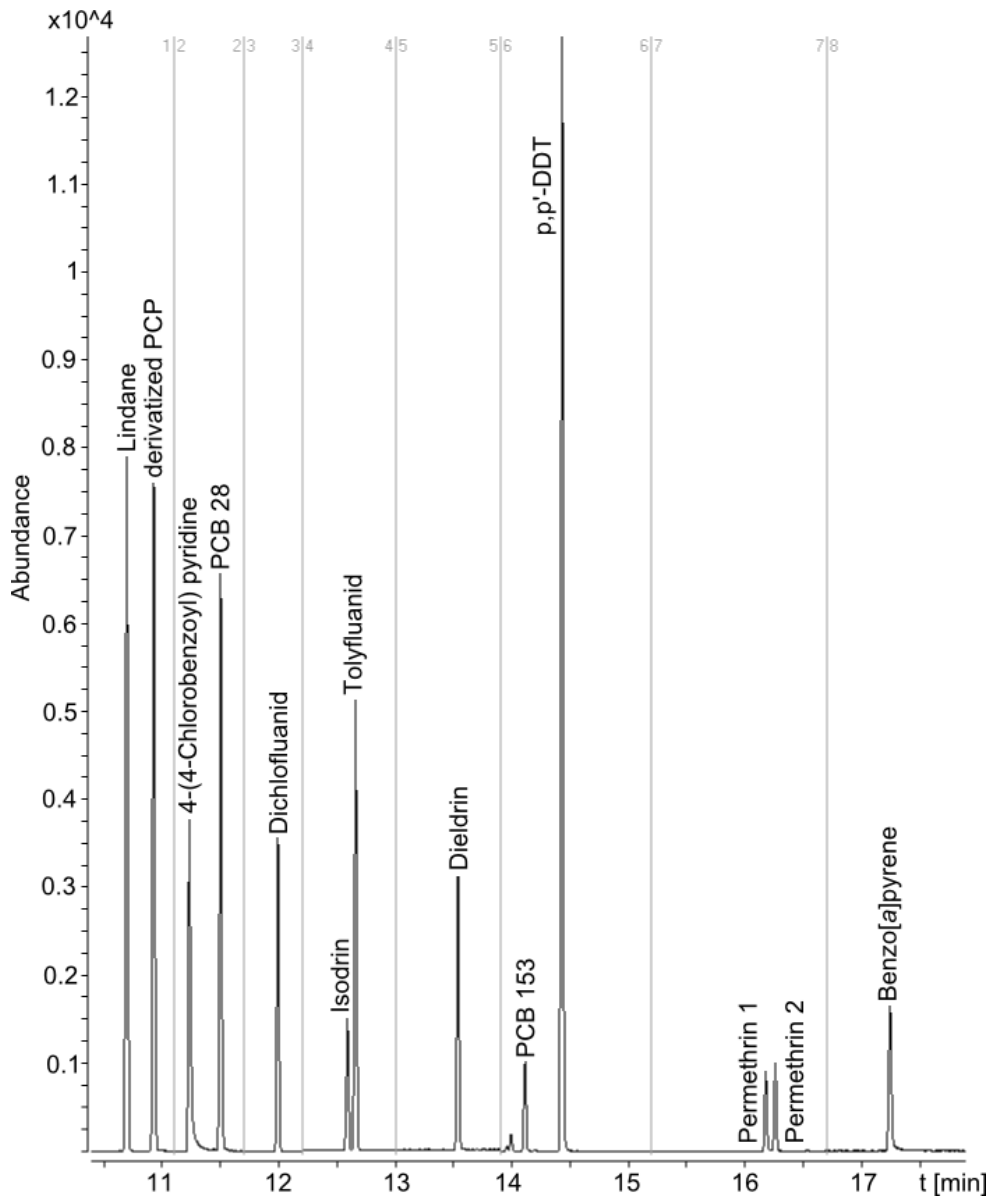


Figure 4.1: MRM-chromatogram of a calibration solution ($c \approx 1.5 \text{ ng } \mu\text{l}^{-1}$)

4.1.2 Statistical parameters of the GC-MS-MS method

4.1.2.1 Limit of detection and limit of quantification

The limits of detection (LoD) and limits of quantification (LoQ) of the GC-MS-MS system were determined in accordance with DIN 32645 [70]. A calibration solution close to the LoQ is necessary for their determination and the calculations are performed using Statist version 2.0 [71] using *Equation 4.1* for the LoD and *Equation 4.2* for the LoQ.

$$x_{LoD} = s_{x_0} \cdot t_{f;a} \sqrt{\left(\frac{1}{m} + \frac{1}{n} + \frac{\bar{x}^2}{Q_x} \right)} \quad \text{Equation 4.1}$$

with $f = n - 2$

$$x_{LoQ} = k \cdot s_{x_0} \cdot t_{f;a/2} \sqrt{\left(\frac{1}{m} + \frac{1}{n} + \frac{(x_{LoQ} - \bar{x})^2}{Q_x} \right)} \quad \text{Equation 4.2}$$

with $f = n - 2$

A good approximation of the LoQ is obtained by substituting x_{LoQ} with $k \cdot x_{LoD}$ [70].

- \bar{X} – arithmetic average of the contents of all calibration samples
- k – relative uncertainty
- m – number of measurements of the analysis sample
- n – number of calibration samples
- Q_x – deviance of x at the calibration
- s_{x_0} – standard *deviation of the method*
- $t_{f;a}$ – quantile of the t-distribution by a one-sided interrogation for a type I error
- $t_{f;a/2}$ – quantile of the t-distribution by a two-sided interrogation for a type I error

The LoD and LoQ values in $\text{ng } \mu\text{l}^{-1}$ for the GC-MS-MS system are shown in *Table 4.2*. *Table 9.9* in *Section 9.3.2* shows the required LoQ values for all used air sampling volumes in $\mu\text{g m}^{-3}$, which were calculated based on the values in *Table 4.2*.

Table 4.2: LoD and LoQ values determined in accordance with DIN 32645 [70]

Compound	LoD [$\text{ng } \mu\text{l}^{-1}$]	LoQ [$\text{ng } \mu\text{l}^{-1}$]
PCP	0.13	0.43
Lindane	0.01	0.03
derivatized PCP	0.01	0.05
PCB 28	0.03	0.09
Dichlofluanid	0.02	0.05
Isodrin	0.01	0.05
Tolyfluanid	0.01	0.05
PCB 153	0.02	0.07
p,p'-DDT	0.01	0.04
Permethrin 1	0.06	0.25
Permethrin 2	0.10	0.37
Benzo[a]pyrene	0.05	0.20

4.1.2.2 Reproducibility

The reproducibility of the GC-MS-MS system was checked for different concentrations with calibration solutions ($c_1 \approx 0.3 \text{ ng } \mu\text{l}^{-1}$; $c_2 \approx 0.6 \text{ ng } \mu\text{l}^{-1}$; $c_3 \approx 3 \text{ ng } \mu\text{l}^{-1}$ and $c_4 \approx 6 \text{ ng } \mu\text{l}^{-1}$) in a multiple determination ($n = 10$). *Table 4.3* shows the standard deviation s and relative standard deviation RSD of the multiple determinations.

Table 4.3: Reproducibility of the GC-MS-MS system ($n = 10$)

Concentration	$c_1 \approx 0.3 \text{ [ng } \mu\text{l}^{-1}]$		$c_2 \approx 0.6 \text{ [ng } \mu\text{l}^{-1}]$	
Compound	s [ng μl^{-1}]	RSD [%]	s [ng μl^{-1}]	RSD [%]
Lindane	0.020	5.56	0.016	3.20
PCP	0.012	3.38	0.015	2.25
PCB 28	0.006	2.17	0.014	2.17
Dichlofluanid	0.005	1.73	0.007	1.01
Isodrin	0.007	2.44	0.010	1.53
Tolyfluanid	0.004	1.40	0.005	0.68
PCB 153	0.008	3.07	0.015	2.41
p,p-DDT	0.012	3.93	0.007	0.99
Permethrin 1	0.006	2.31	0.018	2.22
Permethrin 2	0.011	4.01	0.006	0.66
Benzo[a]pyrene	0.020	6.06	0.005	0.71
Concentration	$c_3 \approx 3 \text{ [ng } \mu\text{l}^{-1}]$		$c_4 \approx 6 \text{ [ng } \mu\text{l}^{-1}]$	
Compound	s [ng μl^{-1}]	RSD [%]	s [ng μl^{-1}]	RSD [%]
Lindane	0.24	6.15	0.50	8.09
PCP	0.30	6.39	0.45	7.19
PCB 28	0.05	1.81	0.17	2.35
Dichlofluanid	0.01	0.43	0.06	0.95
Isodrin	0.03	1.09	0.13	1.71
Tolyfluanid	0.02	0.80	0.06	0.97
PCB 153	0.04	1.49	0.06	0.74
p,p-DDT	0.03	1.20	0.04	0.66
Permethrin 1	0.08	2.65	0.04	0.71
Permethrin 2	0.05	1.88	0.04	0.73
Benzo[a]pyrene	0.06	2.61	0.08	1.29

4.1.2.3 Linearity of the calibration

According to Funk et al. [72] the linearity of the calibrations is checked with Mandel's goodness-of-fit test. This test uses the first order calibration function ($y = a + bx$) and the second order calibration function ($y = a + bx + cx^2$) and includes their residual standard deviations s_y (s_{y_1} and s_{y_2}) (Equation 4.3).

$$s_y = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{N - 2}}$$

Equation 4.3

with $\hat{y}_i = a + bx_i$

The difference of the variances DS^2 (Equation 4.4) is calculated with the residual standard deviations s_{y_1} and s_{y_2} .

$$DS^2 = (N - 2)s_{y_1}^2 - (N - 3)s_{y_2}^2 \quad \text{Equation 4.4}$$

with $f = 1$

The test value TV is calculated with DS^2 (Equation 4.4) for the F-test.

$$TV = \frac{DS^2}{s_{y_2}^2} \quad \text{Equation 4.5}$$

This is compared with the tabular value of F ($f_1 = 1$, $f_2 = N - 3$, $P = 99\%$). If TV is less than or equal to F no significant goodness of fit is achieved with the second order calibration function; a linear calibration function is present.

The linearity was checked for every calibration. If Mandel's goodness-of-fit test was negative for a linear evaluation of the calibration, the considered range was decreased into the relevant operating range. The TV and F -values of every calibration are shown in Table 9.10 to Table 9.21 in Section 9.3.3.

4.2 Adsorbent selection

The second step of the method development was the selection of an appropriate adsorbent to sample selected SVOCs and POMs in the chamber and indoor air. Several adsorbents were examined with regard to their suitability as an air sampling medium for the selected biocides, PCBs and PAHs (see Table 4.4). The adsorbents were either chosen due to their previous successful use for some of the selected SVOCs and POMs or based on the indicated field of application given by the manufacturer. Firstly, the applicability of the adsorbents for their power to elute the aforementioned compounds as a function of recovery rates was checked; subsequently the best adsorbent from this elution test was used for air sampling experiments. Several experiments to test the air sampling quality of the adsorbent were realized in the μ -CTE loaded with solutions of the target compounds.

Table 4.4: List of the tested adsorbents

Adsorbent	Amount of adsorbent [mg]
Silica*	1000
Silica*	500
Styrene divinylbenzene polymer*	500 / 200
Styrene divinylbenzene polymer*	50
Magnesium silicate (MgO ₃ Si)	500
-SiCH ₂ CH ₂ CH ₂ CN (Cyanopropyl)	200
-SiC ₁₈ H ₃₇ (Trifunctional octadecyl)	100
Polyurethane foam	

* Different manufacturers

Solutions of the target compounds (without PCP and p,p'-DDT) were used for the elution tests with the adsorbents mentioned in Table 4.4 and their amounts were correlated to the adsorbent amount. The results of the elution tests are shown in Table 4.5. The 200 mg styrene divinylbenzene (SDVB) polymer is the best adsorbent for the selected SVOCs and POMs. By comparing the results of the SDVB-polymer and the commonly used PUF it can be seen that the SDVB-polymer recovery rates are higher. For the other adsorbents the recovery rates are either too low, too high or an elution of all compounds was not possible.

Table 4.5: Recovery rates [%] of the elution experiments with several adsorbents

Adsorbent	SDVB ⁺ (50 mg) 1	SDVB ⁺ (50 mg) 2	SDVB [#] (200 mg) 1	SDVB [#] (200 mg) 2	SDVB [#] (500 mg)	SDVB [*] (500 mg)
Compound	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Lindane	92	120	92	98	79	104
PCB 28	127	131	95	99	76	-
Dichlofluanid	69	124	98	102	97	-
Isodrin	97	126	98	102	78	118
Tolyfluanid	68	120	96	99	85	-
PCB 153	89	129	101	104	84	99
Permethrin 1	53	126	96	98	74	78
Permethrin 2	72	115	100	102	85	96
Benzo[a]pyrene	57	108	96	98	81	49

Adsorbent	Silica (500 mg)	Silica (1000 mg)	-SiCH ₂ CH ₂ - CH ₂ CN (200 mg)	MgO ₃ Si (500 mg)	-SiC ₁₈ H ₃₇ (100 mg)	PUF	PUF
Compound	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]	Recovery rate [%]
Lindane	111	75	63	80	125	51	46
PCB 28	-	82	54	-	107	74	111
Dichlofluanid	-	109	81	-	110	72	72
Isodrin	126	72	60	91	130	75	73
Tolyfluanid	-	-	71	-	115	76	73
PCB 153	118	82	69	92	141	77	77
Permethrin 1	-	87	49	-	88	90	82
Permethrin 2	-	92	57	-	86	104	95
Benzo[a]pyrene	-	70	65	-	120	98	90

^{†#/*} - SDVB-polymers with different features

The selected SDVB-polymer is equivalent to XAD-2 and consists of a surface-modified polymeric surface with hydrophilic, hydrophobic or pi-pi retention mechanisms. It is generally useful for screening of acidic, basic and neutral compounds by reversed phase and polar and non-polar compounds can also be extracted using this adsorbent [73]. *Figure 4.2* presents the schematic diagram of a cartridge filled with polymer and two filters. The cartridge is made of polypropylene and the filters are made of polyethylene (PE).

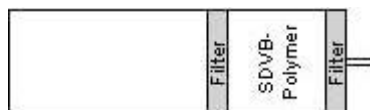


Figure 4.2: Schematic diagram of a cartridge equipped with SDVB-polymer and two PE filters

4.2.1 Determination of the elution volume

Additionally to the selection of an appropriate adsorbent, tests were performed for a work-up of this adsorbent. The necessary amount of solvent needed to moisten the SDVB-polymer and the required amount of solvent for a complete elution of the compounds were ascertained by undertaking duplicate determinations. Elution volumes of 1000 μl , $2 \times 500 \mu\text{l}$, 1500 μl and $3 \times 500 \mu\text{l}$ were tested and the adsorbent was eluted three times with the mentioned amounts to determine whether or not parts of the compounds remain on the adsorbent.

The evaluation of the required elution volume was done based on the peak responses, which were compared for a selection of the elution volumes. The results are shown in *Table 9.22* and *Table 9.23* in *Section 9.3.4*. A complete elution of the SDVB-polymer in the first elution was obtained with an elution volume of $3 \times 500 \mu\text{l}$. 1-2 % remained on the adsorbent after the first elution when using a volume of 1500 μl and by using a total volume of 1000 μl , 1-8 % of the compounds remained on the adsorbent.

4.2.2 Elution test

The elution experiment with the SDVB-polymer was repeated in a fivefold determination in the final stage of this method development to quantify the uncertainty in measurement for the elution process. In *Table 4.6* the results, as recovery rates, are shown but they are different for some compounds compared to the adsorbent selection elution tests, which were performed at the beginning. Several parameters (moistening amount, pre conditioning, elution volume, ISTD concentrations and injection volume, for details see *Section 9.2.2.1*) were changed in the meantime. Lindane, dichlofluanid and tolyfluanid have lower recovery rates in this experiment, whereas benzo[a]pyrene has a higher recovery rate of approximately 125 %. Unfortunately it is not possible to get an elution of PCP from this adsorbent under the given conditions; toluene might be the wrong solvent to desorb PCP from the polymer. PCB 28, isodrin, permethrin 1, permethrin 2 and benzo[a]pyrene have recoveries higher than 100 %, which is inexplicable, because neither

the blank SDVB-polymer nor the blank GC-MS-MS system show any contaminations with these compounds.

Table 4.6: Recovery rates [%] of the elution experiment with the SDVB-polymer in a fivefold determination

Compound	Elution 1 Recovery rate [%]	Elution 2 Recovery rate [%]	Elution 3 Recovery rate [%]	Elution 4 Recovery rate [%]	Elution 5 Recovery rate [%]
Lindane	56	56	59	58	62
PCB 28	102	102	102	106	107
Dichlofluanid	88	88	87	89	89
Isodrin	104	104	104	106	107
Tolyfluanid	86	86	86	88	88
PCB 153	97	97	96	99	99
p,p'-DDT	93	94	94	96	96
Permethrin 1	111	108	106	110	110
Permethrin 2	104	102	101	104	105
Benzo[a]pyrene	122	125	126	129	130

4.3 Emission test chamber measurements

As already described in the literature, the detection of SVOCs in emission test chambers at an ambient temperature requires huge sampling volumes of up to several m³ and their emission process can last up to several months or years [40]. For that reason an air sampling strategy with lower sampling volumes has been developed and experiments were partially performed at higher temperatures. They are important to speed up the emission process of the compounds by forcing the vaporization of the higher boiling SVOCs and POMs into the gaseous phase and therefore get faster results showing sample content and emission behavior. Furthermore, better predictions of the long term emission behavior at ambient temperature are possible e.g. a more precise chronological estimation.

According to the standards (ASTM D 6209-98 [7] and VDI 4301 part 2 [6]) large sampling volumes up to several m³ are required for the air sampling of biocides and PAHs with PUF or XAD-2 for the intended LoQ. The sampling volume of the new air sampling strategy should not exceed one hundred liters, because the sampling time would be large due to the high air flow resistance of the SDVB-polymer and because of the lower air flows as a result of the lower air change rates.

The whole working process is shown schematically in *Figure 4.3*.

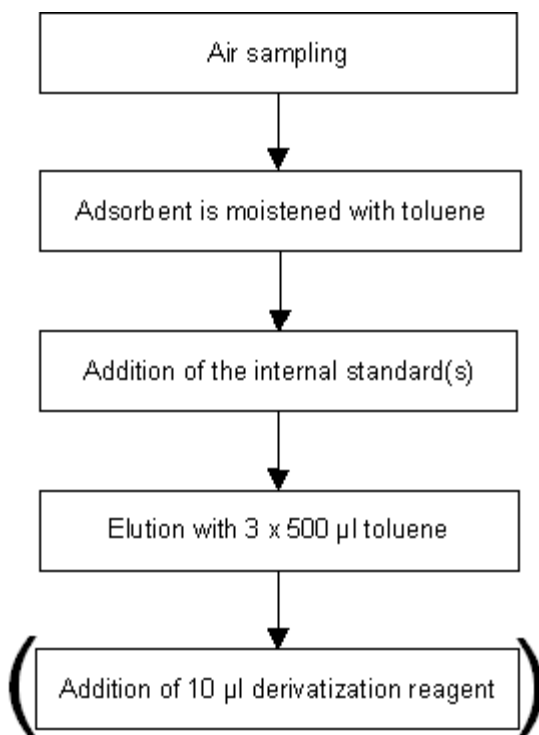


Figure 4.3: Schematic overview of the working process

The emission test chamber measurements were conducted in a μ -CTE, in 27 I showcases and 23 I and 24 I emission test chambers. A detailed description of these chambers was discussed previously in *Section 2.5*. In the following text their advantages for this study are explained.

A μ -CTE was used for air sampling experiments in this study because it can operate in a temperature range from ambient up to 120 °C and it has a low inner surface area. Since experiments at higher temperatures are important to force the vaporization of the higher boiling SVOCs into the gaseous phase, all μ -CTE tests were conducted at 23 °C and 80 °C. Experiments at higher temperatures are also useful for method development and to screen real samples, as well as for simulating air sampling under real conditions (up to 60 °C can occur in showcases).

Since part of this study concerns the development of an air sampling method at low air change rates, work needs to be carried out at these low air change rates. These showcases allow experiments under real life conditions at ambient temperature and furthermore they can be equipped with a clean air- and humidity-instrument to check the influence of relative humidity and air change rates on the emission behavior of the SVOCs and POMs. Simulations at higher temperatures should be done with the μ -CTE or in 23 I

emission test chambers, because the showcases cannot be heated the same way as the other two chambers.

The 23 l and 24 l emission test chambers were selected for experiments of this study, because their volumes are similar to the showcase volume. As the emission test chambers are equipped with ventilators the effects of air circulation can be determined by comparing results with those achieved from the showcase. There may be differences in the adsorption behavior of the emitted biocides, PCBs and PAHs with and without air circulation; however, the air change rate also has an influence on the adsorption behavior. Additionally, the chamber can be heated up and is therefore stored in a container filled with quartz wool and heated with a heating tape.

4.3.1 Air sampling volume

The sampled air volumes in all emission test chamber experiments were between 24-46 l, which were sampled with air flows between 25-35 ml min⁻¹ for the μ -CTE sampling and 100 ml min⁻¹, 300 ml min⁻¹ or 500 ml min⁻¹ for the showcase and emission test chamber samplings.

