Emissions of organic chemicals from materials in car cabins and their potential impact on human health – a comparison with virgin materials

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Content

1. Sammanfattning

En bilkupé består av en mängd olika komponenter och material för optimering av funktion, säkerhet och design. Dessa material är ofta polymera och innehåller kemikalier som över tid kan emitteras och därmed utgöra en risk för exponering av kemikalier för människor i bilmiljö. Högre emissioner sker vid högre temperaturer vilket är vanligt vid soliga sommardagar. Kemikalier kan också släppa i partikulär form när material slits vilket gör att materialytan ökar och medför risk för större molekylär emission. Kemikalier som släpper från material är antingen flyktiga ämnen eller semiflyktiga organiska ämnen (SVOCs). De flyktiga ämnena (VOC) är ganska välstuderade och delvis reglerade i inomhus- och bilmiljöer vilket skiljer dem från SVOCs. SVOCs utgörs tex av flamskyddsmedel, UV-filter kemikalier, processkemikalier, smutsskyddande ämnen och antioxidanter. Flera av dessa ämnen har visat sig kunna orsaka hälsoproblem hos djur och människor som tex att de har hormonstörande eller reproduktionsstörande effekter och därmed bör fasats ut i användning. När nya ämnen ersätter de problematiska eller till och med förbjudna ämnena krävs en ordentlig process vid substitutionen så att bättre hälsoegenskaper uppnås med bibehållen funktion i materialet.

I denna studie har vi tagit fram en metodik för att studera emissioner av organiska ämnen från nya material. Vår målsättning var att med metodiken studera hur kemikalier emitterar från dessa material och identifiera kemikalier som kan vara problematiska i ersättningsmaterial. Dessa material valdes för att representera tänkbara biobaserade material som ersätter petroleumbaserade polymerer och som kan användas i en bilkupé. Vi har tidigare studerat emissioner i kompletta bilar men valde här att ta fram en uppställning i en nerskalad emissionskammare som möjliggör snabbare studier och screening av många material. I denna studie valde vi ett färre antal material från två olika företag och med olika specifikation. Vi valde också att analysera mycket brett utifrån kemiska egenskaper med så kallad non-target screening för att skapa bild över mönster av kemikalier som släpper från materialen. Till detta kopplade vi traditionella VOC-analyser samt multivariat statistik för att studera mönsterskillnader i emissioner.

I projektet har en robust metodik för emissionsmätningar av SVOCs tagits fram, som möjliggör kemisk analys av ett brett spektrum av kemikalier. Protokoll finns nu för att hantera risker för kontaminering mellan prover vilket är centralt vid analyser av delvis

flyktiga ämnen som förekommer i låga koncentrationer. Uppställningen möjliggör analyser på relativt kort tid (15 min) inklusive replikat och analyter fångas upp på sorbent som möjliggör relativt enkel upparbetning analys som kan skräddarsys för önskade substanser.

Den kemiska analysen av de sex olika materialen resulterade i semikvantitativ identifikation av nästan 600 kemikalier. Dessa studerades i en mönsteranalys med principalkomponent analys där det tydligen framgick att kemiska mönster skiljer mellan de olika producenterna men också om materialet var laminerat eller ej. Genom att skala ner datasetet till de mest signifikanta kemikalierna identifierades 95 kemikalier som fortsatt drev ovan beskriven separation mellan materialen. Ett flertal av ämnena som identifierades är naturligt förekommande vilket är rimligt då de studerade polymera materialen är biobaserade. Vi fann vidare representanter för flertal funktioner såsom flamskydd och antioxidanter samt ett fåtal med indikationer på hormonstörande effekter som kräver vidare analys avseende mer noggrann kemisk analys men också en exponeringsbedömning i en bilmiljö. Sammanfattningsvis så finns nu en framtagen metodik som möjliggör studier av emissioner av organiska substanser i polymera material och som erbjuder tester i större skala för vidareutveckling av hållbara material för användning i bilmiljöer.

2. Executive summary

A new methodology for analysis of emissions of small organic volatile chemicals have been developed enabling detailed studies and screening of emission processes. This is critical in the development of more sustainable materials using biobased or recycled polymers. The method was applied on six different materials from two different suppliers and two different techniques, i.e., laminated or unlaminated. Less than 600 chemicals were tentatively identified and analyzed using multivariate statistics. The emission patterns were distinct between suppliers and technique and a list of 95 chemicals emitted from the materials are presented and discussed. Targeted chemicals include representatives of several functionalities including flame retardants and antioxidants. In a next step it is critical to evaluate risk of exposure of these chemicals being used in future materials in a car cabin.

3. Background

Organic chemicals are being released from the materials in the interior of cars from e.g., electronics, textiles, leather, roofing materials and insulation materials. Humans spend on average 5.5% of their time in cars (Klepeis et al., 2001; Matz et al., 2018). They might then be affected by chemicals in the air, both from the incoming air and from interior emissions. Some volatile organic compounds (VOCs) are monitored frequently by the car manufacturer due to requirements on Asian markets.

In recent years several reports have been published on levels of semivolatile organic compounds (SVOCs) in dust and gas phase including particle fraction (Albar et al 2017; Gevao et al 2016; Harrad et al 2016) as was recently reviewed by our research group (Lexén et al 2021). These chemicals are emitted over the life span of the cars and partition between the gas phase and the particulate phase within the car. Chemicals can also be found in material wear like textile fibers and wear from polymeric materials. There are several examples of chemicals in car cabins that have been studied in literature in recent years like flame retardants including polybrominated diphenylethers, polychlorinated biphenyls, plasticizers such as phthalates, and methylsiloxanes (Albar et al 2017; Gevao et al 2016; Harrad et al 2016; Lucattini et al 2018), and organophosphates (Abafe and Martincigh, 2019; Björnsdotter et al 2018).

These chemicals could pose a threat to human health and a great focus has been on so-called endocrine disrupting chemicals (EDCs) (WHO 2012). EDCs can induce adverse health effects by endocrine disruption and exposure could occur through e.g., inhalation, through skin contact or ingestion. Vulnerable groups are children and pregnant women (Bourguignon and Parent, 2010; Khalil et al., 2014; Braun, 2016). Studied effects related to EDCs include obesity, developmental disorders, and effects on the thyroid and reproductive systems. These effects have recently been estimated to cost the EU in the order of 100 billion € annually due to disease and impairment in the population (Trasande et al 2016) and at least 18 billion in the form of obesity and diabetes (Legler et al 2015).

Passengers in a car are protected from outside exposure of chemicals and particulate matter by a filter system including air circulation and sensor guiding for optimized air quality in the car cabin. However, the quality of the filters and functions in the climate systems varies greatly between different car manufactures that may lead to different exposure situations. It is of great importance to ensure good air quality in the car cabin since impurities can be present, like residuals of hazardous chemicals, posing a risk for human health (Biliterwski and Grundmann 2012). Brominated flame retardants have been detected in toys due to the use of recycled plastic in the fabrication process (Ionas et al 2014). This needs to be considered as the amount of recycled plastics increase in use. When it comes to emissions from materials in the car cabin, the focus has been on a few substances and on how much is emitted, but not on the risks of individual chemicals and the complex mixtures of chemicals in the passenger compartment. At Volvo, we now want to investigate how we can improve the air quality in our cars so that our customers can feel safe and secure, with

the materials within the car. This project aimed at strengthening our knowledge base when it comes to the health impact of the air in our cars and in particular with a focus on identifying emissions from materials used in the car cabin in a large extent and the impact of using new materials, including substitution of hazardous chemicals. With gained knowledge risks of health effects from chemicals can be reduced by optimizing the quality of the incoming air and by optimizing the materials in the car.

In polymeric materials and textiles, a large number of chemicals are added to give the material its properties e.g., protection from sunlight, prevent and reduce impact of fires and optimize physical properties (e.g., structure and dirt repellency). Most of these substances are only added to the polymer, i.e., they are not chemically bound and can thus be emitted and migrate to the surrounding environment (Ali et al 2016). Depending on its chemical properties, the substances are distributed between the gas phase and the particle phase, and we know today that a large number of SVOCs can end up in dust (Lucattini et al, 2018, Mercier et al 2011; Zhang et al 2015). Chemicals' propensity to emit or migrate from polymeric materials can be measured using different methodologies or be modeled (Holmgren et al 2012; Wu et al 2016; Xu et al 2012). The distribution between gas and particle phase contributes to that the users in the car are exposed to chemicals both phases (Canbaz et al 2016, van Mourik et al 2016, Xu et al 2016). Assessing the risk of chemicals requires both to measure the exposure and potential effects. Exposure can be measured (biomonitoring) by chemical analysis or estimated using different types of models (Huang et al 2017; Egeghy et al 2016, Weschler et al 2015). In the car interior, both dermal contact, absorption via the skin and inhalation can be relevant related to the substances studied.

The project entitled "Management of potential health effects of airborne pollutants in a car cabin" (44015-1) was initiated in November 2017 (see below) and it has now completed two major sampling campaigns where air and particulate matter were sampled from cars. These studies were designed, among other things, to vary temperature and ventilation in relation to emissions of SVOCs. We sampled four different temperatures in four different cars and the major findings are that the levels of substances increase with increasing temperature and that the chemical composition of the air samples differ with temperature. Data from these campaigns are now being processed for publication in a peer-reviewed article to be submitted during 2022. Volvo Cars also has a project working with energy efficiency and air quality, focused on inorganic gases and particles, to further work with the enhancement of the air quality in the car cabin.

In this complementary project, the focus was on emissions of SVOCs from selected surface materials. We investigated the impact of using different types of bio-attributed surface materials in relation to emissions of SVOCs. Regrettable substitution of hazardous chemicals is a known phenomenon where one hazardous chemical is replaced by less potent but still hazardous chemicals. Sound alternative assessment schemes are required to avoid that (Zheng et al 2019) but in addition large initiatives are now in place for using recycled and renewable materials in a large range of products and materials. Recycled materials may contain chemicals that are phased out or in the process of legislative actions.

It is thus critical to improve our understanding on the fate of chemicals in materials and in particular, the impact on exposure and environmental and human health impacts of chemicals in these materials. The main hypothesis of the project was that smart substitution and use of recycled and renewable materials decrease the chemical hazards for the customers of Volvo and Polestar.

The overall knowledge in this project will increase the knowledge on the emissions from bio-attributed surface materials. We are now breaking ground in this field and the project is, to our knowledge, completely unique in its composition, within the automotive industry in collaboration with academic research. Looking at these two areas separately, the automotive industry has developed methods for measuring certain substances in the cars and for materials. The Academy, for its part, has in depth analytical chemistry expertise and the infrastructure to sample and analyze SVOCs and evaluate their risks. By combining these two, we can investigate chemical risks and the impact of using more sustainable materials. The focus was on emissions of SVOCs from surface materials in order to propose alternatives for the reduction of health risks due to emissions of chemicals. In particular components with large surface area have been studied and those that are located in the car cabin where higher temperatures occur on sunny days. In addition, materials were studied that could be changed to either low emitting materials, recycled or renewable materials or materials where substitution of chemicals is wanted.

From the previous project the list of target substances was used as a basis for the analysis in this project. The complete list can be found in Table 1.

