



Helena Järnström, Sirje Vares & Miimu Airaksinen

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## Abstract

The first part of the project presented in this publication reviews the occurrence of semi-volatile organic compounds (SVOCs) and flame retardants in commonly used building and furnishing materials in Finland. SVOCs included in the review are plasticisers, like phthalates, flame retardants (FRs), like brominated organic compounds and organophosphate esters. In addition, polyaromatic hydrocarbons (PAHs), which are constituents in coal tar/ creosote and have been used for moisture proofing in structures, are also discussed. On the basis of present knowledge, risk assessment for exposure indoors is presented. In addition, sources of SVOCs and the waste potential in the old building stock are clarified. The knowledge for the review was gathered from housing statistics, building product statistics, the chemical registry at The National Product Control Agency's (STTV), The National Board of Antiquities and Historical Monuments in Finland, Finnish Environment Institute (SYKE), and from interviews with the construction product industry.

In the second part of the project, SVOCs were measured from a total of 13 building materials including flooring materials, paints, insulations and a levelling agent (screed). Both short and long term (up to 60 days) emissions were measured by modifying the existing standard sampling method for the measurement of volatile organic compounds (VOCs). Emissions were measured at room temperature 23 °C and at 40 °C. The elevated temperature was considered to simulate real life situations, such as when a floor structure has heating or a surface gets warmed up by direct sunlight.

The results showed that the initial specific emission rates (SER) of SVOCs are typically low, less than 5 µg/m<sup>2</sup>h. An exception was newly prepared foam type polyurethane insulations, which emitted SVOCs up to 65 µg/m<sup>2</sup>h. The SVOC SERs were higher at 40 °C, up to 165 µg/m<sup>2</sup>h. No phthalates were detected from the air samples collected at room temperature during the 60 -day test period. However, 218 µg of a phthalate compound was detected from the solvent used to rinse the walls of the chamber that was used to measure the PVC sample. Also, 72 ng of the fire retardant hexabromocyclododecane (HBCD) was detected from the rinsing samples of the chamber used for measuring the expanded polystyrene (EPS) insulation for FR applications. A commonly used FR, Fyrol PCF (Tris (2-chloroisopropyl) phosphate, TCCP) was detected from air samples taken from the polyurethane insulation (foam type) at 24 µg/m<sup>2</sup>h (as toluene equivalent) after 120 minutes at 40°C. Boron was detected from air samples from the cellulose based insulation material at 0.3–5 µg/m<sup>3</sup>.

The study showed that SVOCs and FRs are emitted at low levels at room temperature from common building materials. However, the variety of compounds emitted and emission ranges varied markedly depending on which building product was measured. SVOC (and VOC) SERs increased markedly when the temperature increased to 40 °C. In real life, such temperatures can be reached on surfaces with direct sunlight during the summer or in cases when floor heating is used. Consequently, exposure assessments for SVOCs in such environments can be assessed better based on the emission results collected during this project. Exposures at room temperature were estimated to <0.1 - <2 µg/kg day. However, the migration of FRs and SVOCs into indoor air is probably less from building materials that are inside a structure, e.g. insulation, which decreases exposure to these compounds indoors.

## Preface

This project was part of the Environmental cluster research projects 2006–2009 financed by the Ministry of Environment in Finland. The supervisors for the project were Chief engineer Kaisa Kauko and Chief engineer Juha-Pekka Maijala. The following construction product industry partners also contributed to the financing of the project: maxit Oy, Upofloor Oy, Saint-Gobain Rakennustuotteet Oy, The Cellulose insulation industry in Finland, The EPS insulation industry in Finland, The Construction Polyurethane Industry of Finland, and Tikkurila Oy. The financiers are greatly acknowledged for making the project possible and for their valuable advice during the project.

The authors want to express their gratitude to Kristina Saarela for her work in initiating this project and to Senior research scientist Tiina Tirkkonen and Technician Eero Luostarinen for their valuable advice during the realisation of it. The sampling and VOC& SVOC analysis work was done by Assistant researcher Kaija Luomanperä, Researcher Jari Kiuru and Technician Helena Vähäkuopus at VTT. The authors are grateful for their contribution in doing the laborious measurements. The authors also want to thank Researcher Sami Huhtala at SYKE, who was responsible for the analyses of the brominated compounds. Building conservation officer Olli Cavén at the The National Board of Antiquities and Historical Monuments in Finland, Senior inspector Ritva Vuorinen at STTV, Marja Hermiö at the Central Statistical Office of Finland as well as Researcher Kaisa Belloni, Senior research scientist Tuomas Paloposki and Senior research scientist Terttu Vainio at VTT, are greatly acknowledged for giving information on relevant building statistics to the review. Finally, the authors want to thank Dr. Cynthia Howard Reed for reviewing the report.

# Contents

Abstract .....	3
Preface .....	4
Abbreviations and definitions .....	7
1. Introduction .....	9
2. Semi volatile organic compounds (SVOCs).....	11
2.1 Chemical structure, properties and production .....	11
2.2 Applications in buildings .....	12
2.3 Regulations given by the authorities.....	13
3. Flame retardants.....	15
3.1 Chemical structure, properties and production .....	15
3.2 Applications in buildings .....	17
3.3 Regulations given by the authorities.....	19
4. Indoor air exposure for SVOCs and flame retardants.....	20
5. Waste potential of SVOCs and flame retardants in the existing building stock .....	25
6. Measurement techniques to determine emission from materials and the indoor air concentration of SVOCs and flame retardants .....	27
6.1 Emission test chambers .....	27
6.2 Sampling and analysis.....	28
7. Emissions of SVOCs from building materials .....	30
7.1 Materials tested .....	30
7.2 Methods.....	31
7.2.1 Sampling.....	31
7.2.2 Analysis .....	33
7.2.2.1 Pre tests.....	33
7.2.2.2 Tenax samples.....	34
7.2.2.3 PUF samples .....	34
7.3 Results .....	34

7.3.1	Pre tests.....	34
7.3.2	Sampling on Tenax TA .....	35
7.3.2.1	Results at 23°C.....	35
7.3.2.2	Results at 40°C.....	38
7.3.3	Sampling on PUF.....	42
7.3.3.1	SVOCs and phthalates .....	42
7.3.3.2	Brominated compounds .....	45
7.3.3.3	Organophosphates .....	45
7.3.3.4	Boron .....	45
7.4	Discussion.....	46
8.	Conclusions and recommendations for further action .....	50
	References .....	54

## Appendices

Appendix A: Chemical product registry search list

Appendix B: Recycling of selected building materials

## Abbreviations and definitions

BAM	Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing, Germany)
BBP	Butylbenzyl phthalate
BFR	Brominated flame retardants
CFC	Chlorine-fluorine-carbon compounds
DBP	Dibutyl phthalate
DCM	Dichloromethane
DEP	Diethyl phthalate
DEHP	Di (ethylhexyl) phthalate
DIBP	Diisobutyl phthalate
DIDP	Diisodecyl phthalate
DIHP	Diisohexyl phthalate
DIOP	Diisooctyl phthalate
DINP	Diisononyl phthalate
DIUP	Diisoundecyl phthalate
DPHP	Dipropylheptyl phthalate
DPP	Diphenylphthalate



DUP	Diundecyl phthalate
ECB	European Chemicals Bureau
ECPI	European Council for Plasticisers and Intermediates
EU	European Union
FLEC	Field and laboratory emission cell
FR	Flame retardant
LCFI	Loose-fill cellulose fibre insulation
LOD	Limit of Detection
LOQ	Limit of Quantification
OECD	Organisation for Economic Co-operation and Development
PAH	Polycyclic aromatic hydrocarbon
PBB	Polybrominated biphenyl
PBDE	Polybrominated diphenylether
PVC	Polyvinyl chloride
SER	Specific emission rate
SVOC	Semi volatile organic compounds
TBBPA	Tetrabromobisphenol A
TCEP	Tri (chloroethyl) phosphate
TCPP	Tris (chloroisopropyl) phosphate
TSVOC	Total semi volatile organic compounds
TTL	Työterveyslaitos (The Finnish Occupational Health Institute)
TVOC	Total volatile organic carbon
WHO	World Health Organisation

# 1. Introduction

The occurrence of semi volatile organic compounds (SVOC) in the indoor environment is under special interest today since health concerns have risen. These compounds might be released to the surroundings from new products as well as from older building materials as a result of wearing. The concern about the health effects has led to the need to evaluate sources and possible exposure routes for these compounds in the indoor environment. Also, the fate of these compounds within the waste management during renovation is of interest.

Common SVOCs in the indoor environment are plasticisers like phtalates, and flame retardants (FRs) like brominated organic compounds and organophosphate esters. In addition, polyaromatic hydrocarbons (PAHs) are constituents in coal tar/ creosote, which have been used for moisture proofing in structures. The indoor air concentration of SVOCs and flame retardants is usually low because of their adsorption to surfaces and dust particles. The probable exposure routes in the indoor environment are skin contact with surfaces, aerosol deposition on skin and respiratory intake. Especially in the case of very young children, the oral and dermal uptake from house dust might be of relevance for risk assessment. It is of importance that the knowledge of the use of these chemicals in the production processes and their behaviour is incorporated to the general information management within the material and building industry.

The Finnish building stock has grown more pronounced since the 1950's (Table 1, Figure 1). Renovation work has been increasing markedly since the 1990's. In 2004, the value of renovation work was about 7 billion euros, which is about 44 % of the total building industry market (Virtanen et al. 2005). Therefore, the waste management of these chemicals is crucial in terms of environmental protection.

Table 1. Building types in Finland in year 2005 (Vainio et al. 2006, [www.tilastokeskus.fi](http://www.tilastokeskus.fi))

<b>Building type</b>	<b>Number (municipally owned/ total)</b>
Residential buildings	12 914/ 1 183 893
Business and office buildings	1 412/ 10 772
Day-care centers	1 318/ no statistics
School buildings	5 881/ 9 005
Public buildings (theater and concert buildings, libraries, museums and exhibition halls, club& society houses, sports and fitness facilities etc.)	2 132/ 13 318
Health care buildings etc.	3 021/ 7 612

## 1. Introduction

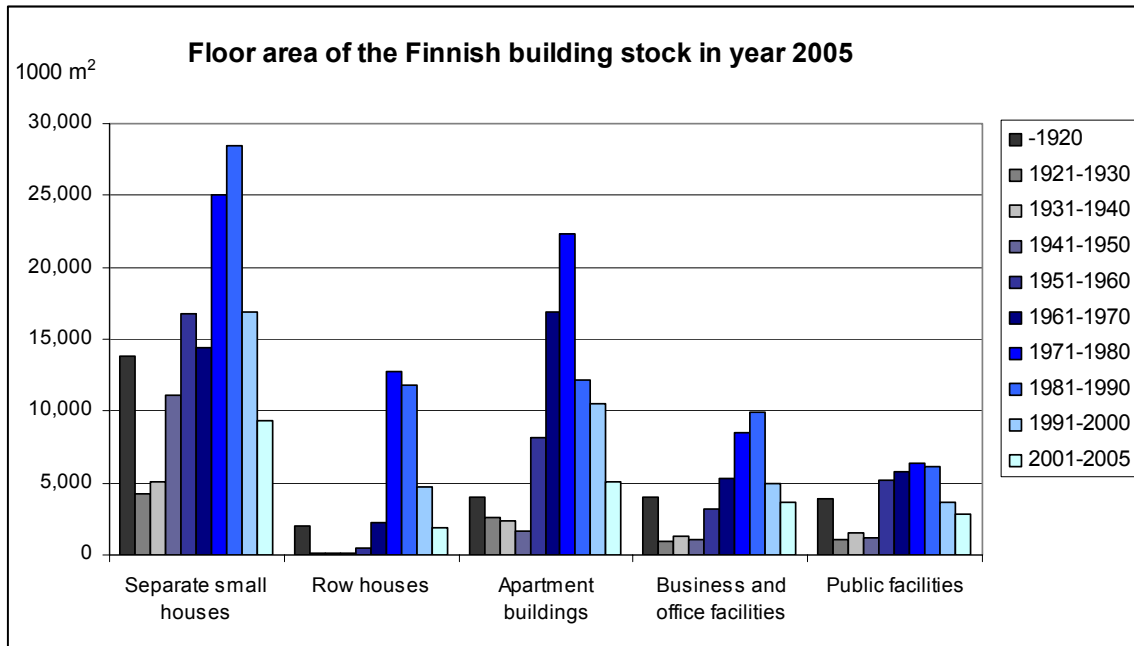


Figure 1. Floor area of the Finnish building stock through year 2005 (VTT 2006a).

This project reviews the occurrence of SVOCs and flame retardants in commonly used building and furnishing materials in Finland, and the need for their use and possible alternative materials or building technology solutions to minimise indoor air exposure. In addition, sources of SVOCs and waste potential in the old building stock are clarified. The knowledge was gathered from housing statistics provided by Terttu Vainio at VTT, Ritva Vuorinen at the chemical registry at STTV, Olli Cavén at The National Board of Antiquities and Historical Monuments in Finland, and from interviews with the construction product industry. The report also includes regulations given by the authorities associated with the materials used in residential, office and public facilities and which contain SVOCs and/or flame retardants. In the last section of the review, the current information available on sampling and analytical techniques for the determination of material emission and indoor air concentrations of SVOCs and flame retardants are summarised for possible incorporation of these compounds to the Finnish material classification. Finally, the emission testing results for 13 different building materials are presented.

## 2. Semi volatile organic compounds (SVOCs)

### 2.1 Chemical structure, properties and production

The World Health Organisation has defined SVOCs as organic compounds with boiling points ranging from 240 °C to 400 °C (WHO 1997). SVOCs considered here are phthalates (PVC plasticiser), polycyclic aromatic hydrocarbons (PAHs), and flame retardants. Flame retardants are discussed separately in Chapter 3. An evaluation of the occurrence of PCB in Finnish buildings has been published earlier (Maijala and Nippala 2002).

**Phthalates**, i.e. phthalate esters are by far the most widely produced plasticisers worldwide. Phthalate esters are manufactured from alcohols such as methanol and ethanol (C1/C2) up to iso-decanol (C13), either as a straight chain or with some branching. There are over 100 commercially available phthalate compounds, which provide a wide range of different properties for different uses such as fast-fusing applications, low viscosity applications, temperature flexibility, high temperature use like high performance cables, etc. (Phthalates Information Centre 2006).

The annual use of phthalates in Europe is about 1 million tons. Di (2-ethylhexyl) phthalate (DEHP) is by far the most commonly used. More than 90 % of phthalates produced in Europe are used to plasticise PVC (polyvinyl chloride) to make flexible PVC products (ECPI 2006). The plasticiser diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) account for around 60 % of all plasticiser use in Western Europe (Phthalates Information Centre 2006).

Typically, C1 and C2 phthalates are used in non-PVC applications. The C3 to C7 phthalates are used in applications where rapid setting and resistance is required, foamed leather cloth and flooring for example. The C8/C9 and C10 phthalates are the most widely used general purpose plasticisers used for such applications as wall covering, flooring and medical applications. The C11 to C13 phthalates are used where high temperature stability is required (Phthalates Information Centre 2006). Table 2 summarises phthalate compounds and their applications registered in Finland by year 2005. A list of phthalate compounds included in the search from the chemical registry is shown in Appendix A.

## 2. Semi volatile organic compounds (SVOCs)

Table 2. Phthalates in chemicals registered in Finland in 2005 (no inf.= no information, STTV 2006).

Phthalate	CAS	Number	Tons	Application
DMP (dimethyl phthalate)	131-11-3	19	280	curing agent, polymerisation initiator
DEP (diethyl phthalate)	84-66-2	6	8	production of medicinal substance, cosmetics
DBP (di-n-butyl phthalate)	84-74-2	51	332	paint, glue, plasticiser
BBP (butylbenzyl phthalate)	85-68-7	27	603	paint, glue
DEHP / DOP (di(2-ethylhexyl) phthalate)	117-81-7	28	757	paint, glue, plasticiser
DINP (diisononyl phthalate)	28553-12-0	18	4	paint, glue, sealing compound
DIDP (diisodecyl phthalate)	26761-40-0	4	2	sealing compound
DUP (diundecyl phthalate)	3648-20-2	7	0.1	printing ink (silk)
DIUP (diisoundecyl phthalate)	85507-79-5	no inf.	no inf.	glue, plasticiser

## PAH compounds

Polynuclear (or polycyclic) aromatic hydrocarbons (PAH) are a group of several hundred different organic compounds with two or more benzene rings. They are highly lipophilic and have low vapour pressures. They are mainly produced as a result of pyrolytic processes, especially the incomplete combustion of organic materials (WHO 2000). Coal tar and its distillation fractions like creosote, crude oil, fuel oil, diesel oil and bitumen contain PAH compounds. Coal tar, creosote and bitumen have been used as a water repellent/barrier and wood preservative.

