In-cabin VOCs:

Sources, health effects, and control methods

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Highlights:

- **Exposure to VOCs in vehicles may cause severe health problems such as: neurological system damage, lung cancer and leukemia.**
- **Interior materials are the main sources of in-cabin VOCs particularly for new cars, which can be gradually replaced by external sources (mainly vehicle exhaust emissions) along with the time of vehicle usage.**
- **The concentrations of TVOCs in new cars can reach up to more than 14,000 μg/m^3, which could cause discomfort feelings and headache even for short-term exposure.**
- **The highest concentration of VOCs, especially for benzene and 1,3-butadiene was in cars, compared to different other indoor microenvironments (homes, offices, restaurants, trains stations, trains, buses, etc) and other means of road transport (train, bus, bicycle).**
- **Many drivers elect to open windows or to have fresh air mode of ventilation to dilute VOCs emitted from internal sources. However, this method can expose the drivers and passengers to high levels of air pollutants, such as particles, present on roadways.**

1. Introduction

Vehicle interior air quality (VIAQ) is becoming an important issue worldwide as commuting by cars is one of the major transport modes by urban inhabitants. The exponential increasing number of vehicles resulting in high levels of vehicular gas and particle emissions, which have become one of the most challenging environment problems. Meanwhile, passengers in cars can have significant enhanced exposure levels of gas pollutants (NO, NO_2, CO, CO_2, and VOCs) and inhalable particulate matters (PM10, PM2.5, and ultrafine particles) [1]–[5]. The exposure to VOCs in vehicles is of increasing concerns due to their severe health effects reported, such as neurological system damage, lung cancer and leukemia [6], especially for new vehicles where VOCs levels are high. Most odors or scents in new cars are due to VOCs. This paper is to give a brief overview of VOCs in vehicles, and health effects due to exposure to VOCs, as well as potential control technologies for those pollutants.

2. VOCs: General background

VOCs (volatile organic compounds) are a big family of carbon-based chemicals with common members of more than 300 types. The definition of VOCs varies from country and organization, but all have the general characters of low boiling point, high vapor pressure, and strong reactivity, especially with respect to photochemical reactions [7]. VOCs can be sourced from natural and from human-made. Most scents and odors indoors, especially for microenvironments such as vehicles, are of VOCs. Organic components are often classified into four groups based on their different boiling point [8].

- Group 1: Very volatile organic compounds (gases), VVOC, with start boiling point < 0 °C;
- Group 2: Volatile organic compounds, VOC, with start boiling point of 50–100 °C;
- Group 3: Semi-volatile organic compounds, SVOC, with start boiling point of 240-260 °C;
- Organic particle matter, PM, with start boiling point of > 380 °C

In this study, the VOCs in vehicles only refer to those organic compounds in Group 1 and Group 2. Main types of VOCs present in vehicle microenvironments include such as: xylenes, toluene, undecane, dodecane, decane, heptane, trimethylbenzene, ethylbenzene, methylcyclohexane, styrene, benzene, formaldehyde, aldehydes, acetaldehyde, etc.

3. In-Cabin VOCs and sources

3.1 Sources of VOCs in vehicle cabins

VOCs inside vehicles have been investigated by plenty of studies. According to a study to investigate 101 Japanese private-use cars, it is identified that a total of 275 pollutants existing in the vehicle microenvironment [9], [10]. For emissions of VOCs into a vehicle, the most important source is from interior materials, which is the main sources particularly for new cars (less than 3 years of usage), as schematic shown in Figure 1. Plastics and rubber that used to produce interior components are of main responsibility. The most commonly used material for vehicle interior equipment is polyester. It has been commonly demonstrated that VOCs can be emitted from components, such as dashboard, steering wheel, insulations (plastics), seats and couch, wrapping of the steering wheel (artificial or natural leather), upholstery, soundproofing, roof ceiling, floor mats, seat covers. Other materials could be polyamide 6 and 6.6, and polypropylene, polyethylene and poly, polyurethane, for productions of floor mats, headrests, and seats. Among all these materials, natural leather is probably the biggest source of emissions of volatile organic compounds [8, and references therein]. The main SVOC found in vehicle cabins are phthalate esters (PES), brominated flame retardants (BFRs) and polycyclic aromatic hydrocarbons (PAHs) [9]. As SVOCs generally account for a large proportion of the material weight and their emission rates are relatively slow, they tend to exist in both new and old vehicles for a long time.