Table 1. Names and function of the 19 target substances

Name	Substance	Example of use/function
Bis(2-propylheptyl) phthalate	Phthalate	Plasticizer
Diundecyl-phthalate	Phthalate	Plasticizer
Triphenyl-phosphate	Phosphate	Flame retardant
Tris[2-chloro-1-(chloromethyl)ethyl] phosphate	Phosphate	Flame retardant
4,4'-Isopropylidenediphenol (bisphenol-A)	Bisphenol	Monomer/polymerisation inhibitor/ antioxidant
4,4'-Methylenediphenol (bisphenol F)	Bisphenol	Monomer/polymerisation inhibitor/ antioxidant
4-(1,1,3,3-Tetramethylbutyl)phenol	Phenol	Monomer/intermediate
Nonylphenol	Phenol	Antioxidant
6,6'-Di-tert-butyl-2,2'-methylenedi-p-cresol	Phenol	Antioxidant
2,6-Di-tert-butyl-p-cresol	Phenol	Antioxidant

(1,1'-Biphenyl)-4,4'-diol	Phenol	Monomer/intermediate
Octabenzone	Phenol	UV stabilizer
Triclosan	Chloro-phenol	biocide
Benzotriazole	Triazole	UV stabilizer
Tetrabromobisphenol A	Bisphenol	Flame retardant
Alkanes, C14-17, chloro	Chlorinated alkanes	Plasticizer/ flame retardant
PFOS	Fluorinated	Repellent
PFOA	Fluorinated	Repellent
N-ethylperfluoro-1-octanesulfonamide	Fluorinated	Repellent

4. Objectives and research questions

The objective for the project was to further build on a knowledge base for supporting the overall goal of decreased exposure to airborne chemicals in a car cabin. The intended research questions in the project were:

- Which parts or materials in a car are the strongest sources for exposure of semivolatile EDCs?
- What impact on levels of chemicals in the car cabin has the use of recycled or renewable materials?
- How can material substitution in car cabins decrease the exposure of EDCs?

These questions were adjusted as the project proceeded to better align with the development of the project. To have a good base for measurements in the project materials used was chosen from a technical perspective with large areas and new development in the area. Due to blank issues with the method, more time was spent on solving this and therefore the number of materials were decreased. To be able to fulfill the goals of the project six types of the same surface material was used, with bio-attributed attributes and different laminations. By testing several grades of the same material, we investigated how the different attributes of the material affected the emissions.

We wanted with this project to further improve the interior environment of a car cabin in terms of air quality and/or levels of hazardous substances and be able to assess different materials. In the ongoing PhD student project, the focus is on the whole interior, while here we focused on assessing different types of surface materials used. The focus lay on developing a method that could be used for comparison of different materials.

This project further improved the research and innovation capacity by adding a single material testing to the scope.

In accordance with the roadmap for Energy and the environment within FFI this focused on the interior surface materials of a car cabin and how it is affected by different material choices. Also, a comparison between different grades of surface materials was carried out.

5. Methods

Chemicals and consumables

Dichloromethane and acetone were purchased from Merck, SupraSolv grade (Darmstadt, Germany), isopropanol from Flucka Optima LC/MS grade (FairLawn, NJ, USA) ethanol and isopropanol from Merch KGaA (Darmstadt).
The mixture of internal standards is given in Table 2, below.

Table 2: Internal standards used to spike the samples

Name	Quantity spiked in the samples (ng)	Producer
Trimethyl-phospate-D9 (TMP-D9)	22.68	CDN Isotope (Pointe-Claire, Canada)
Triethyl-phosphate-D15 (TEP-D15)	25.36	CDN Isotope (Pointe-Claire, Canada)
Tri-n-butyl-phosphate-D27 (TnBP-D27)	23.38	CDN Isotope (Pointe-Claire, Canada)
Tris(chloroethyl) phosphate-D12 (TCEP-D12)	24.02	Toronto Research Chemicals (Toronto, Canada)
Tris(1-chloro-2-propyl) phosphate-D18 (TCPP-D18)	22.86	Toronto Research Chemicals (Toronto, Canada)
Triphenylphosphate-D15 (TPP-D15)	21.2	CDN Isotope (Pointe-Claire, Canada)
Triclosan-D3	28.8	CDN Isotope (Pointe-Claire, Canada)
Bisphenol A-D14	29.42	Sigma Aldrich (Steinheim, Germany)
Octocrylene-D15	28.44	Sigma Aldrich (Steinheim, Germany)
Benzophenone-D10	28.78	Sigma Aldrich (Steinheim, Germany)
Oxybenzone-D3	28.46	Toronto Research Chemicals (Toronto, Canada)
Benzothiazole-D4	25.1	Toronto Research Chemicals (Toronto, Canada)
n-Butylbenzenesulfonamide-D9	24.46	Sigma Aldrich (Steinheim, Germany)
Alpha-Tocopheryl acetate-D9	25.08	Sigma Aldrich (Steinheim, Germany)
Dibutyl phthalate-D4	21.58	Sigma Aldrich (Steinheim, Germany)
Diethyl phthalate-D4	21.34	Sigma Aldrich (Steinheim, Germany)
Di(ethylhexyl) phthalate-D4 (DEHP-D4)	21.34	Sigma Aldrich (Steinheim, Germany)
Dicyclohexyl phthalate-D4	22.82	Sigma Aldrich (Steinheim, Germany)
Dibenzyl phthalate-D4	20.52	Sigma Aldrich (Steinheim, Germany)
4-n-Nonylphenol-D8	23.94	Dr Ehrenstorfer (Augsburg, Germany)

Air samplers consisted of a metal sample holder in which two round plugs of polyurethane foam (PUF, 15 x 15 mm, diameter x length, Special-Plast AB, Sweden) were inserted and used to collect semi-volatile substances emitted from the different materials. PUFs sampler are often used for semivolatile organic compounds (Bidleman et al. 2016). Such samplers can be used alone (as in this work) or in combination with glass fiber filter to retain

particulate compounds while the PUFs itself will capture the gaseous phase compounds (Jantunen et al. 2015 and as in Project 44015-1).
Figure 1 shows the sampling device and how the microchamber is working
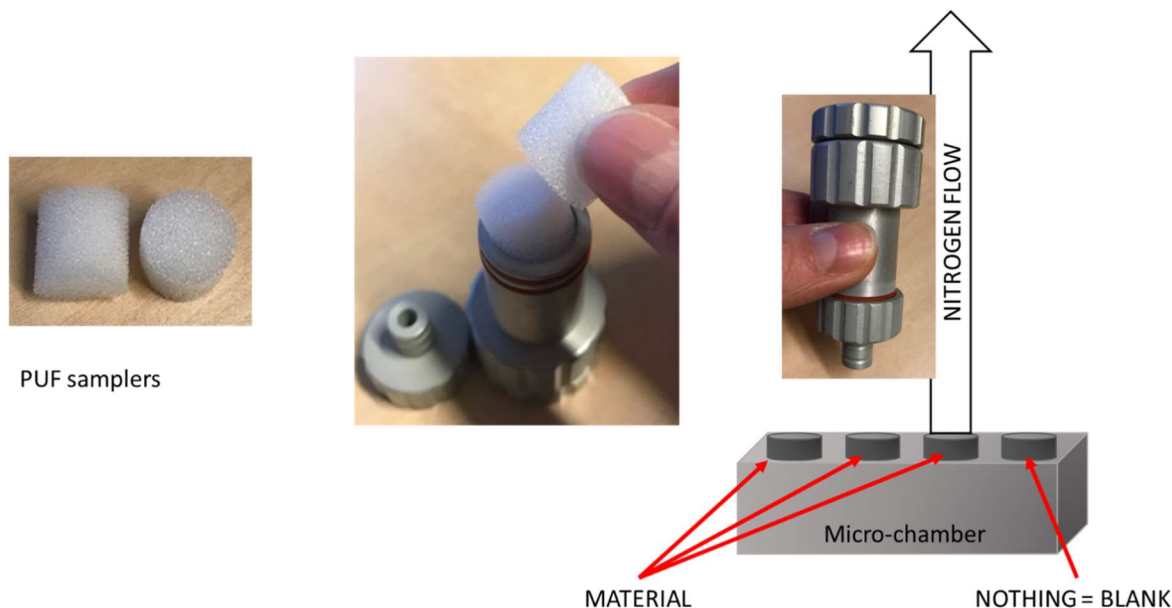

Figure 1: Description of the sampling device.

Microchamber

Micro chamber testing was performed according to ISO 12219-3 (XXX) with some modifications. The micro-chamber used was a Thermal Extractor M-CTE250 from Markes. Before each sampling the chambers were cleaned by raising the temperature to 250°C overnight.

The sample holders, see Figure 1, were cleaned in an ultrasonic bath submerged in isopropanol (1h 40°C) before and between the samplings. The pre-cleaned PUFs were handled under a fume hood to avoid contamination as much as possible. The parcels containing the material was opened right before the sampling. The samples were cut into 60mm disks before placed in the micro-chamber.

The test samples were placed in the micro-chamber at a temperature of 65°C and was left there to equilibrate for 15 min and at a flow rate of 200ml/min. When the 15 min was passed the sampling was started, i.e., the sample holders were attached to the micro-chamber, Figure 2. The duration of the sampling was 2h, at 65°C and a flow rate of 200ml/min. After sampling the PUFs were transferred from the holders and stored in pre-cleaned glass vials for further analysis.
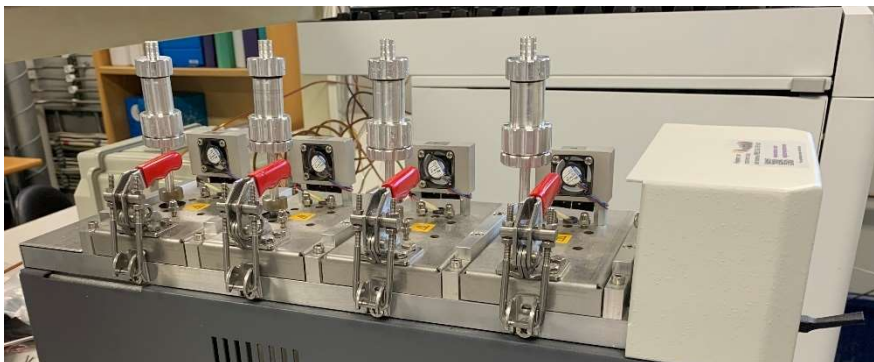
Figure 2. The micro-chamber with the sample holders mounted.

1m3 emission chamber

The 1m3 emission chamber testing was performed principally according to VDA 276 (XXX). The emission chamber used was a VCE 1000 from Vötch. The emission chamber was cleaned by raising the temperature overnight to 130°C. This cleaning procedure was performed between each sampling. 1,5 m2 of each material was cut out and inserted carefully into the chamber. The sample should not touch the walls during the sampling to get a circulated air flow. The chamber is closed and followed by an equilibration state for 2h. After that the sampling is carried out for 10 min, at 65°C, 5% RH and an air exchange of 0.4 l/h. The sampling absorbent used is Tenax TA – tubes. In the 1m3 chamber only VOC analysis was carried out.

Choice of materials

Seats, in cars, represent a large surface area and can be exposed to high temperatures during a sunny day, which leads to increased emissions (manuscript in progress with data from the FFI funded project 44015-1). Therefore, they are considered as a source of SVOCs emission and known material that contain polymeric additives for achieving the wanted attributes. In this project we focused on upholstery materials used in both Polestar and Volvo Cars. Comparison between six different materials, based on their specificities, i.e., bio-attributed phthalate-free was carried out. In Table 3 a summary of the materials can be seen.

Table 3. Materials used, bio-attributed without phthalates.