4.3.2 Micro-chamber

4.3.2.1 Air sampling and breakthrough experiments

The SDVB-polymer air sampling quality and its breakthrough behavior were tested with target compound solutions at 23 °C and 80 °C in μ -CTE experiments and compared with PUF at 80 °C. In addition, the vaporization behaviors of the selected SVOCs were tested in these experiments. This is an important parameter for screening of real samples and for measurements in showcases. Passive sampling is the appropriate air sampling strategy because of the high air change rates in the μ -CTE. The exhaust air flow rate is high enough to sample the air from its air stream at the sampling port in the chamber lid. Furthermore, the breakthrough behavior of both adsorbents was investigated with a second adsorbent in the row. Subsequent to the air sampling the μ -CTE cells were rinsed with solvent to determine if residues of the compounds remained on the chamber surface.

The results of the μ -CTE-experiments at 23 °C and 80 °C obtained by elution of the SDVB-polymer and rinsing of the chamber cells are shown as relative amounts in *Table 4.7*. 14-56 % of lindane with respect to tolyfluaniid evaporated at 23 °C and at 80 °C 10-69 % of all compounds were evaporated and measured in the eluate. In the rinsing eluate 17-93 % of all compounds were detectable at 23 °C but at 80 °C only 10-48 % of PCP, permethrin 1, permethrin 2 and benzo[a]pyrene were measurable. PCP is elutable from the SDVB-polymer after air sampling but not by adding target compound solution on the polymer. As already mentioned above (see *Section 4.2.2*) toluene is an inadequate solvent to elute PCP from the SDVB-polymer. Hence, only the amounts of PCP adsorbed at the PE filter by air sampling are elutable with toluene.

Table 4.7: Results of the air sampling and rinsing experiments in the μ -CTE at 23 °C and 80 °C

Compound	23 °C				80 °C			
	Recovery chamber 1 [%]	Recovery chamber 2 [%]	Recovery chamber 3 [%]	Recovery chamber 4 [%]	Recovery chamber 1 [%]	Recovery chamber 2 [%]	Recovery chamber 3 [%]	Recovery chamber 4 [%]
Elution								
Lindane	56	54	56	56	48	43	45	47
PCP	22	22	24	22	25	23	21	25
PCB 28	38	35	39	37	34	32	31	40
Dichlofluaniid	15	14	15	15	47	47	45	54
Isodrin	44	40	45	44	58	58	55	69
Tolyfluaniid	14	14	14	14	41	42	39	45
PCB 153	-	-	-	-	28	34	25	33
p,p'-DDT	-	-	-	-	32	38	29	35
Permethrin 1	-	-	-	-	21	19	21	18
Permethrin 2	-	-	-	-	21	20	21	20
Benzo[a]pyrene	-	-	-	-	11	10	10	10
Rinsing								
Lindane	17	17	16	17	-	-	-	-
PCP	35	32	32	30	10	10	10	-
PCB 28	26	28	24	23	-	-	-	-
Dichlofluaniid	69	67	65	63	-	-	-	-
Isodrin	38	39	34	33	-	-	-	-
Tolyfluaniid	75	72	70	69	-	-	-	-
PCB 153	93	88	86	86	-	-	-	-
p,p'-DDT	81	77	76	76	-	-	-	-
Permethrin 1	75	71	70	72	22	28	21	18
Permethrin 2	72	69	68	69	28	34	25	23
Benzo[a]pyrene	78	76	75	76	34	48	31	29

When comparing the air sampling ability of the SDVB-polymer and PUF at 80 °C it can be seen that the relative amounts obtained with PUF (*Table 4.8*) are higher for all compounds except for benzo[a]pyrene, which could not be detected in a quantifiable amount.

Table 4.8: Results of the μ -CTE experiment with PUF at 80 °C

Compound	Relative amount chamber 1 [%]	Relative amount chamber 2 [%]
PCP	43	43
Lindane	61	60
PCB 28	73	76
Dichlofluanid	77	75
Isodrin	71	73
Tolyfluanid	71	65
PCB 153	62	58
p,p'-DDT	46	40
Permethrin 1	25	25
Permethrin 2	25	25
Benzo[a]pyrene	-	-

Breakthroughs did not occur through both the SDVB-Polymer and the PUF.

The method recovery was determined for both adsorbents and is shown in *Section 4.4.1*.

The sums of the relative amounts of the elution from the SDVB-polymer and rinsing are between 52-88 % for lindane to tolyfluanid at 23 °C and between 31-58 % at 80 °C for PCP, permethrin 1, permethrin 2 and benzo[a]pyrene. This is lower than 100 % for all compounds but the sums are reproducible in the fourfold determination. Since the relative amounts with PUF are also lower than 100 % and the recovery rates of the first elution experiment (*Table 4.5*) were better with the SDVB-polymer, it was selected for further experiments. It also has an easier work-up process and lower solvent expenses.

4.3.2.2 Comparison of the ISTDs

Labeled ISTDs are the best choice for the quantification and identification of their unlabeled equivalents, because they exhibit similar behaviors e.g. elution behavior from the polymer and column. For that reason the quality of $^{13}\text{C}_6$ lindane as ISTD was compared with the one of 4-(4-chlorobenzoyl) pyridine for lindane, because it is one of the

most important compounds used in this study. The comparison was also undertaken in a μ -CTE experiment with target compound solution at 23 °C.

By quantifying and identifying lindane with $^{13}\text{C}_6$ lindane and 4-(4-chlorobenzoyl) pyridine it can be seen in *Table 4.9* that the relative amounts obtained with $^{13}\text{C}_6$ lindane are about 1.6 times higher than with 4-(4-chlorobenzoyl) pyridine.

Table 4.9: Results of the ISTD comparison

ISTD	Recovery rate lindane [%] chamber 1	Recovery rate lindane [%] chamber 2	Recovery rate lindane [%] chamber 3	Recovery rate lindane [%] chamber 4
4-(4-Chlorobenzoyl) pyridine	51	53	50	52
$^{13}\text{C}_6$ Lindane	78	81	78	78

Even though the recovery rates for lindane are higher when using $^{13}\text{C}_6$ lindane for the evaluation, it would be very expensive to use the corresponding labeled standard for every compound, especially for the evaluation of real samples with any information about the contaminations. For that reason two different unlabeled compounds were selected and used as ISTDs in this study.

4.3.3 Emission test chamber experiments with soaked wood samples

It is difficult to obtain homogenous samples contaminated with all of the selected compounds, therefore wood was soaked manually in order to investigate their emission behavior. Pine (*Pinus sylvestris*) sapwood pieces were used for these experiments and were soaked in solutions of the target compounds. The wood sizes varied depending on the emission test chamber size (all stored at 70 % r. h.):

- μ -CTE: 4.1 cm × 1 cm × 0.5 cm
- showcase and emission test chambers: 11 cm × 4 cm × 1 cm

Different effects on the SVOC and POM emissions were investigated by active and diffusive sampling in the emission test chamber experiments with soaked wood samples for the new low volume air sampling strategy. Firstly the temperature influence was checked in μ -CTE experiments at air change rates of approximately 35 h⁻¹. The effect of air circulation on the emissions of the SVOCs and POMs were the first influences to be investigated in the showcases. In a second experiment the effect of different air change rates and relative humidities were tested and the influence of air circulation on the diffusion process of the compounds was investigated by diffusive sampling. Lastly an active air sampling strategy was tested at air change rates between 0.10-0.26 h⁻¹ with and without air circulation. Experiments in 23 l and 24 l emission test chambers were carried

out to investigate the temperature influence at air change rates of 1.3 h^{-1} and also to test the same active air sampling strategy as in the showcases at an air change rate of 0.2 h^{-1} .

4.3.3.1 Soaked wood in the μ -CTE

The experiment with soaked wood in the μ -CTE was conducted at $23 \text{ }^\circ\text{C}$ and $80 \text{ }^\circ\text{C}$ as a fivefold determination with one sample contained in each chamber cell. Due to the results of computational calculations regarding the flow path and air velocity made by Schripp et al. [60], the samples were placed on one of their larger sides. Since the large sides have the greatest surface area the emission area of the samples was reduced to its minimum. The experiment lasted two days at $23 \text{ }^\circ\text{C}$ and afterwards 36 days at $80 \text{ }^\circ\text{C}$ to investigate the long-term behavior of the SVOC and POM emissions. The breakthrough was checked in this experiment again at $80 \text{ }^\circ\text{C}$ and after removing the samples the chamber jars were rinsed with solvent to determine adsorption of compounds at the chamber surface emitted from the wood.

Only the lower boiling SVOCs (lindane, PCB 28, dichlofluanid and isodrin) could be detected at $23 \text{ }^\circ\text{C}$ by sampling a volume of approximately 43 l. With a sampling volume of approximately 36 l at $80 \text{ }^\circ\text{C}$ the compounds from lindane to permethrin 2, excluding PCB 153 could be detected on the first and second sampling days, whereas on the third and fourth sampling days only lindane to tolyfluanid could be measured, depending on the type of soaked wood sample studied. The concentration reaches its maximum on the first day at $80 \text{ }^\circ\text{C}$ and on the second day the concentration value is similar as it was at $23 \text{ }^\circ\text{C}$. After 35 days at $80 \text{ }^\circ\text{C}$ no emissions could be detected. Unfortunately no PCB 153 and benzo[a]pyrene emissions could be measured, which might be due to their very low volatile character up into the range of POM. The measured concentrations decrease at $80 \text{ }^\circ\text{C}$ from the first air sampling to the last; at $23 \text{ }^\circ\text{C}$ the concentrations are similar on both sampling days. Breakthroughs did not occur at $80 \text{ }^\circ\text{C}$, which was checked on the first and second sampling days, and no compounds were adsorbed at the chamber surface. *Figure 4.4* and *Figure 4.5* show the SE_{Ra} processes of the measured compounds. The necessary parameters for the SE_{Ra} calculation are shown in *Table 4.10*. As shown in both figures the highest SE_{Ra} values are in a range of $40\text{-}300 \mu\text{g m}^{-2}\text{h}^{-1}$ depending on the SVOCs, whereby the lower boiling SVOCs have the higher SE_{Ra} values. The measured concentrations are shown in *Table 9.24* and *Table 9.25* in *Section 9.3.5*.

Table 4.10: Parameters for the calculation of the SE_{Ra}

Parameter	Cell 1	Cell 2	Cell 3	Cell 4	Cell 5
L [$\text{m}^2 \text{m}^{-3}$]	20.50	20.50	20.50	20.50	20.50
n [h^{-1}]	36.00	39.95	35.66	33.80	38.07
q [$\text{m}^3 \text{m}^{-2}\text{h}^{-1}$]	1.76	1.95	1.74	1.65	1.86

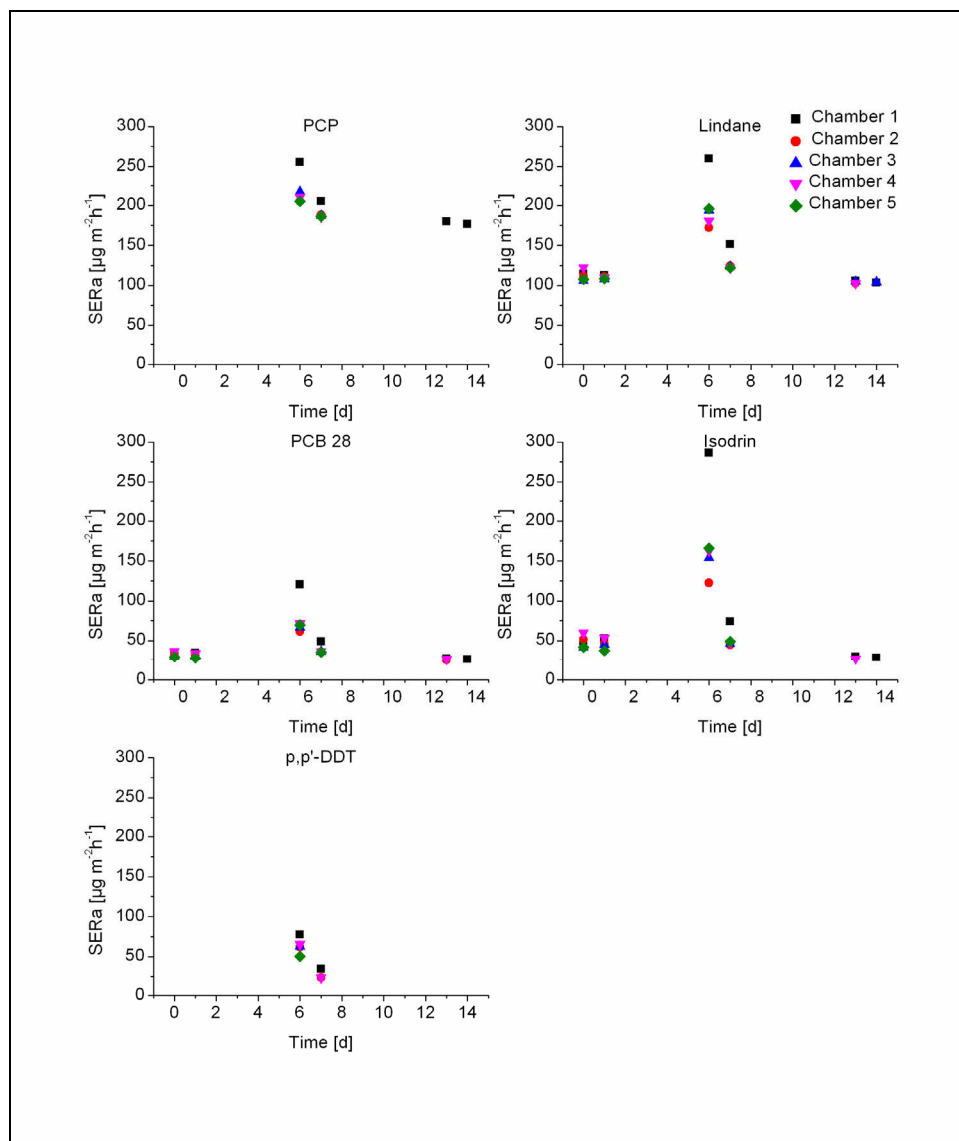


Figure 4.4 SER_a of the μ -CTE experiment with soaked wood samples (PCP, lindane, PCB 28, isodrin and p,p'-DDT). The temperature was increased to 80 °C at day 6.

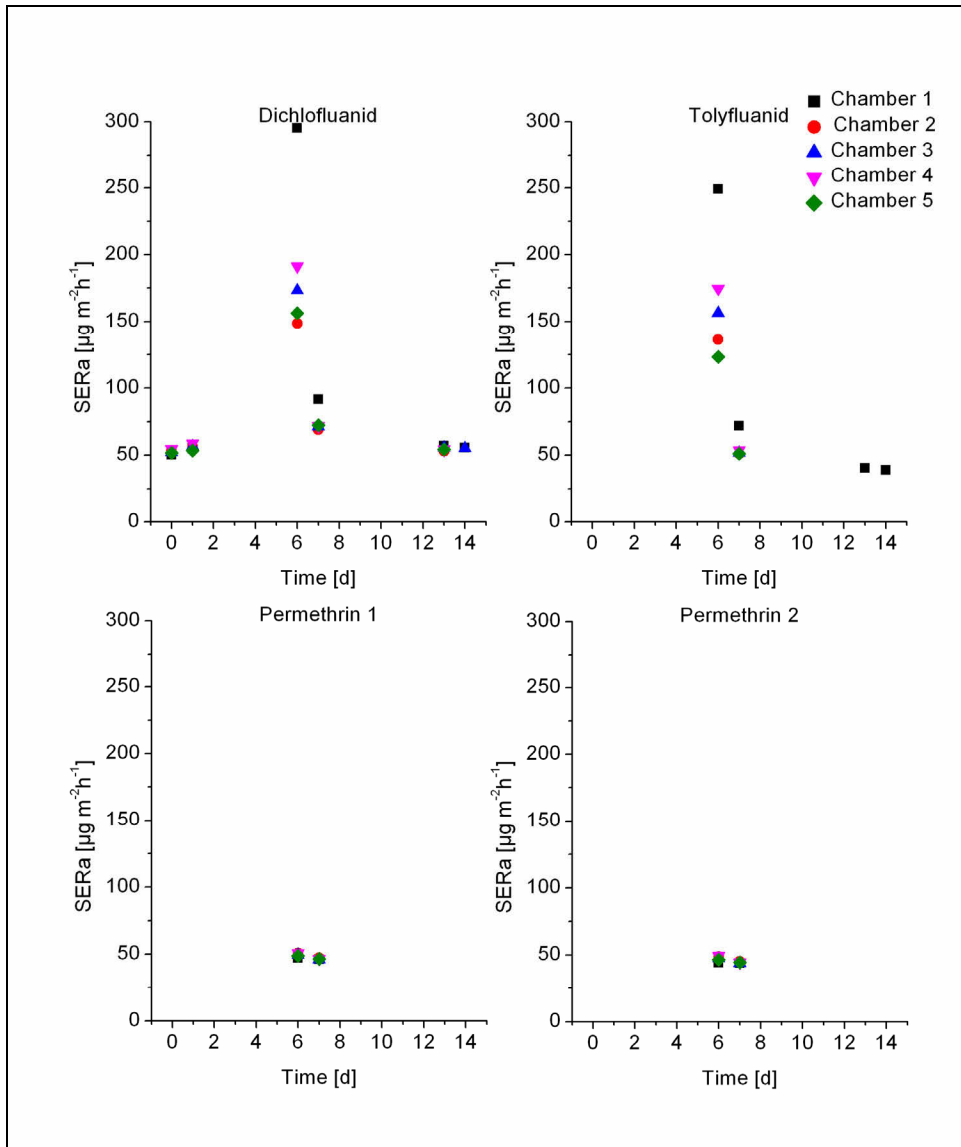


Figure 4.5 SER_a of the μ -CTE experiment with soaked wood samples (dichlofluanid, tolyfluamid, permethrin 1 and permethrin 2). The temperature was increased to 80 °C at day 6.

4.3.3.2 Soaked wood in showcases

The emissions of the soaked wood samples in the showcases were investigated in four test series. In the first series air sampling at air change rates higher than 1 h^{-1} (showcase 1: $n = 2.6 \text{ h}^{-1}$ later 1 h^{-1} ; showcase 2: $n = 1.2 \text{ h}^{-1}$) was performed with and without air circulation. Showcase 2 was equipped with a ventilator in order to generate an air circulation as in the emission test chambers. Every showcase was loaded with four

pine sapwood pieces standing on one of their longer sides and the sampling was done actively with the SDVB-polymer.

The experiments in showcase 1 and 2 lasted between 36 and 55 days depending on the air change rate. In showcase 1 compounds were not detected in the air by sampling with the SDVB-Polymer. In contrast, at least lindane and PCP could be detected by introducing a ventilator into the showcase system working with an air change rate of 1.2 h^{-1} . However, only lindane was detectable on four sampling days (day 4, 7, 15 and 32) and PCP only on one sampling day (day 4). Their $SERa_s$ per sampling day are shown in *Figure 4.6* and *Table 9.26* in *Section 9.3.5* shows the measured concentrations.

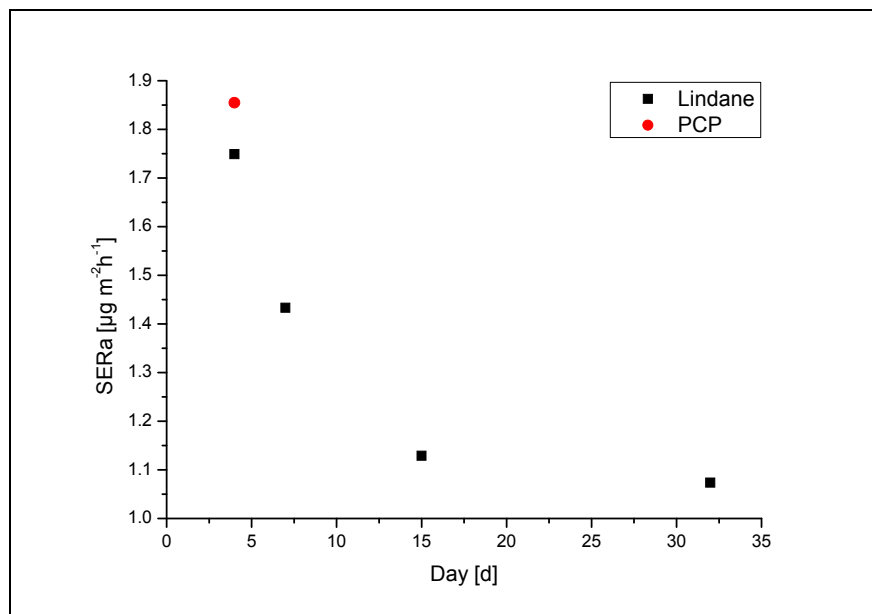


Figure 4.6: $SERa_s$ of showcase 2. The parameters for the $SERa_s$ calculation are the following: $L = 1.59 \text{ m}^2 \text{ m}^{-3}$; $n = 1.2 \text{ h}^{-1}$ and $q = 0.75 \text{ m}^3 \text{ m}^{-2}\text{h}^{-1}$

The influence of the ventilator on the air circulation was investigated by measuring the air flow velocities with a thermoanemometer. In *Figure 4.7* the measuring points of the air flow velocity and the directions of the air flow generated by the ventilator are illustrated.