Although the VOCs in new vehicles are mainly sourced from interior materials, internal sources can be gradually replaced by emissions from external sources along with the time of vehicle usage. That means that in-cabin VOCs for a used car can be sourced from interior materials, and emissions penetrated or suctioned into the cabin from outdoor sources. Fuel combustion in car engines or gas evaporation during refuelling are the main sources of VOCs outdoors or on roadways for vehicles [8]. It has been reported that vehicle exhaust gases are the main sources of human exposure in used vehicles, especially for well-maintained cars in heavy traffic. Benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene (BTEX) are known as markers of vehicle exhaust gases emissions. Formaldehyde and acetaldehyde are also commonly detected as air pollutants inside vehicles, with significant increase observed after refuelling at fuel station [11].

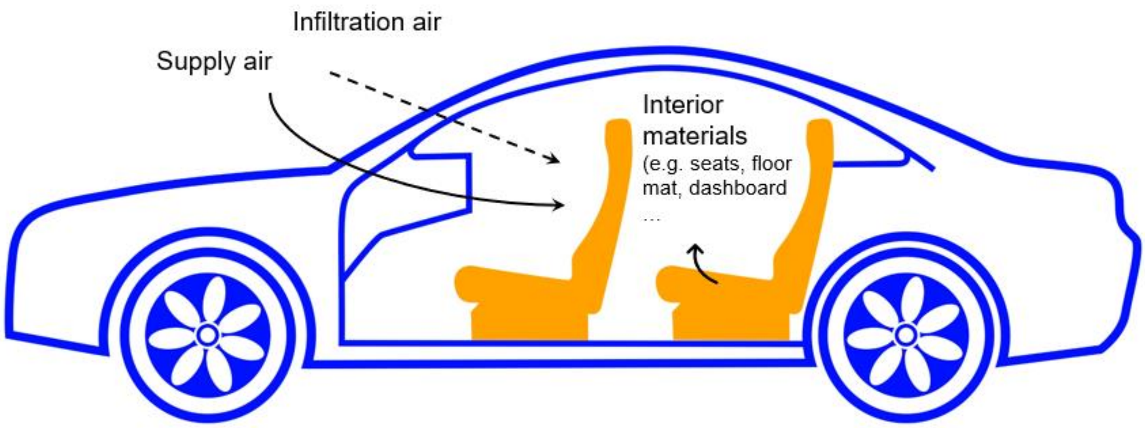

Figure 1. Main sources of VOCs in vehicles: emissions from interior materials are main sources for new cars, while supply air through ventilation system and infiltration air are important external sources for used cars.

3.2 Concentrations of VOCs in vehicles

It has been widely reported that VOCs in vehicles can be much higher than normal ambient air or other indoor environments [9], [12], and can significantly exceed the TVOC (Total volatile organic components) limits of 600 µg/m^3 specified by China's National Standard GB 18883-2002 [4]. Table 1 lists possible health effects due to short-term exposure to VOCs depending on different levels of VOCs. The concentrations of TVOCs in new cars can reach up to more than 14,000 µg/m^3 [8]. Such a level is associated with expected discomfort feelings and possible headache. Concentrations of VOCs inside vehicles are depending on different parameters, such as age of cars, ventilation situation, types of interior materials, air exchange rate, fuel type, refuelling process, moving conditions (parking or static status), interior and ambient temperature and relative humidity [6], [8], [11]. The levels of VOCs are often high for newly manufactured cars, at high interior temperatures, or with low air exchange rate. For example, when the interior temperature is high, it has been demonstrated that the driver is exposed to enhanced temporary VOCs, which happens especially when the drivers open the door to enter the cars[8]. Increased interior temperature leads to enhanced evaporation of organic components from materials, such as toluene for example[6], [8].

