



**Ministry of Environment  
and Food of Denmark**  
Environmental  
Protection Agency

# **Risk assessment of hazardous substances in the indoor environment of cars - a pilot study**

Survey of chemical  
substances in consum-  
er products No. 154

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Sources must be acknowledged.

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# Introduction

This project is part of the Danish EPA's efforts with regard to focusing on consumers' exposure to hazardous chemical substances. In this project, it has been requested to perform a risk assessment of the volatile chemical substances released from car interiors into the car's indoor climate. The basis for the assessment is available literature data and thus, no sampling and chemical analysis has been performed. On this background, the project should be seen as a pilot project for possible further focus and work in the area.

The project has been performed from March 2016 to July 2016 in cooperation between DHI and the Danish Technological Institute.

The project was surveyed by a steering group with the following members:

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# Summary and conclusion

The objective of this project is to get an overview of whether the levels of VOCs in new/ newer cars can pose a health risk. The project is focusing solely on the emission from the interior parts of the cabin, as the indoor air quality affected by external contaminants such as ventilation air containing exhaust residues of fuel and substances evaporated from the fuel system of the car, are not covered by the project.

The interior parts of the car cabin consist of many synthetic materials, which may emit different chemical compounds. The contribution from each material to the concentration in the car's indoor climate depends on the surface area of the material, and whether the surface is covered by other materials.

## *Survey of previous studies of VOCs in cars*

The literature search in this project was targeted peer-reviewed studies that describe the measurements and results of volatile organic compounds (VOCs) in the indoor air of new cars. A broader search on the Internet has been conducted and also the international networks of the project group have also been approached to get access to additional available and non-public information.

The studies selected for inclusion in the survey all had to contain well-described measuring methods considered reliable for its purpose and data should be reported as numerical values. Further focus was on the results of recent studies in the light of the ongoing development and use of materials in car cabins.

Thus, the survey resulted in data from studies from several car manufacturing countries: Poland, Germany, Italy, China, Japan, Taiwan and the United States. Most studies covered middle class cars and VOC content in the cabin, however, car brand or country of production were in many cases not specified.

Most measurements were conducted in cars with doors and windows closed at ambient temperature when parked in the shade, or at elevated temperatures when parked in the sun.

At elevated temperatures of 35 °C, a Chinese study measured 2-3 times higher concentration of VOCs and aldehydes compared to measurement at 24 °C in the car cabin. Furthermore, four studies were found that have measured the emission at 60-65 °C, corresponding to a heated car parked in the sun.

The measurement results of the emissions are listed in Tables 2 - 6 in Chapter 2. As the tables include summaries of the measuring data, only the quantitatively most significant emission components for each substance groups are included.

From the tables it appears that hydrocarbons (aliphatic, alicyclic and aromatic hydrocarbons) with 6-12 carbon atoms are emitted to the greatest extent. Additionally, there are relatively large emissions of aldehydes, ketones, alcohols (including phenol) as well as substances such as methylpyrrolidone, and caprolactam.

However, it can be difficult to make comparisons of the emission levels found in the individual studies, as the cars are different, and different conditions for the measurements are often used. Nevertheless, it is estimated that the total sets of measurements give a good overall indication of the VOCs typically emitted from the interior parts in car cabins.

The specific type of inventory in the car of course plays a major role, and particularly high emission levels were measured in luxury cars with leather upholstery.

It is important to note that there are no recommended or official limit values in the EU regarding emissions in new cars. However, guideline emission values from the automotive industry in China and Japan were found.

#### *Identification of harmful substances*

For making a human health screening of the emitted substances the substances were evaluated partly from their health classification (the EU-harmonised classifications of the substances) and partly from the relevant tolerable exposure levels established for emissions to indoor air. The latter is obtained partly from the EU working group on establishment of tolerable emission concentrations of indoor air (so-called LCI values, Lowest Concentration of Interest) and partly from two recent Danish EPA's reports on assessments of emitted substances from rugs, building materials, interior and toys in children's rooms.

By combining the knowledge of the measured emission levels, the classification of the substances (indicating adverse health effects caused by the substances) and tolerable exposure levels for the substances, the most critical emission components may be identified.

From the listing of the substances found in the literature it can be seen that a large proportion of the substances and groups of substances that evaporate are eye and respiratory tract irritants. This applies e.g. a variety of aldehyde and ketones and to phenol, methylpyrrolidone and caprolactam. Other groups of substances that evaporate in significant quantities are the aliphatic and aromatic hydrocarbons, where primarily the chronic neurotoxic effects of the substances are in focus and of importance for the setting of tolerable exposure levels.

Some of the substances are also classified as carcinogenic. This applies to benzene, naphthalene, formaldehyde and acetaldehyde.

Thus from the human health screening based on human health classification and tolerable exposure levels of the substances the following emission components can be regarded as the most critical components in relation to human health:

- Benzene (carcinogenic)
- Naphthalene (carcinogenic, eye/respiratory irritation)
- Formaldehyde (carcinogenic, eye/respiratory irritation)
- Acrolein (eye/respiratory irritation, tissue damage caused by long-term exposure)
- Crotonaldehyde (eye/respiratory irritation)
- Phenol (eye/respiratory irritation)

#### *Exposure scenarios*

For assessing whether the emissions may exceed the tolerable exposure levels, two user scenarios were set up representing realistic worst-case exposure to the substances:

Scenario 1 (short stay in a hot car):

Entering a hot car placed in the sun, and subsequent brief (maximum 2 minutes) exposure to peak concentrations in the cabin, before venting the cabin:

For assessment of this scenario, emission values measured at 60 to 65 °C found in the literature are used.

### Scenario 2 (daily commuting)

Transport in the car 2 x 1 hour a day at a temperature of 20 °C with windows and ventilation closed, and with an airflow in the cabin of an average of 2 times per hour as a result of the passive venting due to negative pressure inside the car while driving. For assessment of this scenario, emission values measured at approximately 20 - 30 °C found in the literature are used. These values are used even though measurements performed at 30 °C may overestimate the emissions at a cabin temperature of 20 °C.

For each of the two exposure scenarios, the most adequate data in the literature are found for estimating/ calculating the exposure levels of the individual substances. In scenario 2, the concentration built up in the car before entering was found to be of greatest significance for the total exposure over the 2 x 1 hour, as only relatively small amounts will evaporate during the drive for one hour. Rough calculations showed that the average exposure level during one hour corresponded approximately to 50 % of the concentration level when entering the car.

### *Risk assessment*

For both exposure scenarios, the estimated/ calculated exposure levels are compared with the tolerable exposure levels. For a cumulative risk assessment, it is assumed that all relevant substances identified in one or more studies in the literature can be found simultaneously in the emission.

In scenario 1, especially substances that may cause acute effects, such as respiratory tract and eye irritation, are critical, as these effects are often most dependent on the actual concentrations in the air rather than the total exposure over time. For scenario 1, exceedance of the tolerable exposure levels of aldehydes (acrolein and crotonaldehyde) and phenol was found, indicating a risk of short-term discomfort due to eye and respiratory tract irritation in this scenario.

For scenario 2, representing daily commuting in the car for 2 x 1 hours with closed ventilation system and windows, evaporation of aldehydes is also considered to be critical, as the tolerable exposure level regarding long-term exposure to acrolein may be exceeded, indicating the potential for adverse effects on the respiratory system. Phenol is not included in the assessment for this scenario, as no data are available on emission of this substance at lower temperatures.

The assessments have to be interpreted in the context of the circumstances and assumptions made and considering the uncertainties with regard to the exposure estimation.

In scenario 1 the exposure of 2 minutes' duration is compared with tolerable exposure levels applicable to exposure for 24 hours. It is uncertain whether irritation effects will actually occur during 2 minutes of exceedance of this level.

Scenario 2 is considered as a worst-case scenario because of the anticipated very low airflow in a car while driving. Typically, the exposure levels during a normal drive will be significantly lower as a certain air exchange in the cabin will often be required to prevent fog on windows or to obtain fresh breathing air in the cabin.

### *Perspective*

The focus of this project has been on VOCs, and therefore no systematic search for data has been made for other compounds that may be emitted from the cabin material (e.g. certain flame retardants, nitrosamines, biocides (e.g. chlorpyrifos, diazinon, fenobucarb) or other types of SVOCs, which may be difficult substances to analyse/ identify by means of the used methods.

Also the content of SVOCs in the dust of the indoor air of the car are not considered..



The literature identified a number of studies of VOCs in cars from Japan, China and Poland, but not from major car producing countries such as France, Germany and the United States. The most comprehensive and complete information on VOC analyses is found in recent studies from Poland. Only a few studies (from Japan and China) include measurements on formaldehyde, and a single study from China includes measurements on acrolein.

Thus, there are several limitations in the gathered knowledge of emission from car interiors in this project -both in terms of type and number of individual substances measured for, and in terms of car brands relevant for the Danish market. In the present study, we have conducted a thorough literature search and obtained knowledge from the international contacts of the project group members. Therefore, the limitations of the knowledge obtained are probably due to confidentiality and the lack of public access to the results from tests of car interiors in general.

So overall, there seems to be a lack of more systematic knowledge on the emission of VOCs and SVOCs from the interiors of new cars, also covering car brands typical for the Danish market. It is proposed that any further studies must therefore include measuring of aldehydes, VOCs, SVOCs and selected substances of particular concern e.g. formaldehyde, acrolein, crotonaldehyde and phenol, and also including measurements of the chemical content in dust/particles.

Relatively large uncertainties pertain to the development of exposure scenarios for emitted substances into the indoor air of cars, and no specific studies were found investigating the driver's/ passenger's exposure to the emitted compounds from a new car for specific user scenarios.

More precise knowledge of the driver's exposure to different use scenarios could be achieved by using portable measurement devices as data from such measurements would provide the best basis for a proper risk assessment of a person.

# 1. Introduction

## 1.1 Background

The indoor air of cars can be an important source of human exposure. In a study from California, it is assumed that the population daily spends 6-8 % of their time during transport in their cars (Klepies et al., 2001). The literature shows that a large number of volatile organic compounds (VOCs) are released from the interior, particularly in new cars (Yoshida and Matsunaga, 2006a; Yoshida et al., 2006c; Faber et al. 2014; Brodzik et al., 2014). The emission is assumed to come especially from the parts of the car interior consisting of synthetic panels, rubber, synthetic fabrics, rugs, and from applied adhesive and joints.

There is relatively limited knowledge of the health significance of emission from these materials, but studies have shown that the concentration of various organic chemicals can be up to 3 times higher compared to other indoor environments.

## 1.2 Objective

The objective of this project is to get an overview of whether the levels of VOCs in new/ newer cars can pose a health risk to the user. This project focuses solely on the emission from the interior, as the indoor air quality levels in the cabin, caused by external contaminants such as ventilation air containing exhaust residues of fuel and substances from the fuel system, are not covered by the project.

## 1.3 Performance of study

The project is based on literature search and the hereby-obtained data in the area, and is to be considered as a pilot project.

The project and its elements are described in the following chapters with the following content:

### *2 Survey of emission to indoor air of cars*

- Knowledge of materials in new cars and existing measurements of VOCs in new cars. Evaluation of the validity of the analytical results for further assessment.

### *3 Identification of harmful substances and description of exposure scenarios*

- Selection/ identification of VOCs based on their hazardous effects (classification) and knowledge concerning their critical/ tolerable exposure levels.
- Description/ derivation of exposure scenarios for drivers/ passengers.

### *4 Exposure estimation and risk assessment*

- Estimation/ calculation of the exposure levels for the derived exposure scenarios.
- Risk assessment of the exposure scenarios for the selected VOCs.

### *5 Discussion*

- Conclusions and uncertainties.
- Need for further data.

## 1.4 Abbreviations

The following abbreviations are used several times in this report and are presented here for reasons of clarity.

AC	Air Condition
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
BTX	Benzene, Toluene, Xylenes
FID	Flame Ionization Detector
GC	Gas chromatography
LCI	Lowest Concentration of Interest
MS	Mass Spectrometry
RCR	Risc Characterisation Ratio
SVOC	Semi Volatile Organic Compounds
SUV	Sport Utility Vehicle
TD	Thermal Desorption
TVOC	Total Volatile Organic Compounds
Xylenes	Sum af <i>ortho</i> -, <i>meta</i> - and <i>para</i> - xylenes ( <i>o</i> -xylene + <i>m</i> -xylene + <i>p</i> -xylene)
VOC	Volatile Organic Compounds
VVOC	Very Volatile Organic Compounds

## 2. Survey of emission to the indoor air of cars

### 2.1 Method for retrieval of literature

In order to identify the existing knowledge of emission from materials in car cabins, literature search in a variety of knowledge databases has been made as well as retrieval of information from the international network of the project group.

The car cabin is composed of many synthetic materials, which emit different chemical compounds, and the contribution of each material to the concentration in the car's indoor air depends on the surface area in the cabin and whether it has surface directly to the cabin, or it is covered by other materials. Car manufacturers often use their own testing procedures of emission from the materials inside the car. These can be divided into three main types: small material samples, complete (more complex) parts, and the cabin as such of the finished car (Brodzik et al., 2014). The literature search in this project is targeted studies describing the measuring of volatile organic compounds (VOCs) in the cabins of finished cars, as this type of data is more directly applicable for making exposure scenarios.

The literature search was carried out in a number of knowledge databases searching for Danish and foreign scientific studies. The search has primarily been directed at peer-reviewed articles, but has also included books, reports and academic and popular literature. The search has covered the knowledge databases Elsevier - Science, Google scholar, Science.gov, SciVerse Scopus, Springer Link and WorldWideScience.org that includes the world's leading research databases with the most comprehensive collections of scientific, technical and medical journals, books, articles and reference books.