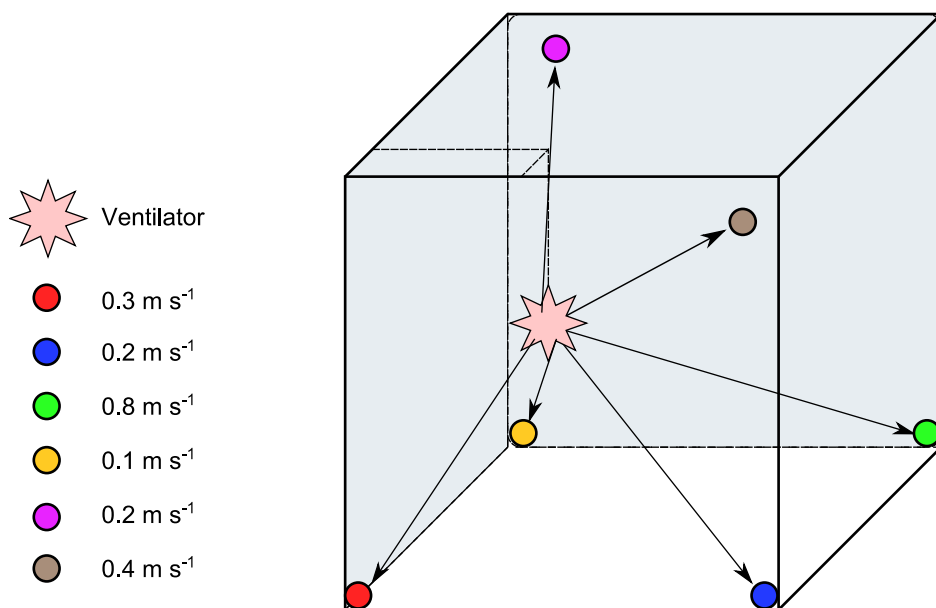


Figure 4.7: Air flow directions and velocities in a showcase equipped with a ventilator

In the second test series the influence of the air change rate and relative humidity on the emission behavior of lindane and PCP was tested in showcases equipped with ventilators, because better results were obtained in the first test series by using a ventilator. Relative humidities of approximately 34 % and 63 % were tested with air change rates of 0.5 h⁻¹ and 1 h⁻¹ at ambient temperature and active air sampling was performed with the SDVB-polymer (see Table 4.11 for experimental parameters).

Table 4.11: Showcase parameters and parameters for the calculation of the SE_{Ra}

Parameter	Showcase 3	Showcase 4	Showcase 5	Showcase 6
L [m ² m ⁻³]	1.59	1.59	1.59	1.59
n [h ⁻¹]	1.00	0.50	1.00	0.50
q [m ³ m ⁻² h ⁻¹]	0.63	0.31	0.63	0.31
r. h. [%]	66	59	34	33

The experiments were stopped after 172 respectively 174 days, although lindane was still emitted by the samples in measurable amounts in the showcases with $n = 1 \text{ h}^{-1}$. During the experiment emissions were measured only at an air change rate of 1 h⁻¹ and neither lindane nor PCP could be detected in a quantifiable amount in both showcases with an air change rate of 0.5 h⁻¹. Nevertheless, only lindane was detectable in both showcases with $n = 1 \text{ h}^{-1}$. The SE_{Ra} s of lindane were calculated with the parameters

shown in *Table 4.11* and are shown in *Figure 4.8* with their average values, which are $2.33 \mu\text{g m}^{-2}\text{h}^{-1}$ for a relative humidity of approximately 66 % and $1.96 \mu\text{g m}^{-2}\text{h}^{-1}$ for a relative humidity of approximately 34 %. *Table 9.27* in *Section 9.3.5* shows the measured concentrations.

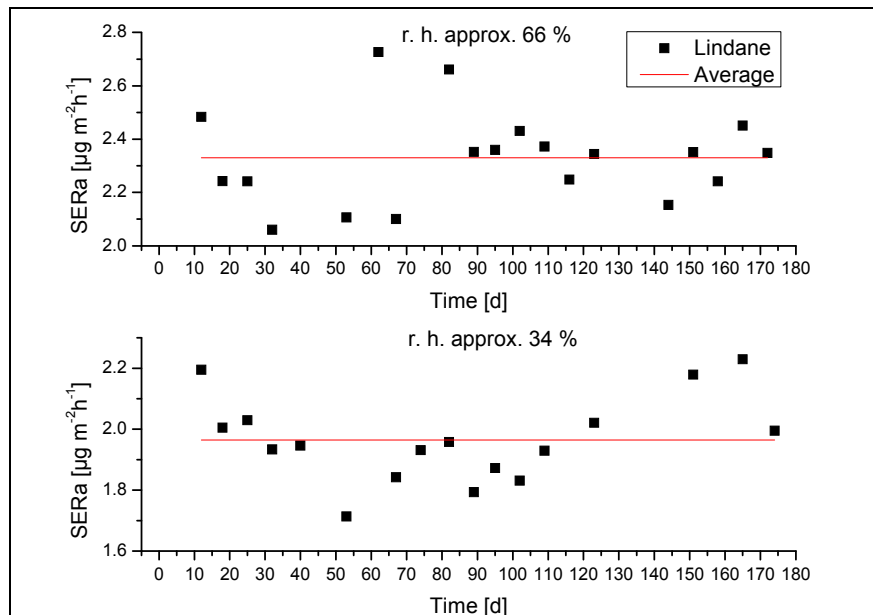


Figure 4.8: SER_a of the experiments in showcase 3 and 5 at air change rates of 1 h^{-1}

The influence of the relative humidity was also investigated in this experiment. Unfortunately it is difficult to decide if the relative humidity has an influence on the emissions of lindane, because the differences in the average values of the SER_a are quite low.

In the third test series the effect of the air circulation on the diffusion of the SVOCs and POMs was determined with object slides as diffusive samplers, which were removed periodically. *Figure 4.9* shows the arrangement of the samples and object slides in the showcases. The air circulation between the object slides might be very low due to little space between them.

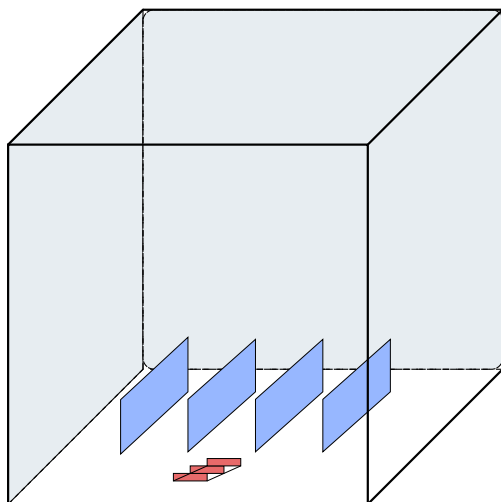


Figure 4.9: Schematic arrangement of samples and object slides in the showcases

The showcases were working with low air change rates and one of them had activated air circulation ($n_{\text{without air circulation}} = 0.02 \text{ h}^{-1}$ and $n_{\text{with air circulation}} = 0.37 \text{ h}^{-1}$) but as illustrated the influence of the ventilator on the air change rate is considerably high. The object slides are used as a removable sink, which can be rinsed off after removing them out of the showcase and the obtained qualitatively results are useful to estimate the diffusion behavior of the compounds with and without air circulation at such low air change rates.

When object slides were used for diffusive sampling in a showcase without air circulation more compounds could be detected at these low air change rates than with active sampling. As can be seen in *Table 4.12* the air circulation might accelerate the diffusion processes of the SVOCs, this is because more compounds are detectable on the object slides of the showcase with air circulation than on the ones without and they can also be detected on the removed object slides. The diffusion processes of lindane and PCP – the lowest semi volatile compounds of this study – are most strongly influenced by the air circulation. The detection days of each SVOC in both showcases are shown in *Table 4.12*.

Table 4.12: Detection days of the SVOCs on the object slides (x - showcase without ventilator; + - showcase with ventilator)

Day	Lindane	PCP	Dichlo- fluanid	Isodrin	Toly- fluanid	p,p'- DDT	Benzo- [a]pyrene
2/3	+	+	x +	+	x +	x +	+
6	+	+	x		x +	x +	
9/10	+	+	x +		x +		+
13		+			x		
16/1 7	+	+				+	+
20		x +					
23/2 4		x +					
27		x +					
30/3 1		x +					
34		x +					

In the fourth test series active air sampling was performed at air change rates between 0.10-0.26 h⁻¹ with the retransfer of the sampled air back into the showcase after passing the adsorbent and the pump. This air sampling strategy was tested in a duplicate determination with and without air circulation at ambient temperature and a relative humidity of approximately 50 %. Two showcases operated without air circulation to simulate active air sampling under real conditions and to determine the influence of the air circulation on the emission behavior by using this air sampling strategy.

The experiment was stopped after 23 days but in this short experimental time quantifiable amounts of the SVOCs and POMs could not be sampled. Lindane was the only compound detected by the MS-MS but in concentrations lower than its LoQ (1.60 µg m⁻³).

4.3.3.3 Soaked wood in 23 I and 24 I emission test chambers

The first experiments with soaked wood samples in emission test chambers were conducted under different conditions regarding the air change rate, relative humidity and temperature (chamber 1 (24 I): n = 1.3 h⁻¹; chamber 2 (23 I): n = 1.3 h⁻¹; chamber 3 (24 I): n = 0.2 h⁻¹). The temperature in chamber 1 and 3 was ambient and the relative humidity was approximately 50 % in chamber 1 and approximately 30 % in chamber 3. The temperature in chamber 2 was in a range of approximately 70-90 °C and the relative humidity was approximately 3 %. As in the previous experiments each chamber was loaded with four wood pieces standing on one of their longer sides and the air sampling

was active with the SDVB-polymer, in chamber 3 ($n = 0.2 \text{ h}^{-1}$) the sampled air was retransferred into the chamber after passing the adsorbent and the pump as in the fourth test series of the showcase experiments.

The influence of ventilators and samples on the air circulation is already described in *Section 2.5.2* but since this time the sample arrangement (*Figure 4.10*) differs from the arrangement discussed previously, the air flow circulation at the chamber bottom should also be different.

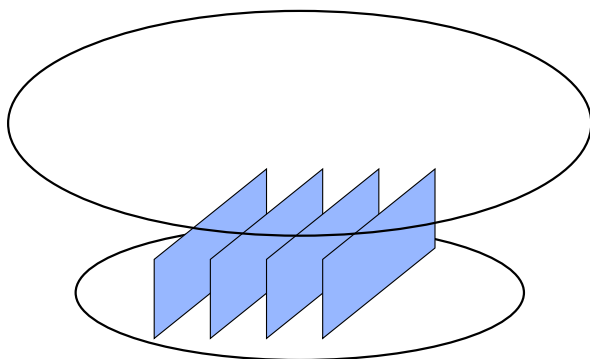


Figure 4.10: Schematic diagram of the sample arrangement in the 23 l and 24 l emission test chambers in the experiments of this study

At ambient temperature in chamber 1 only the lower boiling SVOCs (lindane, PCP, PCB 28, dichlofluand, isodrin and tolyfluand (for concentration details see *Table 9.28* in *Section 9.3.5*)) could be measured in the chamber air for 103 days. The PCP and PCB 28 emissions were very low and only detectable from day 6 to 12 (three sampling days). Dichlofluand, isodrin and tolyfluand were measurable in the chamber air until day 33 respectively day 40. Only lindane was emitted by the self soaked wood samples for 103 days. Lindane and isodrin emissions were already detectable on the first air sampling day (day 1), whereas the emissions of the other lower boiling SVOCs started to be measurable from day 6.

The experimental time in chamber 2 was only 69 days and again only the lower boiling SVOCs (for concentration details see *Table 9.29* in *Section 9.3.5*) were measured in the chamber air, although the temperature was increased to approximately $80 \text{ }^{\circ}\text{C}$. The lindane emissions were measured for 69 days in the chamber air, whereas the other SVOCs were only detectable up to a maximum of 48 days.

The experiment in chamber 3 was the longest with 196 experimental days. As in the other experiments only the lower boiling SVOCs from lindane to tolyfluand were detectable in the chamber air (for concentration details see *Table 9.30* in *Section 9.3.5*) and the emission process of lindane lasted 196 days. Dichlofluand was emitted by the soaked wood samples until day 55 in measureable concentrations but the measurable emissions of all other compounds stopped after 34 to 37 days. Air sampling was active with retransfer of the air back into the chamber after passing the pump.

Comparing the results of the three experiments carried out under different conditions it can be seen that lindane is always the compound with the longest emission process, which might be due to its low semi volatile character compared to the other compounds. Depending on the air change rate and temperature its emission process lasted 69, 103 or 196 days. The experimental time at ambient temperature is two to three times longer than at higher temperatures, depending on the air change rate. The experiment at higher temperature was the shortest one with only 69 experimental days, but this experiment has the highest initial concentration and the shortest emission process, both is a consequence of the high experimental temperature.

One question to consider is why the compounds from lindane to tolyfluanid were the only detectable compounds, even in the experiment at higher temperature. It is a not remarkable behavior for the experiments at ambient temperature; however this is unusual for one of the experiments carried out at a higher temperature. An explanation is given in *Section 6.4*.

For a better comparison of the results the SE_{Ra} s of each compound on each sampling day were calculated. The necessary parameters for this calculation are shown in *Table 4.13*. *Figure 4.11* to *Figure 4.13* show the SE_{Ra} s, which differ depending on the temperature and air change rate. Their differences are most striking at the beginning of the experiments and become more similar throughout. The experiment performed at higher temperature has the highest SE_{Ra} values, whereas the experiment with an air change rate of 0.2 h^{-1} has the lowest values, as expected. Horn et al. [40] published the SE_{Ra} of dichlofluanid, which behavior has a similar behavior to the one presented below.

Table 4.13: Parameters for the calculation of the SE_{Ra} values

Parameter	Chamber 1	Chamber 2	Chamber 3
$L [\text{m}^2 \text{m}^{-3}]$	1.86	1.86	1.86
$n [\text{h}^{-1}]$	1.30	1.30	0.20
$q [\text{m}^3 \text{m}^{-2} \text{h}^{-1}]$	0.70	0.70	0.11

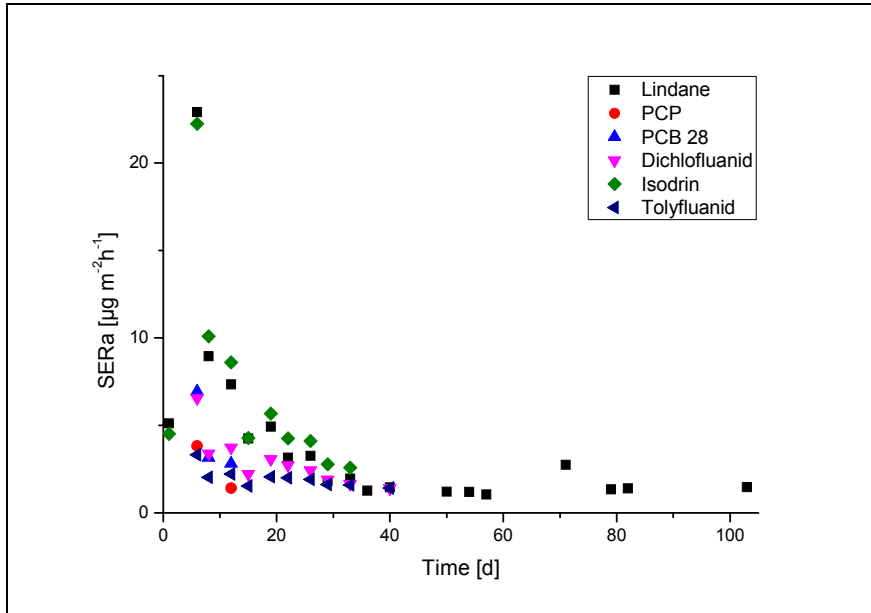


Figure 4.11: SER_a of the lower boiling SVOCs emitted from the self soaked wood samples in chamber 1; $n = 1.3 \text{ h}^{-1}$; ambient temperature

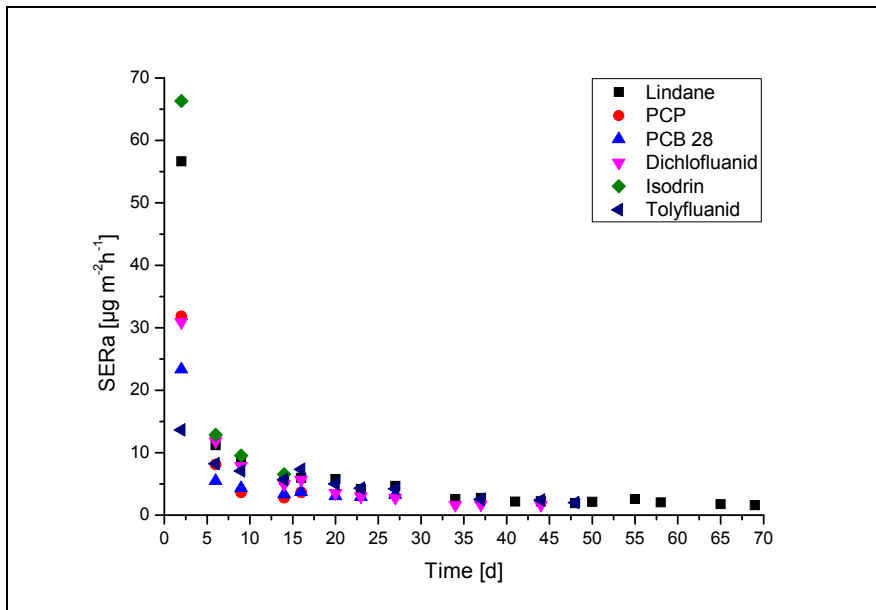


Figure 4.12: SER_a of the lower boiling SVOCs emitted from the self soaked wood samples in chamber 2; $n = 1.3 \text{ h}^{-1}$; 70-90 °C

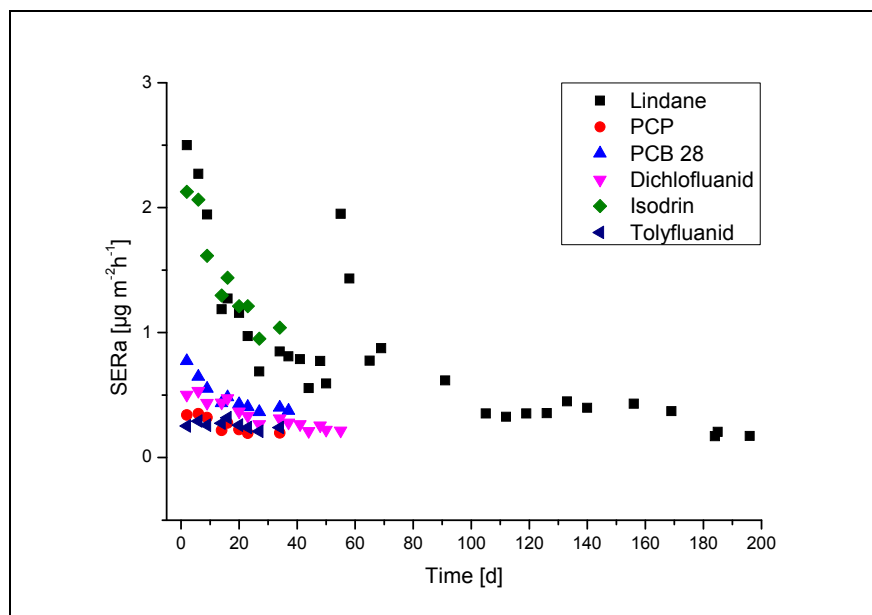


Figure 4.13: SER_a of the lower boiling SVOCs emitted from the self soaked wood samples in chamber 3; $n = 0.2 \text{ h}^{-1}$; ambient temperature

To compare the emission test chamber results further the total concentrations of the measured compounds were calculated and are shown in *Table 4.14*. As already recognizable in *Figure 4.11* to *Figure 4.13* the different investigated conditions have a strong influence on the total emitted concentrations of each compound, although all wood pieces were soaked in the same solution and absorbed a similar amount of solution.

Table 4.14: Total concentrations of all detected compounds in chamber 1, 2 and 3

	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	PCB 28 [$\mu\text{g m}^{-3}$]	Dichlofluaniid [$\mu\text{g m}^{-3}$]	Isodrin [$\mu\text{g m}^{-3}$]	Tolyfluaniid [$\mu\text{g m}^{-3}$]
Chamber 1	110	7	18	41	99	28
Chamber 2	178	71	71	108	136	89
Chamber 3	233	19	44	47	118	21

In a second test an experiment was carried out at an air change rate of $n = 0.003 \text{ h}^{-1}$ at ambient temperature with a relative humidity of 53 %, but without activated air circulation. The chamber was loaded with only one wood piece soaked with technical lindane and technical PCP. Active sampling was performed after 90 days and a volume of 24 l, which corresponds to the chamber volume, was sampled. Only $11.96 \mu\text{g m}^{-3}$ lindane were found in this air volume, which is insignificant compared to the amount (2188 μg) absorbed by the wood by soaking. The SER_a was calculated and is shown in *Table 4.15* with the necessary parameters.