Based on the recent reviewed work of 47 studies, with measurements of more than 1500 vehicles [8], the following conclusions concerning VOCs inside vehicles can be draw:

- The concentrations of VOCs in parked vehicles (static conditions) were significantly higher than in vehicle during the test under normal operation (moving conditions) [6], [8]
- The concentrations of TVOC tested in new cars (with the age under 3 years) ranged from 136 to 14,081 µg/m^3, depending on vehicle models and test conditions;
- Main VOCs compounds in new vehicles, with frequency from high to low, are xylenes, toluene, undecane, dodecane, decane, heptane, trimethylbenzene, ethylbenzene, methylcyclohexane, styrene. (for example, 79% vehicles were tested with elevated concentration level of xylenes)
- The concentration of TVOCs in new vehicles were much higher than in used ones, not only with changes in compounds concentrations, but also changes the quantity of VOCs. A new car can be tested with ten times higher concentration of TVOCs than a 3-years old car with the same type
- The highest concentration of VOCs, especially for benzene and 1,3-butadiene was in cars, compared to different indoor microenvironments (homes, offices, restaurants, trains stations, trains, buses, etc) and other means of road transport (train, bus, bicycle)
- In old cars, TVOC concentrations ranged from 8 to 1130 µg/m^3, with BTEX components most frequently tested (Benzene: 0.75 – 250 µg/m^3, toluene: 32.2 – 770 µg/m^3)

Table 1. Possible health effects due to short-term exposure to TVOC concentration [8]

Concentration of TVOC (µg/m^3)	Possible health effects for short-term exposure
< 200	No irritation or discomfort feelings
200 – 3000	Possible irritation or discomfort feelings
3000 – 25,000	Expected discomfort feelings, possible headache
> 25,000	Possible neurotoxic effects

4. Health effects of exposure to VOCs

Volatile organic components can both influence human comfort, and may even have severe negative health impacts, especially for long-term exposure. Many VOCs are highly toxic and carcinogenic, such as aldehydes, aromatic compounds, polycyclic aromatic hydrocarbons, and ketones etc. For example, low level exposure of aldehyde, especially formaldehyde and acetaldehyde which are the major indoor air pollutants, would cause respiratory issues, such as throat irritation, shortness of breath, eye irritation, fatigue, and chest tightness [7]. Exposure of high concentration or for long-term exposure of low concentration could increase the risk of serious diseases such as nasopharyngeal cancer, pulmonary damage, leukemia, and sick building syndrome [7]. Apart from aldehydes, aromatic compounds can also cause severe health problems, particularly for benzene, which is classified to Group 1 by IARC (the International Agency for Research on Cancer), as shown in Table 2. Low concentration exposure of benzene would induce confusion, tiredness, nausea as well as loss of appetite, memory, and sight. High concentration exposure of benzene can be fatal [7]. A recent study revealed that the exposure of VOCs in current private vehicles (based on the tests of 23 different vehicle models) is associated with cancer risks that are higher than the acceptable risk levels defined by the WHO [4].

Types of VOCs with the greatest potential toxicity to humans in vehicles are listed in Table 2, including their main sources, and major possible effects to human health.

Table 2. Characters of VOCs with the greatest potential toxicity to humans in vehicles [7], [8], [13]

VOC type	Carcinogenic group by the IARC*	Main source in vehicle	Toxicity to humans due to short-term or long-term exposure
Benzene	Group 1**	By-product of combustion, exhaust gas from mobile sources, manufacture of chemicals such as plastics and solvents	Can lead to increased rates of leukemia, lymph cancer and blood cancer, can also result in eye, nose and throat irritation
Formaldehyde	Group 1	Used to produce adhesives used in fiberboard and particle board; also found in foam insulation, and textile finishing treatments	Can cause coughing, wheezing and chest pains, as well as eye, nose and throat irritation, and is associated with lung and nasopharyngeal cancers.
Ethyl benzene	Group 2B	Primarily used in the production of styrene	Has been associated with acute respiratory effects, such as throat and eyes irritation and neurological effects such as dizziness.
Styrene	Group 2B	Used to produce plastics, resins and synthetic rubbers	Has a negative neurotic effect, can cause genetic illness, respiratory problems and throat irritation, eye irritation, and may have a carcinogenic effect
Toluene	---	Used as an additive in vehicle fuels, in paints, varnishes and glues, and in the production of other chemicals.	Has neurological effects, such as muscle weakness, tremors and impairment of speech. Can cause headache, nausea, has impact on awareness
Xylene	---	Used as a solvent in paints and inks, and also in the production of plastics, leather and rubber.	May cause liver and kidney damage, and can also result in dizziness, headache and confusion. Skin contact with xylene can cause irritation and discoloration, as well as dryness, cracking and blistering.
Acetaldehyde	--	Used in fuel compositions and as a solvent for rubber and leather tanning, and also in the production of polyester resins and basic dyes.	Negative effects include irritation of eyes, skin and respiratory track, is known to be toxic, mutagenic or carcinogenic.