The literature search is based on the following keywords: VOC, volatile organic compound, air, indoor, interior, air quality, in-vehicle, car, auto, automobile. In the cases where the search has led to many hits, the search was further focused by combining multiple keywords.

Springer Link, number of hits in the search:

Car interior air quality: 11828

Car interior air quality VOC: 254

Then, the search results (titles) are manually reviewed in order to separate relevant literature for subsequent reading.

The reference lists of the identified relevant articles and searches using the authors names were conducted to search for additional relevant literature.

Google search on Danish words (indeklima, biler, stoffer) yielded 37 600 results. The literature search in Danish resulted in some articles about emission of chemical substances in the indoor air of new cars. Politiken (2009) refers to the former Information Centre for Environment & Health (IMS), pointing out a correlation between the materials in the car cabin and the possible harmful substances that can be found, including phthalates, brominated flame retardants, nickel, chromium, scent freshener and organic solvents. In 2009-2010, the website "bil.guide.dk" four articles mentioning emission from materials in car cabins to the indoor air, and the smell of a new car may be due to harmful volatile substances. However, no concrete measured data are available for use in this study.

The test methods that are the basis for international standards such as ISO 12219-1 were developed in Germany in connection with projects carried out by e.g. TÜV and German car manufacturers (Wensing, 2016). Therefore, it was expected that the literature search would uncover articles describing results of these projects. However, no German studies were identified in the literature search, and therefore a search on Google was performed to find out whether there is any information in addition to the literature. The websites Öko-Test (oekotest.de), Verband der Automobilindustrie (vda.de) and Allgemeiner Deutscher Automobil-Club (adac.de) ADAC were also searched. German keywords were used in combination for further search on Google:

Autos Innenraumluft VOC (5450 hits)  
VOC Neuwagen (54500 hits)  
VOC Innenraum Neuwagen (5760 hits)  
Ergebnisse VOC Innenraum neue Autos (218000 hits)

Some websites were found that discuss a high emission of VOCs in new cars. Reference at several web-sites were made to a study of emission of VOCs, formaldehyde and phthalates in 6 new cars of different brands conducted by the Austrian UBA (GLOBAL 2000, 2005).

Due to lack of public available studies from the major car manufacturing countries like Germany and France, relevant people in the professional networks of the project group were contacted in order to obtain information. Through correspondence with contacts in Germany (Wensing, 2016), France (Mandin, 2016) and Poland (Faber, 2016), it was confirmed that many studies of VOC emission from new cars made by the automotive industry are treated as industrial secrets and are therefore not public available.

Furthermore, the VDA (Verband der Automobilindustrie) in Germany and the Japanese Car Association in Japan were contacted for information.

### **2.1.1 Assessment of the literature**

The Danish car importers (2016) regularly publish statistics on the sales of new cars in Denmark, from which it appears that cars from all around the world are represented. Therefore, the literature was reviewed to see if the majority of car manufacturing countries and brands were represented. A list of car manufacturing countries in the world is shown on the website of the International Organization of Motor Vehicle Manufacturers (OICA) (OICA 2015). The largest car manufacturing countries in the EU are Germany, Poland, France, Spain, Czech Republic, Slovakia and Italy. Overall, the EU produces more cars than the US, Japan and South Korea. China is the largest car manufacturing country in the world. At present, no Chinese car brands are represented on the Danish market, but it is expected that one or more brands will be introduced on the Danish market in the near future (Bil.guide.dk, 2015). Several car manufacturers in and outside the EU have factories in Poland, and considering this fact that makes Poland the second largest car manufacturer in Europe (Faber et al., 2013).

The literature found was evaluated according to the thoroughness of the description of the cars in terms of model, year, age at study, fuel type, interior, and whether additional studies and evaluations have been made of the materials used in the cabin.

The test conditions were evaluated in terms of whether the car was in passive mode, i.e. parked with the engine and ventilation turned off, or the car's ventilation or air conditioning (AC) were active or in recirculation mode or whether the engine was running. Temperature, relative humidity, location of test samples, the tightness of doors and windows, other loose material in the car that are not fixed, interior during and prior to the sampling were also included in the assessment. The sampling and analytical methods were assessed in relation to the collection medium for air samples and the quality of the analytical methods. Collection of air samples for active sampling is preferred, as these represent a well-defined period and for a defined volume of air,

and thus is more suitable for use for an exposure evaluation. Furthermore, sampling site in the car near the breathing zone of the driver or in the middle of the car is preferred.

## 2.2 Measuring volatile substances in cars

The results of the VOC measurements in the indoor air of cars depend on many factors: the age of the car, the materials in the car, tightness of the cabin (in case of leaks in the engine/fuel system petrol fumes may enter from the engine compartment into the passenger compartment, also with the engine switched off), ventilation/ air-conditioning, temperature, humidity, and the ambient conditions of the car (shade, sun). Therefore, in particular over the last 20 years, a continuous development of methods for measuring VOCs in cars has taken place at research institutions and in the industry.

An overview of standard test methods for determining VOCs, SVOCs (Semi Volatile Organic Compounds), aldehydes, phthalates, amines, nitrosamines, and organophosphate esters in car interiors has been prepared by Michael Wensing (2009) distinguishing between measuring the entire interior of the car cabin and material samples.

For several years, the German VDA (Verband der Automobilindustrie) has had internationally recognised methods for determining the emission of smell (VDA-270) and volatile substances, incl. VOCs (VDA-278) from materials and components used in cars. China has a voluntary national standard (GB/T 27630-2011) for testing the emission of selected VOCs and aldehydes from materials designed for cars. Accordingly, several car manufacturers have developed their own methods, test procedures and acceptance criteria for emission of VOCs and odour that are not public available. Examples of application of these procedures: Volvo's materials have been Oeko-Tex 100 certified, i.e. measured for emission of VOCs and odour (Bilguide, 2010), and Ford has allergy tested several models, i.e. measured for contents of allergens, some of which may be VOCs (Bilguide, 2009).

### 2.2.1 Methods and standardised conditions for measuring VOCs

The internationally harmonised standard ISO 12219-1 (2013) describes the procedure for measuring VOCs and carbonyls (incl. VVOCs; Very Volatile Organic Compounds e.g. formaldehyde) in car cabins, including the physical parameters that the car must comply with. According to the ISO standard, a new car should be tested within 28 days after production, i.e. as it leaves the assembly line. Before the test, the car must be stored and transported in a way to avoid high temperatures. A detailed description of the materials used in the cabin (trim) must be included in the test report.

The Japan Automobile Manufacturers Association (JAMA) used a similar test method since 2007, which has now been replaced by ISO 12219-1 for cars. Trucks and buses are still tested with JAMA's test method (JAMA, 2015) as the ISO method only includes cars.

According to ISO 12219-1, the car is placed in a test chamber at 23 °C and 50 % relative humidity (RH). The car is tested in three phases with doors and windows closed. The test phases used are described below:

#### *Ambient mode:*

The car is parked with the engine off and is conditioned with open doors for 1 hour and then with doors and windows closed for ambient temperature at 23 °C for at least 8 hours before sampling of the cabin air. Air samples are taken in duplicate for measuring VOCs and carbonyls (aldehydes) for the last 30 minutes of the period.

#### *Parking mode:*

The car is parked at elevated temperatures for 4 hours (heating takes place with a capacity of 400 W/m<sup>2</sup>). Air samples are taken after 3.5 hours. In the last 30 minutes of the period when the car has been in a high temperature for the longest time samples are taken in duplicate for measuring formaldehyde. The temperature is not defined, but according to Wensing (2009), temperatures of 65 °C can be achieved in the cabin. According to JAMA (2015), temperatures of 40 °C are achieved in the driver's breathing zone by both their own and the ISO test method.

#### *Driving mode:*

The car is started, and the exhaust gases are taken out of the chamber. Ventilation is set to maximum speed, or in case there is an air conditioning (AC), this will be turned on and set to 23 °C. The air is not set to recycling, but to automatic airflow (not defined). Air samples are taken in duplicate measuring VOCs and carbonyls (aldehydes), respectively, the first 30 minutes of the period.

Air samples are taken in the period where the car is conditioned at the relevant temperature. Driving mode simulates worst-case scenario for exposure to VOCs, namely at the start and driving of a car which has been parked in a hot place.

The JAMA method differs from the ISO method by the fact that no samples are collected in ambient mode until the vehicle is heated. In parking mode, air samples are collected after 4.5 hours of heating, i.e. 1 hour longer heating. In driving mode, air samples are collected in the first 15 minutes in cars with the engines running and air conditioning set to recirculate the air, i.e. no airflow in the car. In driving mode, air samples are collected for 30 minutes in trucks and for 120 minutes in buses.

## **2.2.2 Collection and analysis of organic compounds in the air**

When collecting the organic compounds in the air, different types of filters are used with specific collection media for the substances that should be analysed. Substances are collected by leading a controlled airflow through the collection medium at a controlled flow. The methods used in the identified literature are internationally recognised methods, which are described briefly in the following sections. The analyses of volatile substances have a measurement error of 15-30 % (Woolfenden, 2009) and are a combination of the uncertainties by collecting air samples, calibration with reference substances, sample preparation and analytical equipment.

Test medium for collection of VOCs is typically Tenax TA® that binds both polar and non-polar volatile organic substances, or a combination of filters with activated carbon. Volatile organic substances (VOCs, SVOCs and VVOCs) are collected on a filter with high affinity, which typically consists of graphite-carbon black (Carbograph D1) or a porous polymer of 2,6-diphenylene oxide (Tenax TA®) with subsequent analysis by thermal desorption (TD), gas chromatographic separation (GC) and flame ionisation detection with either (FID), or by mass spectrometry (MS). In addition to the identification of VOCs by retention time and reference retention time, identification of unknown substances can be made by using their mass spectra and comparison with Wiley and NIST MS databases. The substances can be quantified using pure reference substances for calibration or as toluene equivalents, where it is estimated that the substance has the same detection response factor as toluene. Standard test methods typically used for VOC measurements are VDA-278, EPA TO15 and ISO 16000-6.

Comparison of collecting media in terms of number of identified VOCs, carried out by Brodzik et al. (2014), shows that Carbograph TD1 identifies a few more VOCs than Tenax TA®.

Very volatile aldehydes as formaldehyde, acetaldehyde, propanal and butanal are VVOCs and cannot be analysed by GC-MS, so they are quantified by collection and derivatization with dinitrophenyl hydrazine (DNPH) with subsequent extraction and analysis on HPLC. Air samples are

collected on DNPH-tubes, and the aldehydes are analysed by HPLC (liquid chromatography) with UV detection. Standard test methods typically used for the collection and analysis of carbonyls (aldehydes and ketones) are VDA-277, EPA TO11A and ISO 16000-3.

ISO 12219-1 (2012) specifies that the VOCs are collected on Tenax TA® and measured by GC in accordance with ISO 16000-6, and carbonyls are collected on DNPH and measured by HPLC according to ISO 16000-3.

General Motors' test method GMW15654 (2013) provides detailed specifications for the collecting air samples and the analysis parameters for determination of VOC concentrations inside the car where the car is tested according to ISO 12219-1. Additional conditions and requirements apply for cars exported to China (HJ/T 400), Japan (JASO Z125) and South Korea (MOLIT 2013-549).

## 2.3 Studies of air quality in cars

Table 1 shows an overview of selected studies measuring VOCs etc. in car indoor air. The references are selected based on how well the methods for measuring VOCs in cars are described, cf. Chapter 2.2, and focus is on results of recent studies in the light of the continuous development and replacement of materials in car cabins over time. Most car manufacturing countries are presented: Poland (PL), Germany (DE), Italy (IT), China (CN), Japan (JP), Taiwan (TW) and the United States (US). Most references have studied middle class cars for VOC content in the cabin. Most studies do not indicate the studied car brand or model. For example, studies conducted in Poland may well have been carried out on other European car brands.

Several references have additional data for used cars, where VOCs are collected after a given mileage; these details do not appear from Table 1. All studies show that concentrations of VOCs decrease with the car's age and the number of travelled kilometers. In this study, recent data are selected for new cars for calculating the worst-case conditions of exposure to VOCs in the indoor air of new cars.

### 2.3.1 Temperature, airflow and other physical conditions

The studies are conducted either at the temperatures of the natural surroundings when parked in the shade, at ambient mode or at elevated temperatures in parking mode when parked in the sun (or lighting of lamps in a hall or chamber). Only two studies have been conducted in chambers, where the environment outside the car is controlled by regulating temperature, humidity, air velocity, airflow and supply of clean filtered air (Wensing, 2009; You et al., 2007). Several studies are performed in driving mode, but they do not address new cars and are not carried out under controlled conditions in a chamber. These studies are not relevant for the present study because VOCs (incl. combustion products, particles, etc.) from the surrounding environment are also measured. One study from Italy is included in Table 1 with data from two newer cars in which the sampling was carried out in parked cars with the windows closed and also in cars while driving with the windows closed (Geiss et al., 2009).

Emissions of VOCs from materials in car cabins are largely dependent on the airflow in the cabin and the air velocity over the materials. While driving at high speed and/ or with the car ventilation at the highest step, the airflow in the cabin is considerably higher than when driving at low speed (Wensing, 2009). Toyota's research center has published a report describing their measuring methods, and here VOCs are measured with the air conditioning system turned on and in recirculation mode as a typical user scenario by urban air pollution (Sato, 2003). ISO 12219-1 (2013) stipulates an airflow in the climate chamber of  $2 \text{ h}^{-1}$  as a minimum, but has not defined ambient air velocity. As car cabins are not completely air tight, the airflow in the car may increase with the air velocity in the surroundings. Most references have measured VOCs in a parked car in ambient mode, but have not measured the airflow in the car or the wind velocity in the surroundings.