## 2.2 Applications in buildings

### Phthalates

Phthalate compounds can be found in the following indoor materials: flooring materials (PVC), vinyl plates, shower curtains, plumbing, wires, cables, sealant ribbon, wall papers, adhesives, paint, electrical equipment, textiles, and coated fabrics. In addition, consumer products like toys and hand grips in tools can contain phthalates.

### Creosote, coal tar

In Finnish construction industry, creosote or coal tar has been used for waterproofing building structures. In old buildings, especially the floors and/or walls of lower floors and cellars have been treated with these chemicals. In addition, proofing with coal tar has been done for brick walls and its joints.

Coal tar has been used in Finnish buildings built until the 1980's. These buildings constitute 73–88 % of the total area of buildings in Finland, which correspond a total floor area of ~350 million m<sup>2</sup> (VTT 2006a). Since 1996, the use of creosote and wood treated with it has been restricted to industrial and professional applications (railroad, power transmission and telephone line support, fences, farming and harbors, The Council of State 1995). Applications, where there is a risk for repetitive dermal exposure or the pollution of nutrition or animal feed, as well as applications indoors, in garden furniture and in gardens is prohibited since 2003 (The Council of State 2003).

The National Board of Antiquities and Historical Monuments in Finland has through its renovation work experience in creosote applications in old buildings. Creosote has been found, for example, in the insulations of the national theatre building, which was built in the beginning 20<sup>th</sup> century. In Valkeala, the floors and walls of an old wooden building was treated with creosote. In Suomenlinna, creosote was found in several buildings built in 1890–1910. Usually it was found on the surface of the ground concrete slab (not reinforced), on which a wooden wall, supported with a platform made of brick, was installed.

### 2.3 Regulations given by the authorities

#### Phthalates

Exposure to some phthalates has been found to increase the risk of cancer, deformations and reproduction disruptions. Newer research has found an increase in rhinitis and eczema as well as asthma (TTL 2006).

The EU has confirmed that two of the most widely-used plasticisers are not classified as hazardous and pose no risks to either human health or the environment from their current use. The publication in the European Union Official Journal of the outcomes of the EU risk assessments for Diisononylphthalate (DINP) and Di-isodecylphthalate (DIDP) state that there is no need for any further measures to regulate the use of these two compounds. The outcome of the risk assessment for the lesser-used specialty plasticiser, DBP, has also been published in the EU's Official Journal. Following the assessment, measures are to be taken within the framework of the IPPC Directive (96/61/EC) and the Occupational Exposure Directive (98/24/EC) (ECPI 2006).

The European Union has confirmed that DEHP poses no general risk to human health in its risk assessment published in 2008 (European Union 2008). For BBP, a risk reduction strategy is to be advised but no further risk reduction measures are recommended for human safety. In 2007, permanent restrictions on the use of phthalate plasticisers in toys came into effect throughout the European Union. DINP and the two phthalates DIDP and DNOP can only be used in toys and childcare articles that cannot be placed in the mouth. DEHP, DBP and BBP will no longer be allowed in any childrens toys or childcare articles (European Union 2005).

## 2. Semi volatile organic compounds (SVOCs)

**PAH compounds** are carcinogenic and no safe level for them can be recommended (WHO 2000). Of the PAH compounds, benzo (A) pyrene is classified as a carcinogen by the International Agency of Cancer (IARC). The use of creosote and wood treated with it has been restricted in Finland since 1996 (The Council of State 1996 and 2003).

## 3. Flame retardants

### 3.1 Chemical structure, properties and production

Flame retardants (FRs) have been found to lengthen escape time, reduce the heat production to 25 %, decrease the combustion of a material by 50 % and decrease the production of toxic flame gases by 30 % (Steukers et al. 2004). Flame retardants are divided into four different groups: 1) inorganic, 2) halogenated organic 3) organic phosphorus containing and 4) nitrogen containing flame retardants (WHO 1997). The bonding of flame retardant compounds in the polymer is of importance when the migration into the environment is considered. The volatilization or leakage is less probable for reactive bonding compared to additive bonding. Table 3 summarizes FRs, their applications and the annual use in Europe in 1999 (WHO 1997, BSEF 2003).

OECD approximated that the annual global production of FRs in 1992 was 600 000 tons (OECD 1994). By 2001, the amount had doubled to 1 217 000 tons (Davenport et al. 2002). The relative portion of organophosphate compounds is expected to increase since the use of polybrominated diphenyls (PBDEs) is nowadays restricted by the authorities. Brominated flame retardants (BFRs) are the largest market group (1998: 39 %, BSEF 2003) because of their low cost and high performance efficiency. There are over 75 different commercial BFRs. Their consumption by final applications is as follows: Electronics and electrical 56 %, building/construction 31 %, textile/other 7 % and transportation 6 % (BSEF 2003). Table 4 summarizes the FRs in chemicals registered in Finland in 2005. A list of the compounds included in the search from the chemical registry is shown in Appendix A.



### 3. Flame retardants

Table 3. Flame retardants, type of bonding in the polymer and annual volumes in Europe in 1999 (WHO 1997, BSEF 2003, no inform.= no information available).

Flame retardant (FR) group	Compound	Applications	Volume estimates (tons)
Inorganic	Metal hydroxides, antimony trioxide, alumina trihydrate, boron compounds, ammonium polyphosphate (APP)	polymers, textiles, papers, cotton, paints, polyamide & phenolic appl.	no inform.
Halogenated organic	Chlorinated FRs (plastics)	plastics (wire & cable appl.), fabrics, paints, coatings	no inform.
	Tetrabromobisphenol (TBBPA)	epoxy resins in printed circuit boards	13 800
	Polybrominated diphenylethers (PBDE): deca (DBDE), octa (OBDE) penta (PBDE)	high impact polystyrene (TV cabinets), thermoplastics, polyolefins, PVC, elastomer	8 160
	Hexabromocyclodecane (HBCD)	polystyrene foam, fire resistant polymers, textiles, furniture, electronics	8 900
	Polybrominated biphenyls (PBB)	plastics, electrical appl., textiles	no inform.
Organic phosphorous containing	Phosphate esters Phosphonium salts Tris (1-chloro-2-propyl) phosphate (TCPP)	cellulosic materials, textiles, PVC-based products, polyurethane foam	no inform.
Nitrogen containing	Melamine compounds	polypropylene, polyethylene, polyamides, terephthalates	no inform.

Table 4. Flame retardant compounds in chemicals registered in Finland in 2005 (STTV 2006).

Flame retardant	CAS	Number of registrations	Tons	Application (as documented in the register)
Alumina trihydrate ATH	21645-51-2	12	0.5	paint, glue, flame retardant, clean-up of waste water
Antimony trioxide (synergist)	1309-64-4	32	182	flame retardant, production of plastics
Sodium antimonate	15432-85-6	not available		flame retardant
Boric acid	10043-35-3	14	42	wood preservative, chemical for photography, flame retardant
TCPP	13674-84-5	16	1571	production of polyurethane, glue, flame retardant
Triphenylphosphate	115 86 6	31	10	lubricant, flame retardant, clipping liquid
Triethylphosphate	78-40-0	9	7	glue, flame retardant
Trioctyl phosphate	78-42-2	6	100	flame retardant, clipping liquid
2-ethylhexyl-diphenyl phosphate	1241-94-7	5	190	flame retardant, lubricant
Melamine	108-78-1	not available		printing ink (silk), flame retardant

## 3.2 Applications in buildings

The brominated FRs have been used in polymers like polystyrene foams, high-impact polystyrene and epoxy resins (Birnbaum & Staskal 2004). TBBPA, deca-BDE and octa-BDE are common BFRs in plastic housings like TVs, PCs and office equipment (BSEF 2003). Kemmlein et al. studied the emission of selected brominated and organophosphate FRs from insulating boards, polyurethane (PU) foams, a mattress and electronic equipment. The content of FRs were < 1 %–20 % and the highest content was measured for the PU foam. TCPP was found to be the most commonly emitted organophosphate FR in polyurethane foam (Kemmlein et al. 2003). The use of BFRs has been clarified quite extensively in the Danish and Swedish building industry (Miljøstyrelsen 2007, Jönsson and Yndemark 2002). The Swedish investigation concluded that BFRs are used in roofing products (rubber membranes and polyethene products), insulations, piping insulations, and installation materials (some cable products, circuit boards etc.). The most common BFRs were HBCD, decaBDE, PBDE and TBBP-A. The annual use of BFRs was 50–100 tons in Denmark.

As a summary, potential sources of FRs in building structures are as follows: insulation materials, i.e. insulation boards, foams, paints, varnishes and glues, and other plastics. In addition, FRs in indoor environments can be found in electrical and electronic equipment (cables, PCs, printers, fax machines, copiers, TVs) and textiles and upholstery foams.

The Finnish building code gives requirements for fire resistance (Ministry of Environment 2002). The requirements do not specify any chemicals for fire retardant purposes. The following summarizes the interviews made among building material manufacturers concerning the use of FRs in building materials produced in Finland. The interviews were made in December 2006–May 2007.

### **Insulations:**

#### The polyurethane industry

The main three polyurethane producers in Finland use FRs in their products. However, the FRs used are considered as less hazardous for health (Rakennuspolyuretaaniteollisuus 2006). Foreign manufacturers commonly use commercial mixtures, which do not specify their FRs.

#### Expanded polystyrene (EPS)

Expanded polystyrene (EPS) is extensively used in building industry because of its durability and insulation properties. EPS insulation is used for example for roofs, facades, ground floor structures, foundations, frost insulation and for civil engineering applications. EPS insulation is manufactured as normal quality and as flame retardant quality (FR quality). Hexabromocyclodecane (HBCD) is used as a fire retardant in EPS raw material. The EPS of FR quality is only used in the applications where fire protection is needed. These kind of applications are for example wall/facade and roof structures in construction. The content of HBCD is 0.7% in the product. EPS applications are mainly in the building frame, i.e. it is not used as a surface or covering material.

### 3. Flame retardants

Seven Finnish producers manufacture EPS insulation materials and one Finnish company produces EPS raw material. EPS raw material is also imported to Finland.

#### Extruded Polystyrene (XPS)

Extruded polystyrene (XPS) is used in roofs, parking levels, ground floor, foundations and frost. One Finnish company produces XPS in Finland. HBCD is used as a flame retardant in XPS products. XPS is also imported to Finland, for example Saint-Gobain Rakennustuotteet Oy markets a XPS product in Finland. The insulation products marketed by Saint-Gobain Rakennustuotteet Oy do not contain any FRs listed in appendix A.

#### Loose-fill and sprayed cellulose based insulations (LCFI)

LCFI-insulations are used for insulating roof, wall and floor structures. Also ventilation ducts can be located in LCFI insulation layers. Boron (borax and boric acid) is added as a FR.

#### Mineral wool

The insulation marketed by Saint-Gobain are made from glass and do not contain FRs. Recycled glass is used up to 60–80 % in manufacturing glass wool insulations. The insulations marketed by Paroc Oy are made of stone material.

#### **Acoustic boards:**

The acoustic boards marketed by Saint-Gobain Ecophon Oy do not contain FRs.

#### **Paints:**

Tikkurila Oy: No flame retardants are added to paints used for indoor application. FRs have been used for paints that are applied on steel constructions, e.g. industrial facilities and ware houses. The constructions are usually finished with paint that does not contain FRs. The most common FRs are polyphosphate and chlorinated paraffin. Also, wooden structure has been finished with paints containing FRs. However, this has not been common in Finland. Some products sold by the Finnish company have been produced in Germany. The possible use of FRs is not known because only compounds with known health effects have to be reported.

Presso Center Oy produces/ markets paints and laquers for fire protection applications. The products are halogen free. Sulfate and phosphate salts are used as FRs. The products are used on steel constructions, wooden structures in the interiors and textiles.

### **Flooring materials:**

Upofloor Oy: PVC and linoleum flooring materials do not contain any FRs

### **Wooden materials**

The common FRs used for wooden materials are inorganic or organic salts (phosphates, sulphates, boric acid and borax, Belloni 2007). In Europe, fire protected wood is used in exterior and interior walls as covering materials (panels etc.), and in the facades.

## **3.3 Regulations given by the authorities**

Many flame retardants currently used are classified as hazardous substances or must be regarded as potentially hazardous to health, so that possible impairments following inhalative, oral, or dermal intake must be evaluated (WHO 1997). The brominated FRs are especially of concern. The clarification work done in the EU concluded that flame retardants should be assessed as separate compounds, i.e., an evaluation for compound groups is not satisfactory. The EU directive 2003/11/EC has restricted the use of penta and octabromodiphenylether. These compounds were banned in the EU from August 2004 (Steukers et al. 2004).

The ROHS (Restriction of the use of Certain Hazardous Substances in Electrical and Electronic Equipment) directive restricts the use of PBB and PBDE in electrical equipments (domestic appliances, information and telecommunication equipment, consumer electronics, electric tools, toys, sports and leisure equipments, automatics, glow lamps, European Union 2003).

The EU risk assessment report concluded recently that there are no health risks of concern for TBBPA (European Chemicals Bureau 2006).

## **4. Indoor air exposure for SVOCs and flame retardants**

The concentration of SVOCs indoors is usually very low,  $10 \mu\text{g}/\text{m}^3$  or less (Wensing et al. 2005). The vapor pressure for SVOCs at normal indoor conditions is low and consequently their partition to particles or on surfaces is higher than to the air (Weschler 2003). The SVOC concentration measured in accordance to the ISO 16000-6 standard (ISO, 2004) in one year old Finnish buildings, which were built during 1999–2002 and in which low emitting, M1 classified (FiSIAQ, 2001) building materials were used ( $n = 14$ ) was on average  $8 \mu\text{g}/\text{m}^3$  (max:  $17 \mu\text{g}/\text{m}^3$ , Figure 2). These buildings had painted walls and the ceiling structure was finished with a leveling agent. A statistically significant higher concentration of SVOCs ( $p < 0.05$ ) was found in apartments with PVC as flooring materials compared to apartments with parquet flooring. The identified SVOCs were alkyl benzenes and isopropyl myristate.

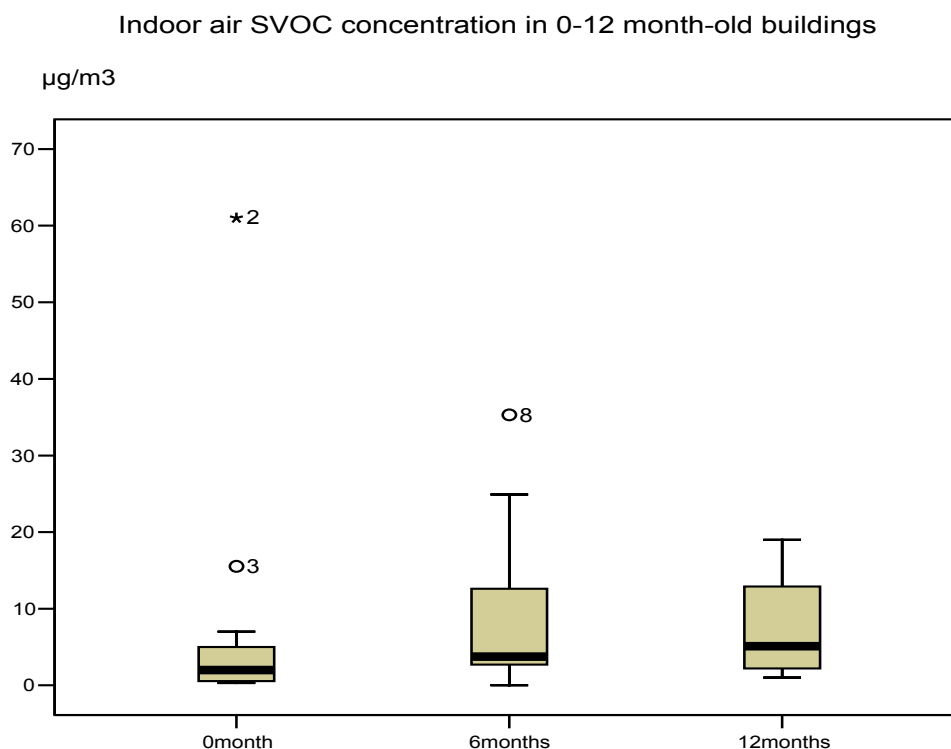


Figure 2. Indoor air SVOC concentration in buildings completed during 2000–2002 in Finland (VTT 2006b). The thick line shows the median value. The box edges are the 25 and 75 percentiles. The lines show the minimum and maximum values, the O stands for outliers (= cases with values between 1.5 and 3 box lengths from the upper or lower edge of the box, the box length is the interquartile range) and the stars stand for extreme values (= cases with values more than 3 box lengths from the upper or lower edge of the box, the box length is the interquartile range).