	Specification
Material 1	Unlaminated Material A
Material 2	Laminated Material A
Material 3	Laminated Material B
Material 4	Unlaminated Material B
Material 5	Unlaminated Material C

| Material 6 | Laminated Material C |

Sampling pre-study

Before sampling, all glassware (including scintillation vials used for polyurethane foam (PUF) transportation or during extraction) were baked for two hours at 550⁰C in a furnace. PUFs samplers were cleaned by soxhlet extraction with acetone overnight, placed in a pre-baked round flask and dried using a rotary evaporator (Heidolph, Schwarbach, Germany) operated at 60⁰C under vacuum (pressure below 200 mbar). The clean and dried PUFs were stored in the burnt vials and stored at room temperature until use. The sample holders and scintillation vial caps were cleaned with three rounds of sonication with 2-propanol, for 20 min, dried under a nitrogen gas flow and packed in pre-baked aluminium foil for the holders. In between sampling of the different materials, the holders were rinsed with ethanol and isopropanol.

We performed a pre-study based on one surface material (petroleum-based product). This was to done to ensure that (i) there are no contamination from the micro chambers disturbing chemical analysis, (ii) sampling time is enough to reach levels above detection limit, (iii) sampling time short enough to prevent breakthrough and the loss of the most volatile compounds, and (iv) equilibration can capture the most and less volatile compounds (too long, the most volatile will be already emitted from the material before the sampling start, too short time the less volatile compounds will not be emitted).

We focused on targeted chemicals presented in Table 1. Sampling times were 1 hour, 2 hours and 4 hours. Equilibration times were 15 min, 30 min and 60 min. Blanks, which consisted of empty micro chamber(s) were performed before the use of the chambers, after sampling with material and overnight cleaning at 200 ⁰C, and after a sampling followed by 1 hour cleaning at 200 ⁰C. Laboratory blanks (sampling site and sample preparation site) were performed as PUFs exposed the laboratories ambient air, mimicking the exposure of PUFs when inserted in the holders, or when PUFs were extracted.

After sampling, the PUFs were transferred to the burnt glass vial and stored at 4⁰C until extraction

- Blank issues

One of the targeted chemicals, 6,6'-di-tert-butyl-2,2'-methylenedi-p-cresol, was found in blanks, in higher quantity than in the samples. To prevent disturbances from background, further cleaning procedures in between sampling events were proposed: (i) cleaning overnight the chamber by heating at 250 ⁰C, (ii) wiping the chamber with isopropanol, and rinsing the holders either with ethanol or isopropanol.

- Final Sampling protocol

The microchamber contains four different emission chambers. For each material, one chamber will remain empty (blank), and the chamber position for the blank will be changed from one material to another one. Before starting, the microchambers will be heated at 250

ºC overnight and wiped with isopropanol. The equilibration time was set at 15 min before the collection of the samples, and sampling time set at 2 hours. After each sampling event the microchambers were heated overnight at 250 ºC and wiped again with isopropanol before the next sampling event. Holders were rinsed in between sampling events with isopropanol and sonication. A laboratory blank consisted of PUFs that were removed from their vial at the sampler preparation time, and at the end of the sampling, when the PUFs are taken from the holders and placed in their vials for storage. This intent to mimic the possible contamination from ambient air during the preparation of the samplers.

Sample extraction

Air samples (PUF) were spiked with the internal standards presented in Table 2 and extracted with 3 rounds of sonication for 30 min with 20 mL of dichloromethane. After each round, extracts were combined and evaporated up to about 300 µL with a BÜCHI Syncore Analyst (BÜCHI Labortechnik GmbH, Essen, Germany). Finally, the samples were transferred in a vial glass insert, spiked with 2 µL of phenanthrene-D10 (2ng in total, Sigma Aldrich, Steinheim, Germany)

Chemical analysis

In order to increase the separation of analytes and to provide cleaner MS spectra, a method was applied with two dimensional-gas chromatography coupled to mass spectrometry (GCxGC-MS). In this set up the instrumentation consisted of a Pegasus BT 4D (GCxGC TOF MS, Leco Corp., St Joseph, MI, USA), equipped with an Agilent Technologies 8890 GC System (Quad jet GCxGC, Palo Alto, CA, USA), a secondary oven, and a modulator. A Rxi-5MS column (30 m, 0.25 mm ID and 0.25 µm film thickness, Restek) was used for the first- dimension, and a Rxi-17SilMS column (1 m, 0.25 mm ID and 0.25 µm film thickness) was used for the second dimension. The system was operated with the ChromaTOF-GC software (version 5.51.50, April 2021, Leco®). Helium was used as gas carrier at a flow of 1 mL/min and 1 µL of each sample extracts and n-alkane standards were injected in a split mode. The inlet spilt ration was set up at 100, the split flow at 100 mL/min and the split inlet total flow was 101 ml/min. The inlet was purged with a 3 mL/min flow and its temperature was 280 °C. The initial temperature of the first oven was set at 80 °C for 1 min and raised at a rate of 7 °C/min then hold at final temperature of 300 °C for 5 min. The secondary oven was operated at + 35 °C offset (relative to the first GC oven temperature) and the modulator with +15 °C off set (relative to the secondary oven temperature). The modulation period (secondary dimension) was 3 s with a 0.9 s hot pulse and a 0.6 s cooling time between stages. The transfer line was set as 300 °C.

The TOF-MS used an electron ionization (EI) operated at 70 eV, mass spectra were recorded from 47 to 500 m/z at an acquisition rate of 100spectra/s and with an acquisition delay of 310 s. The ion source temperature was 250 °C.

VOC analysis

The VOC analysis of the Tenax test tubes were analyzed according to ISO 16000-6 with some modifications. The equipment used was the TD-GC-MS (Thermal Desorption-Gas chromatograph-Mass spectrometer), TD 100-xr Automated thermal desorber from Markes, followed by 7890B GC System + 5977B MSD from Agilent.

The Tenax TA sampling tubes for VOCs were thermally desorbed at a temperature of 300°C. The MS system was calibrated with toluene in methanol. The GS program 40-280°C is then run and the GC-MS data is further computerized analyzed. All results are presented as toluene equivalents.

Data processing strategy of the GCxGC-MS data

As the software ChromatTOF-GC did not provide a solution for peak alignment within the different samples and blanks, a composite sample was created using 20 µL of one replicate for each material and ran twice with the same GC-MS method than the material and blank extracts, and n-alkane mixture (from C10 to C40), used to calibrate the first column dimension and calculate retention time indexes. The hypothesis was that this composite sample would contain all different chemicals from the blanks and different material, and the filtering could be done once (as it is a tedious work) aiming at the creation of a target list that will be used to search all the material replicates and blanks. Figure 3 describes the workflow process. The NIST 2020 EI mass spectral library (NIST 2020), was used to search the acquired spectra in the first composite run. Peaks not assigned with a name were removed from the list of plausible compounds. Only compounds/hits with a name and a score above 700 were kept. The score reflects the EI spectra match between NIST 2020 and the experiment, but also (when available on NIST 2020) the retention time index (RTI) match between NIST 2020 and the experiments. A score of 700 represents a fair score with some deviations in EI spectra, and the higher is the score the more plausible is the associated chemical (e.g. Scores > 900 are excellent and could be considered as a level 2 in the Schymanski (Schymanski et al. 2014) scale for identification confidence.

The remaining hits were manually filtered based on the RTI deviation (experiment vs. NIST 2020), when exceeding +/- 20. When the RTI was not present in the NIST 2020 library then the hit was kept on the list. For hits scoring below 800 a manual spectra inspection was performed, followed by a peak shape check. Finally, column and septa bleed were removed from the list. The first target list was created and ran against the second composite sample. The idea behind running twice the composite sample was to even further decrease the number of hits (e.g. missed split peaks, missed peaks pick up in peaks tailings, non-gaussian peaks, or peaks not found at all).

Blanks and material replicates were searched with the final target list. The results were exported as csv files and aligned using KNIME Software (Berthold et al. 2007) with the nodes csv reader, joiner and csv writer. The obtained csv table was converted into an Excel Table, containing all plausible chemicals distributed within the different material, as well as peak area. A manual review of the aligned data was performed to ensure retention times of the different plausible chemicals were consistent within the different samples and

blanks. The Table was manually assessed, to check when data were missing for a replicate or if only one of the replicates showed a peak area (is it missing because not being present in the sample or was it missed in the search). A plausible chemical, if present in the material was expected to be found in at least two out of three replicates, otherwise it was removed from the table within the corresponding material.

When performing non-target screening, it is impossible to have a proper quantification of the different analytes (no matching internal standards for instance, non-available native standards for calibration…), then semi-quantification is generally used. In this work it was decided to use only one internal standard, which was selected at the middle of the retention time window of the first GC dimension (total run was 2500 s). This was to make sure the internal standard was not affected by evaporation during sample preparation (crucial step were most volatile chemicals can be lost). The Benzophenone-D10 was then used for the normalization. The response factor (RF) of the benzophenone-D10 was determined with the equation (1) and normalized to benzophenone-D10 concentration (Cng/L air) for all plausible analytes with equation (2)

$$RF_{Benzophenone-D10} = Peak\ area_{Benzophenone-D10} / Quantity_{Benzophenone-D10\ spiked} \quad (1)$$

$$C_{plausible\ chemical} = Peak\ area / RF_{Benzophenone-D10} \quad (2)$$

A blank removal was performed using the laboratory blanks obtained during sampling and extraction and the micro-chamber blank (empty from material). The final table containing plausible chemicals and distribution within the different materials was obtained.

Statistics

Principal component analysis (PCA) was performed with the SIMCA software (Version 17, Sartorius). It aimed at finding relationships between observations (here tentatively identified chemicals) and variables (concentrations of these chemicals) in order to derive patterns, outliers, resulting in the clustering of materials that are similar or not. It is a visual representation of how similar the materials are. Average and standard deviation were calculated using Excel (Microsoft, version 10).
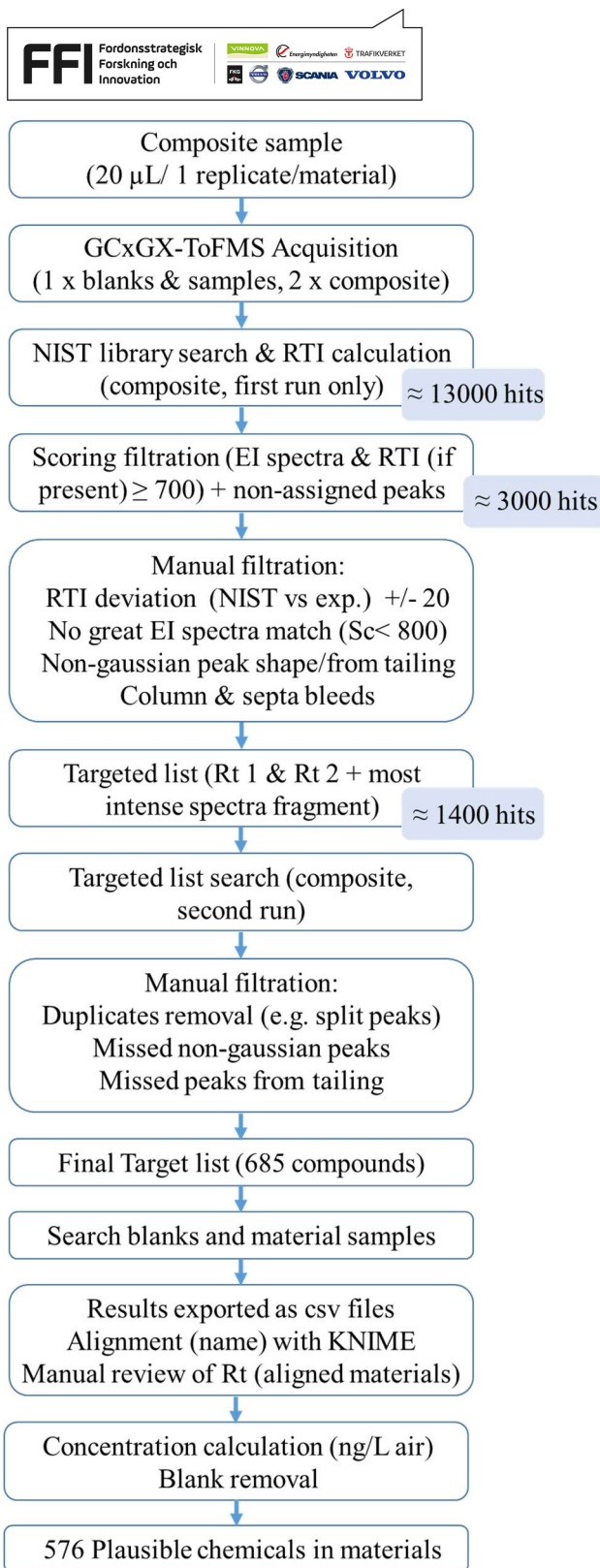
Figure 3: Data processing workflow for acquired GCxGC-MS samples and blanks

6. Goal

The objective of this project was to deliver chemical characterization of the different materials in term of SVOCs emissions (concentration of the different chemicals in the gas phase). The study was based on 19 selected target chemicals (Table 1) for direct comparison between different materials. We also aimed at achieving a more comprehensive chemical assessment of compounds that could leak from material to gas phase by performing a non-target screening based on the NIST 2020 spectral library (National Institute of Standards and Technology, version 2020), that contains more than 700 000 spectra.