From climate chamber measuring, You et al. (2007) found a correlation between the total concentration of volatile organic compounds (TVOC) and the airflow in the cabin as a function of the air velocity in the surroundings. When the air velocity increases from 0.1 to 0.7 m/s, the airflow rate increases from 0.15 to 0.67 h<sup>-1</sup>, whereas the TVOC concentrations decrease from 1780 to 1201 µg/m<sup>3</sup>. At 0.3 m/s, an airflow in the car of 0.41 h<sup>-1</sup> was measured with a TVOC concentration of 1201 µg/m<sup>3</sup>. The VOC measurements in one new and two used cars was performed with controlled air velocity not exceeding 0.3 m/s in the cabin, but unfortunately measuring results were only specified for 20 VOCs, found in the highest concentrations. The measurements showed that TVOC levels may vary up to about 50 % depending on the wind or air velocity in the car surroundings, and furthermore on the effect of the airflow from the car's ventilation system.

### 2.3.2 Analytical results

Although the VOC analyses are conducted by GC methods that can measure all VOCs, only selected VOCs or the 10-20 highest concentrations are typically quantified and reported, although more than 100 VOCs may be detected in new cars. Part of the analytical methods used quantifies only selected chemical substances that target specific typically aromatic hydrocarbons BTX (benzene, toluene, xylenes<sup>1</sup>) or BTEX (benzene, toluene, ethyl benzene, xylenes) and hydrocarbons in general. Only very few references indicate measured concentrations of more polar substances such as carbonyls (aldehydes and ketones), alcohols, glycols, esters, ethers, carboxylic acids, amines, nitrosamines, etc.

Several references report results exclusively in the form of figures and charts, where it is difficult to derive exact figures, so these do not appear from Table 1.

The most thorough studies with the most detailed reporting were performed by Brodzik et al. (2014), Faber et al. (2013a) and Wensing (2009) on European cars, by Yoshida et al. (2006a, 2006b, 2006c) on Japanese cars, and by Xiong et al. (2015) and Chien et al. (2007) on Chinese cars.

Although comparable VOC measurements are used in the studies in the literature, the quantified and reported VOCs vary a lot. Several report a total concentration of VOCs as TVOCs, calculated as the sum of the concentrations of individual VOCs quantified either by calibration curves with reference substances or as toluene equivalents. However, according to ISO 16000-6, TVOCs are calculated as toluene equivalents of the total area of the chromatogram between n-hexane and n-hexadecane, i.e. if there is an accumulation of peaks to a large continuous peaks this cannot be separated chromatographically ("cluster") and will be included in the ISO 16000-6 TVOC, but not as a sum of individual substances. Therefore, it is difficult to compare the TVOC values of different studies.

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<sup>1</sup> Xylenes: Sum of *ortho*-, *meta*- and *para*- xylenes (*o*-xylene + *m*-xylene + *p*-xylene)

**Table 1** Result of literature studies measuring volatile substances including VOCs in car cabins

Cars	Country <sup>1</sup>	Age	Year	Mat <sup>2</sup>	Conditions <sup>3</sup>	Temperature <sup>4</sup>	Collection medium	Method	Findings of VOC	Reference
9	PL	1 day	2012	OK	Outside, ambient	21-25°C	Tenax TA; Carbo-graph 1TD	TD-GC/FID&MS	Total > 260 VOC; 107 VOC all cars	Brodzik et al. (2014)
9	PL	< 1 month	Before 2013	OK	Outside, ambient	18,9-23,8°C	Tenax TA; Carbo-graph 1TD	TD-GC/FID&MS	Total 228 hhv. 200; 105 VOC all cars	Faber et al. (2014)
5	PL	< 1 month	2012	OK	Inside, ambient	20-26°C	Carbograph 1TD	TD-GC/FID&MS	18 VOC <sup>T</sup> and top-10 VOC identified	Faber et al. (2013)
10	PL	< 1 week	Before 2013	OK	Outside, ambient	15°C (middel)	Carbograph 1TD	TD-GC/FID&MS	Benzene, toluene, Xylenes (BTX) <sup>T</sup>	Faber et al. (2013)
4	PL	New	Before 2012	OK	Outside, ambient	25°C	Tenax TA; Carbograph 1TD; Tenax GR/Carbopack B; Carbopack B/C/Carbosieve SIII	TD-GC/FID&MS	144-192 identified VOC (figuree data) and TVOC (table)	Golda-Kopec et al. (2012)
23	IT	2 newer (<1 year)	2007	N	Outside and inside, ambient, parking, driving	Variierer	Radiello passive sampler (VOC, carbonyls, respectively)	TD-GC/FID (HPLC)	16 VOC <sup>T</sup> ; phthalates; aldehydes	Geiss et al. (2009)
1	JP	1 day; (to 3 years)	1999; (2002)	N	Outside, ambient	30-35°C	Active carbon (JUMBO) and Tenax TA/PU DNPB (carbonyls VVOC)	GC/ MS of extract	162 VOC, SVOC and formaldehyde	Yoshida (2006a)
101	JP	< 3 years	2004	N	Outside, ambient	19-35°C	Active carbon (JUMBO) and Tenax TA/PU DNPB (carbonyls VVOC)	GC/ MS of extract	Median-value 101 used cars; VOC	Yoshida (2006b)
101	JP	< 3 years	2004	N	Outside, ambient	19-35°C	Active kul (JUMBO) and Tenax TA/PU DNPB (carbonyls VVOC)	GC/ MS of extract	Median-value 101 used cars; VOC	Yoshida (2006c)
4	TW	< 4 months	2004	OK	Outside, ambient,	25-32°C <sup>3</sup>	Carbotrap 300 (multibed)	TD-GC/FID	12 VOC <sup>T</sup>	Chien (2007)

Cars	Country <sup>1</sup>	Age	Year	Mat <sup>2</sup>	m/u AC		Collection medium	Method	Finds of VOC	Reference
					Conditions <sup>3</sup>	Temperature <sup>4</sup>				
37	CN	1 newer (1,5 months)	2009	Non-leather	Outside, ambient	35°C (1 ny <1,5 md)	Tenax TA	TD-GC/FID	7 VOC <sup>T</sup> ; TVOC	Chen et al. (2014)
3	CN	1 new; 2 used	2007	OK	Chamber, ambient	25°C	Tenax TA	TD-GC/MS	Top 20 VOC; TVOC	You et al. (2007)
3	CN	< 1 month	Before 2015	N	Outside, ambient	24/29/35°C	Tenax TA (other: DNPH)	TD-GC/MS (HPLC)	5 VOC <sup>T</sup> ; 3 aldehydes	Xiong et al. (2015)
2	DE	1 new (<1 month) and 1 (3 years)	Before 2007	N	Chamber, parking	65°C	Tenax TA and diethyl ether (other: DNPH)	TD-GC/FID&MS (HPLC)	47 VOC; 6 aldehydes with 1-4 carbon (C1-C4) – i new car	Buters et al. (2007)
6	DE	New; 20, 40 days, respectively	Before 1996	N	Chamber, parking	65°C	Tenax TA (others: DNPH; Florisil; Silica; Thermo-sorb)	TD-GC/MS (others: GC and HPLC)	Median-value 6 new cars; VOC, aldehydes, phthalates, amines, nitrosamines	Wensing (2009)
6	AT	New	2005	N	Outside, parking, with and without sun	Sun 60°C; Shade N	NA (UBA Wien)	NA (UBA Wien)	Sum VOC Sun: Formaldehyde; phthalate (DEHP)	GLOBAL 2000 (2005)
2	US	< 6 months; 1 used	2003	N	Outside, parking, with sun	Sun 63°C	Anasorb CMS/GCB1/TenaxGR	TD-GC/MS	Top 10 VOC and TVOC	Fedoruk et al. (2003)

<sup>1</sup>Country where the study is performed, two-digit country code. Car brands from other countries may also be produced in this country. PL – Poland; IT – Italy, JP – Japan, TW – Taiwan; CN, China, DE – Germany; AT- Austria; US – USA. N – Not given

<sup>2</sup>Cabin material information

<sup>3</sup>Ambient: Parked with the engine off. Is conditioned with doors and windows closed to ambient temperature before sampling. Sampling is carried out near the driver's breathing zone above the steering wheel or in the middle of the car cabin. Parking: Same conditions as ambient, but with measuring at elevated temperatures. <sup>4</sup>Temperature during sampling with closed air-conditioning (AC).

<sup>†</sup>Targeted analysis, i.e. only analysed for selected substances.

Abbreviations: AC - air conditioning; N – Not given, OK – described

## 2.4 Emission of VOCs

The results from the literature studies are grouped by the actual conditions under which the tests were conducted, approximated ISO's definitions when parking (parking mode), respectively ambient temperatures (ambient mode).

### 2.4.1 Results for parking mode, high temperature

There are 4 studies of VOC emission at high temperatures of about 60-65 °C, corresponding to the temperatures reached in cars parked in the sun (Wensing (2009), Buters et al. (2007), Fedoruk et al. (2003) and Global 2000 (2005)). Table 2 shows a summary. Annex 1 shows more detailed information on specifications of VOCs found in the measurements.

**Table 2** Overview of measured VOCs in new cars at about 60-65 °C (parking mode)

Substance name	CAS-no.	Wensing	Buters	Fedoruk et	Fedoruk et	Global
		(2009)	(2007)	al. (2003)	al. (2003)	(2005)
		6 cars (Median)	New car <sup>1</sup> )	Chevrolet Lumina	Ford Taurus	3 cars
		(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )
Benzene	71-43-2	24	NA	NA	NA	NA
Toluene	108-88-3	275	84,3	NA	239	NA
Ethylbenzene	100-41-4	434	306,4	NA	NA	NA
Xylenes (o,m,p isomers)	-	272	2450,5	NA	NA	NA
Styrene	100-42-5	NA	83,4	264	94	NA
Other aromatic hydrocarbons	-	NA	1945	NA	NA	NA
Aliphatic hydrocarbons	-	NA	3435	1775	98	NA
Aldehydes (VVOC,VOC)	-	199	348	NA	47	250-350
Ketones	-	840	139	NA	NA	NA
Acetone (VVOC keton)	67-64-1	361	238,6	NA	NA	NA
Ethanol (VVOC)	64-17-5	NA	299,6	NA	NA	NA
Phenol	108-95-2	NA	NA	194	124	NA
Esters	-	129	NA	NA	NA	NA
Ethers	-	75	NA	NA	NA	NA
<b>Sum VOC</b>	-	<b>3828</b>	<b>10929</b>	<b>5673</b>	<b>1999</b>	<b>9400</b>

<sup>1</sup>Result of analyses of air samples collected on the media Carbotrap (VOC) and DNPH (carbonyls).

NA: Not analysed

Wensing (2009) measures both VOCs, SVOC phthalates, carbonyls (VVOC aldehydes) and amines in 6 new cars, and the average values of the measurements from these cars are shown in Table 2. Wensing finds that the concentrations decrease the longer the car is stationary after 20 and 40 days, respectively.

In a study by Buters et al. (2007), sampling was conducted from a new car (< 1 month) and a used car (about 3 years) with an airflow of 0.75 m<sup>3</sup>/h at 65 °C, where the purity of the air supply was ensured by filtration through activated carbon and moistening to 50 % RH. Doors and windows were closed and there was internal ventilation in the car to ensure a continuous emission from the interior. Two types of sampling were performed. Direct collection of volatile substances, VOCs on Carbotrap tubes, and carbonyls/lower aldehydes on DNPH tubes. Collecting through four freeze traps, the first being empty in order to remove the water in the air, the next two contained diethyl ether to extract airborne substances, and the latter was empty for catch-

ing remains of evaporated liquids. All liquids in the freeze traps were extracted with diethyl ether, which was then dried over sodium sulfate and evaporated to dryness. This provided extracts used for toxicity testing referred to later in this report in Section 3.1.2. For the collected VOCs, there is no difference between the direct and the diethyl ether sampling, but for several polar substances, including methylpyrrolidone, aldehydes (formaldehyde, acetaldehyde, propanal, butanal, butenal (crotonaldehyde) and others, these cannot be detected in the ether extract. Appendix 1 shows detailed comparison of the results. As the polar substances may also cause toxic effects, and as they are not recovered in the ether extract, questions can be raised to the result of the screenings of toxicity with respect to the impact of these substances.

Fedoruk et al. (2003) performed measurements on two relatively new cars at elevated temperatures and found differences between the 10 VOCs emitted at the highest concentrations. Unfortunately, only the concentrations for the 10 VOCs are reported and not for the rest of the VOCs that emit in lower concentrations; therefore it is difficult to compare the substance groups quantitatively.

Global 2000 (2005) published a summary of emission data on four cars parked in the sun and in the shade. TVOC, phthalates and formaldehyde was measured from sampling at approximately 60 °C. There was no specification of test methods or details of the individual identified VOCs, but since it is the Environmental Protection Agency in Austria (UBA Wien), that made the measurements, the figures are considered trustworthy, and are included in Table 2.

#### **2.4.2 Results for parking, ambient mode**

The studies performed in China and Taiwan are conducted at temperatures of about 25-35 °C, but only with selected VOCs and aldehydes (Table 3). On the same cars, Xiong et al. (2015) measured the emitted levels of benzene, toluene, ethylbenzene, xylene (BTEX), and styrene to be about 2-3 times higher at 35 °C than at 24 °C, which is consistent with the fact that the vapour pressure of the volatile substances increases at elevated temperatures.