## Phthalates

Field studies have shown that phthalate concentrations in residences are on the level  $< 10 \mu\text{g}/\text{m}^3$ . Commonly detected phthalates are DEHP, DBP and BBP. Daily intakes of phthalates (infants) have been estimated to  $0.04\text{--}0.8 \mu\text{g}/\text{kg}$  (inhalative) and  $2.5\text{--}26.8 \mu\text{g}/\text{kg}$  (oral) (Wensing et. al. 2005).

The EU Risk Assessments of the phthalates DEHP, DINP, DIDP and BBP include estimates of exposure to various sectors of the population via a range of exposure scenarios (ECB 2006). The approach adopted for *exposure indoors* is similar for all the phthalates and is exemplified by DEHP. The worst case assumptions made are 1) all surfaces of the room are covered in PVC and the air is saturated with DEHP vapour, 2) three times more DEHP is bound to dust particles in the air than is present as vapour, 3) the concentration of DEHP indoors (at  $20^\circ \text{C}$ ) is  $5.3 \mu\text{g}/\text{m}^3$ , as calculated from the saturated vapour pressure. The amount of DEHP adsorbed onto dust particles is therefore assumed to be  $15.9 \mu\text{g}/\text{m}^3$  ( $3 \times 5.3$ ) and the total air concentration is  $21.2 \mu\text{g}/\text{m}^3$ . The daily exposure to DEHP in indoor environments for adults and children is calculated as follows:

#### 4. Indoor air exposure for SVOCs and flame retardants

$$U_{inh} = \frac{B_{inh} \times C_{inh} \times V_{inh} \times t / 24}{BW} \quad (1)$$

The assumed body weight (BW) for an adult is 60 kg and 8 kg for a child. The inhalation rate, assuming moderate activity ( $V_{inh}$ ) for an adult is 20 m<sup>3</sup>/day and 9.3 m<sup>3</sup>/day for a child.  $U_{inh}$  is the uptake (mg/kg/day),  $B_{inh}$  the bioavailability for inhalation exposure (75 % for adults and 100 % for children),  $C_{inh}$  the air concentration (mg/m<sup>3</sup>) and  $t$  the exposure duration (20h/day for adults and 22 h/day for children). The calculated uptakes are on the basis of Equation 1 above 4.4 µg/kg b.w/day for adults and 22.4 µg/kg b.w/day for children (ECB 2006).

#### PAH compounds

Liquid applied damp proof membrane products containing coal tar can emit VOCs such as naphthalene, acenaphthalene and biphenyl as well as other PAH compounds. These can penetrate into the indoor environment and pose a health risk (Brown et al. 1990, Honkanen 2006). Penetration has often occurred in buildings where a new air exchange system has been installed during renovation. In these cases, the exhaust air flow has been too high compared to the supply air, i.e. infiltration of supply air from the structures has occurred. Other common sources for PAH compounds indoors are traffic and smoking.

About 500 PAH compounds have been detected in air. The most common is naphthalene. PAH compounds have boiling points starting at about 200 °C and therefore their concentration in air is very low, nano- or micrograms per cubic meter. Indoors, PAH compounds are mainly partitioned on particles and surfaces.

The concentrations of PAH compounds varied between 3–38 µg/m<sup>3</sup> (average 13 µg/m<sup>3</sup>) in a renovated Finnish office building, in which with coal tar was left under the new carpeting. Workers in this building complained of bad and stuffy air. The major compounds were naphthalene, phenanthrene, fluoranthene and pyrene (Honkanen et al. 2006). The average naphthalene concentration, measured in the indoor air in 200 randomly chosen residences in Helsinki in 1996–1997, was 0.64 µg/m<sup>3</sup> (Edwards et al. 2001).

The natural background level of the carcinogenic PAH compound benzo [a] pyrene (BaP) is nearly zero and the annual average values in urban outdoor air (without coke-ovens) and measurements indicate that annual means in major urban areas are mainly in the range 1–10 ng/m<sup>3</sup>. Elevated PAH concentrations can be measured from indoor air under special conditions. Benzo [a] pyrene levels of 6 µg/m<sup>3</sup> have been measured in houses without chimneys (WHO 2000).

The daily intake of BaP has been estimated to 400 ng from exposure to a relatively high concentration of 50 ng/m<sup>3</sup>. In cities with adequate smoke control and clean rural areas the daily intake is approximated to a few percent of this amount (WHO 2000). The calculated uptakes are on the basis of Equation 1 above is 0.01 µg/kg b.w/day for adults and 0.05 µg/kg b.w/day for children.

## Polybrominated FRs

**PBDEs** have been found to be ubiquitous in the environment and evidence for bioaccumulation exists. PBDE toxicity decreases as the number of bromines increases. Octa- and deca- PBDE are believed to break down to lower (and more toxic) congeners, i.e. penta- PBDE. The lower brominated congeners are predominant in air samples (Birnbaum and Staskal 2004, Janssen 2005, Wilford et al. 2005). Occupational exposure to PBDEs has been found among electronics-dismantling plant workers and computer technicians (Sjödín et al. 1999, Jakobsson et al. 2005). Recent studies indicate that the indoor environment is potentially the dominant exposure route for PBDEs for young children (toddlers) (Harrad and Diamond 2006).

PBDEs have been found in higher amounts in North American and Japanese dust samples (< 5– 320 µg/g) compared to European samples (< 5–20 µg/g) (Wilford et al. 2005). Indoor air concentrations and relations of PBDEs and PCBs were determined in offices and homes in UK between September 2003 and November 2005. Concentration levels for PCBs were ng/m<sup>3</sup> and for PBDEs pg/m<sup>3</sup>. The variability in PCB& PBDE concentrations *between* rooms (microenvironments) were attributed to room content and ventilation. No clear and consistent evidence of statistically significant relationships between PCB/& PBDE concentration and the number of PCs, electronic devices, number of items of PUF-containing furniture and age of the building was found (Hazrati and Harrad 2006). However, a drop in the PBDE concentration (but not PCB) was coupled to the change of a computer from 1998 to a new one. Higher concentrations of PBDEs have been coupled to computers and PUF containing furniture in other studies (Wilford et al. 2004, Harrad et al. 2004, Gevaio et al. 2006). Seasonal variations are likely to be governed by changes in temperature and ventilation (Hazrati and Harrad 2006). The higher temperature during operation increases emissions from appliances (Kemmllein et al. 2003, Hazrati and Harrad 2006).

Higher PBDE concentrations were measured in urban indoor& outdoor samples compared to rural samples in Toronto, Canada. The samples were taken from window surfaces. The mean concentration in urban indoor window organic films was 34.4 ng/m<sup>2</sup>, which was three times higher than in rural indoor films. Calculated indoor concentrations (using the air-film partition coefficient  $K_{FA}$ ) were 42.1 pg/m<sup>3</sup> for indoor urban sites (Butt et al. 2004).

Wilford et al. investigated PBDEs in both indoor dust and air in Ottawa, Canada. Mean concentration of PBDEs in dust of 68 homes was 5500 ng/g (range 170–170 000 ng/g) and in air of 74 homes 260 pg/m<sup>3</sup> (range 2–3600 pg/m<sup>3</sup>). Penta and deca congeners accounted for about 90 % of the dust compositions. Significant correlations were found between air and dust PBDEs, except for PBDs 183 and 209. The content of organic carbon (OC) in dust samples varied between 9–39%. No correlation between OC and PBDEs was found. Also, no correlation was found between PBDEs and house age, percentage carpeted, the addition of insulation, or new upholstered furniture (Wilford et al. 2004, 2005). Exposure scenarios for PBDEs through intake of air and dust were also made. The daily exposures (95<sup>th</sup> percentile) by inhalation were 23 ng for males and 21 ng for females. The corresponding mean daily dust intakes were estimated to 42 ng for adults and 550 ng for 6 month - 2 years old children (Wilford et al. 2004, 2005).

Kemmllein et al. measured detectable, ng/m<sup>2</sup>h level emissions of brominated FRs from insulating materials, assembly foams, upholstery/mattress and electronics equipment (Kemmllein et al. 2003).



#### 4. Indoor air exposure for SVOCs and flame retardants

##### Organophosphate FRs

Hartmann et al. studied organophosphate FRs and plasticisers in indoor air in 12 locations in Switzerland. TBP, TCEP and TCPP were the most abundant organophosphates and the concentrations were 0.1–150 ng/m<sup>3</sup> in office environments. A risk assessment made in the study concluded that the exposure is tolerable (Hartmann et al. 2004). The intakes for organophosphoric esters has been estimated to < 0.005–3.18 µg/kg (inhalative) and 0.12–1.67 µg/kg (oral) (Wensing et al. 2005). The emission of TCPP from polyurethane foam was between 10–140 ng/m<sup>2</sup>h in a German study. TCEP emission from a printed circuit board at 60 °C and from a PC under operating conditions resulted in a concentration level of 96 ng/m<sup>3</sup> in a 17 m<sup>3</sup> room with 0.5h<sup>-1</sup> air exchange rate (Kemmlin et al. 2003).

Table 5 summarizes measured indoor air concentration levels and estimates for exposure through inhalation as calculated with equation 1 for SVOCs, phthalates, PAHs, polybrominated FRs and organophosphate FRs.

Table 5. Measured indoor air concentration levels and estimates for exposure through inhalation as calculated with equation 1.

Compound	Indoor air concentration	Exposure indoors by alveolar air (adult)/ day
SVOCs (ISO 16000–6)	< 10 µg/m <sup>3</sup>	< 2µg/ kg
Phthalates	< 10 µg/m <sup>3</sup>	
PAHs	< 10 µg/m <sup>3</sup>	
Polybrominated FRs	< 0.5 µg/m <sup>3</sup>	< 0.1 µg/kg
Organophosphate FRs	< 1 µg/m <sup>3</sup>	< 0.2µg/ kg

## 5. Waste potential of SVOCs and flame retardants in the existing building stock

A majority of construction waste is wooden, stone and metal waste. In addition there is waste which includes plastic, contaminated wood as well as chip and other wooden based boards. Due to different classification systems there are inconsistent results for different waste types and their amounts in literature and statistics; part of the construction waste material is classified under the household waste and part of the waste is goes under different items. As for SVOCs and FRs, the waste categories and statistics are insufficient to describe their waste potential in constructions. Only rough estimations can be done as follows.

According to the Statistic Finland 41 % is wooden based waste, 28 % is stone materials, 14 % is metal, 2% is glass and more than 13 % of other waste materials from the total construction waste mass (from renovation + building demolition + building a new buildings). The SVOCs and FRs would mainly fall into the category of other waste materials. Perälä et al 2006 estimated the building waste from new construction in 2004 being a bit less than 0.25 million tons, from the renovation sites (buildings + housing/apartments) 0.9 million tons and from the building demolitions almost 0.45 million tons. Based on these figures, SVOCs and FRs waste potential would be less than 210 000 tons in total mass of building product waste (13%).

According to the Statistic Finland, the waste from construction sector (including buildings, road and water construction) was 21.87 million tons (2005), from which 344 000 tons were hazardous or problem waste (by general definition, a hazardous waste is waste that poses substantial or potential threats to public health or the environment and generally exhibits one or more of these characteristics: carcinogenic, ignitable (i.e., flammable), oxidizing, corrosive, toxic, radioactive, explosive, Tilastokeskus, Table 6). The biggest amount measured in mass scale was mineral waste including landmass (mineral soil materials) and other mineral waste which is not separated in the statistics. The category other mineral wastes include all concrete waste, tiles, ceramic waste, gypsum, insulation materials etc. The category 'mixed waste' includes besides household waste also glass, plastic and wood wastes which may also contain hazardous substances. Detailed information about the recycling of selected materials is given in Appendix B. Figure 3 shows the distribution by waste types from new construction of detached houses, attached houses and multi-story residential building (based on the VTT's calculations).

5. Waste potential of SVOCs and flame retardants in the existing building stock

Table 6. Waste from construction sector (including buildings, road and water construction).

Waste category	Yearly amount (2005)	%
Chemical	1 00 tn	0.0005 %
Metal	212 800 tn	1.0 %
Glass	35 000 tn	0.2 %
Wood	631 000 tn	2.9 %
Electricity and electronic	1 00 tn	0.0005 %
Animals and plants	1000 tn	0.005 %
Mixed waste including household waste	290 200 tn	1.3 %
Mineral based	20 700 200 tn	94.6 %
TOTAL	21 870 400 tn	
from which hazardous waste	343 600 tn	

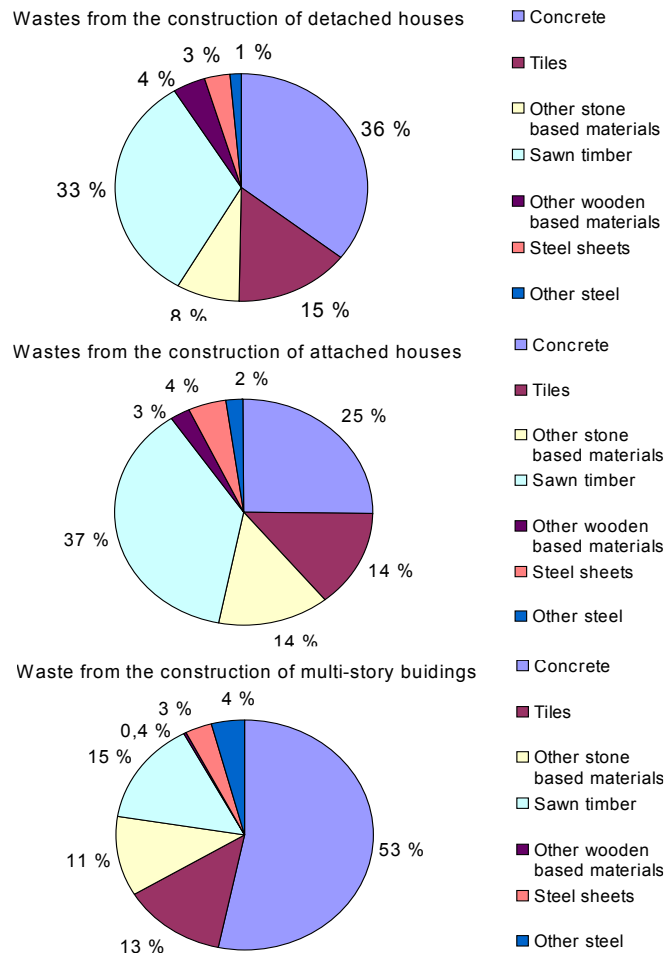


Figure 3. Waste proportions and types from the construction site of new residential buildings. Calculated according to the VTT's waste characteristics.

## 6. Measurement techniques to determine emission from materials and the indoor air concentration of SVOCs and flame retardants

### 6.1 Emission test chambers

Emission testing of VOCs from building products is standardised on an international level (ISO 2006a, 2006b). The measurement of low vapour pressure compounds like SVOCs and flame retardants, are however, more difficult with these techniques because of sink effects, i.e. deposition on surfaces and airborne particles. To minimise sink effects, high loading factors (i.e. sample area  $\text{m}^2$ / test chamber volume  $\text{m}^3$ ) should be used. Table 7 summarises test chamber types and testing conditions in earlier studies.

Table 7. Test chambers and testing conditions for SVOCs and flame retardants (T = temperature, RH = relative humidity, q = area-specific air flow rate, L = loading factor).

Application (reference)	Chamber size	T (°C), RH (%)	q ( $\text{m}^3/\text{m}^2\text{h}$ )	L ( $\text{m}^2/\text{m}^3$ )
POCs, BFRs (Kemmlin et al. 2003)	0.001– 0.02 $\text{m}^3$ and 1 $\text{m}^3$	23°C, 50%  60°C (printed circuit board)	1.24 (insulating board) 5.12 (assembly foam) 1 (upholstery foam) 1.24 (upholstery foam) ~1 (mattress)	1.1–17.7
Biocides (Horn et al. 2003)	0.020–0.023 $\text{m}^3$	23°C, 50%	1–1.25 (carpet) 5 (wood)	5.43–6.25

## 6. Measurement techniques to determine emission from materials and the indoor air concentration of SVOCs and flame retardants

A common feature for SVOC emissions is that they increase slowly until they reach a constant value that persists for a long period of time. For example, the linear emission level for the biocide propiconazole was reached in forty (40) days (Horn et al. 2003).

Wilke et al. made comparisons between four different emission test chambers/ cells and their TVOC and SVOC emissions. Test chamber sizes were 0.02 m<sup>3</sup>–1 m<sup>3</sup> and test cells were 1 litre (BAM cell) and 0.035 litre (FLEC cell). The material was stainless steel and glass. TSVOC was the sum of all compounds eluting after hexadecane. Good comparability was found for VOCs/SVOCs and TVOC/TSVOC.

