Forward Simulation Study on the Emission Characteristics of Volatile Organic Compounds in Cars

Liping Tong¹, *, Shujie Xu¹, Lei Wang¹, Wei Liu¹ and Xuefeng Liu¹

¹China Automotive Data Co., Ltd., China Automotive Technology & Research Center Co., Ltd., Tianjin 300300, China
Email: tongliping@catarc.ac.cn

Abstract. Volatile organic compounds (VOC), represented by formaldehyde and benzene, are highly carcinogenic and teratogenic, and can easily cause dizziness, nausea, vomiting and other illnesses. Their emission characteristics have a significant risk to the physical and mental health of passengers. The forward simulation of the emission characteristics of VOC in cars has become one of the important technical challenges for the automotive industry. In order to solve this problem, the emission and adsorption characteristics of VOC from interior parts of a car were investigated through a multi-interior coexistence experimental system. Based on this, a VOC emission prediction model was proposed in combination with the mass conservation law of VOC in the car and Henry's law of VOC, and validated by engineering amplification for 22 pieces of interior co-existence simulated final assembly experiments, illustrating that the relative standard deviations of the model for VOC in the car were 30.0% (benzene), 50.0% (toluene), -9.8% (ethylbenzene), 10.0% (xylene), -23.5% (formaldehyde), and -28.9% (acetaldehyde), respectively, with good prediction effect, which are able to greatly meet engineering needs.

1. Introduction
By the end of June 2017, the number of vehicle owners in China reached 205 million, with more than 320 million drivers. Drivers and passengers spend billions of hours per day inside a car. This number is predicted to increase at the rate of 7% per year. Under such circumstances, air pollution in an automotive cabin with volatile organic compounds (VOC) as the main component has become a crucial health issue and increasingly attracts attention [1-4]. At the 2013 International Summit on Air Quality and Development in an Automotive Cabin held in Beijing, air pollution in a car was defined as the third greatest indoor environmental pollution hazard towards human health after decoration/furniture pollution and indoor environment PM2.5 pollution. The World Health Organization (WHO) also lists VOC as one of the top ten threats to human health. Their toxicity and excitability can cause irritation and dryness of the eyes, nose, and throat. They can also cause fatigue, headaches, dizziness, memory loss, nausea and skin itching, as well as infant malformations, leukaemia, and cancer in severe cases [5-6]. Therefore, effective control of air quality in an automobile is relevant to everyone’s health and is of great significance to the development of environmental protection in the country and the automotive industry.

At present, VOC emission prediction technology can simulate and predict the amount of VOC emission in an automotive cabin at the research and development stage of a new model, which can help a business to rapidly screen for the interior that complies with the national requirement for the VOC emission limit from the entire vehicle. The model helps to reduce the rectification process of VOC emission as well as the detection cost and improves the air quality inside the car. Hence, the model has great research value and application potential in the automotive industry.
There is much literature on the research of indoor VOC emission prediction models for improving indoor air quality. The prediction model includes an empirical model, semi-empirical model, and theoretical model [7-12]. The theoretical model includes a single-phase mass transfer model, multi-phase mass transfer model, and adsorption-desorption model. However, there is no related report on the prediction research of VOC emission amounts in an actual automobile interior. Compared to indoor VOC emissions, VOC pollutant emission in a car is more critical due to the narrow space, large number of interior parts, various types of materials, and poor ventilation, etc. In addition, due to the significant difference between VOC emissions in a car and indoors, the indoor VOC prediction model cannot be directly applied to a car. After a deep investigation of indoor VOC emission prediction models and a comprehensive inspection of the standard and cost of detection of interior VOC and entire vehicle VOC, we propose the first VOC emission prediction model for the interior of an automobile based on equilibrium adsorption theory. This study, based on the law of conservation of mass and Henry’s law, uses the interior adsorption effect as the key influence factor and validates the prediction results using co-present simulation assembly experiments of 22 key controlled interiors.