The studies performed in Poland are conducted at lower temperatures (15-26 °C) than the Chinese and Taiwanese studies, but with corresponding analytical methods. The studies conducted by Brodzik et al. (2014), Faber et al. (2014), and Yoshida (2006a) report more than 100 identified VOCs at 21-25 °C and 25-35 °C, respectively. In the Tables 3 and 4 the results are separated in various subgroups in order to better compare the measured levels. Due to the findings of the many isomers of hydrocarbons, grouping is made into aliphatic and aromatic hydrocarbons and cycloalkanes.

**Table 3** Overview of measured VOCs in new cars in China and Taiwan at about 24-35 ° C (ambient mode, parked with the engine off)

	Study	Xiong et al (2015)	Xiong et al (2015)	Chen (2014)	Yoshida (2006a)	Yoshida (2006c)	You (2007)	Chien (2007)	Chien (2007)	Chien (2007)	Chien (2007)
	Test	3 cars	3 cars	1 taxi	Nissan Serena	50 cars <sup>4</sup>	1 car	3 SUV (leather)	3 SUV (tex- tile)	3 Sedan (leather)	3 Sedan (textile)
	Temp.	24°C	35°C	35°C	30°C	32°C	25°C	30,9°C	30,9°C	30,7°C	30,7°C
	Rel.Hum			71%RH	60% RH	45% RH	50% RH	43%RH	43%RH	53%RH	53%RH
<b>Measured VOCs</b>	<b>CAS-no.</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>	<b>(µg/m<sup>3</sup>)</b>
Benzene	71-43-2	5.7	14.7	129	6.3	2.8 (0.9-53)	NR	NA	NA	NA	NA
Toluene	108-88-3	70.4	161	309	225.8	40 (12-368)	82	6300	2000	300	2100
Ethylbenzene	100-41-4	9.0	17.5	116	360.9	12 (2.8-62)	NR	77	34	130	1600
Xylenes (sum)	106-42-3	118	189	284	4003	31 (7.2-246)	NR	239	103	NA	13400
Styrene	100-42-5	4.3	14.33	39.5	73.6	11 (1.1-675)	NR	270	150	18	5400
Naphthalene	91-20-3	NA	NA	NA	-	2.2 (0.5-25)	NR				
Arom. hydrocarbons	-	NA	NA	NR	5947	698	NR	792 <sup>1</sup>	195 <sup>1</sup>	185 <sup>1</sup>	1440 <sup>1</sup>
Aliph. hydrocarbons	-	NA	NA	83.1	6012	63	2010	88 <sup>2</sup>	440 <sup>2</sup>	110 <sup>2</sup>	265 <sup>2</sup>
Cycloalkanes	-	NA	NA	NR	515	206	192	NA	NA	NA	NA
Carbonyls	-	NA	NA	NR	56.5	42.7	301	NA	NA	NA	NA
Esters	-	NA	NA	52.3	44.4	7.9	NR	NA	NA	NA	NA
Alcohols	-	NA	NA	NR	162.5	73	314	NA	NA	NA	NA
Terpenes	-	NA	NA	NR	9.0	3.7	200	NA	NA	NA	NA
Halogenated hydro- carbons	-	NA	NA	NR	21.7	12	242	NA	NA	NA	NA
Alkenes	-	NA	NA	NR	768	1.5	90	NA	NA	NA	NA
Sum VOC	-	NA	NA	2254	14081	1201	4950 <sup>3</sup>	NA	NA	NA	NA

Abbreviations: SUV: sport utility vehicle/larger car, NR: not reported (substance not included in the analysis), NA: not analysed

<sup>1</sup>Sum of target substances: Trimethyl benzene, 3 isomers (not total sum of aromatic hydrocarbons)

<sup>2</sup>Sum of target substances: Decane, undecane and tetradecane (not total sum of aliphatic hydrocarbons)

<sup>3</sup>Sum of all substances quantified with reference substance and toluene equivalents > 5 µg/m<sup>3</sup>.

<sup>4</sup>Median of measurements of 50 different new cars (< 1 month).

### 2.4.3 VOCs and materials

According to the literature, high concentrations of hydrocarbons are measured due to the use of synthetic materials for car interiors originating from petrochemical products. Many of the identified substances (low boiling alkanes, benzene, toluene, naphthalene, etc.) may also occur from gasoline or diesel, and therefore data with elevated concentrations of hydrocarbons should be interpreted with caution. Especially when measuring on cars which have been in use.

Most references have no information about the type of fuel used for the car, or whether the fuel tank is empty; only that the car is static/ parked with the engine and ventilation turned off. Because several VOCs also originate from fuel or oil, it is important that the tested cars are checked and that they have no leaks in neither the cabin, fuel tank, engine compartment, etc. Furthermore, it is important that data from newer cars that have been used for a short time, have no leaks, are non-smoking cars, and that materials (not part of the original interior) are removed before the VOC measuring.

Yoshida et al. (2016c) conducted VOC analyses on 101 newer Japanese cars (< 3 years), and by statistical analysis of the results, they found that luxury cars with leather upholstery (seats and steering wheel) had significantly higher concentrations of certain VOCs. This study is not included in Table 3, because these were used cars, but the same author has conducted two studies of completely new cars.

Chien et al. (2007) compared the air quality in an SUV and a sedan with leather and fabric upholstery, respectively (Table 3). The highest concentrations of BTEX were found in the SUV with leather upholstery, i.e. this study shows that the emission depends on the materials. They also measure trimethyl benzenes in the emissions that are not included in Table 3. The emission of 1,2,4-trimethyl benzene is significantly higher from an SUV with leather upholstery ( $580 \mu\text{g}/\text{m}^3$ ) than from an SUV with fabric upholstery ( $69 \mu\text{g}/\text{m}^3$ ).

Chien (2007) found that toluene and xylenes are the typical VOCs derived from acrylic, PU/isocyanate and polychloro butadiene based adhesives. Long chain alkanes (with 14 to 17 carbon atoms) were identified in the fat/ lubricants, and BHT is used as an antioxidant in the manufacture of a number of synthetic materials.

Brodzik et al. (2014) also found that the composition of VOC groups differed depending on the materials used in the car interior (Table 4).

For luxury cars, higher concentrations of VOCs in the cabins were measured. This may be due to more widespread use of leather upholstery, including upholstery on the seats and steering wheel (Janicka et al., 2014). Experience from the Danish Technological Institute emission laboratory shows that the emission from genuine leather can be high and contain a variety of substances, which probably originate from the leather surface treatment. Experience from the laboratory shows that also synthetic leather may have high emission.

Several studies examining a small number of selected VOCs found a correlation between emission of VOCs and the used materials (Faber et al., 2013a, 2013b, Golda-Kopec et al., 2012; Wang and Jia, 2013). The data, however, are usually given in illustrations without numerical values, and the discussion of the data is mostly qualitative. As analysis has not been performed for the entire VOC spectrum, and the materials are not well described, it is difficult to conclude anything based on these studies.



**Table 4** Overview of measured VOCs in new cars at about 21-25 °C (ambient mode, parked with the engine off), grouped by materials.

		<b>Brodzik (2014)</b>	<b>Brodzik (2014)</b>	<b>Brodzik (2014)</b>	<b>Brodzik (2014)</b>	<b>Brodzik (2014)</b>	<b>Faber (2014)</b>	<b>Faber (2014)</b>
Materials:		2 cars (AB) (21-25°C, 48-56%RH)	2 cars (AB) (21-25°C, 48-56%RH)	2 cars (EF) (21-25°C, 48-56%RH)	1 car H (21-25°C, 48-56%RH)	1 pieces I (21-25°C, 48-56%RH)	5 pieces M1 (21,7°C, 44%RH)	4 pieces M2 (21,7°C, 44%RH)
Seat covers:		red sTx; white sL	red sTx; white sL	black sTx; white sTx	black sTx; white sTx	black/white sTx; black sL	black/grey sTx	black suede
Dashboard:		white	white	white	white	white	grey	black
Steering wheel:		white synthetic	white synthetic	white synthetic	black synthetic	black synthetic	black plastic	black plastic
Other:		-	sunroof	sunroof	-	cabriolet	-	-
<b>Volatile substances</b>	<b>CAS-no.</b>	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )
Benzene	71-43-2	7.4	6.8	8.8	9.7	11.3	11.4	11.1
Toluene	108-88-3	24.1	28.2	103.5	110.5	118.1	54.7	44.1
Ethylbenzene	100-41-4	7.6	11.5	33.3	56.8	72.4	7.2	8.8
Xylenes (sum)	106-42-3	40.8	58.6	179.0	356.0	425.4	41.2	44.3
Styrene	100-42-5	Nd	Nd	Nd	Nd	Nd	Nd	4.3
Naphthalene	91-20-3	6.3	6.4	9.0	7.0	7.4	4.8	4.3
Aromatic hydrocarbons	sum	140.2	185.8	478.0	695.1	803.7	181.9	237.0
Cycloalkanes	sum	242.5	422.9	805.0	563.0	640.6	162.0	52.6
Aliphatic hydrocarbons	sum	326.1	527.7	1096.5	1158.3	990.6	612.2	357.3
Carbonyls	sum	18.4	21.0	48.8	77.3	78.7	9.0	6.5
Esters	sum	13.3	17.8	38.6	51.3	61	6.6	7.6
Alcohols	sum	63.4	71.4	110.3	122.6	123.1	54.5	39.6
Terpenes	sum	1.8	2.0	3.5	2.7	2.2	42.2	26.9
Sum VOC	na	894	1389	2767	2933	2945	2109 <sup>1</sup>	1489 <sup>1</sup>

<sup>1</sup>Sum of all substances quantified with reference substances. Other figures relates to toluene equivalents.

Abbreviations: sTx (synthetic textile), sL (synthetic leather)

## 2.5 Emission of other substances

In addition to VOCs, the presence of other substances has been found in car indoor air, including aldehydes, which are very volatile (VVOCs), and other semi-volatile VOCs (SVOCs). Sensory evaluation of the smell in cars, without any specific indication of the substances causing the smell, has also been performed (Sakakibara et al., 1999).

### 2.5.1 Aldehydes

Six studies were found reporting formaldehyde and other volatile aldehydes with 2-4 carbon atoms. Table 5 shows the results.

Because acrolein appears from the measuring program of the Chinese standard GB/T, acrolein is measured in new Chinese cars (Table 5, study by Xiong et al., 2015). The literature search resulted in no further data (specific standards or references) regarding acrolein.

Xiong et al. (2015) measured, in the same three cars, the emitted levels of formaldehyde, acetaldehyde and acrolein to be about 2-3 times higher at 35 °C than at 24 °C, which is consistent with the fact that the vapour pressure of the volatile substances increases at elevated temperatures.

**Table 5** Aldehydes (VVOC)

Substance	CAS-no.	Geiss (2007)	Yo- shida (2006a)	Yo- shida (2006c)	Xiong (2015)	Xiong (2015)	Wensing (2009)	Buters (2007)	Global (2005)
		Temp. varies	30°C	32°C	24°C	35°C	65°C	65°C	60°C
		(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )	(µg/m <sup>3</sup> )
Formaldehyde	50-00-0	24.3- 43.6	46.4	17-67	86.8	216	40	92.4	250-350
Acetaldehyde	75-07-0	12.1- 13.4	NA	NA	20.9	44.6	44	86.8	NA
Acrolein	107-02-8	NA	NA	NA	4.1	9.6	NA	NA	NA
Propanal	123-38-6	3.6-5.3	NA	NA	NA	NA	15	50.5	NA
Butanal	123-72-8	NA	NA	NA	NA	NA	19	12.0	NA
Butenal	4170-30-3	NA	NA	NA	NA	NA	NA	29.4	NA

NA: Not analysed, ND: Not detected

Other studies of aldehydes in cars focused on the general exposure level of the driver when driving in e.g. urban areas. Therefore, these studies cannot be used for new cars (Mapou et al., 2013).

### 2.5.2 SVOC

Yoshida et al. (2006a) found low concentrations of phthalates DMP, DEP, DEHP, DIBP, DBP in a new car as well as in several newer cars (2006c). Global 2000 (2005) found emission of DEHP at 60 °C; however, without specifying the method. Table 6 shows results of the studies for emission of phthalates.

It appears from the figures in Table 6 that the emission of the phthalates DBP and DEHP changes with the temperature, but as it is not the same cars being studied, it cannot be concluded that the concentrations increase with the temperature, even though these SVOCs have a higher vapour pressure at elevated temperatures.

**Table 6** Phthalates

Substance	CAS-no.	Yoshida (2006a)	Yoshida (2006c)	Wensing (2009)	Geiss (2009)	Global (2005)
		30°C (µg/m <sup>3</sup> )	32°C (µg/m <sup>3</sup> )	65°C (µg/m <sup>3</sup> )	<i>varies</i> (µg/m <sup>3</sup> )	60°C (µg/m <sup>3</sup> )
Dimethyl phthalate (DMP) <sup>1</sup>	131-11-3	0.2	0.01-1.8	NA	ND	NA
Diethyl phthalate (DEP) <sup>1</sup>	84-66-2	0.2	0-0.63	NA	ND	NA
di-isobutyl phthalate (DiBP) <sup>2</sup>	84-69-5	0.03	0,02-1.3	NA	NA	NA
Di-n-butyl phthalate (DBP) <sup>2</sup>	84-74-2	0.4	0,12-1.5	0,7	0.196	NA
Diethylhexyl phthalate (DEHP) <sup>2</sup>	117-81-7	0.2	0.04-1.5	NA	0.335	0.340-0.420

<sup>1</sup> VOC ; <sup>2</sup> SVOC

Wenzig (2009) found that higher concentrations of seven organic phosphate esters were emitted at 65 °C than at room temperature (not specified).

