Semi volatile organic compounds and flame retardants – An overview on their occurrence in indoor environments and in Finnish buildings

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SUMMARY
The occurrence of semi volatile organic compounds (SVOC) and flame retardants (FR) have commonly been used in building materials. They might be released to the surroundings from new products as well as a result of wearing. 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.

This project reviewed the occurrence of SVOC compounds and flame retardants in the commonly used building and furnishing materials in Finland. On the basis of present knowledge, risk assessment for exposure indoors is presented.

KEYWORDS
SVOCs, Flame retardants, Building materials

INTRODUCTION
The occurrence of semi volatile organic compounds (SVOC) in the indoor environment is today under special interest since health concerns have risen. The World Health Organization has defined SVOCs as organic compounds with boiling points ranging from 240-260°C to 380-400°C (WHO 1989). Common SVOCs in the indoor environment are plasticizers, like phthalates (DEHP, DBP, DINP, DPP), and flame retardants (FRs), like brominated organic compounds (PBB, PBDE, TBBPA) and organophosphate esters (TCEP, TCPP). In addition, polyaromatic hydrocarbons (PAHs) are constitutes in coal tar/ creosote, which has been used for moisture proofing in structures. SVOC compounds might be released to the surroundings from new products as well 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.

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. 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.

This project reviews the occurrence of SVOC compounds and flame retardants in the commonly used building and furnishing materials in Finland, and the need for their use and possible alternative materials or building technology solutions to minimize indoor air exposure. In addition, sources of SVOC compounds and waste potential in the old building...
stock are clarified. The knowledge 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.

APPLICATIONS IN BUILDINGS
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 toys and hand grips in tools can contain phthalates. The annual use of phthalates in the Finnish industry, as registered by STTV, is up to 2000 tons. The use of plastic flooring materials, possible sources of phthalates, was 4 million m² in 2006 in Finland.

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 m² (VTT, 2006). 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 harbours, The Council of State, 1995). Applications, were 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 in buildings, which were built in the beginning 20th century. Floors and walls of old wooden building have commonly been treated with creosote. Also, creosote has been 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.

Flame retardants have been added to building materials like insulation materials, i.e. insulation boards, PU 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.

Brominated FRs have been used in polymers like polystyrene foams, high-impact polystyrene and epoxy resins (Birnbaum et al., 2004). TBBPA, deca-BDE and octa-BDE are common BFRs in plastic housings like TVs, PCs and office equipment (BSEF, 2000). Kemmlein et al. studied the emission of selected brominated and organophosphate FRs from insulating boards, polyurethane (PU) foams, a mattress and electric 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.
FLAME RETARDANTS IN FINNISH BUILDING MATERIALS
The Finnish building code gives requirements for fire resistance (Ministry of the 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 main three polyurethane producers in Finland use FRs in their products. However, no statistics on volumes are available but the FRs used are considered as less hazardous for health. Foreign manufacturers commonly use commercial mixtures, which do not specify their FRs.

Extended polystyrene (EPS) is extensively used in building industry because of its durability and insulation properties. One manufacturer uses hexabromocyclododecane (HBCD) as a fire retardant used mainly in their EPS insulation products. The content of HBCD is 0.7% in the product. The annual use is 300 tons. The manufacturer also delivers the raw material to another EPS producer in Finland. EPS applications are mainly in the building frame, i.e. it is not used as a surface or covering material.

Extruded polystyrene (XPS) is used in roofs, parking levels, ground floor, foundations and frost. The XPS insulation products marketed in Finland do not contain any halogenated FRs.

Cellulose based insulations are used for insulating roof and wall structures. Also, the insulation can be applied on horizontal ventilation ducts. Boron is added as a FR.

The insulations made of rock material marketed by a leading Finnish manufacturer do not contain FRs.

Acoustic boards: No FRs are used in acoustic boards marketed in Finland.

Paints: 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 warehouses. 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 paint manufacturer have been produced in Germany. The possible use of FRs is not known because only compounds with known health effects have to be reported.

A Finnish company markets paints and lacquers for fire protection applications. The products are halogen – free. Citrate and phosphate salts are used as FRs. The products are used on steel constructions, wooden structures in the interiors and textiles.