Table 4.15: SER_a and the parameters for its calculation

Parameter	Chamber 4
L [$m^2 m^{-3}$]	0.450
n [h^{-1}]	0.003
q [$m^3 m^{-2}h^{-1}$]	0.007
SER_a [$\mu g m^{-2}h^{-1}$]	0.080

4.4 Method validation

4.4.1 Method recovery

4.4.1.1 Recovery of the adsorbent elution/extraction

The method recovery was checked for the elution of the SDVB-polymer ($n = 5$) and extraction of the PUF ($n = 2$), this is shown in *Table 4.16* and *Table 4.17*. The following calculation is used.

$$\text{Recovery } [\%] = \frac{x_a}{x_t} \cdot 100\% \quad \text{Equation 4.6}$$

- x_a – average concentration of n -measurements [$ng \mu l^{-1}$]
- x_t – target concentration on the adsorbent respectively in the μ -CTE cells [$ng \mu l^{-1}$]

Table 4.16: Recovery of the SDVB-polymer elution method ($n = 5$)

Compound	Recovery [%]	RSD [%]
Lindane	58	3.80
PCB 28	104	2.44
Dichlofluanid	88	0.86
Isodrin	105	1.35
Tolyfluanid	87	1.10
PCB 153	98	1.35
p,p'-DDT	95	1.64
Permethrin 1	109	1.99
Permethrin 2	103	1.49
Benzo[a]pyrene	127	2.52

Table 4.17: Recovery of the PUF extraction method ($n = 2$)

Compound	Recovery [%]	RSD [%]
Lindane	51	1,29
PCP	36	4,89
PCB 28	93	28,10
Dichlofluanid	72	0,33
Isodrin	74	2,24
Tolyfluanid	74	2,67
PCB 153	77	0,16
p,p'-DDT	78	0,84
Permethrin 1	86	6,50
Permethrin 2	99	6,72
Benzo[a]pyrene	94	5,33

By comparing the recoveries obtained from both adsorbents it is obvious that the rates are lower with PUF. With the SDVB-polymer recoveries higher than 100 % are obtained for five compounds (PCB 28, isodrin, permethrin 1, permethrin 2 and benzo[a]pyrene) but the blank SDVB-polymer and the blank GC-MS-MS system do not show any contaminations from these compounds. However, all these recoveries were reproducible in a fivefold determination with the SDVB-polymer and in a duplicate determination with PUF.

4.4.1.2 Recovery of the air sampling method

The method recovery (Table 4.18 and Table 4.19) for the air sampling method was checked for μ -CTE experiments (23 °C and 80 °C; SDVB-polymer and PUF) using defined concentrations of target compound solutions. The calculations were also carried out using Equation 4.6 (Section 4.4.1.1).

Table 4.18: Recovery of the air sampling method with the SDVB-polymer (n = 4)

T [°C]	Compound	Recovery [%]	RSD [%]
23	PCP	23	4.53
	Lindane	55	1.99
	PCB 28	37	4.63
	Dichlofluanid	15	2.68
	Isodrin	43	5.45
	Tolyfluanid	14	0.63
80	PCP	24	9.37
	Lindane	46	5.03
	PCB 28	34	11.27
	Dichlofluanid	48	7.75
	Isodrin	60	10.15
	Tolyfluanid	42	6.39
	PCB 153	30	13.86
	p,p'-DDT	33	11.28
	Permethrin 1	20	8.28
	Permethrin 2	20	3.87
	Benzo[a]pyrene	10	5.38

Table 4.19: Recovery of the air sampling method with PUF at 80 °C (n = 2)

Compound	Recovery [%]	RSD [%]
PCP	43	0.08
Lindane	61	2.00
PCB 28	75	2.55
Dichlofluanid	76	1.31
Isodrin	72	1.39
Tolyfluanid	68	6.18
PCB 153	60	5.05
p,p'-DDT	43	10.16
Permethrin 1	25	1.52
Permethrin 2	25	1.66

The method recovery is between 14-55 % when using the SDVB-polymer at 23 °C and between 10-60 % at 80 °C. With PUF recoveries between 25-76 % are obtained. Unfortunately the recoveries of the air sampling method are far below 100 %.

4.4.2 Uncertainty in measurement

The uncertainty in measurement of a method is determined to get information about the quality of the results [74]. In "Guide to the expression of uncertainty in measurement"

(GUM) [75] by Joint Committee for Guides in Metrology and in “*Quantifying Uncertainty in Analytical Measurement*” [74] by EURACHEM/CITAC detailed descriptions to determine the uncertainty in measurement are given. The term uncertainty in measurement is described by GUM [75] as follows: “Parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand”.

The uncertainty in measurement was determined according to the four stepped concept described in EURACHEM/CITAC [74].

- Step 1: Specification of the measurand
- Step 2: Identifying uncertainty sources x_i
- Step 3: Quantifying uncertainty $u(x_i)$
- Step 4: Calculating the combined uncertainty $u_c(y)$

In the following a detailed description of the four stepped concept is given.

- Step 1: Specification of the measurands
 - Analytical result
- Step 2: Identifying uncertainty sources x_i
 - Stock solutions for the calibration
 - Calibration
 - Air sampling
 - Elution of the adsorbent
- Step 3: Quantifying uncertainty $u(x_i)$
 - Stock solutions for the calibration: balance and volumetric flask
 - Calibration: volumetric flask, pipettes and standard deviation of the calibration
 - Air sampling: flow meter (for μ -CTE) or pumps
 - Elution of the adsorbent: pipettes

The uncertainties are quantified by determining their standard uncertainties $u(x_i)$ according to GUM either via a type A or type B evaluation [75].

- “Type A evaluation (of uncertainty): method of evaluation of uncertainty by the statistical analysis of series of observations”
- “Type B evaluation (of uncertainty): method of evaluation of uncertainty by means other than the statistical analysis of series of observations”

All uncertainties were quantified using the type B evaluation and their corresponding errors or uncertainties were taken from calibration certificates or manufacturer's data.

- Step 4: Calculating the combined uncertainty $u_c(y)$

“The combined standard uncertainty $u_c(y)$ is the positive square root of the combined variances $u_c^2(y)$, which is given by

$$u_c^2(y) = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \quad [75] \quad \text{Equation 4.7}$$

where the function f is given by $Y = f(X_1, X_2, \dots, X_n)$ and the standard uncertainties $u(x_i)$ are evaluated either by type A or type B evaluations [75]. “The partial derivatives $\frac{\partial f}{\partial x_i}$ [...] often called sensitivity coefficients, describe how the output estimate y varies with changes in the values of the input estimates x_1, x_2, \dots, x_N . [...]” [75]

“In some cases, the expressions for combining uncertainties reduce to much simpler forms. [...] For models involving only a sum or difference of quantities, e.g. $y = (p + q + r + \dots)$, the combined standard uncertainty $u_c(y)$ is given by

$$u_c(y(p, q, \dots)) = \sqrt{u(p)^2 + u(q)^2 + \dots} \quad [74] \quad \text{Equation 4.8}$$

The last step is to determine the expanded uncertainty $U(y)$ by multiplying the combined uncertainty $u_c(y)$ with the chosen coverage factor k or the Student's t -value (for degrees of freedom $f \leq 30$).

$$U(y) = k \cdot u_c(y) \quad \text{Equation 4.9 [72]}$$

“[...] The expanded uncertainty is required to provide an interval which may be expected to encompass a large fraction of the distribution of values which could reasonably be attributed to the measurand. [...] For most purposes it is recommended that k is set to 2. [...] Where the distributions concerned are normal, a coverage factor of 2 [...] gives an interval containing approximately 95 % of the distribution of values. [...]” [74] The coverage factor $k = 2$ is only valid for $f \geq 30$. If the uncertainty of measurement is determined with fewer data the Student's t -value ($f, P = 95\%$) for the determination of the confidence interval should be used [72]. Equation 4.9 then becomes Equation 4.10.

$$U(y) = t \cdot u_c(y)$$

Equation 4.10

The t -value is dependent on the number of degrees of freedom, which are given by $f = N - 1$ [75]. t -value lists are found in the literature [74, 76].

4.4.2.1 Quantifying uncertainty $u(x_i)$

The quantification of the relevant uncertainties $u(x_i)$ is given in detail below.

Stock solutions for the calibration: Balance and volumetric flask

The measurement uncertainty of the balance is specified as expanded measurement uncertainty ($U(y) = 0.00036\%$) on the calibration certificate. Because its $U(y)$ is very low and its influence on the results is only on the fourth decimal place, it is neglected for the uncertainty in measurement calculation.

The standard uncertainty of the volumetric flask ($10\text{ ml} \pm 0.04\text{ ml}$) is determined according to EURACHEM/CITAC [74]. The volume of the solution in the flask is influenced by the uncertainty in the certified internal volume of the flask and by the flask and solution temperatures differing from the temperature at which the volume of the flask was calibrated.

Calibration: $10\text{ ml} \pm 0.04\text{ ml}$ at $20\text{ }^\circ\text{C}$

The standard uncertainty is calculated assuming a triangular distribution with $\left(\frac{a}{\sqrt{6}}\right)$.

$$u(x_i) = \frac{0.04\text{ ml}}{\sqrt{6}} = 0.02\text{ ml}$$

Temperature:

The volumetric flask is calibrated at $20\text{ }^\circ\text{C}$ but the laboratory temperature is $20\text{ }^\circ\text{C} \pm 3\text{ }^\circ\text{C}$. The uncertainty is determined by the coefficient of volume expansion γ ($\gamma_{\text{Toluene}} = 1.12 \cdot 10^{-3}\text{ K}^{-1}$ at $20\text{ }^\circ\text{C}$) and estimating the temperature range.

$$\pm (10\text{ ml} \cdot 3\text{ }^\circ\text{C} \cdot 1.12 \cdot 10^{-3}\text{ K}^{-1}) = \pm 0.03\text{ ml}$$

The standard uncertainty is calculated assuming a rectangular distribution $\left(\frac{a}{\sqrt{3}}\right)$.

$$u(x_i) = \frac{0.03\text{ ml}}{\sqrt{3}} = 0.02\text{ ml}$$

The standard uncertainty $u(V_{flask})$ and the relative standard uncertainty $u_{rel}(V_{flask})$ of the volume V are calculated with these two contributions.

$$u(V_{flask}) = \sqrt{(0.02 \text{ ml})^2 + (0.02 \text{ ml})^2} = 0.03 \text{ ml}$$

$$u_{rel}(V_{flask}) = \frac{0.03 \text{ ml}}{10 \text{ ml}} \cdot 100 \% = 0.3 \%$$

Calibrations: volumetric flask, pipettes and standard deviation of the procedure

See above for the determination of $u(x_i)$ of the volumetric flask.

The standard uncertainties of the pipettes for the calibrations are calculated assuming a rectangular distribution.

$$1000 \mu\text{l} \pm 8.00 \mu\text{l}: u(x_i) = 4.62 \mu\text{l}; u(x_i)_{rel} = 0.46 \%$$

$$250 \mu\text{l} \pm 2.50 \mu\text{l}: u(x_i) = 1.44 \mu\text{l}; u(x_i)_{rel} = 0.58 \%$$

$$100 \mu\text{l} \pm 1.00 \mu\text{l}: u(x_i) = 0.58 \mu\text{l}; u(x_i)_{rel} = 0.58 \%$$

$$10 \mu\text{l} \pm 0.15 \mu\text{l}: u(x_i) = 0.09 \mu\text{l}; u(x_i)_{rel} = 0.90 \%$$

With these four contributions the standard uncertainty $u(V_{pipettes})$ of the volume V is calculated.

$$u(V_{pipettes}) = \sqrt{(4.62 \mu\text{l})^2 + (1.44 \mu\text{l})^2 + (0.58 \mu\text{l})^2 + (0.09 \mu\text{l})^2} = 4.87 \mu\text{l} = 4.87 \cdot 10^{-3} \text{ ml}$$

$$u_{rel}(V_{pipettes}) = \sqrt{(0.46 \%)^2 + (0.58 \%)^2 + (0.58 \%)^2 + (0.90 \%)^2} = 1.30 \%$$

The standard deviation for the method s_{x_0} is obtained by using DINTTEST [77]. Equation 4.11 is used to calculate the standard coefficient V_{x_0} .

$$V_{x_0} = \frac{s_{x_0}}{\bar{x}} \cdot 100 \%$$

Equation 4.11 [72]

- \bar{x} - Average of the standard concentrations x_i

Air sampling: flow meter (for μ -CTE) and pumps for emission test chambers, showcases and indoor air

The relative standard uncertainty $u_{rel}(x_i)$ of the flow meter is given by the manufacturer as $\pm 1.00 \%$.

The relative error of all used pumps has to be in the range of $\pm 3.00 \%$. As the air sampling was performed using different pumps the error rates were not determined for each separate pump used.

Elution: Pipettes

The standard uncertainties are calculated assuming a rectangular distribution (see above).

$$1000 \mu\text{l} \pm 8.00 \mu\text{l}: u(x_i) = 4.62 \mu\text{l}; u(x_i)_{rel} = 0.46 \%$$

$$100 \mu\text{l} \pm 1.00 \mu\text{l}: u(x_i) = 0.58 \mu\text{l}; u(x_i)_{rel} = 0.58 \%$$

$$10 \mu\text{l} \pm 0.15 \mu\text{l}: u(x_i) = 0.09 \mu\text{l}; u(x_i)_{rel} = 0.90 \%$$

With these three contributions the standard uncertainty $u(V_{pipettes})$ and relative standard uncertainty $u_{rel}(V_{pipettes})$ of the volume V are calculated.

$$u(V_{pipettes}) = \sqrt{(4.62 \mu\text{l})^2 + (0.58 \mu\text{l})^2 + (0.09 \mu\text{l})^2} = 4.66 \mu\text{l} = 4.66 \cdot 10^{-3} \text{ ml}$$

$$u_{rel}(V_{pipettes}) = \sqrt{(0.46 \%)^2 + (0.58 \%)^2 + (0.90 \%)^2} = 1.17 \%$$

The uncertainty in measurement was determined only for a couple of experiments:

- μ -CTE experiments with solutions of the target compounds with the SDVB-polymer (Table 4.21)
- experiment with soaked wood in chamber 3 (Table 4.22)
- experiment with soaked wood in showcase 3-6 (Table 4.23)

Since several different calibrations were used for the evaluation of the experiments the indicated uncertainty in measurement is only valid for experiments evaluated with the same calibration and conducted in the same way. Table 4.20 shows the uncertainty contributions of the stock solutions, calibrations, air sampling and elutions. The standard coefficient of each experiment is given with the combined and expanded uncertainties of the experiments in Table 4.21 to Table 4.23.

Table 4.20: Uncertainty contributions for the determination of the combined uncertainties $u_c(y)$ of the mentioned experiments

Contribution	[%]
$u_{rel}(V_{flask})_{stock}$	0.30
$u_{rel}(V_{pipettes})_{calibration}$	1.30
$u_{rel}(V_{flask})_{calibration}$	0.30
$u_{rel}(V_{pipettes})_{elution}$	1.17
$u_{rel}(V_{flow\ meter})$	1.00
$u_{rel}(V_{pump})$	3.00

Table 4.21: Standard coefficients V_{x_0} , combined uncertainties $u_c(y)$ and expanded uncertainties $U(y)$ of the μ -CTE experiment with target compound solution (SDVB-polymer) ($f = 5$; $t = 2.57$)

Compound	V_{x_0} [%]	$u_c(y)$ [%]	$U(y)$ [%]
Lindane	4,61	5,05	12,99
PCP	5,57	5,94	15,27
PCB 28	4,30	4,77	12,26
Dichlofluanid	10,77	10,97	28,20
Isodrin	5,77	6,13	15,76
Tolyfluanid	11,88	12,06	31,00
PCB 153	5,07	5,47	14,06
p,p'-DDT	10,70	10,90	28,02
Permethrin 1	18,45	18,56	47,72
Permethrin 2	20,18	20,29	52,16
Benzo[a]pyrene	11,63	11,81	30,36

Table 4.22: Standard coefficients V_{x_0} , combined uncertainties $u_c(y)$ and expanded uncertainties $U(y)$ of the experiment with soaked wood in a 24 l emission test chamber (chamber 3) ($f = 5$; $t = 2.57$)

Compound	V_{x_0} [%]	$u_c(y)$ [%]	$U(y)$ [%]
Lindane	4,52	5,72	14,70
PCP	13,04	13,50	34,70
PCB 28	8,29	9,00	23,14
Dichlofluanid	5,71	6,70	17,23
Isodrin	4,52	5,72	14,70
Tolyfluanid	4,67	5,83	15,00
PCB 153	11,96	12,46	32,03
p,p'-DDT	8,10	8,82	22,67
Permethrin 1	2,67	4,40	11,31
Permethrin 2	4,67	5,83	15,00
Benzo[a]pyrene	3,33	4,83	12,42

Table 4.23: Standard coefficients V_{x_0} , combined uncertainties $u_c(y)$ and expanded uncertainties $U(y)$ of the showcase experiments (showcase 3-6) ($f = 5$; $t = 2.57$)

Compound	V_{x_0} [%]	$u_c(y)$ [%]	$U(y)$ [%]
Lindane	4.70	5.86	15.06
PCP	7.96	8.70	22.36

4.4.3 Error and uncertainty

Apart from uncertainty in measurement, the error of the measurement procedure is another parameter for the quality of the measurement results. It is important to distinguish between uncertainty and error; the differences are described in the EURACHEM/CITAC guide [74] and are as follows:

“[...] Error is defined as the difference between an individual result and the true value of the measurand. [...] Uncertainty, on the other hand, takes the form of a range, and, if estimated for an analytical procedure and defined sample type, may apply to all determinations so described. In general, the value of the uncertainty cannot be used to correct a measurement result. [...] An error is regarded as having two components, namely, a random component and a systematic component. Random error typically arises from unpredictable variations of influence quantities. These random effects give rise to variations in repeated observations of the measurand. The random error of an analytical result cannot be compensated for, but it can usually be reduced by increasing the number of observations. [...] Systematic error is defined as a component of error which, in the course of a number of analyses of the same measurand, remains constant or varies in a predictable way. It is independent of the number of measurements made and cannot therefore be reduced by increasing the number of analyses under constant measurement conditions. [...] A further type of error is a spurious error, or blunder. [...] Uncertainties estimated using this guide are not intended to allow for the possibility of spurious errors/blunders.”

4.4.3.1 Maximum error

The maximum error is the sum of the systematic and statistical errors, where the spurious error is not considered [74]. Furthermore, the systematic error is bigger than the statistical error.

The result Y is calculated by the measurands X_i :

$$Y = f(X_1, X_2, \dots, X_i). \quad \text{Equation 4.12 [75]}$$

The error of the measurands X_i is ΔX_i . The maximum error ΔY of Y is given by

$$\Delta Y = \sum_i \frac{\partial Y}{\partial X_i} \Delta X_i. \quad \text{Equation 4.13}$$

If $f(X_1, X_2, \dots, X_i)$ is a product then the maximum error is given by

$$\frac{\Delta Y}{Y} = \sum_i \left| \frac{\Delta X_i}{X_i} \right|. \quad \text{Equation 4.14}$$

Equation 4.14 means that the relative error of the result is from the sum of the relative errors of the measurands X_i .

The maximum error of the procedure consists of several individual errors:

- Error of the stock solution (volumetric flask)
- Error of the stock solution for the calibration solutions (error stock solution, volumetric flask and pipettes)
- Error of the calibration solutions (error stock solution of the calibration solutions and pipettes)
- Error air sampling (error flow meter for μ -CTE and pump for emission test chambers, showcases and indoor air)
- Error elution (error pipettes)

The relative errors given for the flow meter and pumps are added up to the relative error of the procedure.

The formulas for the calculations of the single errors are given below.

Error of the stock solution ΔC_{stock} (volumetric flask V_v):

$$\Delta C_{stock} = \frac{\Delta V_v}{V_v} C_{stock}$$

Error of the stock solution for the calibration solutions ΔC_0 (error stock solution, volumetric flask and pipettes V_p):

$$\Delta C_0 = \left(\frac{\Delta C_{stock}}{C_{stock}} + \frac{\Delta V_v}{V_v} + \frac{\Delta V_p}{V_p} \right) C_0$$

Error of the calibration solutions ΔC_{1-8} (error stock solution of the calibration solutions and pipettes):

$$\Delta C_{1-8} = \left(\frac{\Delta C_0}{C_0} + \frac{\Delta V_p}{V_p} \right) C_{1-8}$$

The relative error of the whole procedure is calculated as follows:

$$\Delta Y = \left(\frac{\Delta C_1}{C_1} + \frac{\Delta C_2}{C_2} + \frac{\Delta C_3}{C_3} + \frac{\Delta C_4}{C_4} + \frac{\Delta C_5}{C_5} + \frac{\Delta C_6}{C_6} + \frac{\Delta C_7}{C_7} + \frac{\Delta V_p}{V_p} \right) Y$$

$$\Delta Y_{rel} = \frac{\Delta Y}{Y} = \left(\frac{\Delta C_1}{C_1} + \frac{\Delta C_2}{C_2} + \frac{\Delta C_3}{C_3} + \frac{\Delta C_4}{C_4} + \frac{\Delta C_5}{C_5} + \frac{\Delta C_6}{C_6} + \frac{\Delta C_7}{C_7} + \frac{\Delta V_p}{V_p} \right) \cdot 100 \%$$

$$\Delta Y_{reltotal} = \Delta Y_{rel} + \Delta V_{rel\text{flowmeter} / \text{relpump}}$$

As the process of determining the maximum error is relatively complex, it was only calculated for the results of the μ -CTE experiments with target compound solution and the results of the experiment in chamber 3 with an air change rate of 0.2 h^{-1} .

The relative error of the μ -CTE results, which are evaluated with a calibration consisting of seven calibration levels, is also depending on the relative error of the flow meter. This results in a relative error of

$$\Delta Y_{rel\ total\ (flow\ meter)} = 18.60\ \%$$

The relative error of the results of the experiment in chamber 3, which are evaluated with a calibration consisting of seven calibration levels, is also depending on the relative error of the pump. This results in a relative error of

$$\Delta Y_{rel\ total\ (pump)} = 22.70\ \%$$

5 Application of the developed method

5.1 Investigation of real samples and indoor air

The investigations of real samples in test chambers and indoor air are an objective of the developed method and it is useful to check its applicability even during the development process. Thus, this method was applied in projects investigating wood samples in the μ -CTE and indoor air quality. The first real samples were already investigated in the μ -CTE after successfully performed tests with target compound solutions. Additional μ -CTE tests and indoor air samplings were also performed though in a later stage of the method development.