A pre-study was performed to assess blanks and exposure time. Blanks appeared to be a larger issue than expected and one material was used for further experiments to improve blanks and make sure the presence of certain chemicals will not compromise the analyses (more in blanks than in samples). A new cleaning protocol was thus, implemented. This material was also used to determine the sampling time along with the equilibration time. Due to the issues with the blanks in the method, one type of material was used with different specifications and origin to evaluate the emissions from different materials.

We expect to provide new knowledge on chemical emissions that can be used for future substitution/use of more benign materials.

Finally, the knowledge gained in this project will be incorporated into the PhD project relating to EDC emission in the entire vehicle along with implementation I car projects for the implementation of future guidelines for material selection along with exposure and risk assessment.

In the long run the knowledge built here will form the foundation in the requirement settings on systems and materials for building next generation cars. This will be done by using the knowledge gain here to see how we further can improve the materials within the car and also which obstacles we see for further transparency discussions.

7. Results and goals fulfillment

Sampling pre-study

In order to sample chemicals emitted from material into the gas phase at a certain temperature (here at 60 °C) it is necessary to expose the material to the heat in order to reach equilibration before starting to collect the air sample. This part of the project aimed at determining how long time we need for the equilibration and for how long we need to take the sample. If this sampling time is too short, we may miss less volatile compounds but if the time is too long we may loose the most volatile ones (flushed from the PUF samplers by the nitrogen flow). In this part we focused on the targeted chemicals presented in Table 1. The times investigated were, 1 hour, 2 and 4 hours. In the case of the 4h sampling time, the analysis was done on separated PUFs (bottom one first PUF to collect the sample, and top) to detect breakthrough. Three chemicals were found in the material samples, 2,6-Di-tert-butyl-p-cresol (BHT), 6'6´-Di-tert-butyl-2-2'-methylenedi-p-cresol (DTB-p-cresol) and bis(2-propylheptyl)phthalate (DPHP). The results with the concentrations obtained at different sampling time and equilibration time are presented in Figure 4. The results show that with 1 hour of sampling time the DPHP is not found, so it requires at least two hours. In the top PUF none of the compounds were found, showing the breakthrough did not occur or in so low quantity that it was not possible to detect the chemicals. As the results did not show a large increase in concentrations with a 4 h sampling, it was decided to use 2 hours for the study comparing the six materials.

Figure 5 shows the results for the equilibration time. Three times were investigated, 15 min, 30 min and 1 hour. As the most volatile compounds are expected to be released from the material quite fast it was hypothesized that they may be lost in case of a long equilibration time, but this was not clearly observed with the BHT, but surprisingly for the DTB-p-cresol compound which is much less volatile. This was also connected to blank issues (described below). It was then decided to use an equilibrium time of 15 min.

So, the final design for the sampling of the six materials was determined to be 15 min equilibration time and collection of the samples during 2 hours.

Blank Issues

We noticed from Figure Y that the DTB-p-cresol fading away with a longer equilibration time, while not the most volatile of the three identified targeted compounds did. Figure 6 explains the reason for this. It appears that this chemical is also highly present in blanks, and after blank subtraction, almost nothing is left in the sample. Another set of experiment was performed in order to compare cleaning method of the microchamber and sampler holders in between sampling events. It was found that heating the microchamber at 250 °C overnight, wiping each chamber with IPA and sonicating the holder also with IPA improved the blank issues with the DTB-p-cresol, even if it did not remove it completely. This new procedure was then adopted for the major sampling of the six materials.
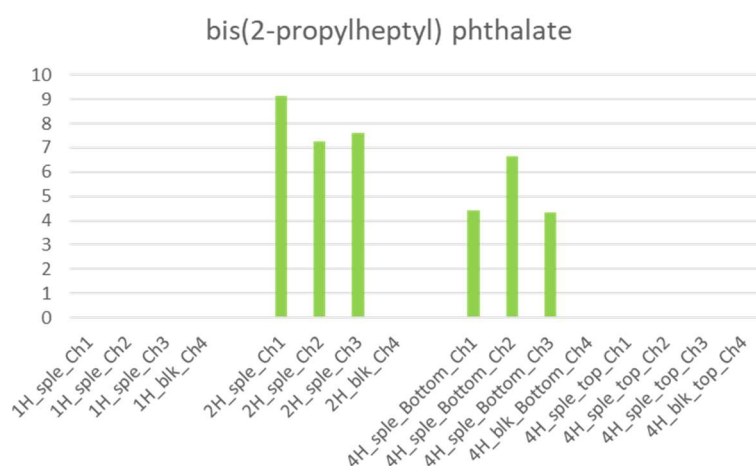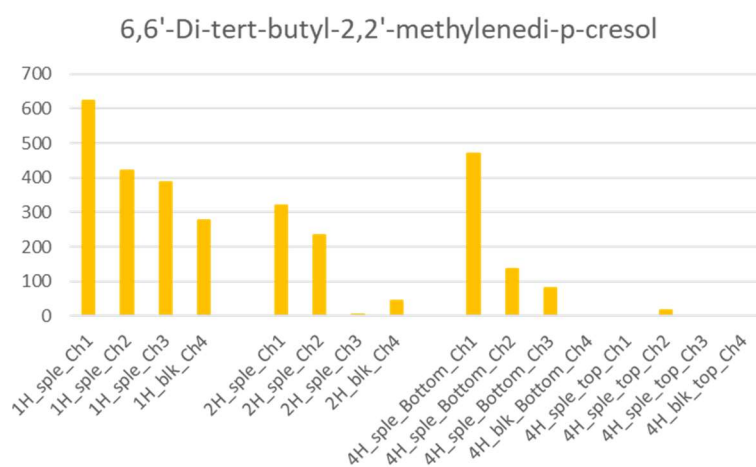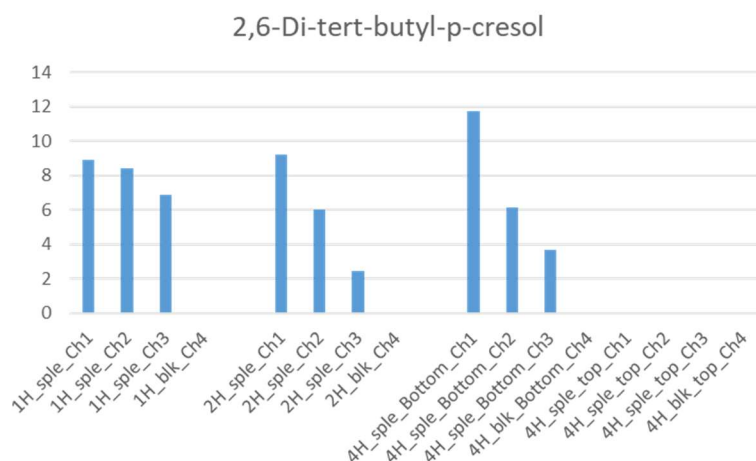
Figure 4: Sampling time for the three detected targeted compounds. Abbreviations: 1H-sple is for 1-hour sample, 2H-sple for 2-hour sample and 4H-sple for 4-hour sample. Ch stands for chamber, as there were four of them and were numbered according to their position.
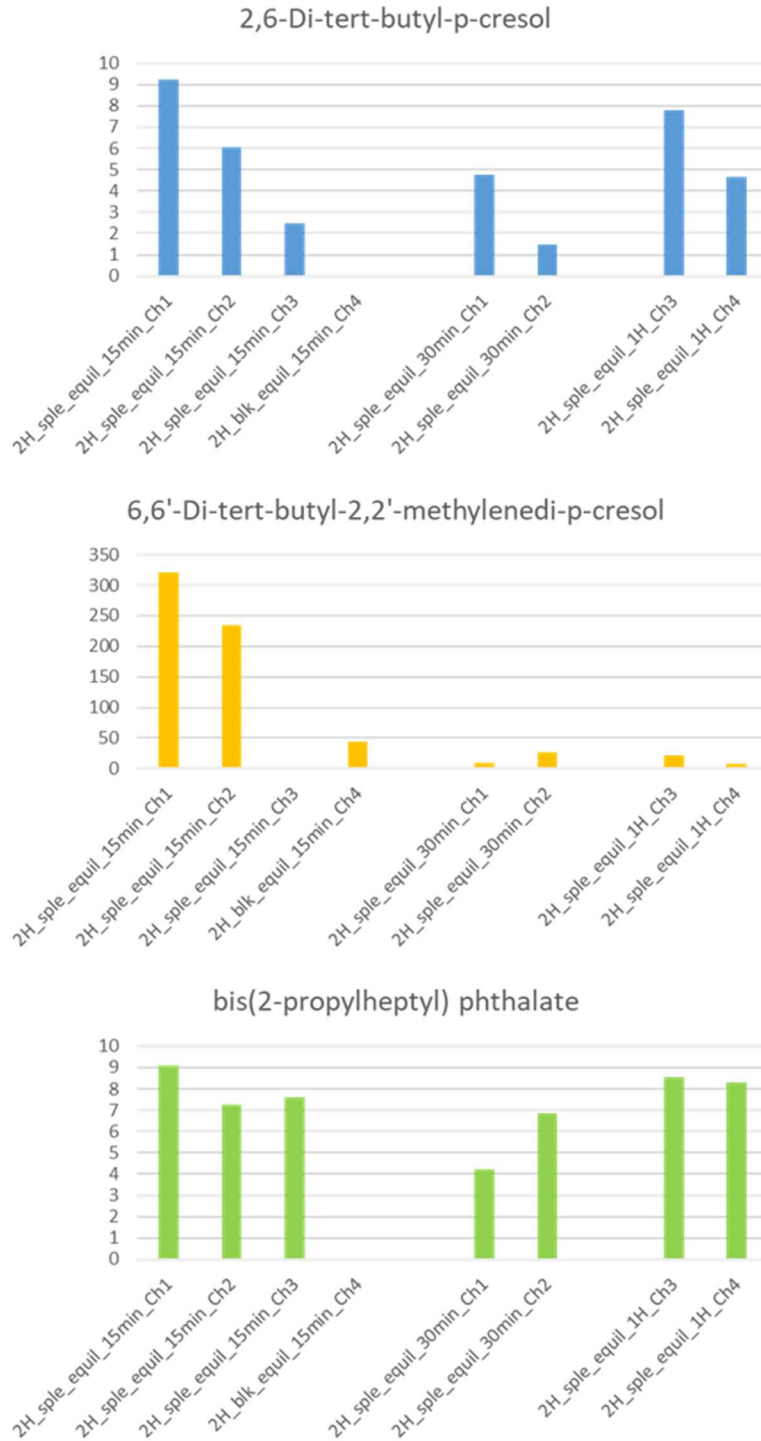
Figure 5:   Equilibration time for the three detected targeted compounds. Abbreviation: equil. stands for equilibration
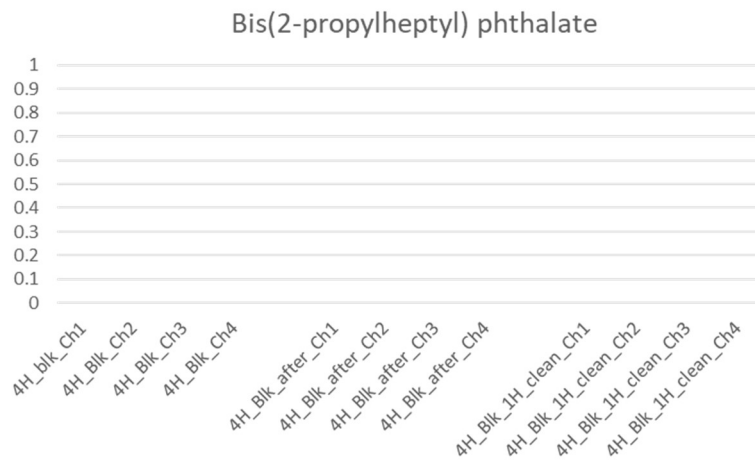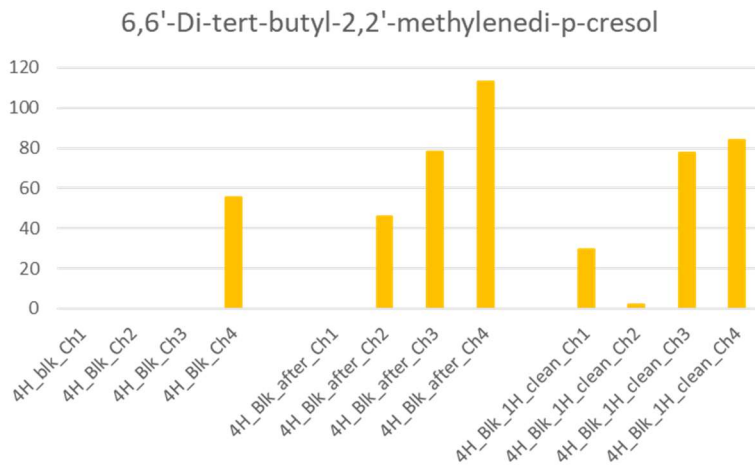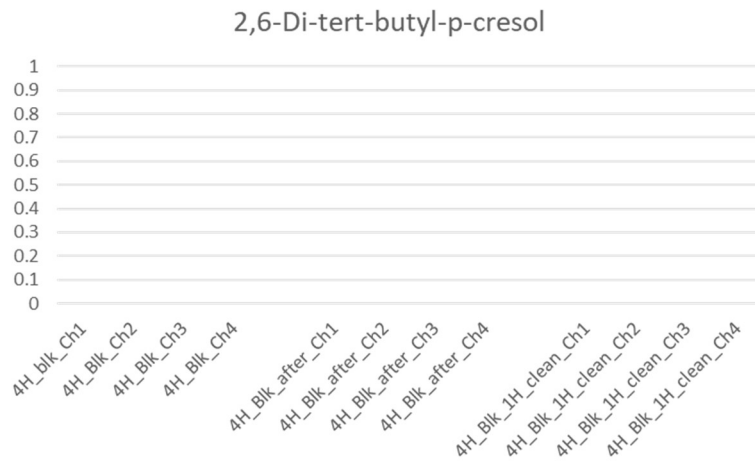
Figure 6: Blank issues. Abbreviations: Blk stand for blank