A Japanese application is to first measure the SVOCs by means of traditional chamber tests. Then, the test sample is removed and the emission test chamber is heated (up to 250 °C) to collect substances that have been absorbed on the inner walls (Katsumata et al. 2005).

### 6.2 Sampling and analysis

Sampling of high boiling compounds like SVOCs and flame retardants is usually done on polyurethane foam (PUF) or a polymer adsorbent (Tenax, XAD). Typical sample volumes are 10–40 m<sup>3</sup>. Passive air samplers have also been utilised and evaluated (Wilford et al. 2005, Hazrati and Harrad 2006). A sample preparation step, i.e. extraction and cleanup is needed prior to analysis with GC/MSD or HPLC (liquid injection). Thermal desorption can be applied if SVOCs are sampled on Tenax TA as in the ISO standard for VOCs (ISO 2004). The optimisation of the parameters for thermal desorption (temperature, flow rates etc) of SVOCs, however, means reduced sensitivity for lower boiling VOCs (Thomas and Uhde 2006).

The effects of extraction parameters on the recovery of phthalates have been studied by Korpi et al. (2007). The overall best performance was obtained by using toluene and ultrasonic treatment for glass fibre filters, Soxhlet extraction and toluene for XAD + glass fibre filter, and dichloromethane and ultrasonic for polyurethane foam (each of the combinations is suitable in terms of extraction recovery).

Large volume injection techniques are recommended to be used in order to increase sensitivity in the analysis of polybrominated diphenyl ethers (PBDEs, Björklund 2003). By selecting a short narrow bore column it is possible to decrease the degradation of high molecular weight PBDEs.

Sampling and analysis techniques found in the literature are summarised in Table 8.

6. Measurement techniques to determine emission from materials and the indoor air concentration of SVOCs and flame retardants

Table 8. Sampling and analysis of SVOCs and flame retardants.

Application and reference	Adsorbent/sampling equipment	Sampling rate and volume (active)/ time (passive)	Preconditioning and analysis	Specifications/ comments
POCs, BFRs in air, test chamber (Kemmlein et al. 2003)	glass tubes with PUF plugs, d = 12 mm, l = 50 mm TEP: glass tubes with Tenax TA	PUF: 15–100 l/h, 2.5–40 m <sup>3</sup> Tenax TA: 100 l/min, 1 l	PUF: Soxhlet extraction (BFR), ultra sonic extraction (POC) Tenax TA : thermal desorption Analysis with GC-MS : DB-5-ms 15 m column (BFR), HP-5-ms 30m column and HPLC (BDP)	LOD : 0.09–1.8 ng/m <sup>3</sup> (BFRs), 3–10.5 ng/m <sup>3</sup> , no breakthrough was observed
PBDEs in air and dust (Wilford et al. 2005)	Air: Passive air samplers on top of a furniture. Dust: Vacuum cleaner bag content was sieved	3 weeks	Both: Extraction and analysis with GC/MS: DB-5-60 m and 15 m columns, negative chemical ionisation mode, m/z: 79 (PBDEs), 81 (PBDE confirmation).	
PBDEs window surfaces (Butt et al. 2004)	Sampling with pre-cleaned laboratory Kim-wipes wetted with dicloro-methane / iso-propyl alcohol	-	Extraction, cleanup, GC-HRMS	
PBDEs in indoor air (Hazrati and Harrad 2006)	PUF passive disk sampler	1 month	Soxhlet extraction, GC/MS analysis (SIM).	BDE 153 and 154 (particle bound) IAC underestimated
POCs in indoor air (Hartmann et al. 2004)	PUF plugs	4 l/min, 14–34 m <sup>3</sup>	Soxhlet extraction, GC/MS analysis (SIM).	recoveries 62–100%
PAH compounds in air samples	XAD	> 1 m <sup>3</sup>	Soxhlet extraction, GC/MS analysis (SIM).	LOD: 0.01 µg/m <sup>3</sup>
Biocides in test chamber (Horn et al. 2003)	PU foam plugs, d=12mm, l=50 mm	115 l/h (max), 20 m <sup>3</sup> (max)	GC-MSD (SIM), column: HP 5 (30x 0.25 x 0.25)	LOD : 4–4000 ng/m <sup>2</sup> h, no breakthrough was observed
Biocides (Yu et al. 2005)			GC- FID/MSD, column: SGE BPX5 30m	

## 7. Emissions of SVOCs from building materials

### 7.1 Materials tested

A total of thirteen different building materials were tested (Table 9). The test specimens were taken directly from the production line and sent within a day to the test laboratory, tightly wrapped without using any plastic materials. The tests were started within < 15 minutes after unwrapping. The immediate testing time point was chosen in order to avoid any contamination of SVOCs from the surroundings during ageing. An exception was made with the two paints tested. These were pre-conditioned in separate environmental chambers at 23 °C and 50 % RH for four weeks in order to ensure proper film formation. The “on site foam type” polyurethane was prepared one the day before the testing was performed and was covered loosely with aluminium overnight.

Table 9. Materials tested.

Abbreviation	Material	Specification
PAINT 1	Paint	For fire retardant appl.
PAINT 2	Paint	Interior wall paint
SCREED	Screed	Interior wall screed
GB	Gypsum board	For interior use
ADV	Acoustic board (thickness 15 mm)	For interior use
MSQ	Acoustic board (thickness 40 mm)	For interior use
PU1	Polyurethane insulation	Foam type
PU2	Polyurethane insulation	Foam type, prepared on site
EPS1	Expanded polystyrene	With fire retardant
EPS2	Expanded polystyrene	No fire retardant
LCFI	Cellulose insulation	Loose-fill cellulose fibre
PVC	Floor covering	PVC
NO PVC	Floor covering	Plastic, does not contain PVC
LINO	Floor covering	Linoleum

## 7.2 Methods

### 7.2.1 Sampling

Two test specimens were prepared for all tested materials (samples 1A and 1B, Figure 4). Emission tests were performed by using 1) a FLEC connected to a 2 litre chamber (Picture 1) and 2) a 2.5 litre glass desiccator (Picture 2). All materials, tubing and fittings were made of stainless steel, glass or Teflon. The air flow was on average 200 ml/min, which resulted in air flow/ area values ( $q/a$ ) between 0.35–1.69  $\text{m}^3/\text{m}^2\text{h}$ . An exception to this was the two paints, which were measured with a higher flow rate ( $q/a \sim 3 \text{ m}^3/\text{m}^2\text{h}$ ). Table 10 summarises  $q/a$  values for the tested materials.



Picture 1. The FLEC chamber.



## 7. Emissions of SVOCs from building materials



Picture 2. The glass desiccators.

Table 10. Test specimen area and  $q/a$  ( $\text{m}^3/\text{m}^2\text{h}$ ) during the emission testing for the tested materials in the FLEC chamber and the desiccator.

Name	Test specimen area, $\text{m}^2$	FLEC $q/a$ , at $23^\circ\text{C}/40^\circ\text{C}$ $\text{m}^3/\text{m}^2\text{h}$ or $\text{m}^3/\text{m}^2\text{g}$	Desiccator $q/a$ , $\text{m}^3/\text{m}^2\text{h}$ or $\text{m}^3/\text{m}^2\text{g}$
Paint 1	0.01	3/ 3.6	1.44
Paint 2	0.01	3/ 1.32	1.44
Screed	0.018	0.69/ 0.77	0.81
GB	0.014	0.83/ 0.97	1.03
ADV	0.018	0.69/ 0.67	0.8
MSQ	0.03	0.39/ 0.40	0.48
PU1	0.035	0.35/ 0.38	0.41
PU2	0.014	0.88/ 0.92	1.03
EPS1	0.026	0.47/ 0.48	0.55
EPS2	0.026	0.53/ 0.54	0.55
LCFI	0.014	1.21/ 1.44	1.5
PVC	0.01	1.19/ 1.35	1.44
no PVC	0.01	1.14/ 1.38	1.44
Linoleum	0.01	1.21/ 1.38	1.44

## 7. Emissions of SVOCs from building materials

Sampling of the outlet air from the FLEC-chamber was done on Tenax TA adsorbents at 23 °C and 40 °C. The samples at the elevated temperature were taken 20, 60 and 120 minutes after the 40 °C was reached, which was in about 10 minutes. Blank samples were collected prior to placing the test specimen in the chamber. In general, sampling was done according to ISO 16 000-6 standard (ISO 2004).

Sampling of the outlet air from the glass desiccator was done on purified polyurethane foam (PUF) for ~ 20 days, which correspond to ~ 7 m<sup>3</sup> samples (= one working day exposure for an adult). The PUF was changed two times, i.e. the total time of sampling was ~ 60 days. Blank samples were collected parallel to the real samples. Finally, a “rinsing sample” was taken by rinsing the desiccator walls with 20 ml of dichloromethane (DCM) after the 60 day sampling period.

	Sample 1A:	Sample 1B:
Chamber:	FLEC	Desiccator
Adsorbent:	Tenax TA	PUF
Temperature:	23oC, 40oC	23oC
Sampling time:	20-120 min	20-60 days
Rinsing sample:	no	yes
Analysis:	1) VOCs C16-C22 2) SVOCs C16-	1) SVOCs incl. Phthalates 2) Brominated compounds 3) Organophosphates 4) Boron

Figure 4. Sampling and analysis scheme (PUF = polyurethane foam).

### 7.2.2 Analysis

#### 7.2.2.1 Pre tests

Before doing specific analysis of the compounds of interest, elementary analysis from all building products was made by X-ray fluorescence analysis (semiquantitative). Especially, the occurrence of bromine was of interest. The PU2 and EPS2 were not analysed since they were included at a later timepoint during the project. In addition, a small amount of the building material was grinded and dissolved in DCM (later referred as “SVOC pre test”). The SVOCs were analysed by a gas chromatograph equipped with a mass selective detector (GC/MSD) after liquid injection (see 7.2.2.3 for the detailed description of the analysis). This step was done in order to reveal any phthalates (and other SVOCs soluble in DCM) in the product itself.

## 7. Emissions of SVOCs from building materials

### 7.2.2.2 Tenax samples

Tenax tubes were thermally desorbed at 260 °C for 6 minutes (cold trap temperature -30°C) and analysed with a gas chromatograph (GC) connected to a mass selective detector (MSD) and flame ionisation detector (FID). The gas chromatograph was equipped with a double-capillary column HP PONA (50 m x 0.2 mm x 0.25 µm) and the sample was split 1:1 in the two columns, which were connected to MSD and FID detectors. The temperature programme of the GC oven was as follows: 40 °C (5 min), 6 °C/ min, 280 °C (5 min), total run time 50 minutes. MSD in SCAN mode was used to identify single VOCs and the FID response was used for quantification. TVOC was calculated as toluene equivalents from the total integrated FID signal between hexane and hexadecane. An external toluene standard was used for calibration. SVOCs were reported as the total integrated area after hexadecane (TSVOC).

### 7.2.2.3 PUF samples

PUF samples were extracted with DCM in a Soxhlet apparatus for eight hours. The extract was divided into three equal parts and the samples were concentrated to 1 ml. Different analysis was performed for the different building material emission samples based on the results from the pre test.

SVOCs (and VOCs) were analysed from the first part by injecting (splitless) 1 µl to a GC/MSD equipped with a HP-5MS (30m x 0.25mm x 0.25µm) column. The temperature programme was as follows: 40 °C (1min), 13 °C/min, 320 °C (10 min). SVOCs and phthalates were calculated from the total integrated area of the MSD detector (SCAN mode) as toluene equivalents.

PBDEs (BDE-17, -47, -66, -99, -100, -85, -153, -154, -183, -203 and -209), HBCD and organophosphates were analysed with a GC/MS system. C<sup>13</sup> labelled internal standards were used for quantification of bromine compounds. Boron was analysed with an ion chromatograph.

## 7.3 Results

### 7.3.1 Pre tests

According to the X-ray fluorescence results, only the EPS1 and paint 1 contained bromine above the detection limit of 0.005 % (0.26 % and 0.02 % respectively). Therefore, the EPS1 emission samples were analysed further for brominated compounds (see Chapter 7.3.3.2). The X-ray analysis also showed that the phosphor content in paint 1 (fire retardant paint) was 7.3 %. This was a significantly higher percentage than in the other materials (0.01–0.5 %). Thus, the paint 1 was analysed for organophosphates (see Chapter 7.3.3.3). The SVOC pre tests showed that only PVC contained phthalates above the blank value.

### 7.3.2 Sampling on Tenax TA

#### 7.3.2.1 Results at 23°C

The TVOC specific emission rates (SER) measured at 23 °C varied between 5–2312  $\mu\text{g}/\text{m}^2\text{h}$  and the TSVOC SER varied between 1–66  $\mu\text{g}/\text{m}^2\text{h}$  (average 7  $\mu\text{g}/\text{m}^2\text{h}$ , Figure 5a and 5b). The highest SVOC concentration was measured from the foam type PU. In general, the SVOCs were difficult to identify from the mass spectra because of low concentration levels. Aliphatic hydrocarbons were however abundant. The VOCs identified were typical for the building products in question, i.e. aldehydes, glycols and glycolethers were main compounds identified (Table 11).

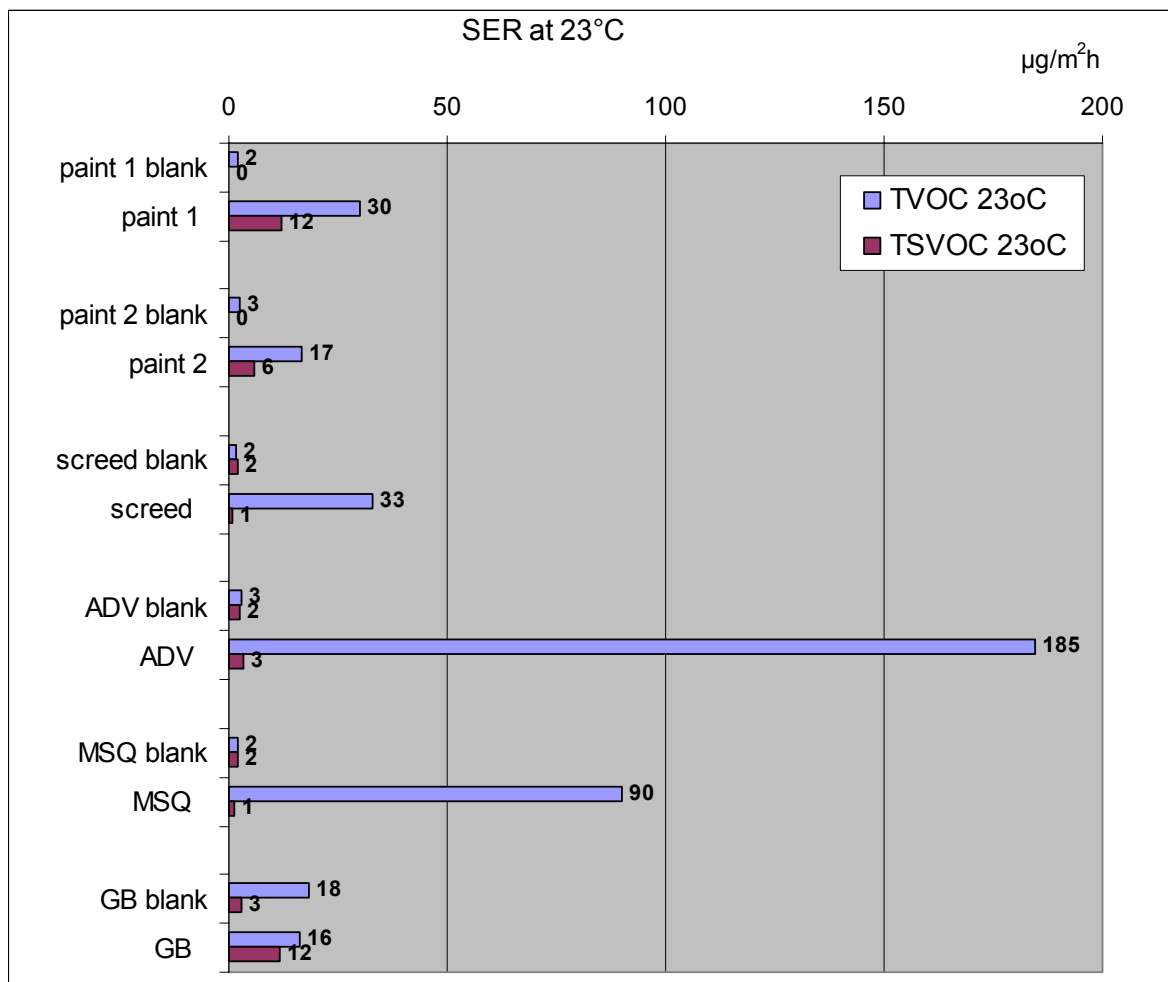


Figure 5a. Specific emission rate (SER,  $\mu\text{g}/\text{m}^2\text{h}$ ) measured at 23 °C.