In some cases the air sampling in the μ -CTE as well as indoors was also performed with Tenax[®] TA (60/80) – a 2,6-diphenylene oxide polymer suitable for thermodesorption (TD). It is a polymer predominately used for air sampling of VOCs, lower boiling SVOCs and higher boiling VVOCs. By using these results an evaluation of the developed air sampling method and its associated outcome is possible. As further dilutions are not necessary for thermodesorption with Tenax[®] TA, the sampled air volume is lower than for the SDVB-polymer. The measurements of the Tenax[®] TA samples were carried out on a GC-MS system from Agilent Technologies (GC: 6890; MS: 5973) with a TD system TDS 3 from Gerstel. The chromatographic separation was realized on a DB-5MS (5% phenyl, 95% dimethylpolysiloxane) column (60 m \times 0.25 mm \times 0.25 μ m).

- CIS temperature program: -101 °C for 0.1 min, 12 °C s⁻¹ to 290 °C for 5 min
- TD temperature program: 40 °C, 40 °C min⁻¹ to 290 °C for 5 min
- GC oven temperature program: 40 °C for 10 min, 3 °C min⁻¹ to 80 °C, 10 °C min⁻¹ to 300 °C for 10 min, 40 °C min⁻¹ to 40 °C (run time 61.83 min)

5.1.1 Investigation of real wood samples in the μ -CTE

Sixteen historic wood samples (*Table 5.1*) dating from the 18th to the 20th century were analyzed. These samples had been treated between 1950 and 1980 with wood preservatives containing among others PCP, lindane and dichlofluanid as active agents. All samples originate from floor or interior equipment from the same estate built between 1870-1900. The origins of sample 01-11 are known in detail (house 1-4) but for sample A-E they are unknown. This fairly precise knowledge of their origin is advantageous for the further analysis, since it is very difficult to obtain homogeneous samples for the required air sampling experiments. In addition, these samples can be heated up to 80 °C in the μ -CTE, accelerating the experimental time.

Table 5.1: Sample number and description of the analyzed wood samples

#	Description	#	Description
01	Floor (House 1)	A	Floor
02	Interior equipment (House 1)	B	Interior equipment
03	Interior equipment (House 1)	C	Interior equipment
04	Interior equipment (House 2)	D	Interior equipment
05	Interior equipment (House 3)	E	Window coating
06	Floor (House 3)		
07	Floor (House 4; ground floor)		
08	Floor (House 4; first floor)		
09	Floor (House 4; second floor)		
10	Floor (House 4; third floor)		
11	Floor (House 4; fourth floor)		

5.1.2 Investigation of wood samples and indoor air quality of a wood-based world heritage site church

During the method development process, determinations of wood protective agents in a world heritage church made solely of wood were undertaken by combining several measurement strategies, see [78, 79]. The small wood splinters (sample 12-17), which have been removed from the church, were investigated in the μ -CTE and indoor air sampling was performed at the places where samples 14 and 15 were removed. Sample 16 is a reference sample, which was treated with Hylotox[®] about 30 years ago. Included in this study were Tenax[®] TA measurements for indoor air sampling and for sample 17 in the μ -CTE.

5.1.3 Air sampling in a museum repository

Further indoor air sampling with the SDVB-polymer and Tenax[®] TA was done in a museum repository, containing several cupboards storing exhibits contaminated with biocides. The air sampling was conducted in a relatively large storage room, two cupboards contained inside this storage room, and in an office located close to the storage room.

5.2 Evaluation of the real samples and indoor air investigations

For the evaluation of the experiments with real samples it is important to bear in mind, that the measured concentrations at higher temperatures might be lower than the true air concentrations in the μ -CTE cells, because of possible condensation processes in the exhaust air outlet or on the chamber lid (for details see Section 6.3). The effect of the condensation was not determined in this study.

5.2.1 Results of the investigation of real wood samples in the μ -CTE

The treatment of the real wood samples with wood preservatives happened more than 30 years ago. Samples 01-11 were the first to be investigated using this developed method and the elution of the SDVB-polymer was carried out with only 1000 μ l toluene at this stage. At 23 °C no SVOCs were detectable through air sampling with the SDVB-polymer. PCP, lindane and dichlofluanid were detectable due to the vaporization into the gas phase at 80 °C in a concentration range between 35-1800 $\mu\text{g m}^{-3}$. Dichlofluanid was measured in the air of eight out of eleven samples; PCP and lindane were present in the μ -CTE air of all eleven samples. See *Table 5.2* for the concentration values at 80 °C. As the samples had been measured other LoD and LoQ values were valid, the associated values are shown in *Table 5.3*.

Table 5.2: Results [$\mu\text{g m}^{-3}$] of the real wood samples (01-11) in the μ -CTE at 80 °C

Day	1	2	1	2	1	2
Compound Sample #	PCP [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]	Dichlofluanid [$\mu\text{g m}^{-3}$]	Dichlofluanid [$\mu\text{g m}^{-3}$]
01	1800	1400	350	200	45	44
02	1600	1000	340	170	80	63
03	79	75	45	35	51	47
04	770	450	79	37	46	50
05	330	230	120	69	1000	920
06	1300	1000	330	220	680	490
07	350	160	89	41	-	-
08	850	300	260	100	39	43
09	300	110	110	38	-	-
10	1400	460	330	140	-	-
11	710	210	160	45	66	55

Table 5.3: LoD and LoQ values for the experiment with real wood samples (01-11)

Compound	LoD [$\text{ng }\mu\text{l}^{-1}$]	LoQ [$\text{ng }\mu\text{l}^{-1}$]	Air sampling volume 50 l
			Elution volume 1000 μ l LoQ [$\mu\text{g m}^{-3}$]
PCP	0.53	1.58	31.60
Lindane	0.13	0.44	8.80
Dichlofluanid	0.07	0.23	4.64

Samples A-E were investigated when the method development was completed, hence the elution was made with 3×500 μ l solvent. As in samples 01-11, PCP and lindane could be detected in all samples investigated at 80 °C in a concentration range between 13-1200 $\mu\text{g m}^{-3}$ and in sample B at 23 °C. Dichlofluanid was measured in two of the five samples at 80 °C and p,p'-DDT in one of the samples but only on the first sampling day. Their concentrations are in the same range as the PCP and lindane concentrations. See *Table 5.4* for the concentration values.

Table 5.4: Results [$\mu\text{g m}^{-3}$] of the real wood samples (A-E) in the μ -CTE at 23 °C and 80 °C

Day	1	2	1	2	1	2	1	2
Compound	PCP	PCP	Lindane	Lindane	Dichlofluanid	Dichlofluanid	p,p'-DDT	p,p'-DDT
Sample #	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]
B (T = 23 °C)	21	22	17	16	-	-	-	-
A (T = 80 °C)	35	35	30	17	-	-	49	47
B (T = 80 °C)	1200	830	420	250	-	-	-	-
C (T = 80 °C)	32	27	42	24	-	-	-	-
D (T = 80 °C)	20	19	15	13	39	-	-	-
E (T = 80 °C)	34	24	50	20	38	38	-	-

A valuation of these results is difficult, because the experiments in the literature for measuring biocide concentrations in air were either conducted at 23 °C in emission test chambers for a longer period of time (up to several month or years [40, 49]) or indoors at ambient temperature.

5.2.2 Results of the real wood samples from a world heritage side church and air sampling in this church

The wood splinters removed from treated wooden elements in the church were investigated in the μ -CTE. In three of the five wood splinters analyzed biocides could be detected by measurements at 80 °C. PCP, lindane, tolyfluanid and p,p'-DDT were emitted by these samples and their concentration values are shown in Table 5.5. Only the chamber air of sample 17 was sampled with Tenax[®] TA, but with a sampling volume eighteen fold lower as with the SDVB-polymer.

Table 5.5: Results of the wood splinters from a church investigated in the μ -CTE at 80 °C on the first sampling day with the SDVB-polymer and Tenax[®] TA

Adsorbent	Sample #	Sampling volume [l]	PCP [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]	Tolyfluanid [$\mu\text{g m}^{-3}$]	p,p'-DDT [$\mu\text{g m}^{-3}$]
SDVB-polymer	12	36.7	-	-	-	-
	13	31.9	-	-	-	-
	14	31.0	-	-	76	-
	15	35.0	350	76	84	-
	16	35.5	-	-	-	20
	17	34.6	44	25	63	-
	Tenax [®] TA	17	2.4	30	3	5

At the places where sample 14 and 15 were removed, indoor air sampling measurements were done. The measured concentrations of PCP are lower than its corresponding LoQ for this sampling volume. Lindane and tolyfluanid could be measured in the indoor air above its LoQ. At these points the air sampling was also done with Tenax[®] TA, for which lower sampling volumes were sufficient. PCP and lindane could be detected above their LoQ with Tenax[®] TA as an adsorbent. Table 5.6 presents the results obtained with both adsorbents.

Table 5.6: Results of the indoor air measurements in the church with the SDVB-polymer and Tenax® TA

Adsorbent	Sample #	Day	Sampling volume [l]	PCP [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]	Tolyfluanid [$\mu\text{g m}^{-3}$]
SDVB-polymer	Origin of 14	1/2	360	< 1.81	-	0.52
	Origin of 15	1/2	360	< 1.81	0.30	0.53
Tenax® TA	Origin of 14	1	25	0.13	-	0.50
	Origin of 14	2	27	0.12	-	0.53
	Origin of 15	1	24	0.61	0.23	0.44
	Origin of 15	2	21	0.71	0.24	0.58

As shown in Table 5.6 the measured tolyfluanid concentrations are similar for the SDVB-polymer and Tenax® TA. However, the sampling volume for the SDVB-polymer is about 14 times higher than for Tenax® TA to obtain similar concentration values. Contrastingly, in the μ -CTE measurements of sample 17 (Table 5.5) lower concentrations were measured with the lower sampling volume for Tenax® TA.

These indoor air concentrations of lindane and PCP are higher than the ones measured by Blessing and Derra [30], who found indoor air concentrations of lindane and PCP of $> 2 \text{ ng m}^{-3}$ from the inside of buildings also treated with wood preservatives in the past. The PCP concentrations of up to 570 ng m^{-3} measured by Schnelle-Kreis et al. [80] indoors, which were treated with PCP containing wood preservatives at least 7 years ago, are similar to the ones in the world heritage side church.

5.2.3 Results of the air sampling in a museum repository

The analyzed air of the two cupboards in the museum repository contains measurable amounts of lindane, which was measured with the SDVB-polymer and Tenax® TA (Table 5.7). Similar concentrations of both adsorbents were measured in the cupboards, again with different air sampling volumes. The amount of sampled air was approximately 20 times higher with the SDVB-polymer.

In the office and the storage room biocides were not detected with any of the adsorbents. Conversely, a lindane concentration of $0.16 \mu\text{g m}^{-3}$ was measured by Schieweck et al. in a storage room of the Lower Saxony State Museum in Hanover (Germany) [81].

Table 5.7: Results of the air sampling in two cupboards of a museum repository

Adsorbent	Sample	Sampling volume [l]	Lindane [$\mu\text{g m}^{-3}$]
SDVB-Polymer	Cupboard 1	61.9	3
	Cupboard 2	62.8	2
Tenax® TA	Cupboard 1	3.2	4
	Cupboard 2	3.2	2

5.2.4 Comparison SDVB-polymer – Tenax[®] TA

In the two above mentioned experiments indoor air sampling and μ -CTE sampling was performed with the SDVB-polymer and partially with Tenax[®] TA. The results obtained with both adsorbents are mainly similar but the required air sampling volumes differ strongly as it is fourteen- to twentyfold lower for Tenax[®] TA than for the SDVB-polymer. A reason for that is the required dilution of the sampled compounds, which is inevitable for the elution of the SDVB-polymer.

Although the sampled air volumes of the new developed method are quite low compared to ASTM D 6209-98 [7] and VDI 4301 part 2 [6], satisfying results are obtained, which was confirmed for at least a few experiments by comparing them with the Tenax[®] TA results.

6 Discussion

6.1 Statistical parameters of the developed GC-MS-MS method

The LoD, LoQ, reproducibility and linearity of the calibration were determined as statistical parameters for the developed GC-MS-MS method (see *Section 4.1.2*).

LoQ values between 0.03-0.09 ng μl^{-1} were obtained for the compounds from lindane to p,p'-DDT, whereas PCP, permethrin 1, permethrin 2 and benzo[a]pyrene have LoQs higher than 0.20 ng μl^{-1} (*Table 4.2* in *Section 4.1.2.1*). PCP is derivatized to improve the selectivity using MS-MS and its LoQ is about nine times lower than of underivatized PCP. However, the LoQ values for the used air sampling volumes are between 1-6 $\mu\text{g m}^{-3}$ for most of the compounds and for the less volatile compounds the LoQ is up to 23 $\mu\text{g m}^{-3}$ depending on the sampled air volume (*Table 9.9* in *Section 9.3.2*). LoQ values and sensitivity of the method are dependent on the air sampling volume (for more details see *Section 6.4*). The higher the sampled air volume the lower the LoQ.

The reproducibility of the GC-MS-MS system was checked with four different solutions ($c_1 \approx 0.3$ ng μl^{-1} ; $c_2 \approx 0.6$ ng μl^{-1} ; $c_3 \approx 3$ ng μl^{-1} and $c_4 \approx 6$ ng μl^{-1} ; *Table 4.3* in *Section 4.1.2.2*) and they are in an acceptable range between 0.43 and 8.09 %, but this differs strongly for some components in the lower concentration range e.g. for p,p'-DDT (c_1 and c_2), permethrin 2 (c_1 and c_2) and benzo[a]pyrene (c_1 and c_2). However, lindane, PCP and PCB 28 have their highest variances at the highest measured concentration and not as expected at c_1 or c_2 , although the concentration ranges of c_1 or c_2 are already up to ten times higher than the LoQ.

By using Mandel's goodness-of-fit test the linearity of every calibration was checked. The *TV* of all compounds in every calibration is lower than their corresponding *F*-value (*Table 9.10* to *Table 9.21* in *Section 9.3.3*), hence all calibrations are linear. This is true for all compounds except for permethrin 2 (low range) of calibration solution 4, because in this case the *TV* is higher than its *F*-value. Furthermore, a quadratic goodness-of-fit is preferable for a better evaluation of some calibrations.

Calibration ranges influence the linearity of the calibrations and its *TV*. Since the ranges are partly very high for the used calibrations, the quality of the linearity might increase by reducing the calibration range. That would also minimize the number of calibrations preferring a quadratic goodness-of-fit.

Considering the four statistical parameters determined for the developed GC-MS-MS method, the method is usable for this study but has to be improved concerning its reproducibility and linearity of the calibrations.

6.2 Elution and extraction experiments

The elution and extraction experiments with target compound solutions were performed with the SDVB-polymer and PUF to compare their elution/extraction qualities (see *Section 4.2*).

During the method development process it became obvious that PCP is not elutable from the SDVB-polymer with toluene as a solvent. As PCP was not available for the adsorbent selection experiments, this could not be realized in the beginning of this study. Since XAD-2 has already been successfully used in the past for the air sampling of PCP using for example diethyl ether as extraction solvent [47], it was obvious that the wrong solvent and not an inadequate adsorbent was selected. For that reason this experiment was repeated using acetone² as the elution solvent to check whether or not PCP is elutable from the polymer with a different solvent. Recovery rates of 47 % were obtained with acetone as the elution solvent, which shows that the SDVB-polymer is an appropriate adsorbent for air sampling of PCP.

Method recoveries of the elution/extraction experiments were determined for the method validation (see *Section 4.4.1.1*) to check their qualities. The elution experiment with the SDVB-polymer was performed once in the beginning and for a second time at the end of the method development, whereby some changes (see *Section 4.2.2*) were made in the meantime. Recovery rates between 95-103 % were obtained for the first experiment (performed without PCP and p,p'-DDT) and for the second experiment recovery rates of 58-127 % were determined with relative standard deviations between 0.86-3.80 %. PCB 153 and permethrin 2 had recovery rates higher than 100 % (103 and 101 %) in the first experiment but in the second experiment PCB 28, isodrin, permethrin 1, permethrin 2 and benzo[a]pyrene had recovery rates which were even higher than in the first experiment especially for benzo[a]pyrene (104, 105, 109, 103 and 126 %). As previously mentioned in *Section 4.2.2* there is no explanation for recovery rates higher than 100 %. On the contrary, the recovery rates for PUF are between 36-99 % with relative standard deviations of 0.16-6.72 % for all SVOCs except for PCB 28 (74 and 111 %, relative standard deviation 28.10 %).

6.3 μ -CTE air sampling experiments with target compound solutions

The air sampling ability of the SDVB-polymer and PUF were compared in μ -CTE experiments at 80 °C (see *Section 4.3.2.1*). In addition to the air sampling quality of the adsorbents, the vaporization behavior of the selected SVOCs and POMs were also tested at 23 °C and at 80 °C. Recovery rates were also determined for the method validation (see *Section 4.4.1.2*). The SDVB-polymer recovery rates at 23 °C (14-55 %, relative standard deviations 0.63-5.45 %) and 80 °C (10-60 %, relative standard deviations 3.87-13.86 %) vary in part from the expected behavior. Lindane has its highest recovery rate at 23 °C and not as expected at 80 °C. PCP and PCB 28 have similar recovery rates at both temperatures, which is not astonishing for PCP but for PCB 28. With PUF better recovery rates were obtained for most of the compounds at 80 °C (25-76 %, relative standard deviations 0.08-10.16 %) especially for PCB 28 and PCB 153, which have recovery rates about 30 and 40 % higher than with the SDVB-polymer. A higher recovery

² Acetone was selected because it was used as solvent for the PUF extraction.

with the SDVB-polymer was only obtained for benzo[a]pyrene, which was the only compound that could not be sampled with PUF.

Although PCP was not detectable in elution experiments with the SDVB-polymer, it was measurable in the eluate of air sampling experiments. A reason for that might be that a small amount of PCP was adsorbed at the PE filter by passing it on its way to the polymer. Therefore, the actual PCP concentrations in the sampled air might be higher but this can only be checked by using a different solvent and that was not done in this study; lower measured air concentrations are the result of this. Hence, all air sampling results of PCP have a further indefinable error.

All compounds except for PCP have their highest recovery rates in the elution/extraction experiments and not in the μ -CTE experiments. Furthermore, the sum of both relative amounts from elution and rinsing or the value from rinsing only do not amount to 100 %. This is important and has to be considered, especially for the evaluation of the experiments with soaked and real wood samples. It can be assumed that the losses are caused by the low volatile respectively POM character of the compounds and their tendency to adsorb on surfaces even at 80 °C. Condensation of the compounds might occur at 80 °C on the chamber lid or in the exhaust air outlet, which the compounds have to pass to desorb on the adsorbent. These two parts of the μ -CTE were not investigated by rinsing. According to this experiment PUF seems to be the adsorbent of choice for the selected compounds except for benzo[a]pyrene due to the obtained recovery rates (*Table 4.7* and *Table 4.8* in *Section 4.3.2.1*). However, the SDVB-polymer was selected as the air sampling adsorbent for this study because it performed better in the first elution test, it is easier to handle and has a lower solvent expense compared to PUF.

Unlabelled ISTDs, 4-(4-chlorobenzoyl) pyridine and dieldrin, were used in this study, because it was only necessary to control the analysis rather than the whole process (including air sampling). To control the whole process from air sampling to elution of the polymer labeled ISTDs are the better choice due to their similar behavior compared to their unlabeled analogues.

6.4 Soaked wood samples in emission test chambers

The experiments with self soaked wood samples were realized in different emission test chamber types and various effects like temperature, air circulation, air change rate and relative humidity on the SVOC and POM emissions were investigated under different conditions (see *Section 4.3.3*).

The temperature influence was investigated in the μ -CTE and in 23 l and 24 l emission test chambers (see *Sections 4.3.3.1* and *4.3.3.3*). Lindane to isodrin were detectable in the μ -CTE at 23 °C, and at 80 °C all compounds from lindane to permethrin 2 were measurable in the μ -CTE air (*Table 9.24* and *Table 9.25* in *Section 9.3.5*). The fact that benzo[a]pyrene was not detectable in the μ -CTE experiments with soaked wood samples, even at 80 °C might be due to its POM character and its associated lower volatility (for more details see *Section 7.1*). Emitted by the soaked wood samples in the 24 l chamber at ambient temperature were lindane to tolyfluamid and at temperatures between 70-90 °C in

the 23 l chamber again these lower volatile SVOCs were the emitted compounds (*Table 9.28* and *Table 9.29* in *Section 9.3.5*). Since the compounds from lindane to permethrin 2 were detected in the μ -CTE at 80 °C it is conspicuous that in the 23 l chamber only the lower boiling SVOCs were detectable. The lower air change rate and the associated lower area specific air change rate in the 23 l chamber might influence the emission behavior of the SVOCs. In these experiments the theoretical assumption was confirmed as the air concentrations in the μ -CTE were always higher than in the bigger emission test chambers because of the higher air change rate per sample surface (area specific air change rate) [60]. As previously mentioned, the concentrations measured at higher temperatures might not necessarily match with the true concentrations because condensation might occur, but the experiments at higher temperatures can also be used for a screening of samples to determine if they are contaminated with biocides, PCBs or PAHs.