Plastics: The PVC and linoleum flooring materials manufactured by a Finnish company do not contain any FRs. Phthalates, however, are used in the production of PVC. Damp proofing plastics (polyethylene) and their support items (HD-polyethylene, SK- fasting) do not contain 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.
EXPOSURE TO SVOCs and FRs INDOORS

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. The daily exposure to DEHP in indoor environments for adults and children is calculated as follows (ECB, 2006):

\[
U_{\text{inh}} = \frac{B_{\text{inh}} \times C_{\text{inh}} \times V_{\text{inh}} \times t / 24}{B \times W}
\]

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 m³/day and 9.3 m³/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/m³) 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). Table 1 summarizes estimates for exposure indoors as calculated with equation 1 for SVOCs, phthalates, PAHs, and FRs. The indoor air concentration levels are estimations from the levels reported in the literature.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Indoor air concentration</th>
<th>Exposure indoors by alveolar air (adult)/ day</th>
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</thead>
<tbody>
<tr>
<td>SVOCs (ISO 16000-6, ISO 2004)</td>
<td>&lt;10 µg/m³</td>
<td>&lt;2µg/ kg</td>
</tr>
<tr>
<td>Phthalates</td>
<td>&lt;10 µg/m³</td>
<td></td>
</tr>
<tr>
<td>PAHs</td>
<td>&lt;10 µg/m³</td>
<td></td>
</tr>
<tr>
<td>Polybrominated FRs</td>
<td>&lt;0.5 µg/m³</td>
<td>&lt;0.1 µg/kg</td>
</tr>
<tr>
<td>Organophosphate FRs</td>
<td>&lt;1 µg/m³</td>
<td>&lt;0.2µg/ kg</td>
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DISCUSSION AND CONCLUSIONS

SVOCs are found in a numerous of building materials. This project concentrates mainly on phthalates, PAH compounds and fire retardants because these are discussed widely nowadays. 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 (Bornehag et al., 2004).

The polybrominated FRs are regarded as potentially hazardous to health, and actions have been taken to restrict the use of these compounds. The EU directive 2003/11/EC has restricted the use of penta and octabromodiphenylether. These compounds were banned in the EU from August 2004 (European Parliament, 2003). From the Finnish chemical registry it was concluded that no halogenated compounds were reported in year 2006. However, the registry only contains chemicals that occur at above 1% in the product. This means that, as in the case for HBCD in EPS, the compound a compound has not always been registered although the annual use of it is several hundred of tons. Table 2 summarizes potential sources of SVOCs and FRs in building products in Finland as found out by the interviews among manufacturers.
Table 2. Summary of SVOCs and FRs in building products in the Finnish market.

<table>
<thead>
<tr>
<th>Product/ product group</th>
<th>Compound</th>
<th>Applications examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic materials</td>
<td>Phthalates</td>
<td>Floor covering materials, cables</td>
</tr>
<tr>
<td>Creosote, bitumen</td>
<td>PAHs</td>
<td>Damp-proofs in structures</td>
</tr>
<tr>
<td>Insulation, polymer based (EPS)</td>
<td>HBCD (FR)</td>
<td>Insulations in building</td>
</tr>
<tr>
<td>Wooden products used as covering materials</td>
<td>Citrate salts (FR), biocides</td>
<td>Interior/ exterior panels</td>
</tr>
<tr>
<td>Paints</td>
<td>Inorganic salts (FR), biocides</td>
<td>All constructions which need fire protection</td>
</tr>
<tr>
<td>Sealings, joints</td>
<td>Biocides</td>
<td>Waterproofing applications</td>
</tr>
</tbody>
</table>

Besides regulative efforts, the demand from consumers and construction companies is essential in terms of decreasing the use of brominated FRs use in the construction industry. Possible measures to reduce the environmental impact of them, when fire safety standards are not reduced, 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 FRs. The implementation of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) in June 2007 obligates that all chemical substances of 1 tons 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. Also, the registration has to be done for substances in products or equipments if the substance is meant to be released from the product or is particularly harmful. 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 (STTV, 2007).

In the future, emission measurement techniques especially designed for SVOC compounds and FRs should be further developed in order to better evaluate emissions from building materials and their contribution to indoor air. During the second part of this project (year 2008), emissions of SVOCs and FRs will be measured from common building materials used today in Finland, i.e. flooring materials (PVC, linoleum), paints, screed products, insulations (PUR, EPS, mineral wool, cellulose based insulations). Emission measurements will be performed by modifying existing standard methods for the measurement of VOCs. Exposure scenarios indoors could then be assessed more accurately. Also, there is clearly a need for life span assessment as well as more health data for these compounds.

ACKNOWLEDGEMENT
This project is financed by the Ministry of the Environment.

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