## 7. Emissions of SVOCs from building materials



Figure 5b. Specific emission rate (SER, μg/m<sup>2</sup>h) measured at 23 °C.

## 7. Emissions of SVOCs from building materials

Table 11. Main compounds identified from the Tenax TA adsorbents at 23°C and 40°C.

Name	Main compounds identified	
	23°C	40°C
Paint 1	Decanal, nonanal	Decanal, nonanal, ethanol- ( 2,2-phenoxyethoxy)
Paint 2	Decanal, nonanal	Decanal, 1,2- propanediol
Screed	Decanal, nonanal ,1,2- propanediol	Oktanal, nonanal ,1,2- propanediol, 2-ethoxy-ethoxyethanol
GB	Decanal, nonanal	Decanal, nonanal, C16-C21 aliphatic hydrocarbons
ADV	1,2- propanediol	1,2- propanediol
MSQ	1,2- propanediol, Ethanol, 2-butoxy-	1,2- propanediol, Ethanol, 2-(2-butoxyethoxy)-, Ethanol, 2-(2-butoxyethoxy) acetate
PU1	Decanal	Cyclohexamine, dimethyl-
PU2	2-methyl- 2-pentenal, tetradecane	2-methyl- 2 -pentenal, tetradecane , tris (1,3-dichloroisopropyl) phosphate
EPS1	Ethylbenzene, styrene, phenylethanone	Ethylbenzene, styrene, phenylethanone
EPS2	Ethylbenzene, styrene, phenylethanone, xylenes	Ethylbenzene, styrene, phenylethanone, xylenes
CELL	hexanal	hexanal, C16 => aliphatic hydrocarbons
PVC	Ethanol,2-butoxy-, phenol, ethanol, 2-(2-ethoxyethoxy)-, 2-pyrrolidone, 1-methyl-, ethanol, 2-(2-butoxyethanol)-, ethanol, phenoxy-, decanal DECANAL (CAS) ETHANOL, 2-PHENOXY- (CAS)	Ethanol, 2-butoxy-, phenol, ethanol, 2-(2-ethoxyethoxy)-, 2-pyrrolidone, 1-methyl-, ethanol, 2-(2-butoxyethanol)-, ethanol, phenoxy-, decanal
no PVC	aliphatic hydrocarbons	aliphatic hydrocarbons
Linoleum	pentanal, hexanal, nonanal, octanal, acetic acid, hexanoic acid	hexanal, nonanal, octanal, hexanoic acid, C16 => aliphatic hydrocarbons

## 7. Emissions of SVOCs from building materials

### 7.3.2.2 Results at 40°C

The emissions measured at 40 °C showed large variations (Figures 6a, b and c). The TVOC SER varied between 10–10 000  $\mu\text{g}/\text{m}^2\text{h}$ . The highest TVOC emission was measured from the PVC. The SVOC SERs were between < 1–150  $\mu\text{g}/\text{m}^2\text{h}$ . The highest SVOC emission was measured from the foam type polyurethane (PU2), cellulose insulation and linoleum. The known fire retardant tris (di-chloroisopropyl) phosphate (Fyrol PCF or TCPP) was identified from the foam type polyurethane. The emission rate of PCF was 24  $\mu\text{g}/\text{m}^2\text{h}$  after 120 minutes at 40 °C. Otherwise, aliphatic hydrocarbons of higher than C16 were identified. Table 11 summarises the main compounds identified at 40 °C.

7. Emissions of SVOCs from building materials

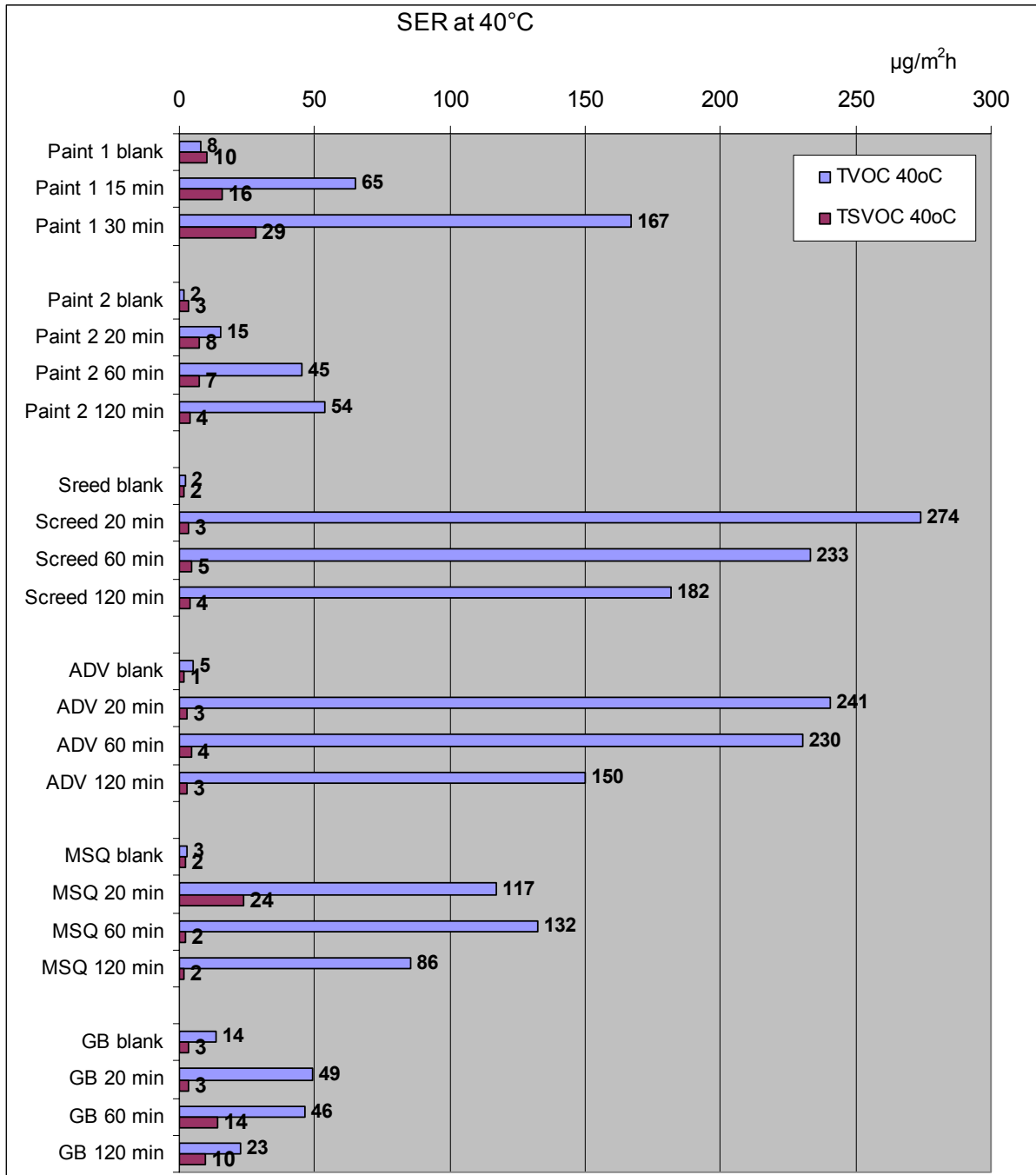


Figure 6a. Specific emission rate (SER, µg/m²h) measured at 40 °C.



7. Emissions of SVOCs from building materials

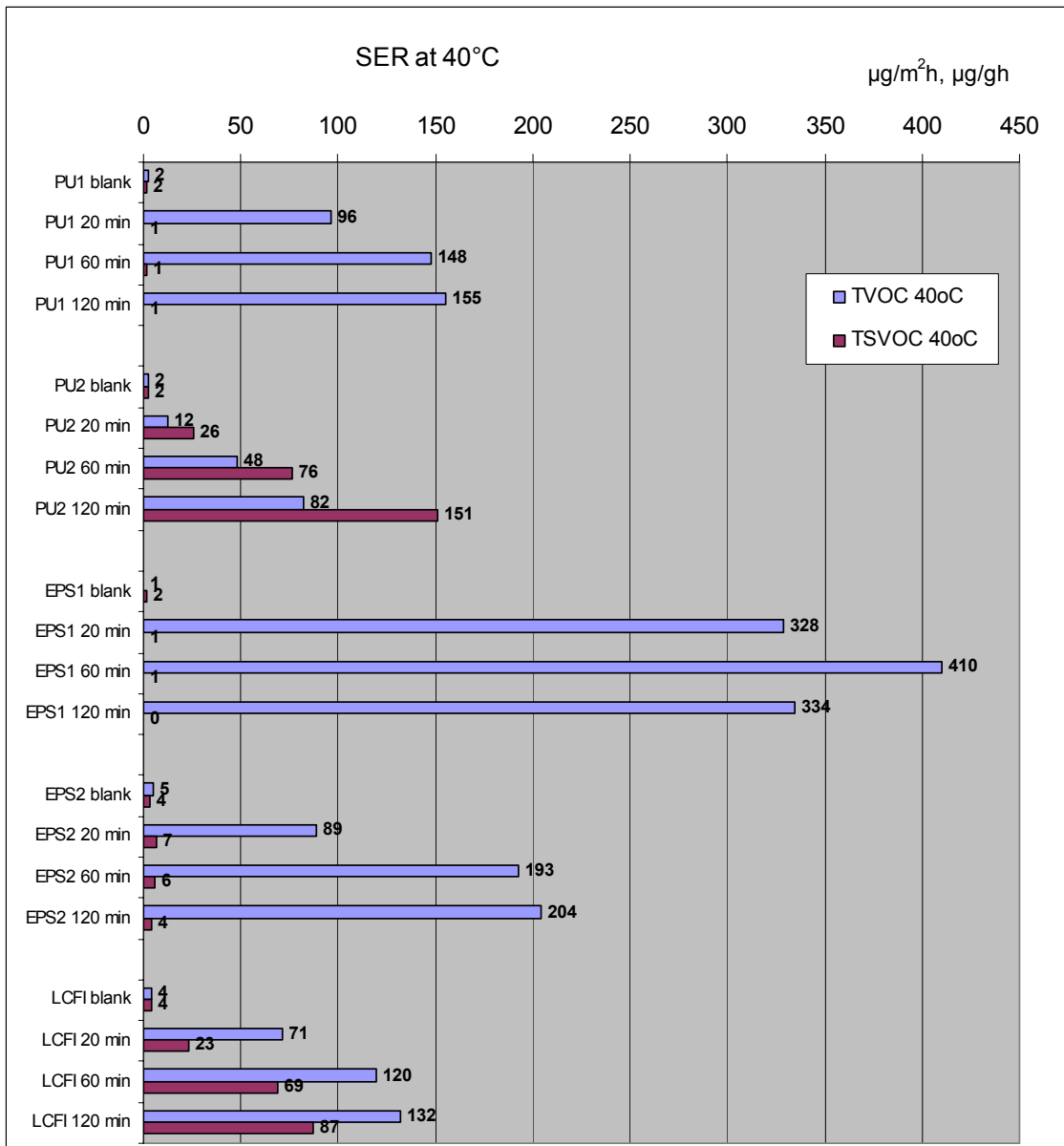


Figure 6b. Specific emission rate (SER, µg/m<sup>2</sup>h or µg/gh for cellulose based insulation) measured at 40° C.

7. Emissions of SVOCs from building materials

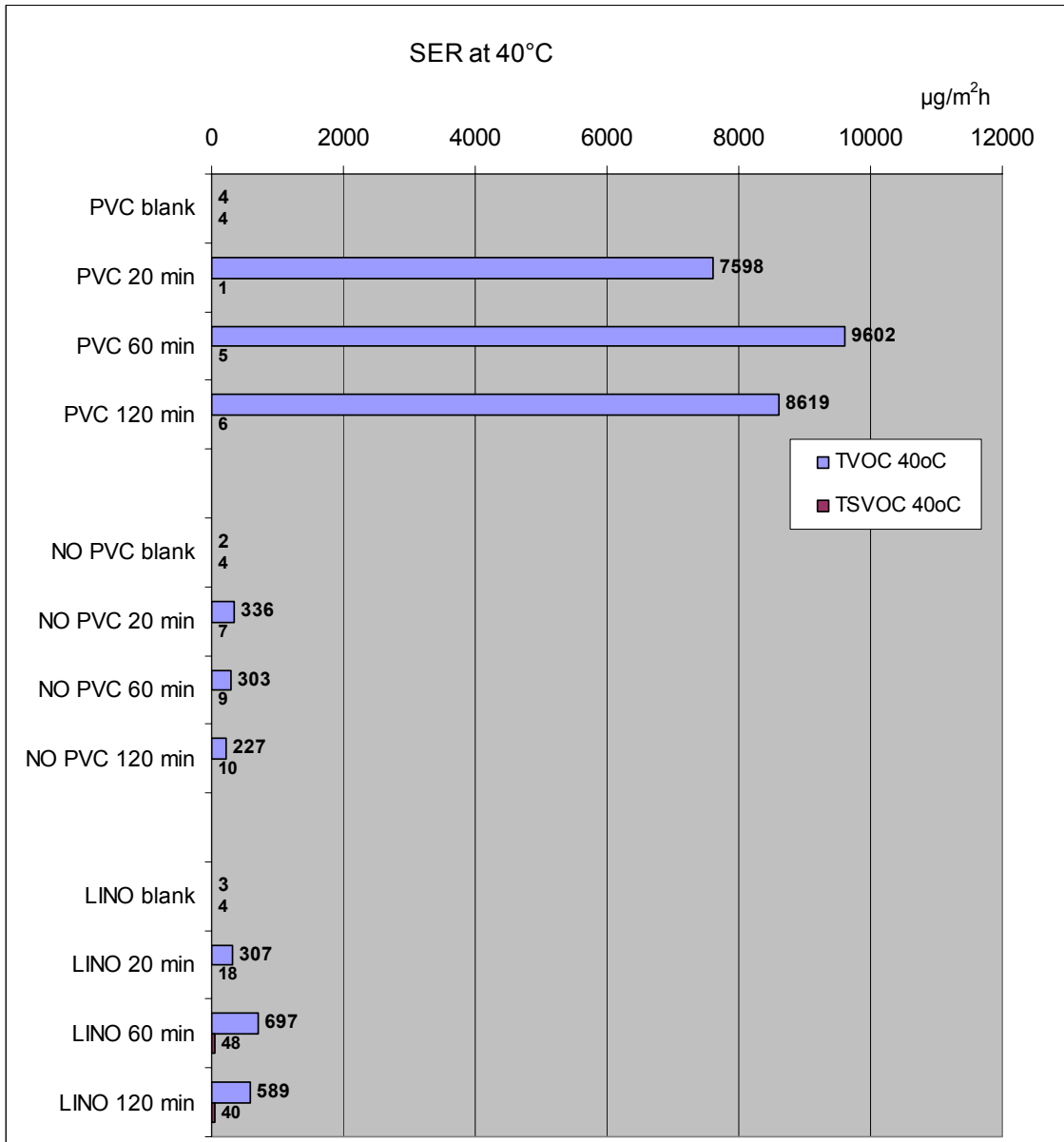


Figure 6c. Specific emission rate (SER, µg/m2h) measured at 40 °C.

## 7. Emissions of SVOCs from building materials

### 7.3.3 Sampling on PUF

#### 7.3.3.1 SVOCs and phthalates

The total amount of SVOCs measured from the PUF samples varied from  $< 10 \mu\text{g}/\text{m}^3$  up to  $500 \mu\text{g}/\text{m}^3$  (Figures 7a–d). Highest concentrations ( $200\text{--}500 \mu\text{g}/\text{m}^3$ ) were measured from paint 1 (20 day sample), screed (20 day sample), cellulose insulation (20&60 day samples) and EPS1 (60 day sample). Very low concentrations were measured from paint 2, polyurethane, no PVC, gypsum board and acoustic board (MSQ). The SVOCs were in general poorly identified. However, hydrocarbon compounds were abundant. Product typical VOCs like glycols and glycolethers were identified from paint and screed products. Likewise, typical VOCs for the flooring materials were also identified.

The amount of SVOCs in the rinsing samples varied between  $< 100\text{--}800 \mu\text{g}$  (Figures 7a–d). Lowest levels of less than  $100 \mu\text{g}$  were measured from the cellulose insulation and the “no PVC”. Phthalate above the blank level was only identified from the PVC rinsing sample ( $218 \mu\text{g}$ ). This phthalate was most likely di-isononylphthalate (DINP), which is used in its production. However, no standard was available to confirm this. Figure 8 shows the GC/MSD chromatogram for the PVC rinsing sample.