* IARC – the International Agency for Research on Cancer

** A category 1 substance is known or presumed to have carcinogenic/mutagenic potential for humans with strong evidence. For category 2A, the agents are probably carcinogenic to humans and the assessment is based primarily on human evidence; for category 2B, the agents are possibly carcinogenic to humans and the assessment is based primarily on animal evidence.

5. Regulations on VOCs in vehicles

Regulations or standards to set levels of VOCs deemed safe for human exposure in new vehicles have been implemented mainly in four countries, they are, Korea, China, Japan, and Russia. A comparison of controlled components and their guideline values can be seen in Table 3. These standards differ in their requirements of which VOC concentrations are measured, as well as their permissible levels. The Russia standard set maximum allowable concentrations on Formaldehyde (0.05 mg/m^3), Nitrogen Dioxide (0.2 mg/m^3), Nitrogen Oxide (0.4 mg/m^3), Carbon Monoxide (5 mg/m^3), Aliphatic hydrocarbons (50 mg/m^3), and Methane (50 mg/m^3), which is not included in Table 3.

Table 3. Comparison of standards on VOC concentrations in vehicles

VOC component	Standard and guideline value (mg/m^3)		
	Korea (since 2007)	China (GB/T 27630, new version since 2016)	Japan (since 2005)
Toluene	1.0	1.0	0.26
Xylene	0.87	1.0	0.87
Formaldehyde	0.25	0.1	0.10
Ethylbenzene	1.6	1.0	3.80
Styrene	0.3	0.26	0.22
Benzene	0.03	0.05	-
Acetaldehyde	-	0.02	0.05
Acrolein (2-propenal)	-	0.05	-
Paradichlorobenzene	-	-	0.24
Tetradecane	-	-	0.33
di-n-butyl phthalate	-	-	0.22
di-2-ethylhexyl phthalate	-	-	0.12

The test methods used in the above-mentioned national standards are different in terms of sample preparation time, sampling duration period, and sampling conditions. This culminate in the development of harmonised methods to quantitate the VOCs emissions and concentrations in vehicles, such as the ISO 12219 part 1-9, published in 2012. Unlike the national standards mentioned above, ISO 12219 series for interior air of road vehicles do not prescribe concentration guideline values for individual VOC components. ISO 12219-1 specifies VOC measurement sampling for passenger vehicles during three distinct modes of vehicle operation (ambient mode, parking mode and driving mode) in order to assess VIAQ under all anticipated operating conditions. While other parts of the standard series define different test methods for VOC emissions from vehicle interior parts and materials.

6. Control Technologies for VOCs

6.1 Overview of control methods for major VOCs

Owing to the toxicity of VOCs to humans and environment, developing of effective VOC control techniques is of great significance. There have been many VOC removal techniques emerged, as illustrated in Figure 2. Preferred methods for controlling VOCs emissions are modifications in process and equipment, which include the substitution of raw materials to reduce VOC input, changes in operating conditions to minimize formation of VOCs, and modifications of equipment to reduce release of VOCs into environment [14]. Alternatively, once VOCs are released from processes, there are lots of control techniques to remove VOCs, which can be generally divided into recovery methods and destruction methods. As can be seen in Figure 2, the destruction methods comprise oxidation and biological treatments. Oxidation techniques, including plasma chemical treatment, photocatalysis, thermal oxidation and catalytic oxidation, are being developed at bench and pilot scale, and some have been commercially wide used, such as catalytic oxidation by using ozone. Biological process is emerging as a cost-effective method for VOC treatment. When it comes to recovery techniques, absorption, adsorption, condensation, and membrane separation are the principle emerged methods.