Mandalakis et al. (2008) conducted a study with sampling of polybrominated flame retardants PBDEs and PBDFs in a study with sampling of cars in use (combined driving and parking) for a longer period of active sampling, i.e. both gaseous substances and substances bound to particles were analysed. Other studies also showed polybrominated flame retardants in the indoor air of cars (Goosey and Harrad, 2011; Harrad et al., 2008; Harrad and Abdallah, 2011; Sónia et al., 2014; Müller et al., 2011).

## 2.6 Recommended limit values for VOCs in cars

In summary literature from various countries describes emission of VOCs in cars, where the main VOCs found in car cabins are BTEX, aliphatic, aromatic and cyclic hydrocarbons. A few studies were also found that include measuring of aldehydes (VVOC), phthalates (VOC/SVOC), and flame retardants (SVOC).

Table 7 shows an overview of indicative VOC limit values used by the automotive industry in Japan and China. Holtkamp (2016) points out that there are no European indicative limit values for VOCs in cars yet and refers to the Chinese and Japanese values.

**Table 7** Indicative limit values for VOCs in new cars in China and Japan

Substance	China	Japan
	GB/T 27630-2011 ( $\mu\text{g}/\text{m}^3$ )	JAMA ( $\mu\text{g}/\text{m}^3$ )
Benzene	110	-
Toluene	1100	260
Ethylbenzene	1500	3800
Xylenes (sum)	1500	870
Styrene	260	220
Formaldehyde	100	100
Acetaldehyde	50	48
Acraldehyde (Acrolein)	50	-
Chlorpyrifos <sup>1</sup>	-	1
Diazinon <sup>1</sup>	-	0.29
Fenobucarb <sup>1</sup>	-	33
Paradichlorobenzene	-	240
Tetradecane	-	330
Di- <i>n</i> -butyl phthalate (DBP)	-	220
Di-ethylhexyl phthalate DEHP)	-	120

<sup>1</sup>Insecticide

Faber (2016) stated: "As far as we are aware, there is no EU or US limit values of VOC concentrations in the cars. But the EU is currently discussing indicative limit values for VOC concentrations in new cars and indicative limit values for EU/international standard are under preparation." According to information presented at the 18th Conference Odour and Emissions of Plastic Materials 2016 (Kassel, Germany), these will be ready by the end of this year. The manufacturers' indicative limit values are confidential.

Xiong et al. (2015) concluded that the detected concentrations of VOCs in Chinese cars did not exceed the Chinese limit values, with the exception of formaldehyde in two cars at elevated temperatures of 29 °C and 35 °C and in one car at 35 °C.

Yoshida et al. (2006c) concluded that the median levels of individual substances for 50 cars were below the WHO guideline values. (WHO values according to Yoshida et al. (2006c): Formaldehyde (100  $\mu\text{g}/\text{m}^3$ , 30 min), toluene, styrene, respectively (260  $\mu\text{g}/\text{m}^3$ , 1 week), xylene (4800  $\mu\text{g}/\text{m}^3$ , 1 week), ethylbenzene (22000  $\mu\text{g}/\text{m}^3$ , 1 year), tetrachloroethylene (250  $\mu\text{g}/\text{m}^3$ , 1 year) and naphthalene (10  $\mu\text{g}/\text{m}^3$ , 1 year)). The measuring results for the 50 cars were given in ranges, from which it appeared that the upper value exceeds the WHO limit values for styrene (675  $\mu\text{g}/\text{m}^3$ ) and naphthalene (25  $\mu\text{g}/\text{m}^3$ ). Yoshida concludes that the total concentration of VOCs (TVOC) is an important parameter for evaluating the air quality of car cabins.

Janicka et al. (2014) compared their measured values in cars with recommended limit values for volatile substances in indoor air RMCL (Recommended Maximum Concentration Limit) according to a Polish Directive (Rozporządzenie, 2003). The Polish RMCL values for acrolein and formaldehyde are 0.9 and 4  $\mu\text{g}/\text{m}^3$ , respectively, and for benzene, toluene, xylene and ethylbenzene, 5, 10, 10 and 38  $\mu\text{g}/\text{m}^3$ , respectively. These limit values are significantly lower than the Chinese and Japanese recommendations in Table 7, but also lower than WHO recommended limits. The background for determining these RMCL values were not specified.

# 3. Identification of harmful substances and exposure scenarios

## 3.1 Hazard assessment

### 3.1.1 Human health screening of emission relevant substances

In connection with a human health screening for substances of highest concern, emphasis is put on the substances with the highest emissions and concentration levels in Tables 2 to 6 and Appendix 1. In the further screening of these substances consideration is also given to the human health classifications as well as to tolerable exposure levels for the substances if these have been established, e.g. in connection with outdoor and indoor environment.

Data for EU-harmonised hazard classification were searched on the ECHA website <http://echa.europa.eu/>.

Data regarding EU values for tolerable emission concentrations to indoor air (so-called LCI values Lowest Concentration of Interest) were found at [http://www.eu-lci.org/EU-LCI\\_Website/EU-LCI\\_Values.html](http://www.eu-lci.org/EU-LCI_Website/EU-LCI_Values.html).

The LCI values indicate the upper levels of emission of a chemical substance to the indoor air not considered to cause any health risk. As the LCI values are calculated in a similar way as DNEL values for the population and consumers under REACH, it is considered relevant to apply the numerical values for the LCI values as tolerable exposure levels (DNEL) for the population.

Furthermore, data were used from the Danish EPA projects "Survey and risk assessment of toluene and other neurotoxic substances in children's rooms" (Danish EPA, 2016a) and "Survey and risk assessment of chemicals in rugs" (Danish EPA, 2016b).

The Danish EPA (2016a) project established tolerable levels of exposure for neurotoxic hydrocarbons, particularly regarding the protection of children, as children are considered particularly sensitive to effects on the central nervous system.

Similarly, the Danish EPA (2016b) project established tolerable exposure levels for e.g. aldehydes and phthalates in connection with children's exposure in the indoor environment. It appears that here, the tolerable values for the aldehydes correspond to the LCI values for aldehydes as children are not, as was the case with the hydrocarbons, considered more susceptible to eye and respiratory irritants than the general population.

Below in Table 8, the substances from Tables 2, 4, 5, 6, and Appendix 1 are listed along with data of the EU-harmonised human health classification and the tolerable exposure levels found for the substances. Table 8 shows in **bold** the tolerable levels, which will subsequently be used in the risk assessment.

For data on hydrocarbons, it was decided to focus on data from Brodzik et al. (2014), Table 4, as these data are considered more representative of European cars than data from Table 3 showing data from cars in China and Taiwan.

**Table 8** Emitted substances and data on human health classifications, tolerable exposure levels and measured levels in car cabins

	CAS	Harmonised EU health Classification*	EU LCI value** µg/m <sup>3</sup>	Danish EPA (2016a+b) µg/m <sup>3</sup>	WHO <sup>(1,2)</sup> µg/m <sup>3</sup>	Measured levels in cars µg/m <sup>3</sup>
<i>Hydrocarbons</i>						
Benzene	71-43-2	Carc. 1A Muta. 1B STOT RE 1 Eye Irrit. 2 Skin Irrit. 2 Asp. Tox. 1	-		0,17 <sup>(1)</sup> (cancer)	11.3 (21-23°C) 23 (60-65°C)
Toluene	108-88-3	Repr. 2 STOT RE 2 STOT SE 3 Skin Irrit. 2 Asp. Tox. 1	2900 (neurotoxicity)	725	260 <sup>(2)</sup> (neurotoxicity)	118 (21-23°C) 275 (60-65°C)
Ethylbenzene	100-41-4	STOT RE 2 Acute Tox. 4 Asp. Tox. 1	850 (neurotoxicity)	200		72.4 (21-23°C) 434 (60-65°C)
Xylenes (o,m,p isomers)	1330-20-7	Acute Tox. 4 Skin Irrit.2	500/ 125 (neurotoxicity)	125 (neurotoxicity)		425 (21-23°C) 2450 (60-65°C)
Styrene	100-42-5	Repr. 2 STOT RE 1 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2	250/ 175 (genotoxicity/neurotoxicity)	175 (neurotoxicity)	260 <sup>(2)</sup> (neurotoxicity)	4.3 (21-23°C) 264 (60-65°C)
Naphthalene	91-20-3	Carc. 2 Acute Tox. 4	10 (cytotoxicity in the airways)		10 <sup>(1)</sup>	7.4 (21-23°C)
C7-C12 hydrocarbons (aromatic hydrocarbons + aliphatic + alicyclic alkanes)	-	STOT RE1 (for white spirit)	-	5700/ 1425 (neurotoxicity)		2436 (21-23°C) 8303 (60-65°C)

## Aldehydes

Formaldehyde	50-00-0	Carc. 1B Muta. 2 Acute Tox. 3 Skin Corr. 1B Skin Sens. 1	<b>100</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)	100 <sup>(1)</sup>	86.8 (24°C) 250-350 (60°C)
Acetaldehyde	75-07-0	Carc. 2 Eye Irrit. 2 STOT SE 3	<b>1200</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		20.9 (24°C) 86.8 (60°C)
Propanal	123-38-6	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2	-	-		15 (30°C) 50.5 (60°C)
Butanal	123-72-8	-	<b>650</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		19 (30°C) 12 (60°C)
Pentanal (valeraldehyde)	110-62-3	-	<b>800</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		7.2 (60°C)
Hexanal	66-25-1	-	<b>900</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		29.8 (60°C)
Nonanal	124-19-6	-	<b>900</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		47 (63°C)
Benzaldehyde	100-52-7	Acute Tox. 4	<b>90</b> <b>(eye/respiratory irritation)</b>	(as the LCI value)		23.8 (65°C)
Acrolein	107-02-8	Skin Corr. 1B Acute Tox. 1	-	<b>0.1 (long-term exp.)</b> <b>7 (short-term exp.)</b> <b>(irritation and cytotoxicity airways)</b>		4.1 (25°C) 9.6 (35°C)
Butenal (crotonaldehyde)	4170-30-3	Muta. 2 STOT RE 2 Acute Tox. 2 Skin Irrit. 2 Eye Dam. 1 STOT SE 3	<b>5</b> <b>(eye/respiratory irritation)</b>			29.4 (65°C)

<b>Phthalates</b>			<b>DNEL-values</b>		
Diisobutylphthalate	84-69-5	Repr. 1B		<b>420 µg/kg bw/d (reprotox)</b>	1.3 (32°C)
Di-n-butylphthalate (DBP)	84-74-2	Repr. 1B	-	<b>6,7 µg/kg bw/d (reprotox)</b>	1.5 (32 °C) 0.7 (60°C)
di-ethylhexylphthalate (DEHP)	117-81-7	Repr. 1B	-	<b>50 µg/kg bw/d (reprotox)</b>	1.5 (32 °C) 0.42 (60°C)
<b>Ketones</b>					
Acetone	67-64-1	Eye Irrit. 2 STOT SE 3	-		361 (60°C)
Ethylmethylketone (2-butanone)	78-93-3	Eye Irrit. 2 STOT SE 3	<b>5000</b>		85 (60°C)
Methylisobutylketone	108-10-1	Eye Irrit. 2 STOT SE 3 Acute Tox. 4	<b>(830/ 3000) (German/ French LCI)</b>		38.1 (60°C)
Methylhexanone	110-12-3	Acute Tox 4	-		117 (60°C)
<b>Other substances</b>					
Ethanol	64-17-5	-	-		300 (65°C)
Phenol	108-95-2	Skin Corr 1B Acute Tox 3 STOT RE 2 Muta 2	<b>(10/ 20) (German/ French LCI)</b>		194 (63°C)
Methylpyrrolidone	872-50-4	Repr 1B Eye Irrit. 2 Skin Irrit. 2 STOT SE 3	<b>400 (Preliminary EU LCI)</b>		425 (65°C)
Caprolactam	105-60-2	Eye Irrit. 2 Skin Irrit. 2 STOT SE 3 Acute Tox 4	<b>300 (respiratory irritation)</b>		96 (60°C)

\*[http://www.eu-lci.org/EU-LCI\\_Website/EU-LCI\\_Values.html](http://www.eu-lci.org/EU-LCI_Website/EU-LCI_Values.html)

\*\* For Acute Tox classification, the most restrictive classification is indicated in case the substance is classified in several Acute Tox categories for different exposure routes

(1) WHO (2000)

(2) WHO (2010)



In relation to the hydrocarbons it can be seen that especially the neurotoxic effects are critical for determining the tolerable exposure levels. An exception is the carcinogenic substances benzene. In the WHO (2010) guidelines for indoor air quality it is indicated that a benzene level of  $0.17 \mu\text{g}/\text{m}^3$  corresponds to an increased lifetime risk of development of cancer of one in a million. Furthermore, it can be mentioned that the EU has set a limit value for benzene for outdoor air at  $1 \mu\text{g}/\text{m}^3$  to protect the population from carcinogenic effects.

For the aldehydes, especially eye and respiratory tract irritation are problematic effects and are the basis for determining their tolerable exposure levels.

In case of ketones and phenol, methylpyrrolidone and caprolactam, the classifications indicate that most likely, the eye and respiratory irritation are the critical effects that may determine their tolerable exposure levels.

For phenol relatively low LCI values of 10 and  $20 \mu\text{g}/\text{m}^3$  have been set in Germany and France, respectively. The background for these values is not immediately apparent. In 2003, the EU Scientific Expert Group on Occupational Exposure Limits has set a 15-minute limit value of  $16 \text{ mg}/\text{m}^3$  and an 8-hour limit value of  $8 \text{ mg}/\text{m}^3$  to protect against mucous membrane effects (SCOEL 2003).