2. The Adsorption Effect on VOC by the Interior
Studies have shown that indoor furniture and building materials, such as carpet and plasterboards, adsorb a certain number of VOC when they emit them. That is, furniture and building materials are both emission sources and adsorption sinks. According to the regulations in HJ/T 400-2007, Determination of VOC and aldehydes/ketones in vehicles, an entire vehicle needs to be parked in a 25.0°C±1.0°C environment for 16 h. To verify that the VOC adsorption effect of the interior of a parked car is as found in furniture and building materials, we studied VOC emission amounts from two and three interiors and compared our results to that of a single interior, as shown in Figure 1. Figure 1(a) shows the VOC emission determination test results from the ceiling and front seat assembly individually and simultaneously. Figure 1(b) shows the VOC emission amount from the front door seal, dashboard assembly, and carpet individually and simultaneously. As seen from Figure 1, for the VOC pollutants toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde, the sum of VOC emissions from the ceiling and front seat assembly individually is significant higher than the VOC emissions when both are present. The sum of VOC emissions from the front door seal, dashboard assembly, and carpet individually is dramatically higher than the VOC emissions when all three are present. Under some situations, the overall VOC emissions from two interiors or three interiors simultaneously is less than that of a single interior. This indicates that the interior can emit VOC and significantly adsorb VOC. This conclusion is consistent with previous research on indoor building materials [11, 13]. At the same time, the adsorption effect of the interior has a significant influence on the prediction of VOC emission. Therefore, the adsorption effect of interiors on VOC is the focus of this study.

Figure 1. Comparison of VOC emission amounts from individual interiors and when several interiors are present. (a) Comparison of VOC emission amounts from 1 interior alone and 2 interiors simultaneously; (b) Comparison of VOC emission amounts from individual interiors and when three are present
3. Construction of a VOC Emission Prediction Model for Several Co-Present Interiors

To build a VOC emission prediction model for multiple co-present interiors, a VOC adsorption physical model was built for two co-present interiors, as shown in Figure 2.

![Figure 2. The physical model of the interior VOC adsorption effect](image)

According to the law of conservation of mass, the mass of VOC before and after emission can be calculated as follows,

\[
\begin{align*}
C_{ax}V + C_{bx}b + C_{mx1}m1 + C_{mx2}m2 &= C_{m01}m1 + C_{m02}m2 \\
&= C_{ax}V + C_{bx}b + C_{mx1}m1 + C_{mx2}m2
\end{align*}
\]

(1)

Where \( C_{ax} \) (\( \mu g/m^3 \)) is the VOC concentration in the air of the sampling bag after a certain time of emission; \( C_{bx} \) (\( \mu g/m^3 \)) is the VOC concentration adsorbed on the sampling bag; \( C_{mx1} \) (\( \mu g/m^3 \)) is the VOC concentration adsorbed on interior 1; \( C_{mx2} \) (\( \mu g/m^3 \)) is the VOC concentration adsorbed on interior 2; \( C_{m01} \) (\( \mu g/m^3 \)) is the initial emission concentration from interior 1; \( C_{m02} \) (\( \mu g/m^3 \)) is the initial emission concentration from interior 2; \( V \) (\( m^3 \)) is the nitrogen volume in the sampling bag; \( V_b \) (\( m^3 \)) is the adsorption volume of the sampling bag; \( V_{m1} \) (\( m^3 \)) is the volume of interior 1; and \( V_{m2} \) (\( m^3 \)) is the volume of interior 2.

When VOC emission from interior 1 and interior 2 reach equilibrium, according to Henry’s law:

\[
K_b = \frac{C_{bx}}{C_{ax}}
\]

(2)

\[
K_1 = \frac{C_{mx1}}{C_{ax}}
\]

(3)

\[
K_2 = \frac{C_{mx2}}{C_{ax}}
\]

(4)