The influence of air circulation on the emission behavior was investigated in showcase experiments by using active and diffusive sampling (see *Section 4.3.3.2*). Air circulation has a high influence on emissions, which was shown by active sampling where no compounds could be measured without air circulation. However, at least lindane and PCP could be detected by active sampling with an air circulation. Air circulation also improved the results obtained by diffusive sampling with object slides. With air circulation more compounds could be detected and they were adsorbed on more object slides.

The impact of the air change rate on the SVOC emission at ambient temperature is very high in showcases. Active air sampling of SVOCs in showcase air worked at air change rates of 1 h^{-1} but it was not working at an air change rate of 0.5 h^{-1} (see *Section 4.3.3.2*). Lindane could be detected under this condition but PCP was not detectable in this experiment at both air change rates. It was assumed that it would take longer for lindane and PCP emissions at an air change rate of 0.5 h^{-1} to be measured due to the lower area specific air change rate, but it was not expected that emissions would not be detected in this experiment. Hence, it is obvious that the air change rate and area specific air change rate have a huge impact on the SVOC emissions from the samples. The lower the air change rates, the lower the area specific air change rates and consequently the emissions of the SVOCs.

Active air sampling with retransfer of the sampled air back into the chamber was successfully performed at an air change rate of 0.2 h^{-1} in a 24 l chamber (see *Section 4.3.3.3*). The emission process at this low air change rate was approximately twice as long as with an air change rate of 1.3 h^{-1} , but the emitted concentration ranges were similar. The same active air sampling strategy was tested in showcases with and without air circulation with air change rates of 0.10 - 0.26 h^{-1} however, none of the SVOCs and POMs were measured in quantifiable amounts (see *Section 4.3.3.2*). In these experiments the quality of the results was not as positively influenced by air circulation as it was in the other showcase experiments. Since this air sampling strategy worked in an emission test chamber with nearly the same air change rate it is astonishing that it does not work in showcases. The highest measurable amounts of all detectable compounds (lindane to tolyfluanid) were sampled in the emission test chamber on the second experimental day. The geometry of both chamber types and the positions of the ventilators are the main variables that have the highest effect on the experimental outcome.

Showcases have a rectangular shape with sidewise installed ventilators whereas 23 l and 24 l emission test chambers have a cylindrical shape with centrally arranged ventilators, which results in different air circulations in both chamber types. In each emission test chamber dead zones – zones with lower up to no air circulation – and zones with stronger air circulation exists. When samples are placed in these zones their emissions are affected and are either lower or higher than in zones with a regular circulation. Dead zones and zones with stronger air circulations can be seen in the flow patterns (*Figure 2.15 to Figure 2.17 in Section 2.5.2*) of the 23 l emission test chambers especially at the chamber's top and bottom but they were measured with differently arranged samples. For showcases, only flow directions and velocities are available (*Figure 4.7 in Section 4.3.3.2*) with no information about dead zones or zones with stronger circulations.

Clausen et al. [82] investigated the influence of the air flow rate in a field and laboratory emission cell on material emissions and discovered that the air flow rate is positively correlated with the air flow over the material surface and the air change rate. Their results show, that the SER_a increases with increasing flow rate, which can also be seen in the results of the 23 l and 24 l emission test chamber experiments (*Figure 4.11 to Figure 4.13 in Section 4.3.3.3*).

The emission behavior of the selected biocides, PCBs and PAHs might not be influenced by relative humidity since the selected SVOCs and POMs are not water-soluble. Only emissions from water-soluble compounds can be affected by different relative humidities. The effect of relative humidity on the SVOC emission was also investigated by Clausen et al. [83] for another water-insoluble SVOC, in which emissions were not influenced by relative humidity in a stainless steel chamber.

Active air sampling was performed in the second experiment in a 23 l emission test chamber after 90 days, although the air change rate was only 0.003 h^{-1} . Only one soaked wood sample was introduced into the chamber (chamber 4), which was soaked in a higher concentrated solution than the other four wood samples for the emission test chamber experiments (chamber 1-3). Due to the different concentrated solutions (target compound solution 5 and 9, *Table 9.4 and Table 9.5 in Section 9.3.1*) and the different number of introduced samples, the ratio of the introduced sample amount and sample surface varies. The total air concentration in chamber 4 must have theoretically been higher but this chamber worked without an activated air circulation, which as demonstrated, influences the emission behavior (see above). All these parameters have an influence on the SER_a , which is much lower for chamber 4 than for chamber 1-3, and primarily dependent on the concentration, air change rate and product loading factor (*Equation 2.3 in Section 2.5*).

The product loading factor (*Table 6.1*) also influences the results, because it is different for each test chamber type depending on the test chamber volume and the introduced sample surface area. It is almost similar for 27 l showcases, 23 l and 24 l emission test chambers but it is about 10 times higher for the μ -CTE. Due to the big differences of the product loading factors between the μ -CTE and the other two test chambers it is obvious that higher concentration values are obtained in the μ -CTE.

Table 6.1: Product loading factors L in different emission test chambers

Chamber type	L [m ² m ⁻³]
μ-CTE	20.50
Showcase	1.59
23 l Emission test chamber	1.86
24 l Emission test chamber	1.78

On the one hand the results are influenced by the investigated parameters but on the other hand they are also influenced by the low air sampling volume and the correlated low sensitivity of the method. The sensitivity is connected to the sampling volume – the lower the sampling volume, the lower the sampled amount on the adsorbent. Usually the higher volatile SVOCs (lindane to tolyfluandid) could be sampled in the three emission test chamber types with volumes between 24-50 l. To check whether it is possible to sample the lower volatile SVOCs with higher sampling volumes, a further experiment in 23 l emission test chambers as well loaded with four soaked wood samples was undertaken and volumes of 100 l and 420 l were sampled one day after loading the chambers. The results did not improve by sampling 100 l but with a volume of 420 l it was possible to measure PCB 153 and p,p'-DDT emissions. Permethrin emissions could not be measured after one day in the emission test chamber air by sampling 420 l. Jann et al. [64] already published that permethrin emissions are not measurable on the first experimental days in test chambers but only after approximately ten days, which is possibly due to its less volatile character or chamber and sample inherent sink-effects. Benzo[a]pyrene emissions were not detectable on the adsorbent because of a missing transport medium (see Section 7.1).

The impact of the low air sampling volume can be seen in the duration of the compound emissions. Lindane was the compound with the longest emission process in 23 l and 24 l emission test chamber experiments and mostly the only detectable compound in the showcase experiments. Since lindane has the second highest vapor pressure of all of the investigated compounds, the emission process must be faster than that of the other compounds with a lower volatility. Hence, the air sampling volume might be too low to sample quantifiable amounts of the other SVOCs and POMs due to their lower emissions and consequently the sensitivity of the method is influenced. The μ-CTE results are similar concerning the emissions of the high and low volatile compounds. PCP and the compounds from tolyfluandid to permethrin 2 cannot be detected on the seventh and eighth day of the μ-CTE experiment at 80 °C, whereas the compounds from lindane to isodrin were mostly detectable at these sampling days. The sampling volumes of all emission test chamber experiments were similar (μ-CTE: 36 l respectively 43 l; emission test chambers: 42 l; showcases: 42 l respectively 30 l) but the air change rates were different (μ-CTE: approximately 35 h⁻¹; emission test chambers: 1.3 h⁻¹ and 0.2 h⁻¹; showcases: approximately 1 h⁻¹, 0.5 h⁻¹ respectively 0.1-0.3 h⁻¹).

Although it is only possible to sample small air volumes due to the given conditions in showcases, the resulting LoQ values have a relatively low sensitivity (1-6 μg m⁻³ for

volumes of 24-50 l) for the higher volatile compounds (lindane to p,p'-DDT). However, LoQs between 4-23 $\mu\text{g m}^{-3}$ are obtained for the less volatile compounds and it is also more difficult to sample them in the test chamber air not least due to their less volatile character.

6.5 Method validation: Uncertainty in measurement and maximum error

The uncertainty in measurement and the maximum error of the method were determined to validate the method. Since the determination of the uncertainty in measurement and maximum error are very complex both parameters were only determined for the most important experiments of this study (see *Sections 4.4.2 and 4.4.3.1*).

μ -CTE experiments with target compound solutions (SDVB-polymer) and the experiments with soaked wood samples in chamber 3 ($n = 0.2 \text{ h}^{-1}$) and in showcase 3-6 ($n = 0.5 \text{ h}^{-1}$ respectively 1 h^{-1} ; r. h. approximately 34 % respectively 63 %) belong to the most important experiments of this study and hence their uncertainty in measurement were determined. These experiments were useful to test air sampling of the SVOCs and POMs with low sampling volumes as well as to test air sampling at low air change rates and the strategy which requires retransfer of the sampled air back into the test chamber. Hence, all relevant aspects of the study were considered for the uncertainty in measurement determination. Each of these experiments have five uncertainty contributions and combined uncertainties $u_c(y)$ up to 9-20 % and expanded uncertainties $U(y)$ of 22-52 % were obtained (*Table 4.21 to Table 4.23 in Section 4.4.2.1*). Since the t -value decreases with increasing degrees of freedom, the number of uncertainty contributions has a high influence on the expanded uncertainties and the contributions have as well an influence on the combined uncertainties.

Relative maximum errors were calculated for the μ -CTE experiments with target compound solutions (SDVB-polymer) and the experiment in chamber 3 ($n = 0.2 \text{ h}^{-1}$), both using a calibration solution consisting of seven calibration levels for the evaluation (see *Section 4.4.3.1*). Further contributions to the relative errors are either the relative error of the flow meter (μ -CTE experiments) or the relative error of the pump (chamber 3). The obtained relative errors are 18.60 % for the μ -CTE experiments and 22.70 % for chamber 3.

7 Conclusion and outlook

7.1 Conclusion

This study proved the suitability of the SDVB-polymer as an adsorbent for air sampling of biocides, PCBs and PAHs. According to the literature [7, 8, 30, 46] cited in *Section 2.3* the SDVB-polymer was already used as single air sampling adsorbent or in combination with PUF for some of the selected compounds. Air volumes up to 60 l were sampled with this polymer and no breakthroughs occurred by sampling air concentrations up to $170 \mu\text{g m}^{-3}$ in the μ -CTE air of self soaked wood samples (see *Section 4.3.3.1*); it is even possible to sample much higher concentrations. 200 mg of SDVB-polymer is suitable for the collection of at least up to $100 \text{ ng } \mu\text{l}^{-1}$ SVOC and POM without breakthroughs, which corresponds to a concentration range of $2500\text{-}6250 \mu\text{g m}^{-3}$ for sampling volumes between 24-60 l. This high concentration range is necessary for the developed method, because concentrations up to $1800 \mu\text{g m}^{-3}$ were measured in the μ -CTE air of real wood samples at 80°C . Since air concentrations increase at 80°C in the μ -CTE, this method is useful to quickly determine if samples are contaminated with the selected compounds.

Low volume air sampling of benzo[a]pyrene, which is the only investigated POM in this study, could not be successfully performed. This was because test chambers are supplied with purified or synthetic air no particles are present in the chambers where POMs could adsorb to be transported onto the adsorbent. Even by rinsing the μ -CTE cells after the investigation of soaked wood samples at 80°C benzo[a]pyrene and the SVOCs were not detectable on the walls. However, it is important to recognize that although the experiment at 80°C lasted for 36 days, between the 8th day (the last emissions were measured on that day) and the 35th day no air sampling was performed (see *Section 4.3.3.1*). In the meantime, the compounds which probably adsorbed on the walls, had enough time to desorb and leave the μ -CTE without being adsorbed on any adsorbent.

The aim of this study – the development of a low volume active air sampling strategy at low air change rates – could successfully be realized in a 24 l emission test chamber but unfortunately not in 27 l showcases (for more details see *Section 6.4*). Active air sampling and their results are influenced by several parameters. First of all the sensitivity of the method has the largest impact on the experimental outcome. Sampling volumes of several hundred liters influence the sensitivity positively but are worse for active air sampling in showcases. Another parameter is the lack of particles (e.g. dust particles) in the purified or synthetic air contained in the chamber promoting the transport especially of POMs (see above). Furthermore, the compound transport in the test chambers is also influenced by air circulation. At last the sink-effect, which increases for higher boiling compounds and the associated stronger adsorption tendencies of the SVOCs and POMs [58], also might have had an impact on the compound transport and consequently on the results. In the results of the third showcase experiment's test series the influence of the sink-effect became obvious. The object slides served as sinks for most of the compounds even though they only adsorbed onto a few of them. However, the influence of the sink-effect on the results of this study was not investigated in further experiments. Difficulties of the SVOC transport are either induced by air circulation, which can be seen in this experiment and in the first test series by comparing the results with and without air circulation (see

Section 4.3.3.2), or eventually by sink-effects. Due to sink-effects the desorption of the compounds adsorbed at surfaces of the chamber material into the chamber air is delayed [58]. Furthermore, it was shown that in 23 l and 24 l emission test chambers and showcase experiment results, the higher boiling SVOCs were not detectable in the chamber air at ambient temperature and at around 70-90 °C. This might also be affected by sink-effects of the higher boiling SVOCs and not only by the low method sensitivity.

Taking all arguments into consideration it can be seen that the developed low volume air sampling method is applicable to investigate samples in the μ -CTE at 23 °C and 80 °C with sampling volumes between approximately 30-50 l. Low volume air sampling in showcases working with low air change rates cannot be performed successfully by now due to the low sensitivity of the method and the low air circulation in real working showcases. Using such a low air sampling volume and air circulation makes it difficult to obtain meaningful results but they are nonetheless useful to get an idea of the investigated parameters and samples.

7.2 Outlook

Before the developed method and air sampling strategy can be used for measurements of real samples in showcases at low air change rates several improvements have to be made, especially concerning the sensitivity of the method.

First of all the elution process has to be optimized to elute PCP from the SDVB-polymer and to improve the lindane recovery rate. As already mentioned in Section 4.2.2 toluene is an inapplicable solvent for the elution of PCP from the SDVB-polymer. Acetone was already tested as solvent to elute PCP (see Section 6.2) but is still not sufficient enough; hence, further solvents (e.g. dichloromethane or diethyl ether) also have to be tested. After the successful determination of an elution solvent for PCP the whole elution process needs to be optimized, because all other compounds, except for lindane, can be eluted with toluene. The elution of lindane might also be optimized with a different solvent. Furthermore, a different ISTD has to be selected for PCP which is derivatized as well to control the derivatization step.

Since condensation of SVOCs and POMs might occur at 80 °C on the μ -CTE lid or in the exhaust air outlet these parts should be rinsed off with solvent, but it might be more difficult than rinsing the chamber jars due to the μ -CTE arrangement. The intensity of sink-effects in all used emission test chamber types should also be investigated to improve low volume air sampling.

The air sampling method and strategy has to be reconsidered especially concerning the air sampling volumes to improve the results. A better sensitivity is achieved by increasing the air sampling volume, because simultaneously the LoD and LoQ decrease with increasing sampling volumes. Sampling volumes in the range of several hundred liters are better suited to sample the selected compounds but they are inappropriate in this range to sample air of showcases working with low air change rates. Nevertheless, an active air sampling strategy with retransfer of the sampled air back into the chamber seems to be still the best active air sampling strategy. This strategy could be improved after

investigating the disturbance of the chamber equilibrium, which occurs by retransferring the sampled air back into the emission test chamber or showcase. For example, its intensity could be investigated by a computational fluid dynamics simulation.

When solutions for all aforementioned parameters are available, active air sampling at low air change rates with retransfer of the sampled air back into the test chamber is a promising air sampling option for showcases working under real conditions.

8 Literature

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9 Appendix

9.1 Chemicals and adsorbents

Compound / adsorbent	Distributor
4-(4-Chlorobenzoyl) pyridine 99 %	Alfa Aesar
Benzo[a]pyrene (pure)	Supelco
Dichlofluamid (PESTANAL [®] , Analytical standard)	Sigma-Aldrich
Dieldrin (PESTANAL [®] , Analytical standard)	Sigma-Aldrich
Isodrin (PESTANAL [®] , Analytical standard)	Sigma-Aldrich
Lindane (PESTANAL [®] , Analytical standard)	Sigma-Aldrich
p,p'-Dichlorodiphenyltrichloroethane (pure)	Sigma-Aldrich
PCB 153 (OEKANAL [®] , Analytical standard)	Sigma-Aldrich
PCB 28 (OEKANAL [®] , Analytical standard)	Sigma-Aldrich
Pentachlorophenol 98 %	Sigma-Aldrich
Permethrin (pure)	Supelco
Tolyfluamid (pure)	Supelco
Acetone (analytical reagent A.R.)	Lab Scan
Toluene (for organic residue analysis)	J.T. Baker
Technical Lindane	VEB Fettchemie
Technical Pentachlorophenol	Schuchardt
¹³ C ₆ Lindane (99 % in Nonane)	Cambridge Isotope Laboratories, Inc.
Silica (1000 mg) (CUSIL)	UCT
Silica (500 mg) (Strata [™] SI-1 Silica)	Phenomenex
SDVB-polymer (200 mg and 500 mg) (Strata [™] X)	Phenomenex
SDVB-polymer (50 mg) (Bond Elut [™] PPL)	Varian
Cyanopropyl adsorbent (200 mg) (Strata [™] CN)	Phenomenex
Magnesium silicate (500 mg) (Strata [™] Florisil [®] (FL-PR))	Phenomenex
Trifunctional octadecyl adsorbent (100 mg) (Bond Elut [™] C18)	Varian
PUF (2.2 cm O.D. × 7.6 cm length; density 0.022 g cm ⁻³)	Supelco

9.2 Experimental part

9.2.1 Calibration solutions

For the preparation of standard mixtures pure substances were used. Known amounts of the compounds were dissolved in toluene in 10 ml volumetric flasks, these are known as the stock solutions. To prepare the target compound solutions a certain amount of stock solution was mixed with toluene in a volumetric flask.

Several calibration solutions with different target compound concentrations were prepared for the calibrations. Different ISTD concentrations were also used. Additionally, the target compound solutions were used for the elution experiments, μ -CTE experiments and for the soaking of wood samples.

The tables in *Section 9.3.1* contain all information about the ISTDs and target compound solutions and about the calibration solutions for the determination of LoD and LoQ.

9.2.1.1 Preparation of calibration solutions

From a target compound solution eight dilutions were prepared and a specific amount of ISTD was added to every dilution level. The volume of the dilution levels was 1000 μ l or 1500 μ l, depending on the elution and extraction volume. Derivatization reagent (400 μ l acetic anhydride and 400 μ l pyridine in 200 μ l toluene) was added to most calibration dilutions to derivatize PCP.

9.2.1.2 Calibration solutions for the LoD and LoQ

Calibration solution 1 (lindane to benzo[a]pyrene), 2 (PCP) and 3 (derivatized PCP) were prepared and measured for the determination of the LoD and LoQ.

9.2.2 Adsorbent

9.2.2.1 Selection of an adsorbent

Depending on the adsorbent amount, a specific amount of toluene was used to moisten the adsorbent before the solution of the target compounds and ISTDs were added onto the adsorbent. The adsorbent elution was made with toluene. The tests were carried out in duplicate for PUF and SDVB-polymer (50 and 200 mg), while for all the other adsorbents a single determination was performed. See *Table 9.1* for experimental details.

Table 9.1: Experimental details for the elution of all tested adsorbents, see Section 9.3.1 for the target compound solutions, ISTD mixtures and ISTDs (number in brackets)

Adsorbent (Amount)	Moistening amount [μl]	Pre-conditioning [μl]	Target compound solution [μl]	ISTD mixture or ISTD [μl]	Solvent amount for elution [μl]
Silica (1000 mg)*	1500	-	200 (4)	150 (1 ^m)	3 × 500
SDVB (500 mg)*	1500	-	200 (4)	150 (1 ^m)	3 × 500
-SiCH ₂ CH ₂ CH ₂ CN (200 mg)*	300	-	200 (4)	150 (1 ^m)	3 × 500
SDVB (200 mg)*	600	2 × 500	100 (4)	20 (2 ^m)	2 × 500
-SiC ₁₈ H ₃₇ (100 mg)*	100	2 × 500	50 (4)	20 (2 ^m)	2 × 500
SDVB (50 mg)*	100	2 × 500	50 (4)	20 (2 ^m)	2 × 500
Silica (500 mg)*	1000	2 × 500	100 (4)	20 (2 ^m)	2 × 500
SDVB (500 mg)*	1500	2 × 500	100 (4)	20 (2 ^m)	2 × 500
Magnesium silicate (MgO ₃ Si) (500 mg)*	500	2 × 500	100 (4)	20 (2 ^m)	2 × 500
Polyurethane foam	-	-	100 (5)	10 (6 + 7)	Extraction**

* Injection volume: 1 μl ; ** see Section 9.2.3.2 for experimental details of the PUF extraction

For the determination of the uncertainty in measurement the elution experiment with the SDBV-polymer (200 mg) was repeated in a fivefold determination. The polymer was moistened with 540 μl toluene before 150 μl target compound solution 5 and each 15 μl ISTD 6 and 7 were added. The elution was made with 3 × 500 μl toluene and the samples were derivatized with 10 μl derivatization reagent (for further details see Section 9.2.3.2).

9.2.2.2 Determination of the elution volume

The SDVB-polymer was moistened with toluene before 100 μl of target compound solution 6 as well as 10 μl of ISTD 1 and 2 for the elution with 1000 μl and 2 × 500 μl toluene were added on the adsorbent. For the elution with 1500 μl and 3 × 500 μl toluene, 150 μl of target compound solution 6 and 15 μl of ISTD 1 and 2 were added onto the adsorbent. The SDVB-polymer was eluted three times with the aforementioned solvent amount and for every elution volume a duplicate determination was made.