For DBP and DEHP, the endocrine disrupting effects and developmental effects are the critical effects that determine the tolerable exposure levels.

Based on the measured levels and the above considerations, the following emitted components are considered the most critical in a human health context:

- Benzene (carcinogenic)
- Naphthalene (carcinogenic, eye and respiratory irritation)
- Formaldehyde (carcinogenic, eye and respiratory irritation)
- Acrolein (eye and respiratory irritation, tissue damage in the respiratory system by long-term exposure)
- Crotonaldehyde (eye and respiratory irritation)
- Phenol (eye and respiratory irritation)

### 3.1.2 Toxicological testing of cabin air from cars

Rather than looking at individual substances from the emission and their toxicological effects, one of the references cited in Section 2.4.1 performed toxicological tests with cabin air sampled from the cars (Buters et al., 2007). In this study, air samples were collected from a new and an old car at a cabin temperature of  $65^\circ\text{C}$ . Air samples containing  $10.9 \text{ mg VOC}/\text{m}^3$  and  $1.2 \text{ mg VOC}/\text{m}^3$  from the new and used car, respectively, were extracted with ether, and the extracts were tested in cell cultures consisting of human keratinocytes, human epithelial lung cells, hamster lung fibroblast cells, and mast cells from bone marrow. Exposure to the extracts did not show any toxic response in the cell cultures, except in mast cells, where an increased IgE level was found for exposure to the extract from the new car. Further, the extracts were tested *in vivo* for allergenic properties in an LLNA test in mice (Local Lymph Node Assay), but with no effect. Thus, the study identified no significant toxic effects that can be used in a hazard and risk assessment context. It should be noted, that the used extraction procedure was not able to extract aldehydes, and therefore potential toxic responses from these could not be detected.

Furthermore, the methods used by Buters et al. in order to assess the effects of air pollution are unusual, and the choices and relevance of the methods is not substantiated in detail in the study. This also makes it difficult to evaluate the significance of the study results. Thus, in connection with further risk assessment in this project it is considered more appropriate to assess the cabin air based on the measured content of the individual components in the air.

## 3.2 Exposure scenario set-up

Among the substances emitting in highest amounts, there is - as mentioned above - a number of substances that may cause serious adverse health effects. For all the substances tolerable exposure levels have been identified than can be used for evaluation of specific exposure scenarios.

### *Exposure route*

The focus of the project is emission of VOCs to cabin air in cars, and therefore, inhalation is considered the predominant and most relevant exposure route for the substances to consider.

For phthalates, known as SVOC substances, exposure will also depend on the content of phthalates in the dust of the cabin, as particularly hand contact with the cabin surfaces will be able to collect dust, which then - especially for young children - may be ingested in connection with sucking the fingers.

### *Target group*

Target group for exposure is both the driver of the car and the passengers. Children are especially considered, because children may be particularly sensitive to exposure from chemical substances (e.g. substances that affect the nervous system or the hormonal system). This is also reflected here as the tolerable levels for the measured neurotoxic substances are set lower than for adults (Danish EPA, 2016a).

For young children (1-3 years of age) and their oral exposure to dust, it is assumed that they consume 100 mg dust per day (Danish EPA, 2016b), primarily through sucking the fingers and objects. This value may be used as a worst-case scenario for intake of cabin dust during stays in the car if relevant data on cabin dust is available.

### *Duration of exposure*

Regarding the duration of the scenario, this is assessed to be highly variable depending on the user's needs for transport in everyday life. Therefore, it was chosen to use a daily residence time in the car of 2 x 1 hour as a starting point for the scenario, as this can be a realistic scenario for people who commute every day. In this scenario, it will partly be relevant to relate to the levels of respiratory and eye irritating substances and partly to substances that by repeated and prolonged exposure may be harmful to health, such as the hydrocarbons.

As the substance concentrations in the cabin will be highly increased when the car has been parked in the sun, it is also important to relate to such elevated levels in the cabin at least for short exposure duration when entering the car and until the car has been ventilated. This scenario especially has to take into consideration the effects from acute-acting substances such as the aldehydes with respect to their irritant effects (eyes/ respiratory system).

### *Exposure levels*

As a basis for estimation of the exposure levels, the following is used:

- - measured data Table 2 (levels (primarily hydrocarbons) after parking in the sun (at 60-65 °C))
- - measured data Table 4 (levels (primarily hydrocarbons) 24 hours after the completion of production (at 21-25 °C))
- - measured data Table 5 (aldehyde levels in cars)
- - measured data Table 6 (phthalate levels (DBP, DEHP) in cars)

For the acute-acting substances (the aldehydes), it will be relevant as a worst-case situation to consider whether the concentration built up in the cabin, to which persons might be exposed at entering the car, may cause nuisance such as irritation.

For substances where it is not the short peak concentrations, but the average concentration over a certain time that is important for the toxic effects, it is more relevant consider the total exposure over a period, e.g. during the 2 x one hour the transport lasts. In such a scenario, the highest exposure is assessed to occur when driving in a car at normal room temperature with the ventilation turned off.

In connection with entering and driving the car at temperatures where ventilation is closed, some air circulation in the cabin will automatically occur as a result of negative pressure in the cabin during driving and small leaks in the car. The air in the car depends on the car's speed and thus the outer wind factor. Further it is dependent of the cabin size and whether the car's ventilation system is set to recirculate the air or not.

The literature indicates large differences with respect to ventilation of car cabins. For cars with windows and doors closed and the ventilation off, an airflow rate is indicated down to one air shift time per hour when the car is stationary. During driving, the airflow increases significantly (Ott et al., 2008; Park et al., 1998; Fruin et al., 2012). From these references, an airflow of approximately 2 times per hour is assessed as a lower level of ventilation during stays/ driving in the car.

Such a scenario could for example be relevant in connection with urban traffic, where the ventilation is set to recirculate to avoid external air pollution.

#### *Estimation of exposure levels during driving*

If the starting concentration, the emission rate, the cabin volume, and the ventilation rate are known, the air concentration at any given time can be calculated by:

$$C_{i(t)} = C_{i(t=0)} \times e^{-\lambda t} + (E_i / V) / \lambda \times (1 - e^{-\lambda t})$$

Where:

$C_{i(t)}$  : concentration of the substance  $i$  at the time  $t$  in the cabin ( $\mu\text{g}/\text{m}^3$ )

$C_{i(t=0)}$  : concentration of  $i$  at the time  $t = 0$  in the cabin ( $\mu\text{g}/\text{m}^3$ ), i.e. concentration when entering

$\lambda$ : airflow in the cabin (times per hour,  $\text{t}^{-1}$ )

$t$ : duration of the stay in the car (hours,  $\text{t}$ )

$E_i$ : emission rate for a substance ( $\mu\text{g}/\text{t}$ )

$V$ : car cabin volume ( $\text{m}^3$ )

Data for the individual parameters, however, can be difficult to obtain from the individual studies. The study by Brodzik et al. (2014) gives the opportunity to come up with an estimate of the emission rate of the substances, as the measured levels are built up within the first 24 hours after finishing the production of the car. I.e. the emission rate  $E_i$  can be calculated from the measured concentration divided by the number of hours the car has been closed before the measurement (as a specific time has not been specified by Brodzik et al. (2014), it is assumed that the cars on average have been stationary 12 hours before the measuring). In addition, Brodzik et al. (2014) state the cabin volume to be approximately  $2.4 \text{ m}^3$  for the cars. If it is assumed that the airflow in the car as described in the scenario above is relatively low, e.g. 2 times per hour, the concentration after 1 hour of stationary/ drive can be calculated.

#### *Example:*

Brodzik et al. (2014) measured the highest toluene level to  $118 \mu\text{g}/\text{m}^3$ , after a car had been stationary with doors and windows closed after the production completion (assumed stationary time 12 hours). The total emission of toluene can be calculated as  $V \times \text{conc} = 2.4 \text{ m}^3 \times 118 \mu\text{g}/\text{m}^3 = 283 \mu\text{g}$  toluene. This corresponds to an emission rate,  $E_i$  of  $283 \mu\text{g} / 12 \text{ hr} = 24 \mu\text{g}/\text{h}$ .

The concentration after an hour in the car at an airflow of 2 times per hour can be calculated as:

$$C_{i(t)} = C_{i(t=0)} \times e^{-\lambda t} + (E_i / V) / \lambda \times (1 - e^{-\lambda t})$$

where the first part of the equation represents the decrease in concentration of the starting concentration of  $118 \mu\text{g}/\text{m}^3$  after 1 hour, and the second part of the equation represents the concentration contribution achieved as a result of the continued emission during 1 hour.  $t=1$ .

$$C_{i(t)} = 118 \mu\text{g}/\text{m}^3 \times e^{-2 \times 1} + (24 \mu\text{g}/\text{h} / 2,4 \text{ m}^3) / 2 \times (1 - e^{-2 \times 1})$$

$$C_{i(t)} = 16 \mu\text{g}/\text{m}^3 + 4,3 \mu\text{g}/\text{m}^3 = 20,3 \mu\text{g}/\text{m}^3$$

This means that the concentration after 1 hour of driving in the car has decreased from  $118 \mu\text{g}/\text{m}^3$  to  $20.3 \mu\text{g}/\text{m}^3$ .

The longer the stay in the car, the last part of the equation  $(1 - e^{-\lambda t})$  will go towards 1 because  $e^{-\lambda t}$  becomes infinitely small with increasing value for  $t$ . The maximum achievable concentration contribution from the emission can be calculated from  $(E_i / V) / \lambda$  corresponding to  $(24 \mu\text{g}/\text{h} / 2,4 \text{ m}^3) / 2 \text{ h}^{-1} = 5 \mu\text{g}/\text{m}^3$ . For larger airflow than 2 times per hour, the contribution will be correspondingly smaller. This means that especially the concentration built up while the car is stationary will be significant for the total exposure, also for the 1 hour drive.

An immediate and rough estimate of the average concentrations during a 1-hour drive can be achieved by adding the initial and final concentrations and divide by 2 (i.e.  $(118 \mu\text{g}/\text{m}^3 + 20.3 \mu\text{g}/\text{m}^3) / 2 = 69 \mu\text{g}/\text{m}^3$ ). This value, however, will be an overestimation, as the graph of the concentration level is sublinear. A more accurate estimate can be obtained by calculating the additional concentrations after 15, 30 and 45 minutes (i.e. dividing the concentration-time curve into several linear intervals). With such an approach, an average concentration of  $57.7 \mu\text{g}/\text{m}^3$  can be calculated  $(118 \mu\text{g}/\text{m}^3 + 73.6 \mu\text{g}/\text{m}^3 + 46.6 \mu\text{g}/\text{m}^3 + 30.2 \mu\text{g}/\text{m}^3 + 20.3 \mu\text{g}/\text{m}^3) / 5 = 57.7 \mu\text{g}/\text{m}^3$ . This corresponds to about 50 % of the starting concentration.

It is not possible from the other studies to estimate emission rates for the emitted substances and thus assess the cabin concentration at various time intervals. On this background, it is reasonable in connection with the exposure calculation and risk assessment for all measurements of other substances at the lower temperatures in the range of 20-30 °C to estimate the average exposure level during 1 hour to 50 % of the measured level when entering the car.

# 4. Exposure assessment and risk assessment

## 4.1 Exposure assessment

As described in the discussion of exposure scenarios, two types of scenarios are considered relevant for exposure assessment:

*Scenario 1 (short stay in a hot car):*

Entering a hot car parked in the sun and short-term (maximum 2 minutes) exposure to the peak concentration in the cabin before it is vented in order to achieve lower temperature:

As assessment basis for this scenario, the measured values by 60 to 65 °C given in Table 8 are used.

*Scenario 2 (daily commuting):*

Transport in the car 2 x 1 hour per day at a temperature of about 20 °C where windows and ventilation are closed and with an airflow in the cabin of 2 times per hour on average.

For exposure assessment for hydrocarbons, the measured levels at 21-23 °C from Table 8 are used. These values are the most recent data found in the literature review in Chapter 2 for cars on the European market. Also the data by Brodzik et al. (2014) make it possible to estimate an emission rate for the substances and thus the concentration process over time in the cabin (as outlined in Section 3.2). As indicated in the example, the average concentration over an hour approximately corresponds to half the starting concentration when entering, so the values in Table 8 can be multiplied by 0.5 to obtain an average exposure estimate.

## 4.2 Risk assessment

The risk assessment of the two exposure scenarios is carried out by comparing the measured/estimated exposure level for the emitted substance with the specified tolerable exposure level for the substance and from this calculate a risk characterisation ratio, RCR:

$$RCR_{(1)} = \text{Exposure level}_{(1)} (\mu\text{g}/\text{m}^3) / \text{Tolerable exposure level}_{(1)} (\mu\text{g}/\text{m}^3)$$

If the calculated RCR value exceeds 1, it means that the exposure exceeds the tolerable level, which reflects that there may be a risk in this particular scenario. If the RCR value is below 1, this indicate that the scenario is not considered to represent a risk..

For substances with similar effects, and where the mode of action may be similar as well a further addition of the RCR contributions of the substances is made in order to evaluate if the total exposure to several substances with the same effects gives rise to risk (i.e.  $RCR_{\text{sum}} > 1$ ):

$$RCR_{\text{sum}} = RCR_1 + RCR_2 + RCR_3 + \dots RCR_n$$

Thus, there may be a risk when contributions from several substances with RCR values below 1 are added.