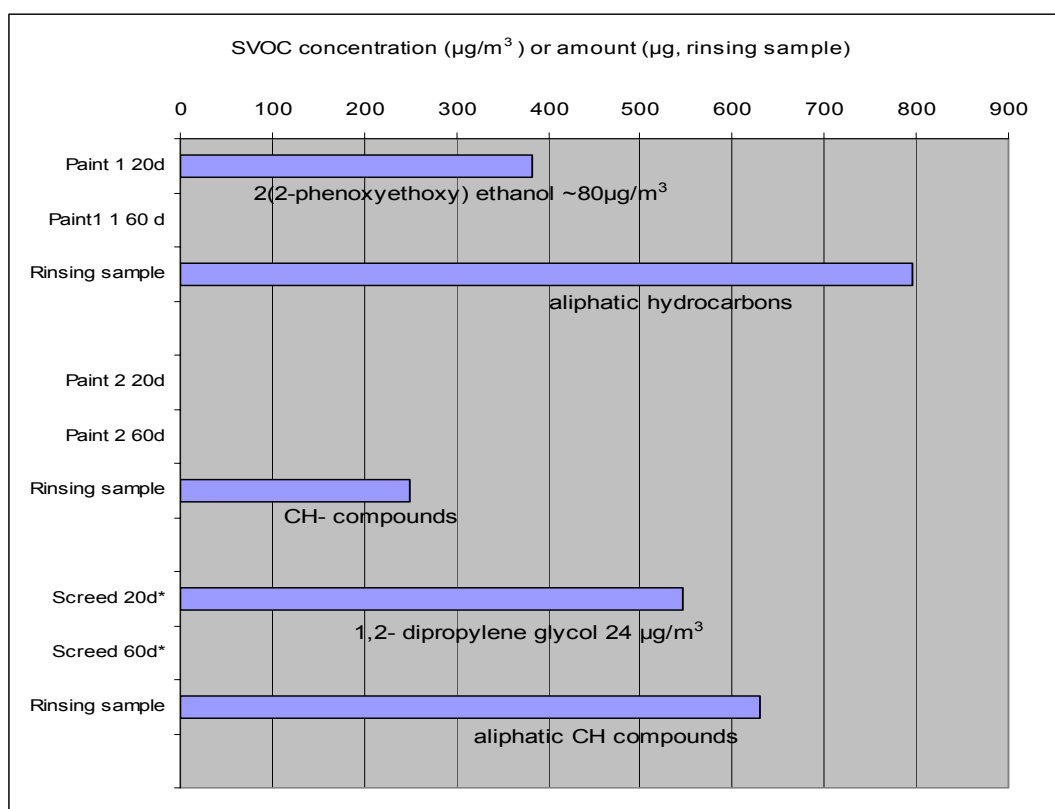


Figure 7a. SVOC concentration or amount measured from the desiccator samples (air & rinsing samples).

## 7. Emissions of SVOCs from building materials

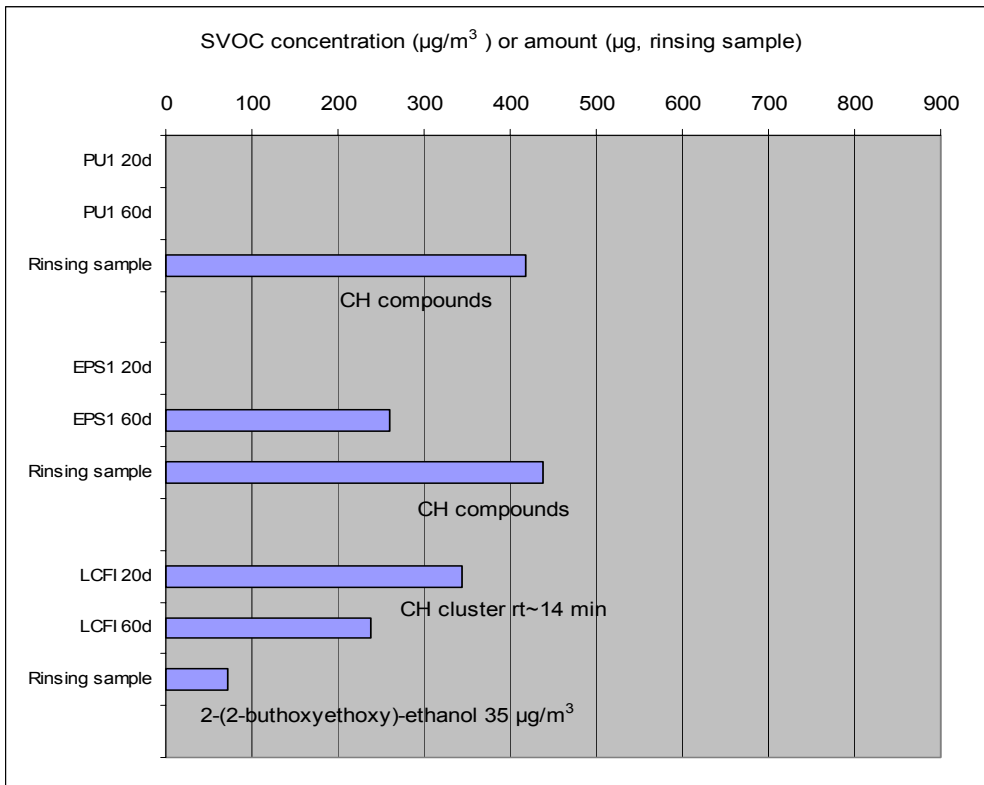


Figure 7b. SVOC concentration or amount measured from the desiccator samples (air & rinsing samples).

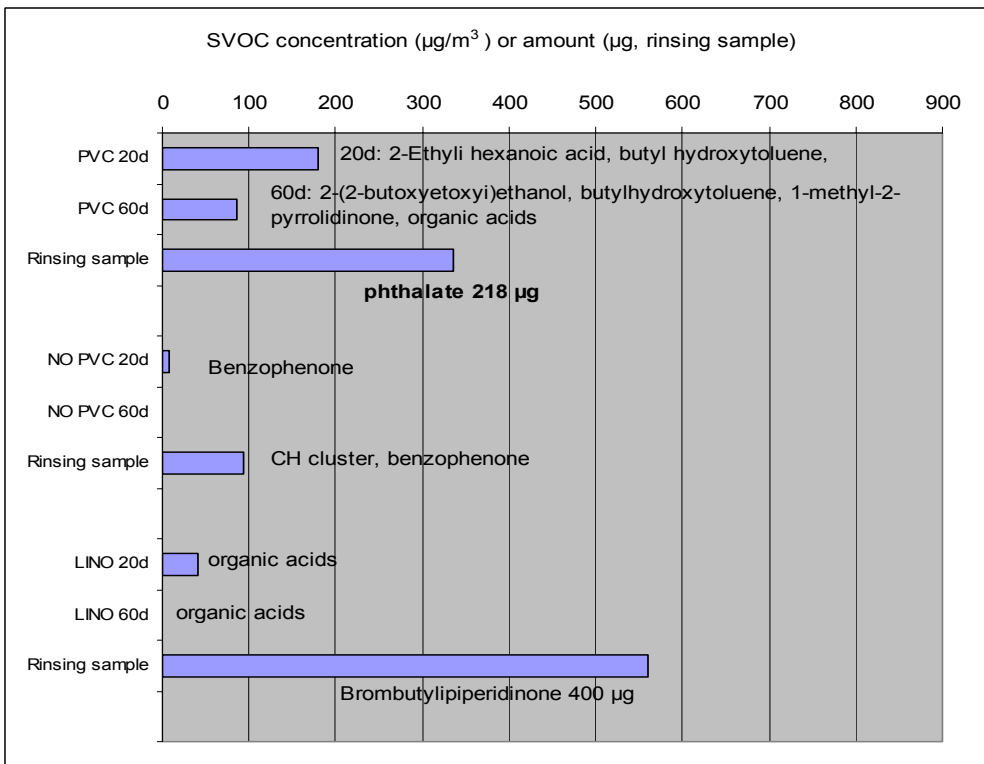


Figure 7c. SVOC concentration or amount measured from the desiccator samples (air & rinsing samples).

## 7. Emissions of SVOCs from building materials

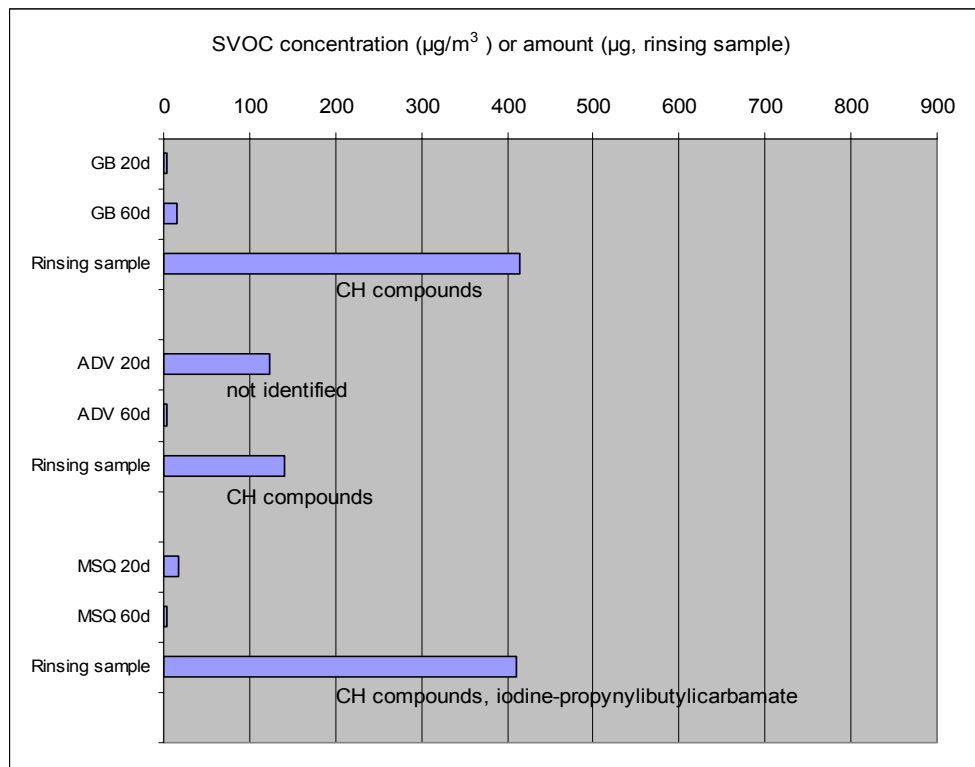


Figure 7d. SVOC concentration or amount measured from the desiccator samples (air & rinsing samples).

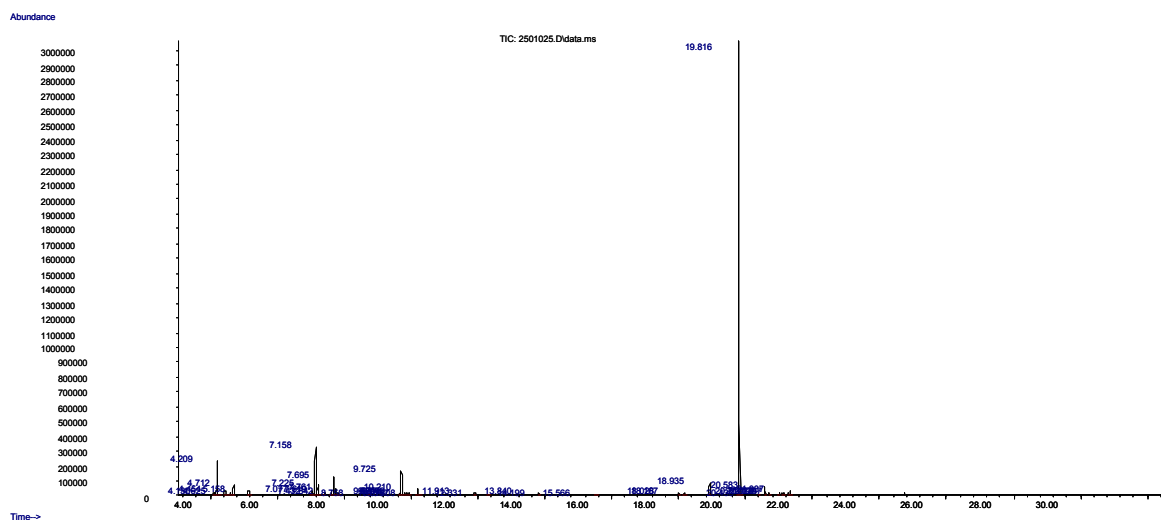


Figure 8. The GC/MSD chromatogram for the PVC rinsing sample, phthalate peak at  $t_r = 19.8$  min.

### 7.3.3.2 Brominated compounds

Only the air samples collected from EPS 1 were analysed for brominated compounds since its bromine content was 0.26% according to the pre test (chapter 7.3.1). As expected, no PBDE compounds were detected from the EPS1 air samples above the limit of quantification ( $4e-4$  ng/m<sup>3</sup>). The congener 209 was detected in the rinsing sample from EPS1, however, the amount was only 0.5 ng. The HBCD concentrations (sum of  $\alpha$ ,  $\beta$  and  $\gamma$  congeners) in the EPS1 air samples were also below of the limit of quantification ( $4e-3$  ng/m<sup>3</sup>). However, the rinsing sample collected from the desiccator walls after the end of the 60 day sampling period contained 72 ng of HBCD (sum of  $\alpha$ ,  $\beta$  and  $\gamma$  congeners).

### 7.3.3.3 Organophosphates

The organophosphates analysed from paint 1 and polyurethane 1 were below the detection limits (<0.04–0.32  $\mu\text{g}/\text{m}^3$  for air samples collected). The concentration levels correspond to emission levels of less than 60–460 ng/m<sup>2</sup>h (paint 1) and 15–140 ng/m<sup>2</sup>h (PU1). Table 12 summarises the concentration levels.

Table 12. The organophosphate concentrations measured in the paint samples collected 20 and 60 days after the test sample was placed in the chamber.

Organophosphate	Concentration ( $\mu\text{g}/\text{m}^3$ )			
	Paint1 20 days, sample V = 6.9 m <sup>3</sup>	Paint1 60 days, sample V = 3.8 m <sup>3</sup>	PU 20 days, sample V = 7.7 m <sup>3</sup>	PU 60 days, sample V = 7.7 m <sup>3</sup>
Tris(chloroisopropyl) phosphate (TCCP)	< 0.17	< 0.32	< 0.16	< 0.16
Triphenylphosphate	< 0.04	< 0.08	< 0.04	< 0.04
Triethylphosphate	< 0.17	< 0.32	< 0.16	< 0.16
Trioctyl phosphate	0.23	< 0.08	< 0.04	0.21
2-ethylhexyl-diphenyl phosphate	< 0.04	< 0.08	< 0.04	< 0.04

### 7.3.3.4 Boron

Boron was measured from the cellulose based insulation emission samples since it was known that boric acid is used as a FR. Boron was identified from the air samples collected from the FLEC at 40 °C for 48 hours and from the glass desiccators at 23 °C 20 and 60 days after the sampling started (Figure 8). The concentration at 23 °C varied between 0.4–0.7  $\mu\text{g}/\text{m}^3$  (SER = 0.6–1  $\mu\text{g}/\text{gh}$ ). At 40 °C, the concentration reached 5  $\mu\text{g}/\text{m}^3$ . This corresponds to a SER of 6  $\mu\text{g}/\text{gh}$ .

## 7. Emissions of SVOCs from building materials

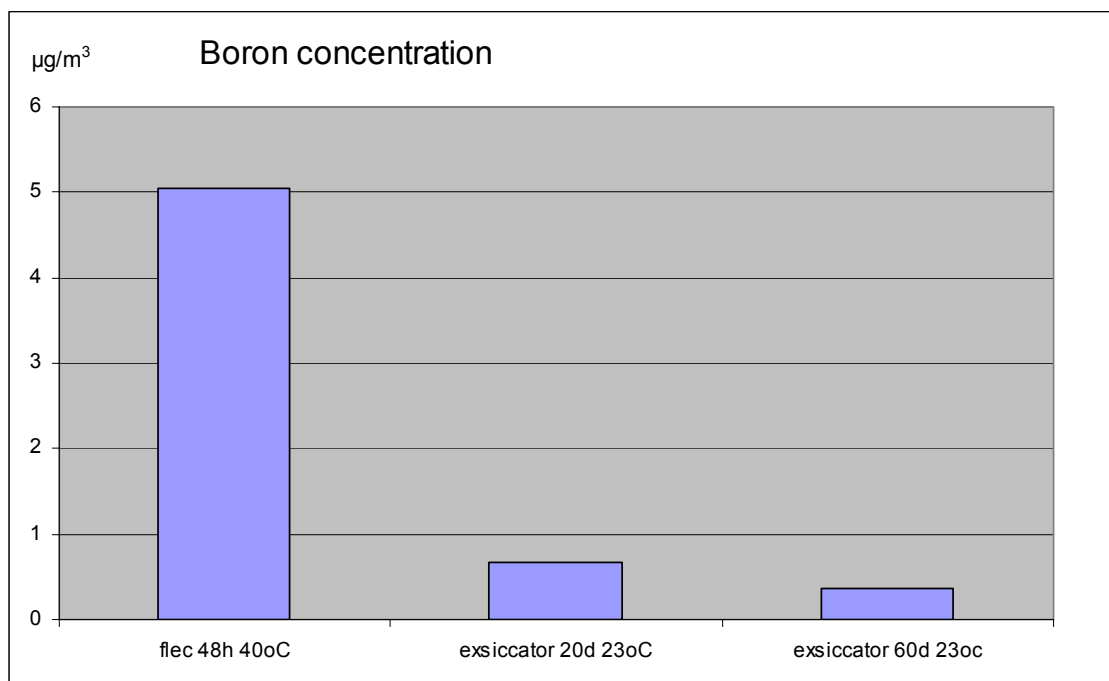


Figure 8. Boron concentration in the cellulose based insulation emission samples.