Where \( K_b \), \( K_1 \), and \( K_2 \) are the solid-gas interface distribution coefficients of VOCs in the sampling bag, interior 1, and interior 2, respectively, which can be obtained by experimental measurement. In this paper, we focus on the adsorption effect of the interior on VOCs. The detailed measurements of \( K_b \), \( K_1 \), and \( K_2 \) are not introduced here, and reference values are used as known and listed below. Combining equations (1) through (4) obtains

\[
C_{ax} = \frac{C_{m01}m1 + C_{m02}m2}{V + K_b V_b + K_1 V_{m1} + K_2 V_{m2}}
\]

(5)

Where \( K_b \), \( K_1 \), \( K_2 \), \( V \), \( V_{m1} \), \( V_{m2} \), and \( V_b \) are known. Therefore, to obtain the VOC concentration, \( C_{ax} \) in the sampling bag, \( C_{m01} \) and \( C_{m02} \) must be measured. These two concentrations can be obtained from the VOC emissions from interior 1 and interior 2 individually, as shown in Figure 3.
Figure 3. VOC emission schematic of interior 1 and interior 2 individually

According to the law of conservation of mass, the VOC emission equations from interior 1 and interior 2, respectively, are as follows:

\[ C_{a1}V_1 + C_{a1}V_1 + C_{a1}V_1 = C_{m1}V_{m1} \]  \hspace{1cm} (6)

\[ C_{a2}V_2 + C_{a2}V_2 + C_{a2}V_2 = C_{m2}V_{m2} \]  \hspace{1cm} (7)

Where \( C_{a1} \) and \( C_{a2} \) (μg/m\(^3\)) are the VOC concentrations in the sampling bag after a certain period of emission from interior 1 and interior 2 individually; \( C_{b1} \) and \( C_{b2} \) are the VOC concentrations adsorbed on the sampling bags; \( C_{m1} \) and \( C_{m2} \) (μg/m\(^3\)) are the VOC concentrations adsorbed on interior 1 and interior 2 when they are alone; \( C_{m01} \) (μg/m\(^3\)) is the initial emission concentration from interior 1; \( C_{m02} \) (μg/m\(^3\)) is the initial emission concentration from interior 2; \( V_1 \) and \( V_2 \) (m\(^3\)) are the nitrogen volume in the sampling bag from interior 1 and interior 2 separately; \( V_{b1} \) and \( V_{b2} \) (m\(^3\)) are the adsorption volume of the sampling bag from interior 1 and interior 2 separately; and the other parameters are the same as above.

When VOC emissions in the sampling bags of interior 1 and interior 2 reach equilibrium, the following equations can be obtained according to Henry’s law,

\[ C_{a1}(V_1 + K_1V_{b1} + K_1V_{m1}) = C_{m1}V_{m1} \]  \hspace{1cm} (8)

\[ C_{a2}(V_2 + K_2V_{b2} + K_2V_{m2}) = C_{m2}V_{m2} \]  \hspace{1cm} (9)

Insertion of equations (8) and (9) into equation (5) obtains the equilibrium concentration of VOC emissions when two interiors are present:

\[ C_{ax} = \frac{C_{a1}(V_1 + K_1V_{b1} + K_1V_{m1}) + C_{a2}(V_2 + K_2V_{b2} + K_2V_{m2}) + ... + C_{an}(V_n + K_nV_{b_n} + K_nV_{m_n})}{V + K_1V_{b1} + K_1V_{m1} + K_2V_{b2} + K_2V_{m2} + ... + K_nV_{b_n} + K_nV_{m_n}} \]  \hspace{1cm} (10)

Equivalent expansion of equation (10) provides the modelling equation of VOC concentration \( C_{axn} \) when \( n \) interiors are present in the bag,

\[ C_{axn} = \frac{C_{a1}(V_1 + K_1V_{b1} + K_1V_{m1}) + C_{a2}(V_2 + K_2V_{b2} + K_2V_{m2}) + ... + C_{an}(V_n + K_nV_{b_n} + K_nV_{m_n})}{V + K_1V_{b1} + K_1V_{m1} + K_2V_{b2} + K_2V_{m2} + ... + K_nV_{b_n} + K_nV_{m_n}} \]  \hspace{1cm} (11)

All parameters on the right side of equation (11) are known. It is known from observation that the VOC equilibrium concentration \( C_{axn} \) for \( n \) interiors in the bag can be predicted from insertion in equation (11) of the VOC concentration of an individual interior.