9.2.3 Air sampling

9.2.3.1 Equipment

The following air sampling pumps were used for this study:

- SKC-pump: SKC Inc. AirCheck XR5000
- AMA-pump: AMA Instruments PN 5500
- DESAGA-pump: DESAGA GS 312

- Pump trolley: Self-designed, consisting of a diaphragm pump and mass flow control devices

The air flow in the μ -CTE experiments was measured with two different flow meters – at first with Bios Definer 220 and later with Electronic Flowmeter Veri-Flow 500 from Agilent Technologies. The Bios Definer 220 normalizes all measured air flows to a temperature of 21.2 °C.

9.2.3.2 General procedures

SDVB-polymer elution: After the air sampling the adsorbent was moistened with toluene and the ISTD was added onto the adsorbent before it was eluted with toluene. Most of the solutions were derivatized for the quantification and identification of PCP.

PUF extraction: After the air sampling the PUF was transferred into a pear-shaped flask and approximately 60-70 ml acetone and 1 ml toluene were added. The foam was extracted in an ultrasonic bath for approximately 45 min. Afterwards the foam was squeezed and rinsed out with approximately 20 ml acetone and an additional 1 ml of toluene was added as well as 10 μ l of each ISTD. The solvent was allowed to evaporate until almost dryness in a rotary evaporator. The residue was transferred into a 1 ml volumetric flask and the remaining solvent was also allowed to evaporate until almost dryness. The pear-shaped flask was rinsed with acetone twice and the solvent was transferred to the volumetric flask and evaporated. The volumetric flask was then filled up to 1 ml with toluene and this solution was transferred into a GC vial. The solutions were derivatized for the quantification and identification of PCP.

Derivatization of PCP: To better determine PCP using MS-MS, the solutions were derivatized with 10 μ l reagent (reagent: 400 μ l acetic anhydride and 400 μ l pyridine in 200 μ l toluene) with sonication for 30 min.

9.2.3.3 Micro-chamber

The air sampling in the μ -CTE experiments lasted 24 h with an air flow between approximately 20-35 ml min⁻¹ (sampling volume in total ~ 30-50 l), controlled with a flow meter for each chamber cell through the adsorbent. One chamber per μ -CTE run was used for blank values.

9.2.3.4 Air sampling and breakthrough experiments

The μ -CTE was set to the desired temperature (23 °C or 80 °C) and afterwards 150 μ l (for SDVB-polymer) respectively 100 μ l (for PUF) target compound solution 5 were injected into the chamber cells. Subsequently the process for air sampling with the

adsorbents was started. The breakthrough was checked with a second adsorbent in series.

- SDVB: T = 23 °C; air flow: ~ 20 ml min⁻¹ (~ 29 l); four chambers
- SDVB: T = 80 °C; air flow: ~ 20 ml min⁻¹ (~ 29 l); four chambers
- PUF: T = 80 °C; air flow: ~ 32 ml min⁻¹ (~ 46 l); four chambers

15 µl ISTD 6 and 7 were added onto the SDVB-polymer and the elution was made with 3 × 500 µl toluene. Furthermore, the chambers were rinsed with 1.5 ml toluene containing 15 µl of ISTD 6 and 7. The solutions were derivatized for the quantification and identification of PCP. For the PUF work-up 10 µl ISTD 6 and 7 were used.

9.2.3.5 Comparison of the ISTDs

The comparison of the labeled and unlabeled ISTD was investigated with 150 µl target compound solution 7 at 23 °C.

- SDVB: T = 23 °C; air flow: ~ 27 ml min⁻¹ (~ 38 l); four chambers

15 µl ISTD 6 and 8 were added onto the SDVB-polymer and the elution was made with 3 × 500 µl toluene.

9.2.4 Air sampling experiments with soaked wood

Soaking: Pine sapwood was soaked in target compound solution 5 for 1 h (30 min per broadside). The samples were weighed before and after soaking and dried in ambient air for a minimum of 24 h.

9.2.4.1 Soaked wood in the µ-CTE

Every µ-CTE cell was loaded with one piece of soaked pine sapwood and was set at 23 °C for two days (air sampling on both days) and afterwards for a period of 36 days at 80 °C (air sampling on day 0, 1, 7, 8, 35 and 36). Breakthrough was checked with a second adsorbent in series on day 0 and 1 at 80 °C.

- T = 23 °C; air flow: ~ 30 ml min⁻¹ (~ 43 l), 2 days
- T = 80 °C; air flow: ~ 25 ml min⁻¹ (~ 36 l), 36 days

15 μl ISTD 4 and 5 were added onto the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. Furthermore, all chambers were rinsed with 1.5 ml toluene containing 15 μl of ISTD 4 and 5.

9.2.4.2 Soaked wood in showcases

Every showcase was loaded with four soaked pine sapwood samples standing on one of their longest sides.

First test series

For the air sampling in showcase 1 sampling volumes of 42 l or 144 l (100 ml min^{-1}) were collected with the SDVB-polymer with a SKC-pump for 55 days.

The experiment in showcase 2 equipped with a ventilator lasted for 36 days. Air sampling with the SDVB-polymer was done with an AMA-pump ($42 \text{ l}; 500 \text{ ml min}^{-1}$). 15 μl ISTD 6 and 7 were added onto the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. The solutions were derivatized for the quantification and identification of PCP.

- Showcase 1:
 - Without air circulation
 - $n = 2.6 \text{ h}^{-1}$ (until day 35), $n = 1.0 \text{ h}^{-1}$ (from day 36)
 - $T = (22 \pm 1) \text{ }^\circ\text{C}$
 - r. h. = $(51 \pm 5) \%$
 - Experimental time: 55 days
 - Air sampling days: 42 l: 2, 6, 9, 13, 16, 20 and 23
144 l: 27, 30, 34, 37, 48 and 55
- Showcase 2:
 - With air circulation
 - $n = 1.2 \text{ h}^{-1}$
 - $T = (26 \pm 1) \text{ }^\circ\text{C}$
 - r. h. = $(48 \pm 1) \%$
 - Experimental time: 36 days
 - Air sampling days: 42 l: 4, 7, 15, 18, 32 and 36

Second test series

The four showcases in the second test series were all equipped with a ventilator and the wood was soaked in target compound solution 9. Active air sampling was done with the SDVB-polymer. Sampling volumes of 30 l (air flow: 100 ml min^{-1} for $n = 0.5 \text{ h}^{-1}$ and 300 ml min^{-1} for $n = 1 \text{ h}^{-1}$) were collected with an AMA-pump and later with the pump trolley. 15 μl ISTD 6 were added onto the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. The solutions were derivatized for the quantification and identification of PCP.

- Showcase 3:
 - With air circulation
 - $n = 1.0 \text{ h}^{-1}$
 - $T = (26 \pm 6) \text{ }^\circ\text{C}$
 - r. h. = $(66 \pm 16) \%$
 - Experimental time: 172 days
 - Air sampling days: 12, 18, 25, 32, 40, 53, 62, 67, 74, 82, 89, 95, 102, 109, 116, 123, 144, 151, 158, 165 and 172
- Showcase 4:
 - With air circulation
 - $n = 0.5 \text{ h}^{-1}$
 - $T = (26 \pm 5) \text{ }^\circ\text{C}$
 - r. h. = $(59 \pm 19) \%$
 - Experimental time: 172 days
 - Air sampling days: 11, 18, 25, 32, 40, 54, 62, 67, 74, 81, 89, 95, 102, 109, 116, 123, 144, 151, 158, 165 and 172
- Showcase 5:
 - With air circulation
 - $n = 1.0 \text{ h}^{-1}$
 - $T = (26 \pm 5) \text{ }^\circ\text{C}$
 - r. h. = $(34 \pm 5) \%$
 - Experimental time: 174 days
 - Air sampling days: 12, 18, 25, 32, 40, 53, 62, 67, 74, 82, 89, 95, 102, 109, 116, 123, 144, 151, 158, 165 and 174

- Showcase 6:
 - With air circulation
 - $n = 0.5 \text{ h}^{-1}$
 - $T = (26 \pm 5) \text{ }^\circ\text{C}$
 - r. h. = $(33 \pm 7) \%$
 - Experimental time: 172 days
 - Air sampling days: 12, 19, 26, 33, 41, 54, 62, 67, 74, 81, 89, 95, 102, 109, 116, 123, 144, 151, 158, 165 and 172

Third test series

Ten object slides were introduced into the showcases together with the soaked wood pieces and were removed periodically. Both sides were rinsed with $2 \times 1000 \mu\text{l}$ toluene through a funnel and the solution was sampled in a flask. Afterwards the funnel was rinsed with $1000 \mu\text{l}$ toluene. $10 \mu\text{l}$ ISTD 6 and 7 were added to the solution and it was evaporated to $1000 \mu\text{l}$. The remaining solution was transferred into a GC vial for measurement and derivatized with $10 \mu\text{l}$ derivatization reagent.

- Showcase 7:
 - Without air circulation
 - $n = 0.02 \text{ h}^{-1}$
 - $T = (22 \pm 1) \text{ }^\circ\text{C}$
 - r. h. = $(50 \pm 1) \%$
 - Experimental time: 34 days
 - Removing of the object slides: 2, 6, 9, 13, 16, 20, 23, 27, 30 and 34
- Showcase 8 :
 - With air circulation
 - $n = 0.37 \text{ h}^{-1}$
 - $T = (25 \pm 1) \text{ }^\circ\text{C}$
 - r. h. = $(14 \pm 12) \%$
 - Experimental time: 34 days
 - Removing of the object slides: 3, 6, 10, 13, 17, 20, 24, 27, 31 and 34

Fourth test series

Two of the four showcases in the fourth test series were equipped with a ventilator and the wood was soaked in target compound solution 5b. Active air sampling was done with the SDVB-polymer. Sampling volumes of 30 l (air flow: 100 ml min⁻¹) were collected with an AMA-pump and the sampled air was retransferred back into the showcase after passing the adsorbent and the pump. 15 µl ISTD 6 and 7 were added onto the adsorbent and the elution was made with 3 × 500 µl toluene. The solutions were derivatized for the quantification and identification of PCP.

- Showcase 9:
 - With air circulation
 - $n = 0.26 \text{ h}^{-1}$
 - $T = (26 \pm 1) \text{ }^{\circ}\text{C}$
 - r. h. = $(49 \pm 1) \%$
 - Experimental time: 23 days
 - Air sampling days: 2, 9, 16 and 23
- Showcase 10:
 - With air circulation
 - $n = 0.19 \text{ h}^{-1}$
 - $T = (26 \pm 1) \text{ }^{\circ}\text{C}$
 - r. h. = $(35 \pm 10) \%$
 - Experimental time: 23 days
 - Air sampling days: 2, 9, 16 and 23
- Showcase 11:
 - Without air circulation
 - $n = 0.20 \text{ h}^{-1}$
 - $T = (25 \pm 1) \text{ }^{\circ}\text{C}$
 - r. h. = $(52 \pm 3) \%$
 - Experimental time: 23 days
 - Air sampling days: 2, 9, 16 and 23

- Showcase 12:
 - Without air circulation
 - $n = 0.10 \text{ h}^{-1}$
 - $T = (26 \pm 2) \text{ }^\circ\text{C}$
 - r. h. = $(47 \pm 14) \%$
 - Experimental time: 23 days
 - Air sampling days: 2, 9, 16 and 23

9.2.4.3 Soaked wood in 23 l and 24 l emission test chambers

First test series

Every emission test chamber was loaded with four soaked pine sapwood samples, which were standing on one of their longest sides, and worked with different air change rates, temperatures and relative humidities. Volumes of 42 l were sampled in the two chambers with $n = 1.3 \text{ h}^{-1}$ first with a SKC-pump (100 ml min^{-1}) and later with an AMA-pump (500 ml min^{-1}). For air sampling in the chamber with $n = 0.2 \text{ h}^{-1}$, an AMA-pump (500 ml min^{-1}) and later the pump trolley (500 ml min^{-1}) were used and the sampled air was retransferred into the chamber after passing the pump. $15 \mu\text{l}$ ISTD 6 and 7 were added on the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. The solutions were derivatized for the quantification and identification of PCP.

- Chamber 1:
 - 24 l emission test chamber
 - $n = 1.3 \text{ h}^{-1}$
 - Ambient temperature
 - Experimental time: 103 days
 - Air sampling days: 1, 6, 8, 12, 15, 19, 22, 26, 29, 33, 36, 40, 50, 54, 57, 61, 64, 68, 71, 79, 82 and 103
- Chamber 2:
 - 23 l emission test chamber
 - $n = 1.3 \text{ h}^{-1}$
 - Higher temperature ($70\text{-}90 \text{ }^\circ\text{C}$)
 - Experimental time: 69 days
 - Air sampling days: 2, 6, 9, 16, 20, 23, 27, 34, 37, 41, 44, 48, 50, 55, 58, 65 and 69

- Chamber 3:
 - 24 l emission test chamber
 - $n = 0.2 \text{ h}^{-1}$
 - Ambient temperature
 - Experimental time: 196 days
 - Air sampling days: 2, 6, 9, 16, 20, 23, 27, 34, 37, 41, 44, 48, 50, 55, 58, 65, 69, 91, 105, 112, 119, 126, 133, 140, 156, 169, 184, 185 and 196

Second test series

The emission test chamber was loaded with one pine sapwood sample soaked in target compound solution 9, which was standing on one of its longest sides. A volume of 24 l (500 ml min^{-1}) was sampled with the pump trolley after 90 days. 15 μl ISTD 6 was added on the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. The solutions were derivatized for the quantification and identification of PCP.

- Chamber 4:
 - Without air circulation
 - 24 l emission test chamber
 - $n = 0.003 \text{ h}^{-1}$
 - $T = (19 \pm 1) \text{ }^\circ\text{C}$
 - r. h. = $(53 \pm 14) \%$
 - Active air sampling after 90 days with the SDVB-polymer

9.2.5 Investigations of real samples and indoor air

9.2.5.1 μ -CTE investigations of real wood samples

The μ -CTE was set to $23 \text{ }^\circ\text{C}$ and the chamber cells were loaded with samples 01-11 respectively A-E. The samples remained in the chambers for the experiments at $80 \text{ }^\circ\text{C}$, which followed the ones at $23 \text{ }^\circ\text{C}$. Air sampling was done on separate days, because a duplicate measurement in parallel using the μ -CTE is not possible.

First samples (01-11)

- $T = 23 \text{ }^\circ\text{C}$; air flow: $\sim 35 \text{ ml min}^{-1}$ ($\sim 50 \text{ l}$)
- $T = 80 \text{ }^\circ\text{C}$; air flow: $\sim 35 \text{ ml min}^{-1}$ ($\sim 50 \text{ l}$)

10 μl ISTD 1 and 2 were added onto the adsorbent and the elution was made with 1000 μl toluene³. 1 μl of the solution was injected for GC-MS-MS measurements.

Second samples (A-E)

- T = 23 °C; air flow: $\sim 30 \text{ ml min}^{-1}$ ($\sim 40 \text{ l}$)
- T = 80 °C; air flow: $\sim 30 \text{ ml min}^{-1}$ ($\sim 40 \text{ l}$)

15 μl ISTD 6 and 7 were added onto the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene. The solutions were derivatized for the quantification and identification of PCP.

9.2.5.2 μ -CTE investigations of real wood samples from a world heritage site church and air sampling in this church

μ -CTE tests

The μ -CTE was set to 23 °C and the chambers were loaded with sample numbers 12-17. The samples remained in the chambers for the experiments at 80 °C, which followed the ones at 23 °C. Again air sampling was done on two separate days (see Section 9.2.5.1).

- T = 23 °C; air flow: $\sim 25 \text{ ml min}^{-1}$ ($\sim 36 \text{ l}$)
- T = 80 °C; air flow: $\sim 25 \text{ ml min}^{-1}$ ($\sim 36 \text{ l}$)

15 μl ISTD 4 and 5 (ISTD 6 and 7 for sample 17) were added onto the adsorbent and the elution was made with $3 \times 500 \mu\text{l}$ toluene.

Indoor air measurements

360 l were sampled on the SDVB-polymer in 6 cycles á 60 l (1 l min^{-1}) on two days with a DESAGA-pump.

- Air sampling origin of sample 14: T = 20 °C; r. h. = 67 %
- Air sampling origin of sample 15: T = 20 °C; r. h. = 67 %

³ This is the only experiment in which an elution volume of 1000 μl was used, as it was one of the first experiments performed during the process development phase. The other experiments of the development process were repeated with the new elution volume.

15 µl ISTD 6 and 7 were added onto the adsorbent and the elution was made with 3 × 500 µl toluene.

9.2.5.3 Air sampling in a museum repository

A volume of 62-63 l (500 ml min^{-1}) was sampled with an AMA-pump on the SDVB-polymer in the office, the storage room and the two cupboards of the museum repository. 15 µl ISTD 6 and 7 were added onto the adsorbent and the elution was made with 3 × 500 µl toluene. The solutions were derivatized for the quantification and identification of PCP.

9.3 Tables

9.3.1 ISTD mixtures, ISTDs, target compound solutions and calibration solutions

Table 9.2: ISTD mixtures

ISTD mixture #	Compound	[ng μl^{-1}]
1 ^m	4-(4-Chlorobenzoyl) pyridine	132
	Dieldrin	120
2 ^m	4-(4-Chlorobenzoyl) pyridine	500
	Dieldrin	505

Table 9.3: ISTDs

ISTD #	Compound	[ng μl^{-1}]
1	4-(4-Chlorobenzoyl) pyridine	1280
2	Dieldrin	920
3	Dieldrin	840
4	4-(4-Chlorobenzoyl) pyridine	1100
5	Dieldrin	1100
6	4-(4-Chlorobenzoyl) pyridine	220
7	Dieldrin	220
8	Lindane (¹³ C ₆ 99 % in Nonane)	100

Table 9.4: Target compound solutions 1-8

Solution of the target compound #	1	2	3	4	5
Compound	[ng μl^{-1}]	[ng μl^{-1}]	[ng μl^{-1}]	[ng μl^{-1}]	[ng μl^{-1}]
PCP	1.3	2.5	7.0		70.0
Lindane	1.3			107.2	62.0
PCB 28	1.3			100.8	33.0
Dichlofluanid	1.3			100.8	62.0
Isodrin	1.5			101.5	62.0
Tolyfluanid	1.1			99.0	66.0
PCB 153	0.9			102.0	33.0
p,p'-DDT	1.1				62.0
Permethrin	1.6			110.6	66.0
Benzo[a]pyrene	1.0			102.0	58.0
Solution of the target compound #	5b	6	7	8	
Compound	[ng μl^{-1}]	[ng μl^{-1}]	[ng μl^{-1}]	[ng μl^{-1}]	
PCP	70.0	101.6		14.0	
Lindane	62.0	93.8	49.6	12.4	
PCB 28	36.9	100.8		11.5	
Dichlofluanid	62.0	100.8		12.4	
Isodrin	62.0	101.5		12.4	
Tolyfluanid	66.0	99.0		13.2	
PCB 153	32.4	93.5		11.5	
p,p'-DDT	62.0	100.8		12.4	
Permethrin	66.0	94.8		13.2	
Benzo[a]pyrene	58.0	102.0		11.6	

Table 9.5: Target compound solution 9

Solution of the target compound #	9
Compound	[ng μl^{-1}]
technical PCP	418.4
technical Lindane	429.1

Table 9.6: Calibration solution 1 for the determination of the LoD and LoQ

Calibration level (1000 μl)	1	2	3	4	5	6	7	8
Compound	[ng μl^{-1}]							
Lindane	1.3	0.7	0.3	0.13	0.07	0.03	0.01	0.007
PCB 28	1.3	0.6	0.3	0.13	0.06	0.03	0.01	0.006
Dichlofluanid	1.3	0.6	0.3	0.13	0.06	0.03	0.01	0.006
Isodrin	1.5	0.7	0.4	0.15	0.07	0.03	0.01	0.007
Tolyfluanid	1.1	0.6	0.3	0.11	0.06	0.02	0.01	0.006
PCB 153	0.9	0.4	0.2	0.09	0.04	0.02	0.01	0.004
p,p'-DDT	1.1	0.6	0.3	0.11	0.06	0.02	0.01	0.006
Permethrin	1.6	0.8	0.4	0.16	0.08	0.03	0.02	0.008
Benzo[a]pyrene	1.0	0.5	0.3	0.10	0.05	0.02	0.01	0.005

Table 9.7: Calibration solution 2 for the determination of the LoD and LoQ of PCP

Calibration level (1000 μl)	1	2	3	4	5	6	7	8
Compound	[ng μl^{-1}]							
PCP	2.5	2.0	1.5	1.02	0.76	0.51	0.25	0.13

Table 9.8: Calibration solution 3 for the determination of the LoD and LoQ of derivatized PCP

Calibration level (1000 μl)	1	2	3	4	5	6	7
Compound	[ng μl^{-1}]						
PCP	0.7	0.4	0.14	0.07	0.04	0.02	0.01