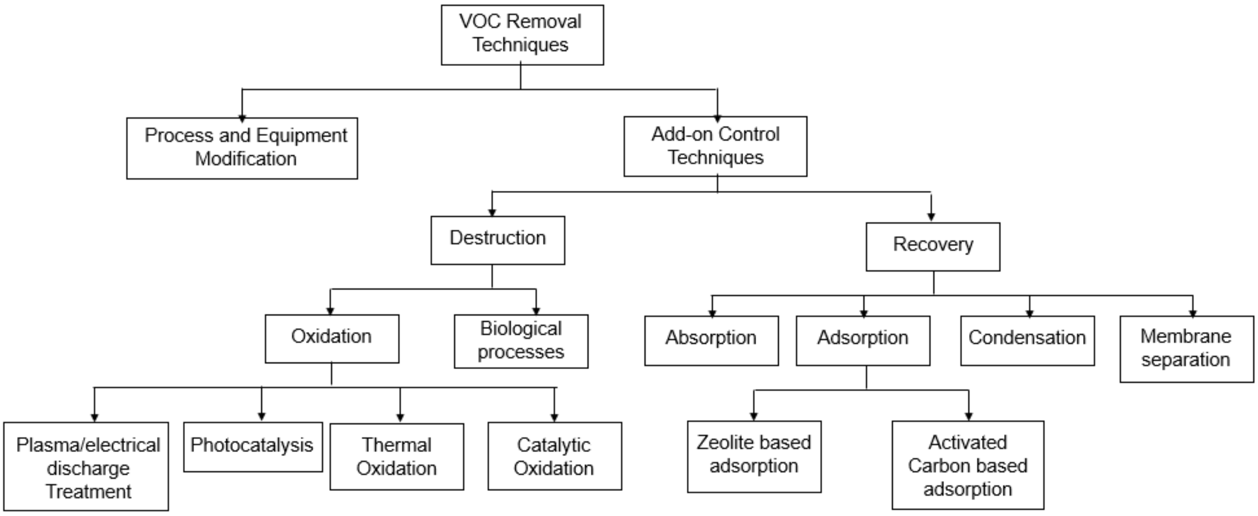

Figure 2. Flowchart showing different VOC control techniques [14]

The choice of a specific control technology for VOCs should consider the concentrations of VOCs to be treated, and other factors related to the technology, such as the removal efficiency, cost, recovery of materials, energy reuse, secondary waste generation, operation conditions, etc. In Table 4, some characters concerning the choice of a specific technology are summarized in terms of their market sales scale, reuse of materials, secondary waste products, energy consumption, and a suitable VOCs concentration. The merits and demerits of different types of VOCs removal technologies are listed in Table 5.

Table 4. Technological characteristics of VOC removal methods [7]

Methods	Market sales	Reuse	Waste generation	Energy consumption	Suitable for VOCs concentration
Incineration	**High**	No	CO, NOx	Moderate	20% - 25%
Condensation	**High**	Yes	-	High	>5000 ppm
Biological degradation	Nc*	No	Acetaldehyde, Propanal, Acetone	Low	<5000 ppm
Absorption	Low	Yes	Spent absorbent	Moderate	-
Adsorption	**High**	Yes	Spent adsorbent	Moderate	700-10000 ppm
Plasma catalysis	Nc*	No	Formic acid, Carboxylic acids, NOx, O3	High	-
Photocatalytic oxidation	Low-moderate	No	Strong oxidant OH radicals	Moderate	-
Ozone-catalytic oxidation	**High**	No	Secondary organic aerosols	High	-
Membrane	Nc*	Yes	Clogged membranes	High	<25%

* Not widely commercialized

Table 5. Merits and demerits of emerging VOCs removal technologies [14]

Technique		Attainable removal efficiency	Merits	Demerits
Oxidation processes	Plasma treatment	90%	This treatment especially is more beneficial for low concentrations of VOCs, having advantage of energy saving and no production of dioxin	In general needs very huge electrical energy, solvents cannot be recovered for reuse.
	Photocatalysis	90-100%	Sunlight can be used to activate low-cost photocatalyst. Amenable for scale-up. Wider application scope	Reaction rates need to be enhanced by 10-to 100-fold for cost-effectiveness
	Thermal oxidation	95-99%	Energy recovery is possible	Halogenated and other oxidation compounds may require additional control equipment downstream
	Catalytic oxidation	90-98%	Energy recovery is possible	Efficiency is sensitive to operating conditions. Certain compounds can poison the catalyst. May require additional control equipment downstream
Biological processes		60-95%	Requires less initial investment, less non-harmful secondary waste, and nonhazardous	Slow, and selective microbes decompose selective organics, thus requires a mixed culture of microbes (which is difficult). No recovery of material
Absorption		90-98%	Wastewater product can be recovered	Requires rigorous maintenance. May require pretreatment of VOCs. Design could be difficult due to lack of equilibrium data.
Adsorption	Zeolite based adsorption		nonflammable, thermal-stable, and hydrophobic, allowing selective adsorption of some compounds while excluding others, effective in more than	The cost of hydrophobic zeolite is still very high, restricted availability