4. Determination of the Equilibrium Time of VOC Emission

According to the derivation of equation (11), \( C_{axn} \) is the equilibrium concentration of VOC emissions. Therefore, the precondition of using equation (11) to predict the VOC concentration in the car is that the entire vehicle has been in a sampling environment of 25°C for 16 h to reach emission equilibrium. To verify that equation (11) can be used for predicting VOC emissions in a car, the dynamic emission processes of VOC from several individual interiors were investigated. Here, the VOC emission process from a dashboard assembly is used as an example, as shown in Figure 4. The bag sampling method was used for VOC emission measurement on a dashboard assembly at 25°C and air samples...
were taken at 1 h, 2 h, 4 h, 7 h, 10 h, and 24 h using a Tenax tube and DNPH tube from the bag to obtain data for VOC emission over time. The change in VOC emission over time can be observed by curve fitting, and the time to reach equilibrium can be clearly determined. Figures 4(a), (b), (c), (d), and (e) show that the emissions of toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde from the dashboard assembly reach equilibrium after 16 h at 25°C. Due to the presence of multiple interiors in the vehicle, VOC emission is accelerated. The VOC emission rate in the entire vehicle is faster than that from individual interiors. Hence, it is assumed that VOC emission reaches equilibrium after 16 h at 25°C for the entire vehicle, and equation (11) can be used for the VOC emission prediction in the car.

![Graphs of VOC emissions](image)

**Figure 4.** The plot of dynamic VOC emission from typical interiors against elapsed time.
5. Validation of VOC Emission Prediction Model in the Presence of Multiple Interiors

To validate the accuracy of equation (11) for VOC emission predictions, VOC emission tests were performed in the presence of two or three of the five typical vehicle interiors: the ceiling, front seat assembly, front door seal, dashboard assembly, and carpet. The results are shown in Table 1 and Table 2. $K$, the distribution coefficient of VOC on the solid gas interface, was obtained for each interior from experimental measurements. See the references for detailed information [14-15]. From the relative ($(C_{ax}^{predicted} - C_{ax}^{measured}) / C_{ax}^{measured}$ × 100%) and absolute $(C_{ax}^{predicted} - C_{ax}^{measured})$ (in Table 1 and 2) prediction error, the prediction model equation (11) showed excellent prediction ability for ethylbenzene and xylene with relative prediction errors of ±17%. It has a higher relative prediction error for benzene and toluene but a lower absolute prediction error. The relative prediction error for acetaldehyde is between -30% and -35%. The prediction for formaldehyde is relatively poor, with a relative prediction error between 10% and 90% (830% corresponding to an absolute value of 4.2 µg/m$^3$, a low absolute prediction error).

The prediction equation (11) exhibits excellent VOC emission prediction results for the experiments when two and three interiors are present simultaneously. Therefore, to investigate VOC emission by the entire vehicle using the prediction model, a VOC emission experiment using 22 key controlling interiors was performed to simulate VOC emission from the entire vehicle (Figure 5). The measured values and predicted values were compared to verify the accuracy of the VOC emission prediction model. Figure 5 shows that the errors of the simulation for benzene, toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde are 32%, 50%, -10%, 10%, -24%, and -29%, respectively. Aside from benzene and toluene, the prediction results are excellent, with errors for all components within ±30%, which meets the industrial application requirement. The large prediction errors for benzene and toluene are due to the relatively low measured content of these two components. The measured concentration values exhibit a larger error, especially for benzene. The measured value is near the detection limits of the instrument and mostly undetected, which significantly affects the accuracy of the prediction.