9.3.2 Limits of quantification

Table 9.9: LoQ values for all air sampling volumes

Air sampling volume [l]	24	29	30	36	38	40	42
Elution volume [µl]	1500	1500	1500	1500	1500	1500	1500
	LoQ	LoQ	LoQ	LoQ	LoQ	LoQ	LoQ
	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]
PCP	27.13	22.45	21.70	18.08	17.13	16.28	15.50
Lindane	2.00	1.66	1.60	1.33	1.26	1.20	1.14
deriv. PCP	2.81	2.33	2.25	1.88	1.78	1.69	1.61
PCB 28	5.75	4.76	4.60	3.83	3.63	3.45	3.29
Dichlofluanid	3.31	2.74	2.65	2.21	2.09	1.99	1.89
Isodrin	3.38	2.79	2.70	2.25	2.13	2.03	1.93
Tolyfluanid	3.25	2.69	2.60	2.17	2.05	1.95	1.86
PCB 153	4.38	3.62	3.50	2.92	2.76	2.63	2.50
p,p'-DDT	2.19	1.81	1.75	1.46	1.38	1.31	1.25
Permethrin 1	15.81	13.09	12.65	10.54	9.99	9.49	9.04
Permethrin 2	23.06	19.09	18.45	15.38	14.57	13.84	13.18
Benzo[<i>a</i>]pyrene	12.44	10.29	9.95	8.29	7.86	7.46	7.11
Air sampling volume [l]	43	46	50	62	63	360	
Elution volume [µl]	1500	1000	1000	1500	1500	1500	
	LoQ	LoQ	LoQ	LoQ	LoQ	LoQ	
	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	[µg m ⁻³]	
PCP	15.14	9.43	8.68	10.50	10.33	1.81	
Lindane	1.12	0.70	0.64	0.77	0.76	0.13	
deriv. PCP	1.57	0.98	0.90	1.09	1.07	0.19	
PCB 28	3.21	2.00	1.84	2.23	2.19	0.38	
Dichlofluanid	1.85	1.15	1.06	1.28	1.26	0.22	
Isodrin	1.88	1.17	1.08	1.31	1.29	0.23	
Tolyfluanid	1.81	1.13	1.04	1.26	1.24	0.22	
PCB 153	2.44	1.52	1.40	1.69	1.67	0.29	
p,p'-DDT	1.22	0.76	0.70	0.85	0.83	0.15	
Permethrin 1	8.83	5.50	5.06	6.12	6.02	1.05	
Permethrin 2	12.87	8.02	7.38	8.93	8.79	1.54	
Benzo[<i>a</i>]pyrene	6.94	4.33	3.98	4.81	4.74	0.83	

9.3.3 Linearity of the calibration

Table 9.10: TV and F-value for calibration solution 1, 2 and 3

Compound	TV	F-value
PCP	10.02	21.19
derivatized PCP	1.46	98.50
Lindane	0.00	21.19
PCB 28	0.40	98.50
Dichlofluanid	0.30	34.11
Isodrin	0.40	98.50
Tolyfluanid	5.74	98.50
PCB 153	15.45	4052.18
p,p'-DDT	3.24	34.11
Permethrin 1	1593.66	4052.18
Permethrin 2	1.98	98.50
Benzo[a]pyrene	0.51	4052.18

Table 9.11: TV and F-value for calibration solution 4

Compound	TV	F-value
PCP	18.69	21.19
Lindane	12.36	21.19
PCB 28	0.60	21.19
Dichlofluanid (high range)	43.46	4052.18
Dichlofluanid (low range)	4.87	4052.18
Isodrin	4.89	21.19
Tolyfluanid	74.55	98.50
PCB 153	16.01	21.19
p,p'-DDT (high range)	275.83	4052.18
p,p'-DDT (low range)	7.28	4052.18
Permethrin 1 (high range)	552.61	4052.18
Permethrin 1 (low range)	0.81	98.50
Permethrin 2 (high range)	4227.44	4052.18
Permethrin 2 (low range)	9.41	98.50
Benzo[a]pyrene (high range)	2414.22	4052.18
Benzo[a]pyrene (low range)	1117.29	4052.18

Table 9.12: TV and F-value for calibration solution 5

Compound	TV	F-value
PCP	1.54	21.19
Lindane	0.56	21.19
PCB 28	1.10	21.19
Dichlofluanid	8.01	21.19
Isodrin	2.61	21.19
Tolyfluanid	8.39	21.19
PCB 153	0.69	21.19
p,p'-DDT	9.40	21.19
Permethrin 1	18.99	98.50
Permethrin 2	28.77	98.50
Benzo[a]pyrene	14.54	21.19

Table 9.13: TV and F-value for calibration solution 6

Compound	TV	F-value
PCP	24.07	34.11
Lindane	0.00	21.19
PCB 28	7.12	21.19
Dichlofluanid	5.91	21.19
Isodrin	6.27	21.19
Tolyfluanid	0.61	21.19
PCB 153	15.60	21.19
p,p'-DDT	10.50	21.19
Permethrin 1	7.82	34.11
Permethrin 2	19.01	34.11
Benzo[a]pyrene	2.59	34.11

Table 9.14: TV and F-value for calibration solution 7

Compound	TV	F-value
Lindane	0.40	16.25

Table 9.15: TV and F-value for calibration solution 8

Compound	TV	F-value
PCP	11.55	21.19
Lindane	0.14	21.19
PCB 28	0.26	21.19
Dichlofluanid	2.17	21.19
Isodrin	0.00	21.19
Tolyfluanid	2.03	21.19
PCB 153	0.54	21.19
p,p'-DDT	1.79	21.19
Permethrin 1	0.44	98.50
Permethrin 2	12.33	21.19
Benzo[a]pyrene	1.67	21.19

Table 9.16: TV and F-value for calibration solution 9

Compound	TV	F-value
PCP	19.62	34.11
Lindane	15.07	21.19
PCB 28	22.86	34.11
Dichlofluanid	16.02	21.19
Isodrin	12.45	21.19
Tolyfluanid	12.40	21.19
PCB 153	29.67	34.11
p,p'-DDT	14.42	21.19
Permethrin 1	1.88	21.19
Permethrin 2	0.69	21.19
Benzo[a]pyrene	0.01	21.19

Table 9.17: TV and F-value for calibration solution 10

Compound	TV	F-value
PCP	19.27	21.19
Lindane	14.35	16.25

Table 9.18: TV and F-value for calibration solution 11

Compound	TV	F-value
PCP	14.01	34.11
Lindane	0.79	34.11
PCB 28	298.11	4052.18
Dichlofluanid	100.72	4052.18
Isodrin	0.51	98.50
Tolyfluanid	1.85	98.50
PCB 153	22.35	34.11
p,p'-DDT	462.51	4052.18
Permethrin 1	16.09	34.11
Permethrin 2	21.43	34.11
Benzo[a]pyrene	26.93	98.50

Table 9.19: TV and F-value for calibration solution 12

Compound	TV	F-value
PCP	0.11	21.19
Lindane	14.80	21.19
PCB 28	0.74	21.19
Dichlofluanid	17.29	34.11
Isodrin	9.05	21.19
Tolyfluanid	0.02	21.19
PCB 153	6.93	21.19
p,p'-DDT	9.42	21.19
Permethrin 1	0.07	21.19
Permethrin 2	0.01	21.19
Benzo[a]pyrene	0.04	21.19

Table 9.20: TV and F-value for calibration solution 13

Compound	TV	F-value
PCP	56.38	98.50
Lindane	12.08	16.25
PCB 28	11.28	98.50
Dichlofluanid (high range)	20.59	34.11
Dichlofluanid (low range)	11.32	98.50
Isodrin	1.58	98.50
Tolyfluanid	14.69	98.50
PCB 153	27.36	98.50
p,p'-DDT	19.18	98.50
Permethrin 1	14.44	16.25
Permethrin 2	9.64	16.25
Benzo[a]pyrene	26.79	98.50

Table 9.21: TV and F-value for calibration solution 14

Compound	TV	F-value
PCP	0.19	21.19
Lindane	0.00	16.25
PCB 28	1.15	16.25
Dichlofluanid	11.76	16.25
Isodrin	0.25	16.25
Tolyfluanid	12.87	16.25
PCB 153	3.30	16.25
p,p'-DDT	3.15	21.19
Permethrin 1	12.18	16.25
Permethrin 2	0.03	21.19
Benzo[a]pyrene	12.29	16.25

9.3.4 Elution volume

Table 9.22: Results of the determination for the required elution volume of the SDVB-polymer with 1000 µl and 2 × 500 µl toluene

Elution volume [µl]	Compound	SDVB-polymer 1			SDVB-polymer 2		
		1. Elution [%]	2. Elution [%]	3. Elution [%]	1. Elution [%]	2. Elution [%]	3. Elution [%]
1000	Lindane	96	4	0	96	4	0
	4-(4-Chlorobenzoyl) pyridine	94	6	0	92	8	0
	PCB 28	97	3	0	96	4	0
	Dichlofluamid	97	3	0	97	3	0
	Isodrin	97	3	0	96	4	0
	Tolyfluamid	97	2	0	97	3	0
	Dieldrin	94	6	0	80	19	0
	PCB 153	97	3	0	97	3	0
	p,p-DDT	98	2	0	98	2	0
	Permethrin 1	98	2	0	98	2	0
	Permethrin 2	98	2	0	98	2	0
	Benzo[<i>a</i>]pyrene	95	5	0	95	5	0
	Lindane	97	3	0	98	2	0
	4-(4-Chlorobenzoyl) pyridine	94	6	0	95	5	0
2×500	PCB 28	97	3	0	98	2	0
	Dichlofluamid	98	2	0	99	1	0
	Isodrin	97	2	0	98	2	0
	Tolyfluamid	98	2	0	99	1	0
	Dieldrin	94	6	0	94	6	0
	PCB 153	98	2	0	98	2	0
	p,p-DDT	98	2	0	99	1	0
	Permethrin 1	98	2	0	99	1	0
	Permethrin 2	98	2	0	99	1	0
	Benzo[<i>a</i>]pyrene	96	4	0	97	3	0

Table 9.23: Results of the determination for the required elution volume of the SDVB-polymer with 1500 µl and 3 × 500 µl toluene

Elution volume [µl]	Compound	SDVB-polymer 1			SDVB-polymer 2		
		1. Elution [%]	2. Elution [%]	3. Elution [%]	1. Elution [%]	2. Elution [%]	3. Elution [%]
1500	Lindane	99	1	0	99	1	0
	4-(4-Chlorobenzoyl) pyridine	98	2	0	99	1	0
	PCB 28	99	1	0	99	1	0
	Dichlofluaniid	99	1	0	99	1	0
	Isodrin	99	1	0	99	1	0
	Tolyfluaniid	99	1	0	99	1	0
	Dieldrin	98	2	0	98	2	0
	PCB 153	99	1	0	99	1	0
	p,p-DDT	99	1	0	99	1	0
	Permethrin 1	99	1	0	99	1	0
	Permethrin 2	99	1	0	99	1	0
	Benzof[a]pyrene	99	1	0	99	1	0
	Lindane	100	0	0	100	0	0
	4-(4-Chlorobenzoyl) pyridine	100	0	0	100	0	0
3×500	PCB 28	100	0	0	100	0	0
	Dichlofluaniid	100	0	0	100	0	0
	Isodrin	100	0	0	100	0	0
	Tolyfluaniid	100	0	0	100	0	0
	Dieldrin	100	0	0	100	0	0
	PCB 153	100	0	0	100	0	0
	p,p-DDT	100	0	0	100	0	0
	Permethrin 1	100	0	0	100	0	0
	Permethrin 2	100	0	0	100	0	0
	Benzof[a]pyrene	100	0	0	100	0	0

9.3.5 Results of soaked wood samples in emission test chambers

Table 9.24: Concentration values [$\mu\text{g m}^{-3}$], standard deviation s and relative standard deviation RSD of the experiment with soaked wood in the μ -CTE at 23 °C and 80 °C (lindane to isodrin)

Compound	Day	0		1		7		8	
		23		80					
Concentration	T [°C]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]
Lindane	Chamber 1	65	64	150	86	60	59		
	Chamber 2	57	57	88	64	53	-		
	Chamber 3	61	62	110	71	60	60		
	Chamber 4	74	66	110	74	62	-		
	Chamber 5	58	58	110	66	-	-		
	Average	63	61	114	72	59	60		
	s [$\mu\text{g m}^{-3}$]	7	4	22	9	4	1		
	RSD [%]	11	6	20	12	7	1		
PCP	Chamber 1	-	-	150	120	100	100		
	Chamber 2	-	-	110	67	-	-		
	Chamber 3	-	-	130	110	-	-		
	Chamber 4	-	-	130	110	-	-		
	Chamber 5	-	-	110	100	-	-		
	Average			126	101	100	100		
	s [$\mu\text{g m}^{-3}$]			17	20				
	RSD [%]			13	20				
PCB 28	Chamber 1	19	19	69	28	15	15		
	Chamber 2	17	16	31	18	13	-		
	Chamber 3	17	18	38	21	-	-		
	Chamber 4	22	20	43	22	16	-		
	Chamber 5	16	15	37	19	-	-		
	Average	18	18	44	22	15	15		
	s [$\mu\text{g m}^{-3}$]	2	2	15	4	2			
	RSD [%]	13	12	34	18	10			
Dichlofluanid	Chamber 1	29	31	170	52	33	32		
	Chamber 2	27	29	76	35	27	-		
	Chamber 3	30	33	100	41	32	32		
	Chamber 4	33	36	120	44	33	-		
	Chamber 5	28	29	84	39	29	-		
	Average	29	32	110	42	31	32		
	s [$\mu\text{g m}^{-3}$]	2	3	38	6	3	0		
	RSD [%]	8	9	34	15	9	0		
Isodrin	Chamber 1	28	30	160	42	17	16		
	Chamber 2	26	24	63	23	-	-		
	Chamber 3	24	26	88	27	-	-		
	Chamber 4	36	32	99	28	16	-		
	Chamber 5	23	20	89	26	-	-		
	Average	27	26	100	29	17	16		
	s [$\mu\text{g m}^{-3}$]	5	5	36	7	1			
	RSD [%]	19	18	36	25	4			

Table 9.25: Concentration values [$\mu\text{g m}^{-3}$], standard deviation s and relative standard deviation RSD of the experiment with soaked wood in the μ -CTE at 23 °C and 80 °C (tolyfluanid to permethrin 2)

Compound	Day	0	1	0	1	7	8
	T [°C]	23		80			
Concentration		[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]	[$\mu\text{g m}^{-3}$]
Tolyfluanid	Chamber 1	-	-	140	41	23	22
	Chamber 2	-	-	70	26	-	-
	Chamber 3	-	-	90	30	-	-
	Chamber 4	-	-	110	33	-	-
	Chamber 5	-	-	66	28	-	-
	Average			95	32	23	22
	s [$\mu\text{g m}^{-3}$]			31	6		
	RSD [%]			32	19		
p,p'-DDT	Chamber 1	-	-	44	20	-	-
	Chamber 2	-	-	32	12	-	-
	Chamber 3	-	-	36	-	-	-
	Chamber 4	-	-	40	14	-	-
	Chamber 5	-	-	27	-	-	-
	Average			36	15		
	s [$\mu\text{g m}^{-3}$]			7	4		
	RSD [%]			19	27		
Permethrin 1	Chamber 1	-	-	27	26	-	-
	Chamber 2	-	-	26	24	-	-
	Chamber 3	-	-	29	26	-	-
	Chamber 4	-	-	31	28	-	-
	Chamber 5	-	-	26	25	-	-
	Average			28	26		
	s [$\mu\text{g m}^{-3}$]			2	1		
	RSD [%]			8	6		
Permethrin 2	Chamber 1	-	-	25	25	-	-
	Chamber 2	-	-	25	23	-	-
	Chamber 3	-	-	27	25	-	-
	Chamber 4	-	-	30	27	-	-
	Chamber 5	-	-	25	24	-	-
	Average			26	25		
	s [$\mu\text{g m}^{-3}$]			2	1		
	RSD [%]			8	6		

Table 9.26: Concentration values [$\mu\text{g m}^{-3}$] of the experiments in showcase 1 and 2

Day	Showcase 1		Showcase 2	
	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]
4	-	-	2	2
7	-	-	2	-
15	-	-	2	-
18	-	-	-	-
32	-	-	1	-

Table 9.27: Concentration values [$\mu\text{g m}^{-3}$] of the experiments in showcase 3 and 5

Day	Showcase 3	Showcase 5
	Lindane [$\mu\text{g m}^{-3}$]	Lindane [$\mu\text{g m}^{-3}$]
12	4	3
18	4	3
25	4	3
32	3	3
40	-	3
53	3	3
62	4	-
67	3	3
74	-	3
82	4	3
89	4	3
95	4	3
102	4	3
109	4	3
116	4	-
123	4	3
144	3	-
151	4	3
158	4	-
165	4	4
172	4	-
174		3

Table 9.28: Concentration values [$\mu\text{g m}^{-3}$] of the 24 l emission test chamber experiment (chamber 1; $n = 1.3 \text{ h}^{-1}$; ambient temperature)

Day	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	PCB 28 [$\mu\text{g m}^{-3}$]	Dichlofluanid [$\mu\text{g m}^{-3}$]	Isodrin [$\mu\text{g m}^{-3}$]	Tolyfluanid [$\mu\text{g m}^{-3}$]
1	7	-	-	-	6	-
6	33	5	10	9	32	5
8	13	-	5	5	14	3
12	10	2	4	5	12	3
15	6	-	-	3	6	2
19	7	-	-	4	8	3
22	5	-	-	4	6	3
26	5	-	-	3	6	3
29	3	-	-	3	4	2
33	3	-	-	2	4	2
36	2	-	-	-	-	-
40	2	-	-	2	-	2
50	2	-	-	-	-	-
54	2	-	-	-	-	-
57	1	-	-	-	-	-
61	-	-	-	-	-	-
64	-	-	-	-	-	-
68	-	-	-	-	-	-
71	4	-	-	-	-	-
79	2	-	-	-	-	-
82	2	-	-	-	-	-
103	2	-	-	-	-	-

Table 9.29: Concentration values [$\mu\text{g m}^{-3}$] of the 23 l emission test chamber experiment (chamber 2; $n = 1.3 \text{ h}^{-1}$; 70-90 °C)

Day	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	PCB 28 [$\mu\text{g m}^{-3}$]	Dichlofluanid [$\mu\text{g m}^{-3}$]	Isodrin [$\mu\text{g m}^{-3}$]	Tolyfluanid [$\mu\text{g m}^{-3}$]
2	81	45	33	44	95	19
6	16	12	8	17	18	12
9	13	5	6	11	14	10
14	8	4	5	7	9	8
16	9	5	5	8	-	10
20	8	-	4	5	-	7
23	6	-	4	4	-	6
27	7	-	5	4	-	6
34	4	-	-	2	-	-
37	4	-	-	2	-	4
41	3	-	-	-	-	-
44	3	-	-	2	-	3
48	3	-	-	-	-	3
50	3	-	-	-	-	-
55	4	-	-	-	-	-
58	3	-	-	-	-	-
65	2	-	-	-	-	-
69	2	-	-	-	-	-

Table 9.30: Concentration values [$\mu\text{g m}^{-3}$] of the 24 l emission test chamber experiment (chamber 3; $n = 0.2 \text{ h}^{-1}$; ambient temperature)

Day	Lindane [$\mu\text{g m}^{-3}$]	PCP [$\mu\text{g m}^{-3}$]	PCB 28 [$\mu\text{g m}^{-3}$]	Dichlofluanid [$\mu\text{g m}^{-3}$]	Isodrin [$\mu\text{g m}^{-3}$]	Tolyfluanid [$\mu\text{g m}^{-3}$]
2	23	3	7	5	19	2
6	21	3	6	5	19	3
9	18	3	5	4	15	2
14	11	2	4	4	12	3
16	12	3	4	4	13	3
20	11	2	4	3	11	2
23	9	2	4	3	11	2
27	6	-	3	2	9	2
34	8	2	4	3	9	2
37	7	-	3	3	-	-
41	7	-	-	2	-	-
44	5	-	-	2	-	-
48	7	-	-	2	-	-
50	5	-	-	2	-	-
55	18	-	-	2	-	-
58	13	-	-	-	-	-
65	7	-	-	-	-	-
69	8	-	-	-	-	-
91	6	-	-	-	-	-
105	3	-	-	-	-	-
112	3	-	-	-	-	-
119	3	-	-	-	-	-
126	3	-	-	-	-	-
133	4	-	-	-	-	-
140	4	-	-	-	-	-
156	4	-	-	-	-	-
169	3	-	-	-	-	-
184	2	-	-	-	-	-
185	2	-	-	-	-	-
196	2	-	-	-	-	-

9.4 Abbreviations

μ-CTE	Micro-Chamber
c	Concentration
CE	Collision energy
CIS	Cooled injection system
cis-Permethrin	Permethrin 1
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
f	Degrees of freedom
GC	Gas chromatography / Gas chromatograph
GUM	Guide to the expression of uncertainty in measurement
ISTD	Internal standard
L	Product loading factor
LoD	Limit of detection
LoQ	Limit of quantification
MRM	Multiple reaction monitoring
MS	Mass spectrometry / Mass spectrometer
n	Air change rate
PAH	Polycyclic aromatic hydrocarbons
PCB	Polychlorinated biphenyls
PCP	Pentachlorophenol
PE	Polyethylene
POM	Particulate organic matter
POG	Polymer-coated glass sampler
PUF	Polyurethane foam
q	Area specific air flow rate
r. h.	Relative humidity
RSD	Relative standard deviation
s	Standard deviation
SDVB	Styrene divinylbenzene
SER _a	Area specific emission rate
SIM	Selected ion monitoring
SPMD	Semi-permeable membrane devices
SPME	Solid-phase microextraction

SVOC	Semi volatile organic compounds
T	Temperature
TD	Thermodesorption
trans-Permethrin	Permethrin 2
TV	Test value
VOC	Volatile organic compounds

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