## 7.4 Discussion

### *General remarks on the emission results*

The studied materials showed a large diversity when it comes to their VOC and SVOC emissions both in terms of emission levels and compounds emitted. However, it seemed that aliphatic hydrocarbons are the most abundant SVOCs measured.

The TVOC and TSVOC emissions increased by a factor of four and two respectively, when the temperature increased from 23 °C to 40 °C. The elevated temperature was used in order to increase the emissions of SVOCs for better detection. Also, real life situations like direct sunlight may cause temperatures up to 70 °C on surfaces indoors. In fact, the known fire retardant tris (dichloroisopropyl) phosphate (TCCP) was identified from the polyurethane foam from the Tenax TA sample taken 120 minutes after the temperature reached 40 °C. The phosphate content in the PU sample was 0.5 % according to the elementary analysis.

Phosphate FRs were also expected from the Paint 1, which had a phosphor content of 7.3 %. However, no organophosphates were detected from air samples above LOQs which were, depending on sample volume, < 0.04–0.32  $\mu\text{g}/\text{m}^3$ .

A brominated FR, namely HBCD, was detected above LOQ only in the rinsing sample from the desiccator rinsing samples in which the EPS with FR (EPS 1) was measured. The amount of HBCD (sum of three congeners) was 72 ng.

A phthalate was detected above blank values only from the desiccator rinsing samples in which the PVC was measured. The results showed that the sorption of this compound on chamber walls is sig-

nificant for the time period of 60 days. The amount on the walls corresponded to an average concentration of  $0.01 \mu\text{g}/\text{m}^3$  throughout the sampling period of 60 days.

In addition, boron was detected from the cellulose insulation air samples. The mechanism of boron transfer to the air samples was not clarified further during this project, however, its concentration increased by 5 times when the temperature was raised to  $40^\circ\text{C}$ .

Figure 9 summarises the percentage of SVOC mass (not SER) distributed between the air samples collected during the 60 day test period on the PUF and the rinsing samples from the exsiccator walls after the 60 days. Large variations could be seen, i.e. depending on the product the SVOC mass on chamber walls varied between  $< 5$ –100 %.

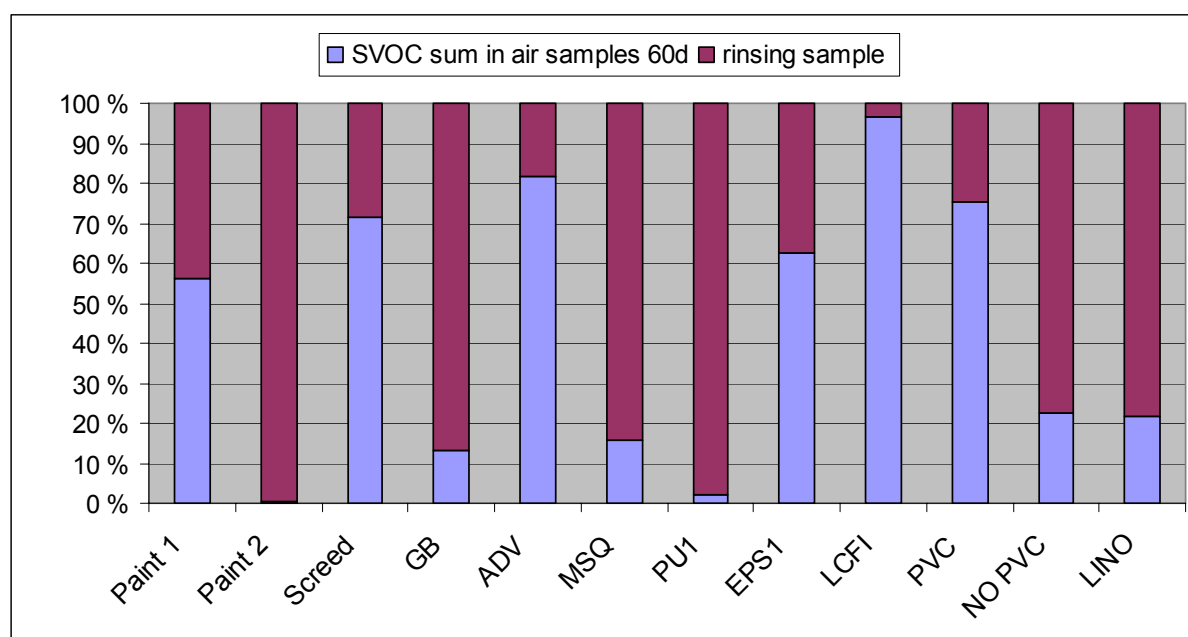


Figure 9. The percentage of SVOC mass in the air samples (sum of 0–60 day results) and the rinsing samples (= deposition on chamber walls).

#### *Correlations between the different sampling methods for SVOCs*

The TVOC and TSVOC SERs measured from the Tenax TA and PUF samples at  $23^\circ\text{C}$  were compared (an average of the PUF samples during the 60 day test period was used in the calculations). The PUF TSVOC and Tenax TA TSVOC result correlated positively (0.839, Figure 10). The correlation was statistically significant ( $p < 0.01$ ). The TVOC result correlated negatively with the TSVOC results from the Tenax TA samples, however, the correlation was not statistically significant. The TSVOC measured from the Tenax TA was 1–74 % from the PUF TSVOC, except for PU1 and gypsum board, for which the percentages were 186 % and 120 % respectively. The Tenax TA TSVOC varied between  $2$ – $66 \mu\text{g}/\text{m}^2\text{h}$  and the TSVOC measured from the PUFs varied between  $1$ – $435 \mu\text{g}/\text{m}^2\text{h}$ . The  $435 \mu\text{g}/\text{m}^2\text{h}$  SER was measured from the cellulose based insulation which was five times the amount in the Tenax TA (TVOC+TSVOC). Otherwise, the amount of SVOCs (and VOCs) measured from the PUF was 5–35 % of the Tenax TA result (TVOC+TSVOC).



## 7. Emissions of SVOCs from building materials

It could be concluded that the different sampling methods do show correlation for TSVOC taking into account the large variations within the SER levels. The results implied that the SVOCs calculated from the 2 litre Tenax TA sample collected in the beginning of the test period does give some implication of the 60 day SVOCs result collected on the PUF. However, because of small sample size (n=8, samples with internal standard interference were excluded from the statistical analysis) no general conclusions should be drawn. At this point it should be further noticed that the quantification from Tenax TA samples was made from the FID whereas the results from the PUF were quantified from the MSD.

		Correlations		
		TenaxTVOC SER	TenaxTSVOC SER	PufTSVOC SER
TenaxTVOC SER	Pearson Correlation	1	-0.257	0.218
	Sig. (2-tailed)		0.539	0.604
	N	8	8	8
TenaxTSVOC SER	Pearson Correlation	-0.257	1	<b>.839**</b>
	Sig. (2-tailed)	0.539		0.009
	N	8	8	8
PufTSVOC SER	Pearson Correlation	0.218	<b>.839**</b>	1
	Sig. (2-tailed)	0.604	0.009	
	N	8	8	8

\*\* . Correlation is significant at the 0.01 level (2-tailed).

Figure 10. Pearson correlations between TVOC and SVOC SER measured from the Tenax TA and PUF samples.

Figure 11 concludes the correlation tests between the Tenax TA results at 23 °C and 40 °C (TVOC+TSVOC) and PUF results at 23 °C (TSVOC). The TVOC measured at 40 °C 20, 60 and 120 minutes after the temperature reached 40 °C showed strong correlation with the TVOC measured at 23 °C (Tenax TA samples, 0.978–0.984,  $p < 0.01$ ). The TSVOC measured 60 and 120 minutes after the temperature reached 40 °C correlated with the TSVOC measured from the Tenax TA at 23 °C (0.857–0.927,  $p < 0.01$ ). Also, the TSVOC measured from the PUF at 23 °C had a statistically significant correlation between the TSVOC measured 120 minutes after reaching 40 °C. These results imply that the Tenax TA results at 40 °C does correlate with the TVOC and SVOC results at room temperature. In the experiment presented here, the best time point for sample collection was 120 minutes.

## 7. Emissions of SVOCs from building materials

	40oC samples:	TenaxTVOC40oC	TenaxTSVOC40oC
TenaxTVOC40oC	20 minute sample		-0.355
	60 minute sample		-0.211
	120 minute sample		-0.172
TenaxTSVOC40oC	20 minute sample	-0.355	
	60 minute sample	-0.211	
	120 minute sample	-0.172	
TenaxTVOC23oC 20 min sample	20 minute sample	<b>.978**</b>	-0.289
	60 minute sample	<b>.984**</b>	-0.151
	120 minute sample	<b>.983**</b>	-0.149
TenaxTSVOC23oC 20 min sample	20 minute sample	-0.238	0.484
	60 minute sample	-0.233	<b>.857**</b>
	120 minute sample	-0.228	<b>.927**</b>
PufTSVOC23oC average of 60 day sampling	20 minute sample	0.252	0.356
	60 minute sample	0.544	0.698
	120 minute sample	0.259	<b>.817*</b>
** . Correlation is significant at the 0.01 level (2-tailed).			

Figure 11. Pearson correlations between TVOC and SVOC SER measured from the Tenax TA and PUF samples at 23 °C and 40 °C.

### Validation tests

Validation of a test method means that the repeatability of the method is well defined, i.e. the results are within certain known limits. Parallel testing with the FLEC chamber was done for the polyurethane and cellulose based insulations since their emissions represented a good range in terms of VOC and SVOC emissions (Table 13). The samples were prepared as identical as possible and they were equal of age. The Tenax TA sampling volumes were 2–3 litres. The relative standard deviations varied between 1.3–22 % for concentration levels between 10–400 µg/m<sup>3</sup>.

Table 13. Results from parallel testing with the FLEC.

	Cellulose based insulation (µg/m <sup>3</sup> )			Polyurethane insulation(µg/m <sup>3</sup> )		
	FLEC 1	FLEC 2	STEDV%	FLEC 1	FLEC 2	STEDV%
TVOC 23°C	35	36	1.4	151	110	22
40°C 20 min	54	45	13	244	260	4
40°C 60 min	88	78	8	405	369	7
40°C 120 min	91	93	1.3	426	387	7
SVOC 23°C	7	5	17	7.4	8.6	11
40°C 20 min	14	18	18	14	12	11
40°C 60 min	46	49	4	13	11	12
40°C 120 min	57	64	9	14	17	14

## 8. Conclusions and recommendations for further action

This publication reviewed the occurrence of SVOCs and flame retardants in the Finnish building industry, the regulations concerning them as well as exposure scenarios for exposure to these compounds indoors. The summary was made in order to clarify the possible need of both restricting the use of these compounds and for the waste management especially in renovation.

SVOCs are found in a numerous of building materials. This report concentrated mainly on the SVOCs phthalates and PAH compounds because these are discussed widely nowadays. Phthalates have been used as plasticisers in flooring materials whereas PAH compounds can penetrate into indoor air from damp proofing used in the structures in older buildings. PAH compounds are carcinogenic whereas the health effects of phthalates are still under review. Studies concluding that negative health effects arise from exposure to phthalates, however, have been published. Exposure scenarios estimate that the inhalative exposure for these compounds is less than 2 µg/kg/day for an adult. The phthalates can be replaced with other compounds, but often these too are classified as SVOCs and therefore they are as persistent as phthalates in the indoor environment. The annual use of phthalates in the Finnish industry, as registered by STTV, is up to 2000 tons.

The brominated FRs are regarded as potentially hazardous to health, and actions have been taken to restrict the use of these compounds. From the chemical registry held by STTV it was concluded that no halogenated FRs were used in Finland in year 2006. However, the registry only contains chemicals that occur at above 1 % in the product. The registration procedure has in this aspect changed since the implementation of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) within the European Union in 2007. REACH obligates that all chemical substances that are produced in 1 ton or more per year falling under the REACH system need to be registered by manufacturers and importers to the Chemicals Agency, otherwise they cannot be manufactured and/or imported. In Europe, ~30 000 such chemicals are in use and ~300 new chemicals are taken into use annually. The registration requires that the manufacturers and importers present information about the dangerous properties of the chemical, its methods of use and methods for safe handling. The use of the most dangerous chemicals will be authorized. These chemicals are those that have long term and severe effects, like carcinogens and persistent environmental pollutants ([www.ymparisto.fi](http://www.ymparisto.fi) 2007).

Besides regulative efforts, the demand from consumers and construction companies is essential in terms of decreasing the use of brominated FRs in the construction industry. Possible measures to reduce the environmental impact of brominated flame retardants, when fire safety standards are not re-

## 8. Conclusions and recommendations for further action

duced, are replacing them with other, less dangerous FRs, using alternative technological solutions or other working methods to maintain fire safety standards, and using materials that are not flammable in themselves instead of materials containing brominated flame retardants. However, as in the case of EPS for FR applications, at the moment HBCD is the best available fire retardant according to the EPS industry. There is currently no technically and commercially feasible alternative flame retardant, with a proven better environmental profile.

From the interviews made among the domestic building product manufacturers it could be concluded that not all chemicals used in their products are known for the manufacturers. Domestic producers often use imported raw materials, for which specifications are lacking. A summary table of SVOCs and FRs on the Finnish market is presented below. No data exists for the waste potential for the specific product groups. However, the “mixed waste” (includes plastics) is estimated to be less than 300 000 tons/ year.

Table 14. Summary of SVOCs and FRs in building products and their applications in the Finnish market.

<b>Product/ product group</b>	<b>Compound</b>	<b>Applications examples</b>
Plastic materials	Phthalates	Floor covering materials, cables
Creosote, bitumen	PAHs	Damp-proofs in structures
Insulation, polymere based (EPS for FR applications) and PU	HBCD (FR), TCPP	Insulations in building
Wooden products used as covering materials	Sitrate salts (FR)	Interior/ exterior panels
Paints	Inorganic salts (FR), b	All constructions which need fire protection

Clearly, there are a lot of challenges in measuring SVOC emissions from building products and setting limit values for them. Firstly, the diversity of materials and their chemical constituents as well as matrixes is enormous. Secondly, the concentration levels of SVOCs are low and therefore, sophisticated measurement techniques are needed to detect them from air samples or deposition samples. Also, the contamination of samples with SVOCs and FRs from the environment is a challenge. Moreover, the impact on IAQ for different types of materials may vary a lot. For example, the impact of SVOCs emitted from inside a structure (like insulation) on IAQ is presumably less than for the more volatile compounds since SVOCs are easily deposited on surfaces. In addition, the health effects of SVOCs and FRs are not known well enough.

Nevertheless, long term occurrence of SVOCs and FRs indoors may possess a health risk. It seems as if the definition of the compounds of interest would be the right approach for any regulatory actions. Based on such a definition, exposure limits indoors would be set and further, emission limit values for different building product types. If no health effects have been proven, a pre cautionary type of limit value would be set until more health data evolves.

The results presented in this publication show that SVOCs and FRs are emitted from building products normally used. However, the emission levels are low and therefore the exposure levels concluded

## 8. Conclusions and recommendations for further action

in Table 5 (or even lower) are confirmed. The results also showed that in real life situations, like direct sunlight and the use floor heating, elevated emissions and significantly higher exposures may occur.

The importance of blank samples was pronounced because of the low levels of SVOCs measured. For example, the tubing and fittings in the analysis equipment is a common source of contaminants. Any contamination of the surroundings was avoided by measuring samples directly, i.e. no ageing of the products were done. The sampling at elevated temperatures on Tenax TA proved to be a suitable method for detecting the flame retardant tris (dichloroisopropyl) phosphate (TCCP) from the PU insulation. The repeatability for the emission testing at temperatures 23 °C and 40 °C was good.