### Table 1. Predicted VOC emissions for two interiors present simultaneously

| Name             | VOC       | $K$ | $C_a$ $\mu g/m^3$ | Predicted $C_{ax}$ $\mu g/m^3$ | Measured $C_{ax}$ $\mu g/m^3$ | Relative prediction error $\%$ | Absolute prediction error $\mu g/m^3$ |
|------------------|-----------|-----|-------------------|-------------------------------|-------------------------------|--------------------------------|----------------------------------|
| Ceiling assembly | Benzene   | 543 | 0.5               | 5.5                           | 5.5                           | 1.2                            | 0.0                              |
|                  | Toluene   | 389 | 0.5               | 4.2                           | 6                             | -29.3                          | -1.8                             |
|                  | Ethylbenzene | 1690 | 23       | 26.4                          | 30                           | -11.9                          | -3.6                             |
|                  | Xylene    | 311 | 170              | 181.1                         | 162                          | 11.8                           | 19.1                             |
|                  | Formaldehyde | 1923 | 26       | 4.7                           | 0.5                          | 830.6                          | 4.2                              |
|                  | Acetaldehyde | 168  | 42              | 13.2                         | 19                           | -30.3                          | -5.8                             |
|                  | Benzene   | 4196 | 0.5              |                               |                               |                                |                                  |
|                  | Toluene   | 235 | 5.0              |                               |                               |                                |                                  |
|                  | Ethylbenzene | 114  | 25              |                               |                               |                                |                                  |
|                  | Xylene    | 166 | 143              |                               |                               |                                |                                  |
|                  | Formaldehyde | 1923 | 0.5       |                               |                               |                                |                                  |
|                  | Acetaldehyde | 643  | 9               |                               |                               |                                |                                  |
Table 2. The VOC emission prediction results from the coexistence of three interiors

| Name          | VOC      | $K$  | $C_a$ $\mu g/m^3$ | Predicted $C_{ax}$ $\mu g/m^3$ | Measured $C_{ax}$ $\mu g/m^3$ | Relative prediction error $\%$ | Absolute prediction error $\mu g/m^3$ |
|---------------|----------|------|-------------------|---------------------------------|--------------------------------|-------------------------------|----------------------------------------|
| Front door    |          |      |                   |                                 |                                 |                               |                                        |
| seal          | Benzene  | 27   | 0.5               | 0.7                             | 0.5                             | 30.7                          | 0.2                                    |
|               | Toluene  | 1429 | 0.5               | 1.7                             | 4                               | -58.0                         | -2.3                                   |
|               | Ethylbenzene | 2729 | 9                 | 11.5                            | 11                              | 4.3                           | 0.5                                    |
|               | Xylene   | 3326 | 74                | 89.6                            | 77                              | 16.4                          | 12.6                                   |
|               | Formaldehyde | 2152 | 10                | 52.5                            | 37                              | 41.8                          | 15.5                                   |
|               | Acetaldehyde | 506  | 0.5               | 11.8                            | 18                              | -34.7                         | -6.2                                   |
| Dashboard     | Benzene  | 3    | 0.5               | 0.5                             | 59                              | 4                             |                                        |
|               | Toluene  | 59   | 0.5               | 0.5                             | 104                             | 11                            |                                        |
|               | Ethylbenzene | 104  | 11                | 11                              | 104                             | 11                            |                                        |
|               | Xylene   | 203  | 81                | 203                             | 203                             | 81                            |                                        |
|               | Formaldehyde | 2074 | 61                | 2074                            | 2074                            | 61                            |                                        |
|               | Acetaldehyde | 23   | 7                 | 23                              | 23                              | 7                             |                                        |
|               | Benzene  | 1511 | 0.5               | 1511                            | 1511                            | 0.5                           |                                        |
|               | Toluene  | 577  | 0.5               | 577                             | 577                             | 0.5                           |                                        |
|               | Ethylbenzene | 1102 | 10                | 1102                            | 1102                            | 10                            |                                        |
|               | Xylene   | 291  | 72                | 291                             | 291                             | 72                            |                                        |
|               | Formaldehyde | 1604 | 25                | 1604                            | 1604                            | 25                            |                                        |
|               | Acetaldehyde | 111  | 15                | 111                             | 111                             | 15                            |                                        |