Chemical identification

The workflow presented above enabled the identification of about 570 chemicals (after blank removal), with a level of confidence of 2 (when a NIST 2020 spectral match and RTI match returned a similarity score of 900 or more), plausible structure, or with a level of confidence of 3 (tentative candidate, for any score below 900). This level of confidence is based on the Schymanski scale (Schymanki et al. 2014). We identified chemicals like tris(2-chloropropyl)phosphate, triisobutylphosphate, used as flame retardants, benzophenone, benzotriazole and 2,6-di-tert-butyl-p-cresol, used as antioxidant/UV stabilizers, and some polyaromatic hydrocarbons (PAHs) such as acenaphtene, anthracene and fluorene, which can result from heat or are used in the production of dyes or plastic for instance.

The results of the PCA on all 570 chemicals are presented in Figure 7. It shows clear clustering of the six materials. Materials are labelled from 1 to 6 according to their rank in the experiments (M1 is the first material which was sampled, M2 the second…). Table 3 shows the specificities of the six materials. Material M1 and M2 are provided by supplier A, while material M3, M4, M5 and M6 are provided by supplier B. Material M1 and M2 are the same material but M1 is unlaminated while M2 is laminated. This also applies to M3 and M4 (same material, laminated, unlaminated, respectively), and M5 and M6 (unlaminated, laminated, respectively). We can clearly see that material M1 and M2 are two very unique materials in terms of chemical profiles and concentrations. Materials M4 and M5 (unlaminated) are very similar as they cluster together. Finally, in the fourth section, materials M3 and M6 (laminated) show some similarities. Based on this information, Figure 7 shows that the largest chemical variation (38%) is connected to the supplier (clustering of material M1 and M2, supplier A, (t[1] negative values) vs M3 to M6, supplier B, (t[1] positive values) on the X axis), even if the same bio-attribute source is used by both supplier (pine oil). The material itself (laminated or unlaminated) is the second most important chemical variation (24%), with positive t[2] values for the laminated materials (clustering material M2, M3 and M6) and negative t[2]values (clustering material M1, M4 and M5) on the Y axis.

The next step was to understand what chemicals were driving this clustering. It was quite overwhelming to go through 570 compounds. For this reason, standard deviation on all materials and replicates were calculate relatively to the average (all materials and replicates). Different thresholds were applied, like removing chemicals showing a standard deviation relative to the average of 20%, 34%, 68 %, 75% and 95%, resulting in the discard of 70, 130, 345, 380 and 475 compounds, respectively. To make sure these different cuts were not changing the clustering, PCA were performed at each step. As no clustering was changed, it was decided to go for the compounds showing the most drastic changes, and we used the 95% of standard deviation cut (Figure 8). The final list of the chemical drivers of the separation of the clusters includes 96 chemicals and are listed in Table 4. Figure 8 shows that the main chemical variation is due to the supplier (X axe clustering, 56%)) and

the material (laminated or unlaminated) drives the second most important chemical variation (Y axe clustering, 21%), as seen in Figure 7.

Table 4 and Figure 8 show that the differences between the six materials is highly correlated to the presence of 96 driver chemicals. As said above, the supplier induced the highest chemical variation (Figure 8, 56% variation on X axis), resulting in material M1 and M2 (supplier A) being very different from the four others (supplier B). This can be explained with the presence of certain chemicals at much higher level in materials M1 and M2 in comparison to materials M3 to M6. Indeed, there are 15 chemicals found predominantly in material M1 and M2 (10 chemicals with concentrations higher than 1 ng/L) while barely detected or not detected at all in the other 4 materials from supplier B. Amongst these 10 chemicals, 2,6-dimethyl-8-octanol (20 and 7.5 ng/L in M1 and M2, respectively), 2-decanol (8 and 4,7 ng/L), acenaphthylene (3.1 and 2.3 ng/L), acetic acid, 1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl ester (2.6 and 4.4 ng/L), benzoic acid, 2-methylpropyl ester (5.3 and 2.9 ng/L), ethanol, 2-(2-butoxyethoxy)- (42 and 28.3 ng/L) and ethanol, 2-phenoxy- (9.2 and 2.6 ng/L) are detected at much higher concentration then 1 ng/L.

The second variation is correlated to the type of material, unlaminated material (M1, M4 and M5) versus laminated materials (M2, M3 and M6), as seen on Figure 8 (Variation of 21 % on the Y axe). Table 4 shows the chemicals that are present in laminated or unlaminated materials. There are 10 chemicals that are mainly detected in laminated materials (M2, M3 and M6) with concentrations above 1 ng/L. For instance, 1,2-benzenedicarbonitrile, 1,3-benzenedicarboxylic acid, diethyl ester, 1-propanol, 2-(2-hydroxypropoxy)- (mostly in M2), 2-propanol, 1,1'-oxybis-, 3-pyridinecarbonitrile, benzene, 1,1'-ethylidenebis-, benzene, 1-methyl-2-(phenylmethyl)-, benzene, 1-methyl-3-(phenylmethyl)-, benzonitrile, Benzonitrile, 4-amino- and phenol are mainly in laminated materials. In unlaminated material (M1, mostly), (S)-(+)-6-methyl-1-octanol, 1-phenoxypropan-2-ol, acetic acid, phenylmethyl ester, benzene, 1-(1,5-dimethylhexyl)-4-methyl-, caprolactam and decanal are dominating with concentration higher than 1 ng/L (up to 9.2 ng/L for the caprolactam).

We know that these 6 materials should not contain phthalates, but phthalic acid, decyl nonyl ester (in M2 and M5) and 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester (in M2, M3 and M6) were found at very low levels (see Table 4). During data processing, slight differences in integration of mass spectral peaks (used for concentration calculation) can occur, especially for low levels, resulting in higher concentration in one sample in comparison to the blank. We also cannot rule out that the industry producing the material does not use these phthalates for other products and thus, the presence would also result from cross contaminations, which are unavoidable. Dimethylphthalate was found in all materials from supplier B (data not shown), at concentrations around 1 ng/L for the laminated materials and around 3 ng/L air for the unlaminated materials. Dimethylphthalate is present in a lot of different type of materials (plastic, insect repellants, lacquer coating, safety glass and so on) and if used as well in the factory of the supplier, its presence in the phthalate-free material can be due to cross contaminations.

Material M1 shows concentration higher than 1 ng/L air (relative to Benzophenone-D10) for 18 chemicals, with 16 of them dominating in M1 in comparison to the other materials, they are highlighted in light grey in Table 4. Amongst them, six chemicals, 2,6-Dimethyl-8-octanol, 2-Decanol, Benzoic acid, 2-methylpropyl ester, Caprolactam, Ethanol, 2-(2-butoxyethoxy)- and Ethanol, 2-phenoxy- have concentration higher than 5 ng/L air (about 20, 8, 5, 9, 42 and 9 ng/L respectively). Since this material does not contain phthalates, other plasticizer or compounds used in their manufacture like 2-decanol and linoleic acid ethyl ester (unique compound to M1) can be found, from the information we have on the different chemicals. Caprolactam and phenol are used in the manufacture of synthetic fibers, like nylon. In this material, we detected carvone (used in fragrances or as antimicrobial for instance), decanal (used in flavoring and fragrances, and important component of citrus) and heptanal and these are substances also found in plants for instance, which would explain their presence here since the material is wood-based. Also, we detected some more compounds entering in the production of dyes and plastics (acenaphthylene, benzyl acetate and ethanol, 2-(2-butoxyethoxy)-) and finally some chemicals used as insecticides or insect repellents (ethanol, 2-phenoxy- (glycol ether) and acenaphtylene). This could be connected to the wood itself used as a base for the materials.