Also, the actual data indicate that many substances are measured simultaneously, so addition considerations must be considered highly relevant.

#### 4.2.1 Risk assessment of scenario 1 (short stay in a hot car)

In this scenario, it is particularly relevant to focus on the acute toxic effects, i.e. irritation of the eyes and respiratory tract, as these effects are strongly concentration dependent and even short-term exposure to increased levels may cause effects. Thus the risk assessment is focused on acute irritation effects, as the most critical effects. Table 8 indicates that relevant substances for acute irritation effects are: aldehydes, ketones, methylpyrrolidone, caprolactam, and phenol.

Below in Table 9, the measured levels and the tolerable levels are indicated for the substances and the calculated RCR values, and RCR values above 1 (risk) are highlighted in **bold**.

**Table 9** Risk assessment for scenario 1 regarding peak concentrations of emitted eye and respiratory tracts irritants.

	CAS	Harmo- nised EU health classifica- tion*	Tolerable exposure levels  µg/m <sup>3</sup>	Measured levels in cars  µg/m <sup>3</sup>	RCR value
<b>Aldehydes</b>					
Formaldehyde	50-00-0	Carc. 1B Muta. 2 Acute Tox. 3 Skin Corr. 1B Skin Sens. 1	100  (eye/respiratory irrita- tion)	250-350 (60°C)	<b>2.5 – 3.5</b>
Acetaldehyde	75-07-0	Carc. 2 Eye Irrit. 2 STOT SE 3	1200  (eye/respiratory irrita- tion)	86,8 (60°C)	0.07
Propanal	123-38-6	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2	-	50,5 (60°C)	-
Butanal	123-72-8	-	650  (eye/respiratory irrita- tion)	12 (60°C)	0.02
Pentanal (valeraldehyde)	110-62-3	-	800  (eye/respiratory irrita- tion)	7,2 (60°C)	0.001
Hexanal	66-25-1	-	900  (eye/respiratory irrita- tion)	29,8 (60°C)	0.03
Nonanal	124-19-6	-	900  (eye/respiratory irrita- tion)	47 (63°C)	0.05
Benzaldehyde	100-52-7	Acute Tox. 4	90  (eye/respiratory irrita- tion)	23,8 (65°C)	0.27

Acrolein	107-02-8	Skin Corr. 1B Acute Tox. 1	7 (short-term value, EPA 2016)	9,6 (35°C)	<b>1.37</b>
Butenal (crotonaldehyde)	4170-30-3	Muta. 2 STOT RE 2 Acute Tox. 2 Skin Irrit. 2 Eye Dam. 1 STOT SE 3	5 (eye/respiratory irritation)	29,4 (65°C)	<b>5.9</b>
<b>Ketones</b>					
Acetone	67-64-1	Eye Irrit. 2 STOT SE 3	-	361 (60°C)	
Ethylmethylketone (2-butanon)	78-93-3	Eye Irrit. 2 STOT SE 3	5000	85 (60°C)	0.02
Methylisobutylketone	108-10-1	Eye Irrit. 2 STOT SE 3 Acute Tox. 4	(830/ 3000) (German/ French LCI)	38,1 (60°C)	0.045
Methylhexanone	110-12-3	Acute Tox 4	-	117 (60°C)	-
<b>Other substances</b>					
Methylpyrrolidone	872-50-4	Repr 1B Eye Irrit. 2 Skin Irrit. 2 STOT SE 3	400 (Preliminary EU LCI)	425 (65°C)	<b>1.1</b>
Caprolactam	105-60-2	Eye Irrit. 2 Skin Irrit. 2 STOT SE 3 Acute Tox 4	300 (respiratory irritation)	96 (60°C)	0.32
<i>Sum RCR for irritation potential</i>					<b>10.6 – 11.6</b>
Phenol	108-95-2	Skin Corr 1B Acute Tox 3 STOT RE 2 Muta 2	10 (German LCI)	194 (63°C)	<b>19.4</b>

*RCR-values > 1 are highlighted in bold.*

As can be seen, the RCR values are higher than 1 for the substances formaldehyde, acrolein, crotonaldehyde, and methylpyrrolidone, indicating that there may be a risk of eye/ respiratory irritation from these substances. It should also be noted that for acrolein, the peak concentration of 9.6 µg/m<sup>3</sup> is measured at 35 °C (no data for higher temperatures), so the level is likely to be significantly higher at about 60 °C, and thus may lead to an even higher RCR value.

If the RCR contributions of all the respiratory irritants are added, an overall RCR value of 10.6 to 11.6 is achieved, which further reinforces the risk of irritation.

The background for the low German LCI value for phenol of  $10 \mu\text{g}/\text{m}^3$  has not been found (and which results in a very high RCR value of 19.4). Possibly the low LCI value intends to protect against eye – and respiratory tract irritation as well..

Although it is a very short-term exposure scenario, the high RCR values indicate that it is likely to feel irritation from the eyes and the respiratory tract when entering a hot car due to emission of these substances. Such a sensation of irritation will be very short lived, as the start of ventilation and venting would quickly reduce the levels significantly within the first minutes.

Such high levels of emitted irritants is likely to happen especially in the first months of a car's 'lifetime' when it is parked in the sun with the windows closed and the ventilation turned off.

#### *Hydrocarbons*

Exposure to hydrocarbons (see Table 8) is estimated to have only minor impact in connection with the risk for irritation in this scenario. For hydrocarbons, the chronic neurotoxic effects are considered the most critical effects. For this type of effects it is not considered relevant to compare peak concentrations with tolerable exposure levels for the substances as the tolerable exposure levels are intended to protect against chronic effects, for which the average daily exposure is more important than very short peak concentrations. For brief (about 2 minutes) exposure especially to elevated levels of hydrocarbons (as in scenario 1) this is considered to provide an insignificant additional contribution to the overall exposure compared to prolonged stays (2 hours in scenario 2) with more moderately elevated levels.

However, some aromatic hydrocarbons may for short-term exposure at elevated levels cause irritation to the eyes and the respiratory tract. These effects appear, however, at levels significantly above the odour concentrations for the substances. Xylenes and styrene are the most odour potent aromatic hydrocarbons from Table 8. The literature indicates odour thresholds of  $160 \mu\text{g}/\text{m}^3$  and  $130 \mu\text{g}/\text{m}^3$  for these two substances, respectively, meaning that these substances can be recognized by odour at the indicated peak concentrations.

#### **Overall assessment scenario 1**

For this scenario it is found that there may be a risk for short-term irritation of the eyes and the respiratory tract - primarily as a result of exposure to the increased levels of aldehydes as well as contributions from other irritants (e.g. phenol and methylpyrrolidone).

#### **4.2.2 Risk assessment of scenario 2 (daily commuting)**

In this scenario, the average exposure levels of the substances during 2 x 1 hour's drive are compared to the tolerable exposure levels for the substances. As the tolerable exposure levels normally pertain to an average 24 hour average exposure, the estimated 1 hour exposure values are converted to daily values, which is indicated in the column "average exposure over one day". In this scenario, the following effects were considered the most critical ones in the risk assessment: carcinogenic effects (benzene, naphthalene, formaldehyde, acetaldehyde), chronic neurotoxic effects (hydrocarbons), impact on the eyes and the respiratory system regarding irritation/ cytotoxic effects (aldehydes, naphthalene). For phthalates, the developmental effects are considered as the most critical effects.

Table 10 shows the measured levels (transformed to 24-hour levels) and the tolerable levels for the substances as well as the calculated RCR values. RCR values above 1 (risk) are highlighted in **bold**.



**Table 10** Risk assessment of scenario 2 regarding daily average exposure to emitted substances.

	CAS	Harmo-nised EU classification	Tolerable exposure levels; Danish EPA (2016a+b) $\mu\text{g}/\text{m}^3$	Measured levels in cars $\mu\text{g}/\text{m}^3$	Average 24-h exposure* $\mu\text{g}/\text{m}^3$	RCR
<i>Hydrocarbons, carcinogenic effect</i>						
Benzene	71-43-2	Carc. 1A Muta. 1B STOT RE 1 Eye Irrit. 2 Skin Irrit. 2 Asp. Tox. 1	0.17 (WHO 2010 (cancer))	11.3 (21-23°C)	0.47	<b>2,76</b>
Naphthalene	91-20-3	Carc. 2 Acute Tox. 4	10 (WHO 2000)	7.4 (21-23°C)	0.31	0.03
<i>Hydrocarbons, neurotoxicity</i>						
Toluene	108-88-3	Repr. 2 STOT RE 2 STOT SE 3 Skin Irrit. 2 Asp. Tox. 1	725 (neurotoxicity)	118 (21-23°C)	4.92	0.007
Ethylbenzene	100-41-4	STOT RE 2 Acute Tox. 4 Asp. Tox. 1	200 (neurotoxicity)	72.4 (21-23°C)	3.0	0.015
Xylenes ( <i>o</i> -, <i>m</i> -, <i>p</i> -isomers)	1330-20-7	Acute Tox. 4 Skin Irrit. 2	125 (neurotoxicity)	425 (21-23°C)	17.8	0.14
Styrene	100-42-5	Repr. 2 STOT RE 1 Acute Tox. 4 Skin Irrit. 2 Eye Irrit. 2	175 (neurotoxicity)	4.3 (21-23°C)	0.18	0.001
<i>RCR<sub>sum</sub> (neurotoxicity)</i>						0,163

C7-C12 hydrocarbons	-	STOT RE1 (white spirit)	1425 (neurotoxicity)	2436 (21-23°C)	102	0.07
Corr.t. aromatic hydrocarbons + aliphatic + alicyclic alkanes						
<i>Aldehydes, eye and respiratory irritant and carcinogenic effects</i>						
Formaldehyde	50-00-0	Carc. 1B Muta. 2 Acute Tox. 3 Skin Corr. 1B Skin Sens. 1	100	86.8 (24°C)	3.6	0.04
Acetaldehyde	75-07-0	Carc. 2 Eye Irrit. 2 STOT SE 3	1200	20.9 (24°C)	0.87	0.0007
Propanal	123-38-6	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2	650	15 (30°C)	0.63	0.001
Butanal	123-72-8	-	650	19 (30°C)	0.04	0.00006
Acrolein	107-02-8	Skin Corr. 1B Acute Tox. 1	0.1 long-term value	4.1 (25°C)	0.17	1.7
<i>RCR<sub>sum</sub> aldehydes</i>						1.74
<i>Phthalates, reproduction toxic effects</i>			<b>RAC/ECHA</b>			
Diisobutylphthalate	84-69-5	Repr. 1B	420 µg/kg bw/d	0.054 (30°C)	0.0013** µg/kg IgV/d	0.000003
Di-n-butylphthalate (DBP)	84-74-2	Repr. 1B	6,7 µg/kg bw/d	0.063 (30°C)	0.0015** µg/kg IgV/d	0.0002
di-ethylhexyl phthalate (DEHP)	117-81-7	Repr. 1B	50 µg/kg bw/d	0.063 (30°C)	0.0015** µg/kg IgV/d	0.00005
<i>RCR<sub>sum</sub> phthalates</i>						0.00025

\* The average concentration contribution per day is calculated from the measured concentration x 0.5 (to achieve average over one hour) x 24 / 24 h

\*\* calculated dose after 2-hour inhalation for a pregnant woman with an inhalation volume of 0.2 L/min/kg (NMR 2011)

For the individual substances, it can be seen that benzene (carcinogenic effect) and acrolein (cytotoxic effects in the respiratory tract) exceed an RCR value of 1. In addition, the sum of RCR values for aldehydes exceeds the value of 1 (this is primarily due to the RCR for acrolein).

For hydrocarbons and neurotoxic effects, the RCR contribution for xylene represents by far the largest part with an RCR value of 0.14.

For the phthalates, the inhalation exposure is far below the tolerable levels for the substances ( $RCR_{sum} = 0.00025$ ).

#### *Benzene*

The RCR value for benzene should be seen in the context that the tolerable level of exposure of  $0.17 \mu\text{g}/\text{m}^3$  is an exposure level that through lifelong exposure corresponds to an increased lifetime risk of cancer of 1 in a million.

For ambient air in EU limit value for benzene of  $1 \mu\text{g}/\text{m}^3$  has been set (DME 2011), which is a value that both consider human health aspects as well as current background levels of benzene in ambient air in cities. In general it is not considered that benzene emission from car cabin materials will be the main source of exposure to benzene, as the air in dense traffic contain significantly higher levels than  $0.17 \mu\text{g}/\text{m}^3$ . Even small leaks in the fuel system may lead to significantly higher levels of benzene in the cabin than measured here, where the measurements only reflects benzene emission from the cabin components.

#### *Acrolein*

Acrolein is different from the other aldehydes as the alkyl chain is unsaturated, i.e. there is a double bond in the molecular structure, making the substance more reactive (Danish EPA, 2016b). At very low exposure levels, acute respiratory irritation in humans was observed (by short-term exposure), and prolonged exposure may progress to tissue damage in the lungs, which is observed in laboratory animals. In an assessment by WHO/ CICAD (2002) a tolerable exposure level of  $0.1\text{-}0.5 \mu\text{g}/\text{m}^3$  for long-term exposure was suggested, while the American organisation ATSDR proposed a tolerable exposure level of  $7 \mu\text{g}/\text{m}^3$  for shorter exposure duration less than 14 days (ATSDR 2007).

#### *Other aldehydes*

Table 9 shows that the highest RCR value with respect to the peak concentrations is obtained for the aldehyde crotonaldehyde, which like acrolein has an unsaturated alkyl chain, and therefore is particularly reactive. However, no measuring data have been found for this substance at lower temperatures, but even relatively low emission of this substance would result in an RCR value above 1, as the tolerable exposure level for the substance is  $5 \mu\text{g}/\text{m}^3$ .