Figure 5. Validation of VOC emission predictions using a 22 interior simulated assembly test

Overall, application of the VOC emission prediction model to multiple interiors can be expanded to the inside of the entire vehicle. However, the VOC emissions of the entire vehicle are affected by the concentration decrease, the overall airtightness, the shelter effect of various interior parts, and the relative humidity difference, etc [16]. These factors were not considered in this prediction model. In addition, due to the large difference between the interior part materials, processing technology, storage conditions, and VOC detection conditions, etc., of different automotive manufacturers, the measured VOC concentration had large errors. Due to the above two reasons, the current prediction model equation (11) shows some reference value to the entire vehicle VOC emission prediction but still needs further amendments to meet industrial application requirements.

6. Conclusions
This study proposed a VOC emission prediction model which is derived based on the law of conservation of mass and Henry’s law. Tests using the co-presence of two interiors and three interiors show that the model exhibits excellent prediction ability for ethylbenzene and xylene with a relative
prediction error of ±17%. It shows a higher relative prediction error for benzene and toluene but a lower absolute prediction error. The relative prediction error for acetaldehyde is between -30% and -35%. The prediction for formaldehyde is comparatively poor, with a relative error between 10% to 90%. A simulated assembly test using 22 interiors showed that the differences between the simulation and test for benzene, toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde are 30%, 50%, -9.8%, 10%, -23.5%, and -28.9%, respectively. Overall, the proposed equilibrium adsorption model has excellent prediction results for VOC emissions when multiple interiors are present. It meets the requirements of industrial application and provides a sufficient theoretical basis for predicting VOC emissions in the entire vehicle cabin. In addition, compared to other VOC emission prediction mass transfer models and adsorption desorption models, the present model uses the measured results of VOC emissions of interiors parts from manufacturers directly, which makes efficient use of VOC detection results and reduces detection costs for the automotive industry. Therefore, this model exhibits great application potential and is expected to achieve the forward design of VOC emissions of an entire vehicle in the R&D phase of a new model.

7. Acknowledgments
This research was supported by China Automotive Technology & Research Center Co., Ltd.,

8. References
[1] Cao J, Weschler C J, Luo J, et al. 2016 Environmental science & technology 50(2): 825
[2] Zheming Tong, Hao Liu. 2020 Sustainability 12(14) 5526
[3] Yue, T, Yue, X, Chai, F, et al. 2017 Atmospheric Environment 151: 62-69
[4] Wang Haimei, Zheng Jihu, Yang Tao, et al. 2020 Environment International 142: 105817
[5] Nicole Zulauf, Janis Dröge, Doris Klingelhöfer, et al. 2019 International Journal of Environmental Research and Public Health 16: 2441
[6] Bo Lianga, Xiang Yua, Haipeng Mi, et al. 2019 Atmospheric Pollution Research 10(5): 1677-1684
[7] Little J C, Hodgson A T, Gadgil A J. 1994 Atmospheric Environment 28(2): 227-234
[8] Zhang Xu, Cao Jianping, Wei Jingya, et al. 2018 Building and Environment 143: 570-578
[9] Lee, C, Haghighat, F, Ghaly, et al. 2005 Indoor air 15(3): 183-196
[10] Zhang, Y, Xiong J, Mo J, et al. 2015 Indoor air 26(1): 39-60
[11] Cao, J, Weschler, C, Luo, J, et al. 2016 Environmental science & technology 50(2): 825
[12] Tong-Bou Chang, Jer-Jia Sheu, Jhong-Wei Huang, et al. 2018 Transportation Research Part D 62: 433-440
[13] Matthews T G, Hawthorne A R, Thompson C V, 1987 Environmental science & technology 21 629-34
[14] Xiong J, Chen W, Smith J F, Zhang Y, et al. 2009 Atmospheric Environment 43(26) 4102-4107
[15] Deng Q, Yang X, Zhang J S, 2010 HVAC&R Research 16 (1) 95-105
[16] Huang H, Haghighat F, Blondeau P, 2006 Indoor air 16 (3) 236-47