			90% RH, recovery of compounds	
	Activated carbon-based adsorption		Flexible and inexpensive to operate, recovery of compounds	Difficult to regenerate for high-boiling solvents, promote polymerization or oxidation of some solvents to toxic or insoluble compounds, susceptible to moisture, and some compounds (ketones, aldehydes, and esters) can clog the pores, thus decreasing the efficiency
Condensation		70-85%	Product recovery can offset annual operating costs	Requires rigorous maintenance. Not recommended for the materials having boiling points above 33 Celsius degree
Membrane		90-99%	No further treatment, solvent can be recovered	Membranes are costly due to the requirement of vacuum pumps and refrigeration equipment, and possible additional separation systems

Carbon adsorption is a very common method of VOCs emission control due to the low cost and high efficiency which is related to the large surface area of activated carbon. VOC molecules are physically adsorbed to the surface of the carbon. Moisture is one of the crucial parameters and dictates the efficiency and effectiveness of the process. The applications of activated carbon present some disadvantages as they are flammable, are difficult to regenerate for high-boiling solvents, promote polymerization or oxidation of some solvents to toxic or insoluble compounds, and require humidity control.

6.2 Control technologies of VOCs in vehicles

Active carbon filters used inside HVAC air intake system is one of the main technologies used by many automotive industries. The efficiency of such method is not only depending on the efficiency of the carbon infused cabin air filters but is also highly related to target sources of VOCs inside vehicles. VOCs from outdoor air may be effectively controlled with a carbon filter integrated in the ventilation system, but the efficiency on internal sources can be very limited [9]. Alternatively, new materials with lower VOC emission potential is recommended to be used to minimize in-cabin VOC sources for new cars [15]. Optimization of refuelling process can reduce the external emission sources of VOCs that can penetrate cabins. Proper setting of ventilation conditions is another method to effectively lower interior VOCs with fan on and recirculation off while driving [6]. Since the ambient carbon dioxide concentration and VOCs concentrations are much lower than in-cabin levels, many drivers elected to drive with windows open to increase the air exchange between inside cabins and outside to dilute VOCs and CO2 emitted from internal sources. However, this method can expose the drivers and passengers to high levels of air pollutants, such as particles, present on roadways [1], [9].

7. Conclusion

Driven by toxicity and negative effects of VOCs on humans and environments, elevated attentions have been paid on VOCs in vehicles, where concentrations of those organic components can be high due to both internal and external sources. Sources of VOCs emissions can differ in new and used cars. The concentration of TVOCs in new vehicles were much higher than in used ones, not only with changes in compounds concentrations, but also changes the quantity of VOCs. Off-gas emissions from interior materials are the main sources of VOCs in new cars, while these internal sources can be gradually replaced by external sources in used cars. Vehicle exhaust emissions are the main external sources, containing the majority of BTEX. Concentrations of VOCs inside vehicles are depending on different parameters, such as age of cars, ventilation situation, types of interior materials, air exchange rate, fuel type, refuelling process, moving conditions (parking or static status), interior and ambient temperature and relative humidity. In new cars, the concentrations of TVOCs can range from 136 to 14,081 μg/m^3, depending on vehicle models and test conditions. The high levels of VOCs concentrations in vehicles are of great concern if considering their impact on humans. Many types of VOCs that are commonly detected in vehicles are toxicity and can even have severe health effects, such as negative neurotic effect and carcinogenic effect. Regulations on VOCs in vehicles are available in four countries, but it is likely that legislative regulations concerning vehicle interior air quality will be introduced by more and more countries. This will be not only depending on the increased recognition of health risks connected with the exposure of VOCs, but also on the harmonized test methodologies. A couple of technologies are available both on the industrial market and in the research level for the removal of VOCs, however, there is very limited effective methods to control those organic components in vehicles by far.

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