Among the remaining aldehydes formaldehyde contribute with the highest RCR value of 0.04.

#### *Phthalates*

From the estimated RCR values for phthalates ( $RCR_{sum} = 0.00025$ ), it can be seen that the exposure is far below any risk.

#### **Overall assessment scenario 2**

For this scenario, the group of aldehydes -and especially acrolein- is found to cause exposure levels in the car cabin that may result in risk towards adverse effects from the respiratory tract. It should be noted that the risk of possible emission of phenol is not included in the assessment, as there are no emission data for phenol at temperatures relevant for this scenario.

### 4.2.3 Discussion of the risk assessments

#### 4.2.3.1 Uncertainties, limitations and lack of knowledge

##### *Exposure scenarios and exposure assessment*

There is a high degree of uncertainties associated with setting up exposure scenarios for the emitted substances in the indoor air of cars. In this project, it has been crucial to focus solely on exposure to the emissions from the cabin materials in new cars and not to assess the overall air quality while driving. The air quality in the cabin while driving will also be affected by any emission from the fuel system of the car and from exhaust fumes from other vehicles.

As no studies were found that specifically examine the driver's/ passenger's exposure to emission components of a new car in specific user scenarios, it has been necessary to make a number of assumptions for establishing the two scenarios listed in this report (e.g. with respect to duration of exposure and airflow in the cabin). The scenarios illustrate short-term exposure to highly elevated levels when entering a car that had been parked in the sun and also an average exposure for 2 hours per day when driving a car at normal temperature without using ventilation and with the windows closed.

Finally, there are uncertainties in the conversion of measured data from various references to exposure values in the scenarios. The measurement data from the various references has not been obtained under identical circumstances, so the measured levels included in the references are not fully comparable. However, we consider that the assumptions made reflect realistic worst-case conditions.

##### *Hazard and risk assessment*

The hazard and risk assessment is carried out at a screening level, as the hazard assessment is limited to hazard classification of the substances and data from a limited selection of literature/sources giving information concerning tolerable exposure levels.

For the risk assessment, tolerable exposure levels related to 24-hour continuous exposure have been used both to assess very short exposure duration in scenario 1 (2 minutes) as well as the average daily exposure in scenario 2. This makes especially the assessment of scenario 1 very conservative.

Despite these uncertainties, which largely affects the assessment of the various substances in the same way, it is evaluated that it has been possible by the screening performed to identify the most critical substances in connection with emissions from interiors in new cars.

#### 4.2.3.2 Conclusion of the risk assessment

*Scenario 1* represents short-term exposure to high levels of emitted substances in connection with entering a heated car that has been parked in the sun. For this scenario it is estimated that there may be a risk of short-term discomfort as a result of eye and respiratory tract irritation. This is primarily due to emission of aldehydes, where especially emissions of acrolein and crotonaldehyde are crucial, and also due to the emission of phenol.

*Scenario 2* represents daily commuting in the car 2 x 1 hour with closed ventilation system and closed windows. For this scenario, emission of aldehydes is also considered critical, as here the tolerable exposure level in relation to long-term exposure may be exceeded for acrolein indicating a potential risk for adverse effects of the respiratory tract.

It should be emphasised that both scenarios should be considered as worst-case scenarios, and that the exposure levels can be significantly reduced by venting the car either by briefly opening the windows or by turning on the ventilation system.

# 5. Discussion and perspective

## 5.1 Limitations regarding existing knowledge on emissions in cabin air in new cars

The purpose of this pilot project was to identify relevant literature and provide an overview of the most important substances/ components that evaporate from the cabin materials of new cars. From the literature data found focus has been on listing the substances that were dominating in the emissions.

As detection of different substances requires different collection and analysis methods, there may be a bias in substances reported in the literature, as there will often be a tendency to focus on substances, e.g. BTEX, previously found. It cannot be excluded that some critical emission components have been overlooked in the literature.

Furthermore, the selected focus for this project has been VOCs, and therefore no systematic search has been made for data for SVOCs or other components in the cabin materials, or dust that might be affecting the indoor air of the car, such as certain flame retardants, nitrosamines or biocides (chlorpyrifos, diazinon, fenobucarb) and other types of semi-volatile or polar substances that are difficult substances to analyse by means of the methods used. For example, nitrosamines have harmful and carcinogenic effects and are known to emit from recycled materials of rubber products, including floor mats (which can also be found in new cars).

The literature identified a number of studies of VOCs in the indoor air of new cars from Japan, China and Poland, but strangely enough not from major car producing countries such as France, Germany and the United States. The most comprehensive and complete information on VOC analyses is found in recent studies from Poland. Only a few studies from Japan, China, Germany and Austria, respectively, include formaldehyde, and one study (from China) include measurement on acrolein. So, there is a lack of more systematic knowledge of the emission for the various car brands relevant for the Danish market.

There are no studies of new cars for acetic acid or acrolein recently identified in rugs consisting of textiles and rubber, also found in car interiors (EPA, 2016b).

Some studies have been found for phthalates, brominated flame retardants and phosphate esters, but the level of these in new cars is unknown.

Thus, there are limitations in relation to the gathered knowledge of emission from car interiors in this project – both in terms of type and number of individual substances, and in terms of car brands relevant for the Danish market. Given the scale of the conducted literature search and knowledge obtained from international contacts of the project group, the limitations are especially considered to be due to lack of public access to the results.

For obtaining increased knowledge regarding the emission of VOCs and SVOCs from new cars, there is a need for more systematic measurements of the emission from different car brands within their first life year.

## 5.2 Substances of particular concern in indoor air of cars

In this pilot project, the substances found to be emitted in the car cabins are especially considered to be critical in connection with eye and respiratory tract irritation (e.g. aldehydes, phenol, methylpyrrolidone and caprolactam). Another chemical group also evaporating in significant quantities is aliphatic and aromatic hydrocarbons, for which the most critical effects are considered to be chronic neurotoxic effects.

Some of the substances are also classified as carcinogens, such as benzene, naphthalene, formaldehyde and acetaldehyde.

The most critical substances, i.e. the substances with the lowest tolerable exposure levels, are:

- Benzene
- Naphthalene
- Formaldehyde
- Acrolein
- Crotonaldehyde
- Phenol

## 5.3 Uncertainties and conclusions

Relatively large uncertainties pertain to the development of exposure scenarios for emitted substances into the indoor air of cars, and no specific studies were found investigating the driver's/ passenger's exposure to the emitted compounds from a new car for specific user scenarios.

When establishing a short-term exposure scenario (a person entering a heated car that has been parked in the sun and short-term exposure before the car has been vented) and a repeated scenario for longer duration (driving for 2 x 1 hour each day with closed windows and closed ventilation), it was necessary to incorporate a number of assumptions in the scenarios, making the exposure estimates uncertain. However, this affects all the substances in the same way, and therefore the scenarios are still considered to provide a reliable impression of the substances' relative importance in relation to which substances are the most problematic in each scenario.

When assessing the two scenarios, eye irritation and respiratory tract irritation are considered the most critical effects. For the short-term scenario with entry into the overheated car, relatively high levels of eye and respiratory tract irritants may be accumulated in the cabin, which may cause risk for short-term irritation and nuisance for the driver and the passengers.

With regard to long-term exposure when entering and driving a car with closed ventilation at normal cabin temperature, there is a slight risk that the driver/ passengers will be exposed to unacceptably high levels of the emitted volatile substances. Here concentrations when entering will be significantly lower than in the first scenario, and - regardless of closed ventilation system - there will be a certain air circulation in the cabin due to the negative pressure that occurs while driving.

## 5.4 Need for further studies

Based on the available knowledge collected from literature and the assessments made in this pilot study, it can be concluded that there is a lack of more systematic knowledge of the emission of VOCs and SVOCs from interiors of new cars, especially for car brands typical for the Danish market. Any further studies should therefore include measurements of aldehydes, VOCs, SVOCs and also specifically addressing substances of very high concern e.g. formaldehyde, acrolein, crotonaldehyde and phenol. Further the chemical analysis of the dust in the

cabin should be considered. This will provide a more solid basis for risk assessment than the present one.

For obtaining increased knowledge, the measurements should be made in new cars received in Denmark directly from the factory, so that they represent the practically lowest age of the cars when delivered to customers. Further, it is suggested to perform the measurements as has already been done by several in the present project i.e. with outdoor parking in the shade (ambient mode). Such measurements can be supplemented with measurements carried out at elevated temperature in order to represent the situation of entering a car that has been parked in the sun.

In order to obtain increased knowledge about the decline in the concentrations of chemical substances in the car indoor air in connection with starting and driving a car and turning on the ventilation/ air conditioning or opening a window, the above proposed measurements can be supplemented with measuring during the first few minutes of the drive for obtaining realistic data on everyday exposure to the volatile substances.

In case of measuring very high emission levels, it may be relevant with further analyses in the car's first life year to follow the decline in emissions from the car interior over time.

More precise knowledge of the driver's exposure to different use scenarios could be achieved by using portable measurement devices as data from such measurements would provide the best basis for a proper risk assessment of a person.

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# Appendix 1.

Table regarding emission data.

	CAS- no.	Wensing (2009)	Buters (2007)	Buters (2007)	Fedoruk et al. (2003)	Fedoruk et al. (2003)	Global (2005)	Global (2005)	Global (2005)
		6 cars (Median)	New car (direct analysis)	New car (ether extract)	Chevrolet Lumina	Ford Taurus	Opel Astra	Mercedes E220	Renault Megane
		( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )	( $\mu\text{g}/\text{m}^3$ )
<b>Aromatic hydrocarbons</b>									
Benzene	71-43-2	24	ND	ND					
Toluene	108-88-3	275	84.3	111.3		239			
Ethylbenzene	100-41-4	434	306.4	311.6					
Xylenes ( <i>o</i> -, <i>m</i> -, <i>p</i> -isomers)	-	272	2450.5	2170.5					
Styrene	100-42-5	ND	83.4	79.7	264	94			
Other aromatic hydrocarbons	-		1945	1934					
<b>Aliphatic hydrocarbons</b>	-		3435	5022	1775	98			
<b>Aldehydes</b>									
Formaldehyde	50-00-0	40	92.4	ND	NA	NA	260	350	250
Acetaldehyde	75-07-0	44	86.8	ND	NA	NA	NA	NA	NA
Propanal	123-38-6	15	50.5	ND	NA	NA	NA	NA	NA
Butanal	123-72-8	19	12.0	ND	NA	NA	NA	NA	NA
Butenal	4170-30-3		29.4	ND	NA	NA	NA	NA	NA
Pentanal	110-62-3	29	7.2	ND					
Hexanal	66-25-1	42	29.8	ND					
Nonanal	124-19-6					47			
Benzaldehyde	100-52-7	10	23.8	ND					
3-/4-Methylbenzaldehyde	620-23-5/104-87-0		15.6	ND					
<b>Ketones</b>									
Acetone	67-64-1	361	238.6	NA					

Methylethyl ketone	78-93-3	85								
Methylisobutyl ketone	108-10-1	755	37.8	38.1						
Methylhexanone	110-12-3		100.7	116.7						
<b>Other VOCs</b>										
Ethanol	64-17-5		299.6	NA						
Phenol	108-95-2				194	124				
1-Butanol	71-36-3	3.4								
2-Methoxy ethanol	109-86-4	2.6								
2-Ethoxy ethanol	110-80-5	68								
2-Butoxy ethanol		4.4								
2-Etoxyethyl acetate		25								
2-Butoxyethyl acetate		104								
Methylpyrrolidon	872-50-4	-	425.1	ND						
1-methyl-2-pyrrolidone						81				
Caprolactam						96				
2-Ethyl hexanoic acid						83				
2-(2-Butoxyethoxy)-ethanol						49				
<b>SVOC</b>										
Di-n-butyl phthalate (DBP)		0.7	NA	NA	NA	NA				
Di-ethylhexyl phthalate (DEHP)		ND	NA	NA	NA	NA	420	340	390	
<b>Other specific substances</b>										
Dimethylamine		9	NA	NA	NA	NA	NA	NA	NA	
Diethylamine		9.6	NA	NA	NA	NA	NA	NA	NA	
Di-n-butylamine		54	NA	NA	NA	NA	NA	NA	NA	
N-nitrosodimethylamine		0.2	NA	NA	NA	NA	NA	NA	NA	
<b>TVOC/Sum VOC</b>		<b>-</b>	<b>3828</b>	<b>10929</b>	<b>10865</b>	<b>5673</b>	<b>1999</b>	<b>9400</b>	<b>5100</b>	<b>15000</b>

## **Risk assessment of hazardous substances in the indoor environment of cars - a pilot study**

The objective of the project is to get an overview of whether the levels of Volatile organic compounds (VOC) in new cars can pose a health risk.

The interior parts of the car cabin consist of many synthetic materials, which may emit different chemical compounds. The contribution from each material to the car's indoor climate depends on the surface area of the material, and whether the surface is covered by other materials.

The project reviews studies that describe the measurements and results of VOC in the indoor air of new cars and uses these as basis for the risk assessments.

Substances with eye and respiratory tract irritation effects (e.g. aldehydes, phenol, methylpyrrolidone and caprolactam) and substances with neurotoxic effects (e.g. aliphatic and aromatic hydrocarbons) were detected in the studies.

The report concludes that when entering an overheated car, relatively high levels of eye and respiratory tract irritants may be accumulated in the cabin, which may cause risk for short-term eye irritation and respiratory tract irritation for the driver and the passengers.

Emissions of other substances are considered not to cause any health hazard for the driver and the passengers.



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