In material M2, 21 chemicals have a concentration higher than 1 ng/L air (relative to benzophenone-D10), but 5 of them with much higher concentrations (1-octanol,3,7-dimethyl, 2,6-dimethyl-8-octanol, 1-Propanol, 2-(2-hydroxypropoxy)-, benzonitrile, benzonitrile-4-amino and ethanol, 2-(2-butoxyethoxy)-, with concentrations of about 7, 12, 7, 6 and 28 ng/L air, respectively). This material even if unique (see PCA results, figures 7 and 8) it shares some similarity with material M1, with chemicals present at a very high concentration (2,6-dimethyl-8-octanol, ethanol, 2-(2-butoxyethoxy)-) but also at concentration above 1 ng/L. Two plasticizers were detected at higher concentrations, the 2-decanol, 2-Propanol, 1,1'-oxybis- (dipropyleneglycol) (4.7 and 2.4 ng/L air, respectively). This fabric contains several substances, a-terpineol, D-carvone at higher level and many others at lower concentrations (below 1 ng/L air), like borneol, terpinen-4-ol for instance, that are present in natural products (e.g. in plant oils).

Materials M3 and M6 cluster in the PCA and these two materials share chemicals at very similar concentrations, most likely due to the fact they are both laminated fabrics. Twelve compounds were detected with concentrations higher than 1 ng/L, and 3 of them with concentrations over 5 ng/L, 1,3-benzenedicarboxylic acid, diethylester, benzene, 1-methyl-2-(phenylmethyl)- and phenol. The presence of the 1,3-benzendicarboxylic acid, diethylester occurs at concentrations of 8 and 12 ng/L for M3 and M6, respectively. Phenol is particularly high in these materials and is used in the production of nylon. In these materials few chemicals are also detected in plants, like the pentanoic acid (1.4 ng/L in M6) with some other at lower levels (carvone, decanal, nonanal and octanol, for instance).

Material M4 and M5 seems to be identical materials as all replicates cluster together (we know they are not the same material), but also relatively similar to material M3/M6 (Figure 7 and 8). In these two materials, the phenol is the only chemical occurring at concentration higher than 1 ng/L. The rest is rather similar to the concentrations in material M3 and M6

(e.g. 2-decanol). Material M4 and M5 contain also naturally occurring compounds (e.g. a-terpineol, benzaldehyde-3,4-dimethyl, D-carvone).
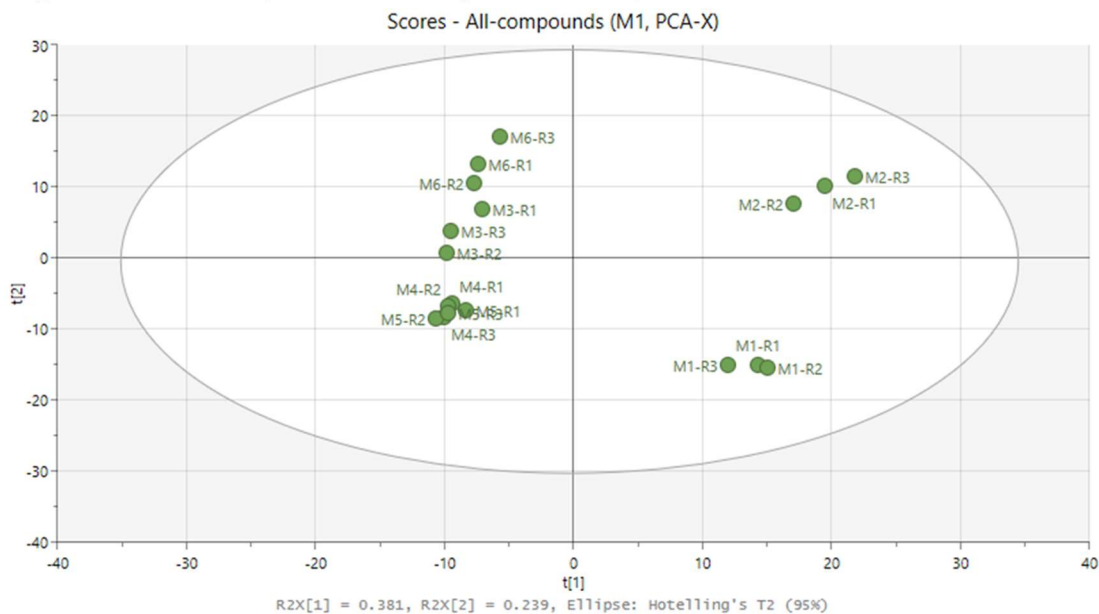
Figure 7: PCA with all chemicals (plausible structure and tentative candidates) for the triplicates (R1 to R3) for the six materials (M1 to M6). t[1] is the first principal component describing the largest variation in the data (38%), and t[2] the second largest variation (24%) in the data set.
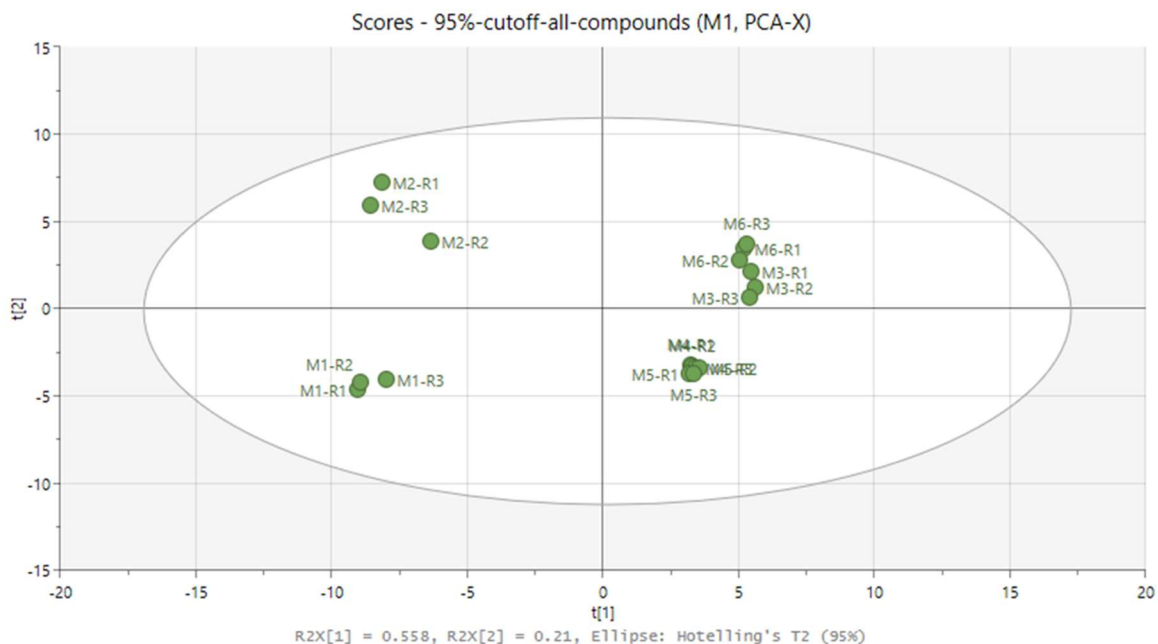
Figure 8: PCA with the chemicals remaining after a 95 % cutoff. t[1] is the first principal component describing the largest variation in the data (56%), and t[2] the second largest variation (21%) in the data set.

Table 4: Chemicals showing the most extreme deviation in each material. (-) when the standard deviation was not calculated due to only one replicate remained after blank subtraction

Name	Similarity (confidence)	Concentrations (ng/L relative to benzophenone D10) (stdev %)						Possible chemical uses in industries
		M1	M2	M3	M4	M5	M6	
(R)-(1-Cyclopentylpropane-1,3-diyl)dibenzene	706 (3)	0.0168 (126)	-	-	-	-	-	
(S)-(+)-6-Methyl-1-octanol	887 (3)	1.9354 (25)	0.8453 (14)	0.1147 (19)	0.1662 (44)	0.0498 (-)	0.724 (36)	
[1]Benzothiopyrano[4,3-b]benzo[e]indole	715 (3)	-	-	-	0.0005 (88)	-	-	
1,1'-Biphenyl, 3,4-diethyl-	786 (3)	0.0215 (14)	0.0183 (23)	0.2939 (39)	0.0781 (31)	0.1061 (6)	0.4142 (8)	
1,2-Benzenedicarbonitrile	938 (2)	0.0794 (8)	2.0634 (23)	1.988 (21)	0.0379 (17)	0.0374 (23)	2.8084 (10)	
1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester (Diisobutyl phthalate)	936 (2)	-	0.1724 (-)	0.8694 (43)	-	-	0.0534 (109)	Plasticizer
1,2-Ethanediol, monoacetate	701 (3)	-	-	-	-	-	0.0363 (-)	
1,3-Benzenedicarboxylic acid, diethyl ester (diethylisophthalate)	862 (3)	0.0802 (6)	0.043 (51)	7.9338 (34)	0.0807 (13)	0.0806 (19)	12.4877 (4)	Plasticizer
1,3-Dicyclohexylurea	924 (2)	-	-	0.0042 (-)	0.002 (-)	0.0174 (-)	-	
1-Docosene	749 (3)	-	0.0004 (-)	0.0012 (127)	0.0003 (2)	0.004 (111)	-	

Compound	RI							Use
1-Hexadecanol	882 (3)	0.2459 (104)	0.1419 (38)	-	-	-	0.0289 (134)	Mainly it is used as an opacifier, emulsifier, and thickening agent that alter the thickness of the liquid, and increase and stabilize the foaming capacity.
1H-Indene, 2,3-dihydro-1,1,4,5-tetramethyl-	810 (3)	-	0.1212 (29)	0.0105 (23)	-	-	-	
1-Methyl-2-n-hexylbenzene	803 (3)	0.2678 (3)	0.2221 (14)	0.0421 (35)	0.0117 (2)	0.0149 (56)	0.0438 (17)	
1-Octanol, 3,7-dimethyl-	865 (3)	-	2.9462 (8)	-	0.2395 (9)	0.2999 (29)	0.2148 (60)	
2,6-Dimethyl-1-octanol	790 (3)	20.0143 (4)	7.4805 (60)	-	0.1856 (7)	-	-	
1-Phenoxypropan-2-ol	871 (3)	2.0197 (9)	0.6381 (23)	0.0096 (15)	-	-	0.0212 (39)	
1-Propanol, 2-(2-hydroxypropoxy)-	892 (3)	-	12.5849 (42)	0.2545 (61)	0.0729 (84)	-	0.1954 (-)	
2(3H)-Furanone, 5-heptyldihydro-	831 (3)	0.0312 (12)	0.0844 (14)	0.0075 (95)	0.011 (41)	0.0086 (40)	0.012 (14)	
2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester	909 (2)	0.149 (13)	0.0788 (74)	0.0121 (113)	-	0.0212 (14)	0.0061 (34)	
2-Decanol	841 (3)	8.0171 (4)	4.6795 (10)	0.5361 (18)	0.5125 (8)	0.5611 (10)	0.6777 (7)	Decanol is used in the manufacture of plasticizers, lubricants, surfactants and solvents.
2-Decanone	862 (3)	2.6733 (4)	1.761 (11)	0.3468 (18)	0.0698 (19)	0.1685 (13)	0.5404 (11)	
2-Ethylhexyl salicylate	932 (2)	-	-	-	-	-	0.715 (-)	Ethylhexyl salicylate is a UV-filter which protects