For measuring SVOC emissions from building products, a pre step measuring the elemental constituents is recommended. Products containing phosphor or bromine (e.g. above 0.1 %) would then be tested further for the occurrence of brominated compounds and organophosphates. Similarly, phthalates should be pre tested from the material itself.

In conclusion, the following scheme is proposed for the measurement of SVOCs from building products:

1. Pre test 1: elementary analysis (bromine, phosphorus etc.). Emission testing is performed if the content is > 0.1 % according to specifications in Table 15 and 16. If content is < 0.1 %, emission testing is performed according to Table 16.
2. Pre test 2: phthalate occurrence. Emission testing is performed if phthalate is identified above blank values according to specifications in Table 15. If no phthalate is detected, emission testing is performed according to Table 16.

Table 15. Emission testing of SVOCs and FRs (A).

Compound	Sampling	Analysis	LOD
Brominated FRs	Chamber size: < 2.5 dm <sup>3</sup> . Q/A: ISO 16 000-9 Collection media: PUF samples, minimum sample volume 5 m <sup>3</sup>	GC/MS-MS	2e-3–2e-4 ng/m <sup>3</sup>
Organophosphates		GC/MS	0.04–0.0008 µg/m <sup>3</sup>
Phthalates (and TSVOCs)		GC/MS	~ 0.005µg/m <sup>3</sup>

Table 16. Emission testing of SVOCs and FRs (B).

Compound	Sampling	Analysis	LOD
TSVOC	Chamber size: < 2.5 dm <sup>3</sup> . Q/A: ISO 16 000-9 Collection media: PUF samples, minimum sample volume 5 m <sup>3</sup>	GC/MS	~ 0.005µg/m <sup>3</sup>
TSVOC	Chamber size: < 2.5 dm <sup>3</sup> . Q/A: ISO 16 000-9 Collection media: Tenax TA sam- ples, minimum sample volume 2 litres	GC/MS-FID	~ 1µg/m <sup>3</sup>

## 8. Conclusions and recommendations for further action

Finally, this study found research need for the future on SVOCs and FRs as follows. More results on measured emissions of SVOCs and FRs from building products are needed. This requires that a standard measurement method for SVOCs and FRs, including validation data like uncertainty calculations, is developed. The contribution of the emissions to the indoor air and exposure scenarios indoors could then be better evaluated. In addition, specific data on the waste potential as well as life span assessment and extensive health evaluation for these compounds within the built environment is still lacking.

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## Appendix A: Chemical product registry search list

The following compounds were included in the search from the chemical registry at STTV.

<b>Phthalates</b>	<b>CAS</b>
C1 DMP (dimethyl phthalate)	131-11-3
C2 DEP (diethyl phthalate)	84-66-2
C3 DPP (dipropyl phthalate)	131-18-0
C4 DBP (di-n-butyl phthalate)	84-74-2
DIBP (diisobutyl phthalate)	3001-15-8
C4 / C6 BBP (butylbenzyl phthalate)	85-68-7
C7 DIHP (diisohexyl phthalate)	68515-50-4
C6 / C8 / C10 610P (six-ten phthalate)	
C7 DIHP (diisoheptyl phthalate)	71888-89-6
C7 / C9 79P (seven-nine phthalate)	
C8 DEHP / DOP (di(2-ethylhexyl) phthalate)	117-81-7
DIOP (diisooctyl phthalate)	27554-26-3
C8 / C10 810P (eight-ten phthalate)	
C9 DINP (diisononyl phthalate)	28553-12-0
C9 / C11 911P (nine-eleven phthalate)	
C10 DIDP (diisodecyl phthalate)	26761-40-0
DPHP (dipropylheptyl phthalate)	84294-98-4
C10 / C12 1012P (ten-twelve phthalate)	
C11 DUP (diundecyl phthalate)	3648-20-2
DIUP (diisoundecyl phthalate)	85507-79-5

### Flame retardants

#### Inorganic:

Alumina trihydrate ATH	21645-51-2
antimony trioxide (synergist)	1309-64-4
antimony oxides and antimonates	
sodium antimonate	15432-85-6
boric acid	10043-35-3
sodium borate	1330-43-4
zinc borate	12536-65-1
ammonium polyphosphate APP	68333-79-9

#### Halogenated:

tetrabromobisphenol (TBBPA)	79-94-7
polybrominated diphenylethers (PBDE):	32534-81-8

## Appendix A: Chemical product registry search list

decabromodiphenyl ether (DBDE)	13654-09-6
octabromodiphenylether (OBDE)	32536-52-0
pentabromodiphenylether (pentaBDE)	32534-81-9
	3194-55-6,
hexabromocyclodecane (HBCD)	25637-99-4
polybrominated biphenyls (PBB)	67774-32-7
<u>Organophosphorus:</u>	
TCPP	13674-84-5
phosphate esters	
triphenylphosphate	115 86 6
triethylphosphate	78-40-0
trioctyl phosphate	78-42-2
2-ethylhexyl-diphenyl phosphate	1241-94-7
<u>Nitrogen based:</u>	
melamine	108-78-1
melamine cyanurate	37640-57-6
melamine phosphate	20208-95-1

## **Appendix B: Recycling of selected building materials**

This appendix summarises the recycling data available for selected building materials that are considered to be sources of SVOCs and FRs.

### **1 Joint sealing compounds in concrete structures in buildings**

PCB-compounds have been added to the joint sealing (elastic polysulphides) until at least 1974, possibly to the end of 70's. Majority of the 1970 and 1960 buildings joint sealing have been renewed. In 1980 and 1990 it was typical to install a new sealing on the old ones without removing those. Sealings containing PCB, or butyl are also used in roof and window joints. (Haukijärvi and Pentti 2000).

In addition to PCB also lead and polychlorinated biphenyls were used in joint sealings as hardeners (lead) or plasticisers (polychlorinated biphenyls).

According to field test, the PCB concentrations in joint sealing are 50 mg/kg, which is the limit value for hazardous problem waste. For lead concentration the limit value is 1500 mg/kg (Pyy & Lyly 1998). According to the same study the PCB concentrations in the ground soil were higher than recommended limit values in the environments where PCB containing joint sealing was used. PCB was also found in concrete samples close to joints.

PCB and lead are classified as hazardous problem waste. Thus recycling and re-use is not possible or very limited.

### **2 Masonry products, light weight clay aggregate blocks**

Masonry products and light weight clay aggregate blocks are typically re-used as crushed land fillings (excluding the insulation material). Some blocks contain EPS or polyurethane insulation material. Typically one wall m<sup>2</sup> weights 140–170 kg of which 4–6 kg is insulation. When bricks are used in foundations bitumen coating is used to protect against moisture.

### 3 Damp proofs and water vapour resistance layers

In old buildings coal pitch was used as damp proof and water vapour resistance layer. Typically coal pitch is found in floors (ground and intermediate floors), foundations and walls against ground soil, swimming pools etc. In the demolition of building structures, treated with coal pitch, the most problematic compounds are poly aromatic hydrocarbons (PAH compounds), which are classified as carcinogenic. The structures with coal pitch are not suitable for re-use.

### 4 Thermal insulation materials

#### **Mineral wool**

Glass wool consists 95% of recycled glass and the natural stones and 5% of resin and oil. Glass wools (and other mineral wools) are non-combustible.

#### **Cellulose based insulation**

Cellulose based insulation materials can be used as layers or blow inside a structure. When blowing technique is used water and glue is added to the material. Cellulose based insulation is made from recycled news paper. During the manufacturing process boron is added against mould and fire. Insulation can be reused or used as fillings in land but since Boron can dissolve the amount of material compared to the ground soil should be considered. The limit value for boron in terms of PNEC value (Predicted No Effect Concentration) is 2.5 mg/kgdry (Braunschweiler 1993, Koivisto 1998). In normal conditions the boron concentration in ground soil can be 2–100(–300) mg/kg depending on soil type and climate.

#### **Polystyrene**

EPS (Expanded polystyrene) insulation layers consist of small polystyrene pearls including pentane gas. EPS does not include styrene monomers. The expanded gas is evaporated during manufacturing process. Polystyrene is not water soluble. There are several options to treat EPS building and demolition waste, each with environmental, technical and economic implications to consider when choosing the best option to implement at specific sites. Generally, the most beneficial is direct re-use by grinding clean EPS waste and adding it to virgin material during production. This waste can also be used to improve soil condition. Alternatively, EPS can be melted and extruded to make compact polystyrene, for items such as plant pots, coat hangers and a wood substitute. Medium toughened polystyrene from which sheets for thermoformed articles, such as trays, can also be made. As part of mixed plastic waste, EPS can be recycled to make, for example, park benches, fence posts and road signs, ensuring the plastic material has a long and useful second life. EPS can also be used for the recovery of energy, usually in the form of heat from incineration. This gives EPS-waste a genuine post-consumer use. The calorific value of EPS available for heat recovery is slightly more than that of coal by weight.

## **Polyurethane**

Polyols and di-isocyanates are the pre-stages of polyurethane. In building materials difenylmethane-di-isocyanate (MDI) is typically used. The amount of catalyst, pigments and surface activated ingredients are typically 1–2%, the fire resistance and propellant gas amount is 2–20% of the weight.

Until now CFC (chlorine-fluorine-carbon) compounds are not collected for building products. Part of the polyurethane insulation materials could be recovered and used in the manufacturing of new insulation products or in soil construction.

20% of the CFC is emitted by diffusion to the environment during 30 to 50 years time span. Also other gases are diffused in a small amounts e.g. the pentane which is typically used today in polyurethane insulations. That can possibly cause slightly elevated VOC emissions. On the other hand, aerosols are less used today.

## **5 Boards**

### **Gypsum boards**

Gypsum boards can be recycled. The weight of a gypsum board is typically 9.0 and 11.7 kg/m<sup>2</sup> depending of the type of the board. Recycled gypsum boards are crushed and used as raw material together with raw gypsum for new boards.

### **Concrete fibre boards (asbestos)**

Asbestos was widely used in 1960–70s, but the use of asbestos started already in 1920. Asbestos was used in several products such as sealing, air ducts, thermal insulation, floor coverings, water proof layers, paints, plasters etc. The most harmful asbestos applications are shotcrete materials and insulation materials, since they release asbestos fibres more easily (the asbestos is not bind to the base material). Undamaged asbestos materials are not harmful for building users.

## **6 Flooring materials**

The yearly use of different flooring materials was 6 million m<sup>2</sup> for parquet and laminate and 4 million m<sup>2</sup> for plastic, linoleum carpets as well as ceramic tiles.

### **Plastic floorings**

The main raw material of plastic floorings is PVC, which is chlorinated hydrocarbon polymer. The polymer is produced from vinyl chloride. In addition, other plastic materials like polyethene and poly-



## Appendix B: Selected materials and their recycling

propylene, and fillers like dolomite, talc, calcium carbonate and quartz sand are used. The additives used include plasticisers, stabilizers, pigments etc.

The weight of flooring product used in residential buildings is 1400–1500 g/m<sup>2</sup>. The products that are used in office and in public buildings weight roughly 4000 g/m<sup>2</sup> (plastic plates) and 2700–3300 g/m<sup>2</sup> (plastic carpets). The floorings used in moist and wet conditions weight typically 2300–2400 g/m<sup>2</sup>. The loss of materials in assembling of floorings is typically roughly 10%.

The alternative ways to remove the product from service are placing to dumping place, decomposting, incineration and recycling or reuse. The incineration of plastic materials as well as co-combustion in municipal solid waste combustion plants has been studied and results have been published by for example APME.

The biggest European manufacturers of flooring product belong to the European Resilient Flooring Manufacturer's Institute (ERFMI). The organisation has committed to support the recycling floorings. Vinyloop is a new industrial method of recycling of floorings. It is a combination of mechanical and chemical recycling methods with help of which recovered plastic can be produced from flooring waste.

The Vinyloop PVC recycling process separates the usable PVC compound from other materials (other plastics, rubber, metal, textile...) by selective dissolution and filtration and precipitates it into micro-granules of PVC compound. This regenerated PVC compound (R-PVC) that can be re-processed by extrusion, injection or calendaring. The process works on an industrial scale.

Vinyloop is not classified as a "chemical recycling technology" but rather as a "mechanical technology" because it conserves the molecular structure of the components. By simply dissolving the PVC compound and bringing it back to a solid state by precipitation, Vinyloop uses far less non renewable energy than competitive chemical recycling technologies.

In Finland a recycling system for assembling waste of flooring materials is organised by a company. The assembling waste is assorted and made use of as a bottom layer in the production of plates.

## 7 Bitumen

Nowadays the bitumen waste is not recycled. However, there could be some re-use options in filling lands. For roof materials the waste dump is 5.6 kg/m<sup>2</sup>.

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## Appendix B: Selected materials and their recycling

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Author(s) Helena Järnström, Sirje Vares, Miimu Airaksinen		
Title <b>Semi volatile organic compounds and flame retardants Occurrence in indoor environments and risk assessment for indoor exposure</b>		
Abstract The first part of the project presented in this publication reviews the occurrence of semi-volatile organic compounds (SVOCs) and flame retardants in commonly used building and furnishing materials in Finland. SVOCs included in the review are plasticisers, like phthalates, flame retardants (FRs), like brominated organic compounds and organophosphate esters. In addition, polycyclic aromatic hydrocarbons (PAHs), which are constituents in coal tar/ creosote and have been used for moisture proofing in structures, are also discussed. On the basis of present knowledge, risk assessment for exposure indoors is presented. In addition, sources of SVOCs and waste potential in the old building stock are clarified. The knowledge for the review was gathered from housing statistics, building product statistics, the chemical registry at The National Product Control Agency's (STTV), The National Board of Antiquities and Historical Monuments in Finland, Finnish Environment Institute (SYKE), and from interviews with the construction product industry. In the second part of the project, SVOCs were measured from a total of 13 building materials including flooring materials, paints, insulations and a levelling agent (screed). Both short and long term (up to 60 days) emissions were measured by modifying the existing standard sampling method for the measurement of volatile organic compounds (VOCs). Emissions were measured at room temperature and at 40 °C. The elevated temperature was considered to simulate real life situations, such as when a surface gets warmed up by direct sunlight. The results showed that the initial specific emission rates (SER) of SVOCs are typically low, less than 5 µg/m <sup>2</sup> h. An exception was newly prepared foam type polyurethane insulations, which emitted SVOCs up to 65 µg/m <sup>2</sup> h. The SVOC SERs were higher at 40 °C, up to 165 µg/m <sup>2</sup> h. No phthalates were detected from the air samples collected during the 60 -day test period. However, 218 µg of a phthalate compound was detected from the solvent used to rinse the walls of the chamber that was used to measure the PVC sample. Also, 72 ng of the fire retardant hexabromocyclododecane (HBCD) was detected from the rinsing samples of the chamber used for measuring the expanded polystyrene (EPS) insulation for FR applications. A commonly used FR, Fyrol PCF (Tris (2-chloroisopropyl) phosphate, TCCP) was detected from air samples taken from the polyurethane insulation (foam type) at 24 µg/m <sup>2</sup> h (as toluene equivalent) after 120 minutes at 40°C. Boron was detected from air samples from the cellulose based insulation material at 0.3–5 µg/m <sup>3</sup> . The study showed that SVOCs and FRs are emitted at low levels at room temperature from common building materials. However, the variety of compounds emitted and emission ranges varied markedly. SVOC (and VOC) SERs increased markedly when the temperature increased to 40 °C. In real life, such temperatures can be reached on surfaces with direct sunlight during the summer or in cases when floor heating is used. Consequently, exposure assessments for SVOCs in such environments can be assessed better based on the emission results collected during this project. Exposures at room temperature were estimated to <0.1 - <2 µg/kg day. However, the migration of FRs and SVOCs into indoor air is probably less than this from building materials that are inside a structure, e.g. insulation, which decreases exposure to these compounds indoors.		
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Series title and ISSN VTT Tiedotteita – Research Notes 1455-0865 (URL: <a href="http://www.vtt.fi/publications/index.jsp">http://www.vtt.fi/publications/index.jsp</a> )		Project number 31646
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Keywords SVOC, material emission, exposure indoors		Publisher VTT Technical Research Centre of Finland P.O.Box 1000, FI-02044 VTT, Finland Phone internat. +358 20 722 4520 Fax +358 20 722 4374



This project reviews the occurrence of SVOC compounds and flame retardants in the commonly used building and furnishing materials in Finland. The knowledge for the review was gathered from housing statistics, building product statistics, the chemical registry at The National Product Control Agency's (STTV), The National Board of Antiquities and Historical Monuments in Finland, Finnish Environment Institute (SYKE), and from interviews with the construction product industry. In addition, emissions of SVOCs and flame retardants were measured from the most commonly used building materials. On the basis of present knowledge, risk assessment for exposure indoors is presented.