Name	RI							Description
								against UVB rays. It is regulated by EU and FDA (USA) to be used up to 5 % in cosmetic products such as sunscreen
2-Mercaptobenzothiazole	858 (3)	0.0005 (-)	-	-	-	0.0003 (-)	0.0055 (61)	Industrially it is found in rubber products such as the lining for fuel tanks, caulking, electrical cords, plugs, gas masks, safety goggles, conveyor belts, shock absorbers, springs, mats, aprons, earphones, stethoscopes, rubber bands, erasers, rubber sheeting, non-slip waistbands, mattresses and anti-slip carpet ...
2-Methylhexacosane	732 (3)	-	0.0171 (-)	-	-	-	-	
2-Propanol, 1,1'-oxybis- (dipropyleneglycol)	941 (2)	-	2.3662 (27)	-	-	0.0366 (15)	0.366 (25)	Used as a plasticizer, an intermediate in industrial chemical reactions, as a polymerization initiator or monomer, and as a solvent
2-Propyl-1-pentanol, chlorodifluoroacetate	743 (3)	2.534 (6)	1.8492 (5)	0.1494 (62)	0.2459 (5)	0.5002 (14)	0.4691 (42)	
3(2H)-Pyridazinone, 6-methyl-	726 (3)	-	-	-	-	0.0012 (78)	0.0609 (110)	
3-Hexyne-2,5-diol, 2,5-dimethyl-	871 (3)	0.1434 (5)	0.3376 (41)	0.0044 (51)	-	-	0.0202 (39)	

3H-Indazol-3-one, 1,2-dihydro-	768 (3)	0.5453 (6)	1.1826 (23)	0.1731 (41)	0.1461 (27)	0.1799 (21)	0.2125 (14)	
3-Phenyl-2-pentenenitrile	787 (3)	0.0349 (43)	0.4124 (14)	0.0405 (64)	-	-	-	
3-Pyridinecarbonitrile	964 (2)	0.0327 (6)	0.9518 (18)	0.6468 (13)	0.011 (16)	0.0098 (28)	1.1742 (17)	Intermediate in the manufacturing of Pharmaceuticals. It is also used as an intermediate in the agrochemical industries, as a cosmetic additive and as a food chemical in the manufacture of nicotinic acid and nicotinamide.
4-Ethylidene-pent-2-enedinitrile	806 (3)	-	0.0493 (55)	0.0079 (61)	-	-	0.0147 (16)	
7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydro-1-phenanthrenol (isomer 2)	837 (3)	0.0001 (-)	-	0.0004 (-)	-	0.0014 (135)	-	
Acenaphthylene	926 (2)	3.1476 (2)	2.2753 (8)	0.3134 (25)	0.0898 (12)	0.0852 (14)	0.6451 (9)	Used in dye synthesis, insecticides, fungicides, and in the manufacture of plastics.
Acetic acid, 1,7,7-trimethyl-bicyclo[2.2.1]hept-2-yl ester	919 (2)	2.5935 (9)	4.4105 (10)	0.2884 (16)	0.4358 (6)	0.4663 (8)	0.6773 (6)	
Acetic acid, 2-phenylethyl ester	824 (3)	0.3459 (4)	0.3438 (10)	0.0277 (20)	0.0175 (10)	0.017 (10)	0.0388 (4)	Cosmetics & PCPs

Acetic acid, phenylmethyl ester (Benzyl acetate)	934 (2)	1.2275 (3)	0.5946 (7)	0.0041 (1)	-	-	0.0351 (26)	Benzyl acetate is also used as a solvent in plastics and resin, cellulose acetate, nitrate, oils, lacquers, polishes and inks.
Amberonne (isomer 2)	907 (2)	0.9544 (10)	0.8013 (17)	0.0469 (51)	-	0.1625 (56)	0.0564 (23)	It is a synthetic woody odorant and is used as a fragrance ingredient in perfumes, laundry products and cosmetics
Phenanthrene	939 (2)	0.8331 (6)	0.9969 (13)	0.0606 (24)	0.0846 (48)	0.0538 (18)	0.0443 (17)	Used to make dyes, plastics and pesticides, explosives and drugs.
a-Terpineol	724 (3)	0.7865 (4)	2.8165 (68)	0.0164 (-)	0.1729 (3)	-	0.0241 (69)	Natural in pine oil- Has insecticide properties
Benzaldehyde, 3,4-dimethyl-	829 (3)	0.516 (15)	0.2896 (12)	0.0578 (19)	0.0147 (80)	0.0029 (95)	0.059 (26)	Natural substances, used in flavor
Benzaldehyde, 4-(1-methylethyl)-	892 (3)	0.104 (109)	0.063 (56)	0.0267 (-)	-	-	-	Naturally found in eucalyptus
Benzaldehyde, 4-hydroxy-	892 (3)	-	0.0316 (-)	-	-	-	-	Pharma uses
Benzene, 1-(1,5-dimethylhexyl)-4-methyl-	877 (3)	1.1029 (9)	0.2082 (12)	0.1748 (22)	0.1279 (10)	0.0948 (9)	0.2061 (6)	
Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis-	861 (3)	0.0368 (141)	0.0122 (14)	0.078 (39)	0.0352 (60)	0.0154 (105)	0.0175 (6)	
Benzene, 1,1'-ethylidenebis-	892 (3)	-	-	4.727 (11)	0.1636 (14)	0.1616 (11)	4.5926 (9)	
Benzene, 1,3-diethenyl-	836 (3)	0.2023 (10)	0.293 (3)	0.0079 (2)	0.0062 (7)	0.0059 (8)	0.0113 (26)	Divinylbenzene improves the high temperature strength of adhesive

Benzene, 1-methyl-2-(phenylmethyl)-	923 (2)	0.0302 (13)	0.0386 (16)	5.5461 (20)	0.1751 (11)	0.2127 (10)	4.9685 (7)	
Benzene, 1-methyl-3-(phenylmethyl)-	924 (2)	0.0171 (23)	0.0272 (22)	4.2805 (19)	0.1015 (15)	0.1468 (7)	3.895 (6)	
Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	779 (3)	0.1549 (8)	0.4658 (11)	0.0778 (20)	0.0318 (12)	0.0222 (24)	0.097 (10)	
Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester	836 (3)	0.0057 (10)	0.0816 (122)	0.0285 (61)	0.0296 (17)	0.0218 (19)	0.0071 (18)	Benzenepropanoic Acid Ester is used primarily as an antioxidant in plastics and as a thermal stabilizer.
Benzo[b]thiophene, 2,5-dimethyl-	886 (3)	0.1669 (10)	0.0673 (10)	0.0026 (70)	0.0024 (45)	0.0051 (46)	0.0041 (25)	
Benzo[b]thiophene, 3,5-dimethyl-	767 (3)	0.1938 (9)	0.1487 (8)	0.012 (22)	0.0108 (6)	0.0127 (3)	0.0133 (5)	
Benzo[ghi]fluoranthene	813 (3)	0.0006 (49)	-	-	-	0.0037 (-)	0.0007 (-)	
Benzoic acid, 2-methylpropyl ester	931 (2)	5.2659 (3)	2.9193 (6)	0.0903 (20)	0.0545 (13)	0.0478 (38)	0.0803 (24)	Flavor and fragrances
Benzoic acid, octyl ester	946 (2)	0.438 (8)	-	0.0731 (45)	0.061 (8)	0.0741 (29)	0.1021 (5)	
Benzonitrile	949 (2)	1.0781 (3)	6.5882 (18)	8.9383 (8)	0.5085 (5)	0.4341 (11)	12.7391 (12)	Is used as an intermediate for rubber chemicals and as a solvent for nitrile rubber, specialty lacquers, many resins, polymers and for many anhydrous metallic salts
Benzonitrile, 4-amino-	765 (3)	0.1207 (11)	6.0122 (29)	4.0004 (22)	0.0067 (22)	0.0024 (114)	5.765 (11)	

Butanedioic acid, dimethyl ester	949 (2)	0.2604 (5)	1.0767 (16)	0.1644 (10)	0.0725 (13)	0.0429 (26)	0.1511 (16)	It also has wide range of industrial applications such as Functional fluids (open systems), Intermediates, Paint additives and Coating additives, Pigments Solvents, Viscosity adjustors.
Caffeine	704 (3)	-	-	0.0053 (134)	-	0.0007 (-)	0.0053 (73)	Beverage, cosmetics
Caprolactam	948 (2)	9.478 (16)	-	-	0.0377 (113)	-	0.2629 (79)	Caprolactam is primarily used in the manufacture of synthetic fibers - Conventionally, caprolactam is produced by oxidizing cyclohexane, or from phenol or toluene.
Carbonic acid, hexadecyl phenyl ester	850 (3)	-	0.0939 (-)	0.8393 (-)	0.0379 (-)	0.1337 (-)	0.2207 (80)	
Carbonic acid, pentadecyl phenyl ester	736 (3)	-	0.0285 (-)	0.2435 (-)	-	-	0.0686 (-)	
Cyclopenta[g]-2-benzopyran, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl- (Galaxolide)	838 (3)	0.0449 (14)	0.0699 (16)	0.0044 (25)	0.0033 (60)	0.0028 (15)	0.0051 (17)	Synthetic musk with a clean sweet musky floral woody odor used in fragrances.
D-Carvone	846 (3)	1.0335 (7)	1.0011 (9)	0.0157 (67)	0.0348 (15)	0.0303 (12)	0.0324 (23)	Naturally occurring. Used in fragrance perfumes - Its use as a fragrance and flavor, potato sprouting inhibitor, antimicrobial agent, building block, biochemical

								environmental indicator and in medical applications
Decanal	946 (2)	2.4051 (7)	0.4702 (34)	0.1101 (95)	-	-	0.1338 (102)	Decanal occurs naturally and is used in fragrances and flavoring. Decanal occurs in nature and is an important component in citrus
Diphenylmethane	921 (2)	0.0133 (12)	0.0221 (8)	0.2925 (19)	0.0406 (15)	0.0386 (18)	0.3312 (9)	It is used in the preparation of a polymerization initiator
Ethanol, 2-(2-butoxyethoxy)-	933 (2)	42.0849 (3)	28.3079 (11)	3.6813 (12)	0.7277 (13)	0.5155 (18)	5.4038 (12)	It is also used as a coalescing agent in latex paints; solvent for stamp pad inks; dye solvent; solvent in high baked enamels; dispersant; diluent for hydraulic
Ethanol, 2-phenoxy-	937 (2)	9.1882 (8)	2.6479 (37)	0.1414 (75)	-	-	0.2549 (13)	Phenoxyethanol is a colorless liquid with a pleasant odor. It is a glycol ether used as a perfume fixative, insect repellent, antiseptic, solvent, preservative, and also as an anesthetic in fish aquaculture.
Ethyl 3-cyanobenzoate	806 (3)	-	-	0.1611 (31)	0.0021 (84)	0.0024 (73)	0.2524 (4)	
Furan, 2-pentyl-	789 (3)	-	0.0287 (-)	-	-	-	-	It is found in many heat-processed foods and drinks. It has a role as an Aspergillus metabolite, a human urinary metabolite, a volatile oil component, an insect repellent, a flavoring agent, a

								plant growth stimulator and a bacterial metabolite.
Heptanal	826 (3)	0.1181 (-)	-	-	-	-	-	Precursor to components in perfumes and lubricants - can be found in essential oils naturally
Indane	854 (3)	0.2 (14)	0.2707 (42)	0.0152 (87)	-	-	0.0338 (29)	
Indene	913 (2)	0.0471 (9)	0.2753 (15)	0.0302 (26)	-	-	0.0556 (58)	The principal industrial use of indene is in the production of indene/coumarone thermoplastic resins - Natural product
Isoborneol	718 (3)	0.3354 (5)	0.954 (12)	0.0603 (45)	0.1507 (14)	0.1332 (28)	0.0561 (-)	Naturally occurring. Used in fragrance perfumes
Isopropyl myristate	932 (2)	-	-	-	-	-	0.3574 (-)	Used in lice/flea treatment
Linoleic acid ethyl ester	768 (3)	0.0072 (-)	-	-	-	-	-	used as lubricants and plasticizer
Methanethioamide, N,N-dimethyl-	889 (3)	-	-	-	-	0.0108 (-)	-	Pesticide/biocide
Methyl dehydroabietate	896 (3)	-	-	-	-	0.0255 (-)	-	Adhesive in food packaging
Methyl tetradecanoate	851 (3)	0.1539 (12)	0.1185 (32)	0.0073 (86)	0.0279 (41)	0.0155 (83)	0.022 (56)	Fatty acid, metabolite in plants - used in cosmetics flavoring and soaps
Naphtho[2,1-b]furan, dodecahydro-3a,6,6,9a-tetramethyl-	942 (2)	0.1268 (13)	0.0634 (20)	0.0131 (13)	0.0179 (28)	0.0173 (44)	0.0107 (27)	Flavor and fragrance

Name	RI							Description
Nonanal	934 (2)	0.1505 (58)	-	0.5873 (152)	-	-	0.5858 (88)	Occurs in naturally. Used as pesticide (mosquitoes repellent)
Octadecanamide	873 (3)	-	-	0.1418 (-)	-	-	-	It is used for the synthesis of organic chemicals and surfactants used in detergent, ore floating agent, fabric softener, anti-static agent, germicide- naturally produced
Octahydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-dione-, (5aR,10aR)	913 (2)	0.0037 (138)	0.0005 (-)	-	-	-	0.0351 (-)	
Octanal	850 (3)	-	-	-	-	-	0.1186 (-)	Naturally occurring in citrus. Used in fragrances
o-Terphenyl	848 (3)	0.0003 (2)	0.002 (115)	0.0014 (-)	-	0.0007 (55)	0.0011 (63)	Used as textile dye carrier and intermediates for lubricants
Pentanoic acid	899 (3)	0.0555 (-)	-	0.0498 (-)	0.1095 (32)	0.2619 (61)	1.3877 (18)	Used in the synthesis of esters- naturally produced by fungi in rotting wood
Phenol	969 (2)	1.2983 (5)	2.2583 (55)	8.5048 (11)	1.6 (21)	1.2116 (6)	11.275 (15)	Manufacture of nylon and other synthetic fibers. Also used to kill bacteria/fungi
Phenol, 2-methyl-	945 (2)	-	0.1464 (103)	-	-	-	0.0026 (-)	Used as a precursor for other compounds
Phosphine oxide, methyldiphenyl-	861 (3)	-	-	-	-	0.0008 (-)	-	
Phthalic acid, decyl nonyl ester	845 (3)	-	0.4917 (13)	-	-	0.0102 (59)	-	Plasticizer

Piperonal	909 (2)	0.1968 (13)	0.0529 (23)	0.0137 (132)	0.0028 (50)	-	0.0079 (7)	Naturally present in plants (dill vanilla, violet flowers, and black pepper). Used in fragrances
Quinoline, 1,2-dihydro-2,2,4-trimethyl-	876 (3)	0.0155 (38)	0.3602 (16)	0.0192 (53)	0.0138 (14)	0.0121 (58)	0.0143 (27)	
Sulfoximine, N-[(dimethylamino)carbonyl]-S-methyl-S-phenyl-	788 (3)	0.0018 (105)	0.0003 (69)	0.0006 (-)	-	-	-	
Terpinen-4-ol	843 (3)	-	0.2836 (9)	0.0052 (79)	0.0362 (5)	-	-	Natural, from plants
Triethyl phosphate	901 (2)	0.5012 (5)	2.4514 (12)	0.0221 (22)	0.0309 (5)	0.0332 (21)	0.0753 (64)	Flame retardant

VOC results

All six materials were also analyzed for TVOC and some specific substances, in accordance with internal Volvo standards. There are small variations between the six materials. The greats difference can be seen in TVOC (total volatile organic compounds), were material 1 and 2 show considerably higher values (around 9000 $\mu g/m^3$) compared to material 3-6 (around 3000 $\mu g/m^3$).
The results from these samplings are in accordance with what we normally measure for these kinds of materials at the lab at Volvo Cars.

Goal fulfillment

This project has laid a great foundation for further research to increase the knowledge in the field. However, when it comes to implementation in development projects it has been shown to be time consuming and expensive to carry out this kind of analysis on a regular basis. Therefore, other measures need to be taken to implement the knowledge in car development. There are different tracks on how this can be done, and this is under investigation and will be tested mostly in the Mistra SafeChem project but also in the FFI funded project 44015-1.

The project has worked towards the goal of FFI regarding Swedish technique and knowledge, by combining two fields that have not been working that much previously and by incorporating the area of bio-attributed materials. This project is also knowledge building in the understanding of exposures from materials of different grades. By publishing data of this kind, we are to our knowledge first.
We have also been addressing the program goal of Environmental and health effects, by looking at emission profiles from different materials and investigate the possibility to further address the issue of chemicals in materials and its release to the surrounding environment. This area is still in early stages, however the speed of this field in high and it will be incorporated in the goal conflict addressed, circular economy and use of recycled materials. And this project can be used in the discussion on how to address this to further speed up the transition to circular use.

8. Publication and spread

Knowledge and Result distribution

How have the results been spread or will be spread?	Mark with X	Comment
Increased knowledge in the area	X	Increased knowledge both in the area of methods and how the emission patterns from selected surface materials look
Results to be moved to other advanced technical development projects.	X	The results from this project will be used both in the FFI funded project 44015-1 and in Mistra SafeChem (se information below).
Results to be moved to product development		The results show that analysis these substances are difficult and time consuming. Therefore, other measure are investigated to be used in product development
Introduction to market	N/A	
To be used in investigations /regulation/ permit matters / political decisions		The research is of basic character.

The connects to the other research projects will give the results a greater take out. We will also continue internally to work with the results gather to implement it in product development and the understanding of the shift from virgin materials to bio-attributed materials.

Publications

The results obtained in this project will be published in scientific peer-reviewed journal. Name of the different materials will not be included but rather listed as Material 1, Material 2…and with a short description of the material specifications.

9. Conclusion and further work

This project established sampling techniques for microchamber emissions and analytical methods for future work on single material when analyzing SVOC's.

The results showed that the suppliers and also the type of material (laminated or unlaminated) can influence the emissions, even if the six materials have very similar bio-attributes. It is also important to keep in mind that unexpected chemicals can be present in these types of materials, since the materials are based on natural sources (e.g. pine oil in this case). Indeed, chemicals that can occur in nature were detected alongside with insect repellents. The presence of such chemicals can be related to agricultural areas, where pesticides and other insect repellents are spread (atmospheric depositions/transportation). This project is one of the first steps in the investigation of emission from more natural and sustainable sources towards a transition from petroleum-based materials to bio-attributed materials. However, it is clear that further studies are needed to investigate and conclude how to address unexpected chemicals, especially the anthropogenic compounds (e.g. biocides that could be used in agriculture and spread in the environment) for future uses in car interiors.

Volvo and Polestar will also use the results internally to further address how to work with bio-attributed materials and use the knowledge to continue the discussion regarding trace levels of substances in materials. This will also be addressed in the light for circular use of materials.

As written in the application these results will be taken into consideration in the FFI funded project 44015-1. By further looking into the substances found in the complete vehicle and compare that to the material testing carried out here. Along with that the results will be used in a case study in the Mistra SafeChem project where there is focus on chemical content in the surface materials tested and an making a toxicology focused LCA (Life cycle assessment) to be able to rank the chemicals that need substitution.

10. Partners and Contactpersons

Partner	Contact person	Email address
Umeå University	Patrik Andersson	Patrik.andersson@umu.se
Polestar	Henrik Edman	Henrik.edman@polestar.com
Volvo Cars	Maria Bernander	Maria.bernadner@volvocars.com

From each of the partners several persons have been involved. Besides the contact persons, at Umeå University Christine Gallampois have been responsible for the analysis and results. At Polestar Lisa Bolin have been involved in discussions regarding the project and at Volvo Cars, Hanna Sundqvist and Annelie Synnerdahl have been responsible for sampling and VOC analysis, Jeffrey Phan for planning and discussion and there has also been involvement from persons at the surface material group, mainly Farshad Toomadj, when deciding on materials and discussion regarding them. All in all, the project was led by Volvo Cars and Maria Bernander and the equality in the project was 40% men and 60% women.

11.   References

Abafe and Martincigh,. Chemosphere 230, (2019) 239–247

Albar *et al.* Microchemical Journal, 132 (2017) 227-232

Ali *et al.* Science of the Total Environment, 569–570 (2016) 269–277

Berthold *et al*. 2009. KNIME – The Konstanz Information Miner: Version 2.0 and beyond. SIGKDD Explor. Newsl. 11(1) (2009) 26-31

Bidleman *et al*. Chemosphere 159, (2016) 126-131

Biliterwski and Grundmann. RISKCYCLE Conference-Risk-Based Management of Chemicals and Products in a Circular Economy at Global Scale, Dresden, 8–9. 5. 2012, Conference proceedings (2012)

Björnsdotter *et al*. Environ. Int. 112, (2018) 59–67.

Bourguinon and Parent. Current Opinion in Pediatrics, 22 (2010) 470-7

Braun, Nature Reviews Endocrinology, Nov. 18 (2016),

Canbaz *et al*. Indoor Air, 26 (2016) 403-413

Egeghy *et al.* Environment Health Perspectives, 124 (2016) 697-702

Gevao *et al.* Indoor and Built Environment, 25 (2016) 106-113

Harrad *et al.* Chemosphere, 146 (2016) 346-353

Holmgren *et al.* Science of the Total Environment, 437 (2012) 306-314

Huang *et al.* Science of the Total Environment, 574 (2017) 1182-1208

Ionas *et al*. Environment International, 65 (2014) 54-62

ISO 12219-3:2012

ISO 16000 6:2011

Jantunen *et al.* Environ. Sci. Technol 49 (23), (2015)13844-13852

Khalil *et al*. Current Opinion in Pharmacology, 19 (2014) 120-124

Klepeis, *et al.* 2001. J. Eposure Sci. Environ. Epidemiol. 11 (3), (2001) 231–252.

Legler *et al.* Journal of Clinical Endocrinology & Metabolism, 100 (2015) 1278-1288

Lexén *et al.* Environ Int 157, (2021) 106847

Lucattini *et al.* Chemosphere, 201 (2018) 466-482

Matz *et al*., Air Qual. Atmos. Health 11 (2), (2018) 209–220

Mercier *et al.* Environmental Science and Technology, 45 (2011) 6716-6727

NIST 2020, National Institute of Standards and Technology, Gaithersburg, MD, USA

van Mourik *et al.* Environmental Science and Technology, 50 (2016) 7752-7760

Schymanski *et al.* Environ. Sci. Technol. 48 (4), (2014) 2097-2098

Trasande *et al.* Andrology, 4 (2016) 565-572

Weschler *et al.* Environment Health Perspectives, 123 (2015), 928.−934.

WHO (2012), http://www.who.int/ceh/publications/endocrine/en/

Wu *et al.* Building and Environment, 95 (2016) 126-132

VDA 276

Xu *et al.* Environmental Science and Technology, 46 (2012) 12534-12541

Xu *et al.* Chemosphere, 155 (2016) 415-428

Zhang *et al.* Environmental Science and Technology, 49 (2015) 10099-10107

Zheng *et al.* Environmental Science and Technology, 53 (2019) 6341-6351