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Improvement of the Theoretical Model for Evaluating Evaporative Emissions in Parking and Refueling Events of Gasoline Fleets Based on Thermodynamics

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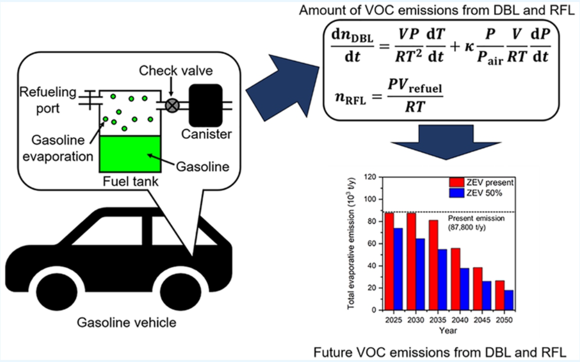
ABSTRACT: Evaporative emissions from gasoline vehicles are known as an emission source of volatile organic compounds that are the precursors of tropospheric ozone and secondary organic aerosols. We formulated new estimation models based on thermodynamics for two main evaporation processes, namely diurnal breathing loss (DBL) and refueling loss (RFL) from gasoline vehicles. The models enable us to evaluate real-world evaporative emissions using the fuel composition and environmental temperature as input parameters. The proposed models well replicated the experimental results of the canister breakthrough emission from DBL (DBLb) and RFL obtained in previous experimental studies. The evaporative DBLb and RFL emissions in Japan in 2015 were then estimated using the new models. The evaporative emission from DBLb was approximately 8800 t/y, and that from RFL was 73,300 t/y. In addition, we estimated the variation in fuel evaporative emissions due to the market penetration of zero-emission vehicles. Even if the sale of gasoline vehicles is banned from 2035, the evaporative emissions of DBLb and RFL from gasoline vehicles will only be halved after 2040. The two models proposed for estimating the DBLb and RFL in this study are expected to be applied in the evaluation of the emission inventories of volatile organic compounds in future work.



1. INTRODUCTION

Road transportation is known to be a main contributor to both air pollution and global warming. There is a worldwide trend of battery-based vehicles, so-called zero-emission vehicles (ZEVs) including electric and fuel-cell vehicles, being introduced as the solution to environmental issues relating to the use of fuel-based vehicles.[1−5] Despite this, it is mainly economically developed countries, such as the United States, the United Kingdom, countries in the European Union, Japan, South Korea, and China, that are planning to introduce ZEVs, even though the issues of air pollution and greenhouse gas emissions due to road transportation are expected to affect all countries in the future. Furthermore, it may take more than 20 years to replace all fuel-based fleets with ZEVs, even in developed countries. The investigation of vehicular emissions and their atmospheric impact thus remains important in the field of atmospheric science, and many studies have focused on these topics.

Vehicular exhaust emissions can be categorized into two groups, namely, tailpipe emissions and evaporative emissions. Tailpipe emissions are defined as the emissions released by fuel combustion in the internal engine combustion chamber to obtain the driving force, and many studies have investigated the atmospheric impact and reduction technologies.[6−9] Meanwhile, evaporative emissions are defined as the emissions of gasoline evaporation from fuel tanks and fuel-related parts and include the emissions of volatile organic compounds (VOCs). VOCs are precursors of tropospheric ozone and secondary organic aerosol-related $PM_{2.5}$ created by intense sunlight and high temperature. The treatment of tailpipe emissions led by both governments and manufacturers has reduced tailpipe emissions, and the focus has significantly recently shifted to the reduction of non-tailpipe emissions including evaporative emissions. Evaporative emission processes can be categorized into five types: The diurnal breathing loss (DBL), hot-soak loss (HSL), refueling loss (RFL), puff loss (PL; evaporative emissions released during the fuel-cap removal of vehicle refueling[10]), and running loss (RL). The present study focuses on the DBL and RFL as they are one of the major sources of VOCs from evaporative emissions of gasoline vehicles and are regulated in many countries. These two emission processes are described in this section, whereas previous studies can be referred to for the remaining three

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evaporative emissions.[10−12] The DBL is an evaporative emission from a fuel tank due to a diurnal temperature change during parking events and can be divided into permeation and breakthrough emissions. Permeation is the evaporative emission from fuel-related parts. Apart from permeation, evaporative emission occurs from the vacant space of the fuel tank owing to a diurnal temperature change in parking events to prevent the breakage of the fuel tank caused by the increase of internal pressure. The evaporative emissions from the fuel tank are first adsorbed by a canister containing activated carbon. The adsorption capacity of evaporative emissions is exceeded by long-term parking events, after that evaporative emissions are directly emitted into the atmosphere. These emissions are referred to as breakthrough emission. Comprehensive studies on the DBL have investigated the emission behaviors, the detailed VOC composition, a statistical method to evaluate the amount of evaporation combined with the parking frequency, and modeling for the evaluation of the amount of evaporation.[13−21] For example, Martini et al.[14] raised concerns over the previous type approval measurements of DBL and suggested improving the testing procedure from 1-day DBL to 2-day DBL to make an agreement with the real-world parking frequency. In terms of the effect of DBL on atmospheric pollution, a study on the effect of evaporative emissions from the DBL on atmospheric ozone and $PM_{2.5}$ generation in a metropolitan area of Japan using a chemical transport model concluded that the DBL maximally contributes 3 ppb of hourly ozone formation, which corresponds to 5% of the environmental standard in Japan (a maximum of 0.06 ppm per hour[22]), and indicated the potential effects on humans and crops.[23] The RFL is emitted in the process of refueling a tank with gasoline. In this process, gasoline vapor accumulated in the empty space of the fuel tank is pushed up by the refueling liquid and released into the atmosphere. To prevent evaporation during refueling, two technologies, namely the so-called Stage II and onboard refueling vapor recovery technologies,[24] have been adopted in the United States, Canada, and China (starting 2023, in Brazil, and discussed in the EU). Japan has been implementing Stage II technology since 2018 but the technology has not yet been adopted at all service stations,[25] and the RFL still accounts for 14% of the stationary source of VOC emissions in Japan.

It is thus important to study the basic characteristics of the DBL and RFL in assessing emission reduction strategies. The purpose of this study is to improve the theoretical models used to evaluate evaporative emissions released into the atmosphere from the breakthrough of the DBL and RFL processes that have been proposed in previous studies.[26,27] The previously proposed models have two shortcomings. First, the models for the DBL emission include nonphysical regression parameters that are determined by fitting to experimental results. The semi-empirical parameters have been determined in previous experiments, and there is no evidence that the proposed models can be applied to other environmental conditions. Second, models of the DBL and RFL only evaluate the amount of total evaporation and do not evaluate VOC compositions, the information of which is required in the fields of atmospheric science and air quality management. A study on PL emissions accounted for these two problems by implementing overall thermodynamic parameters of gasoline fuel based on Raoult's law and Charles' law coupled with the Antoine equation and accurately reproduced experimental results of PL emissions without fitting parameters.[10] In the present study, an approach similar to that adopted by Hata et al.[10] was applied to breakthrough DBL and RFL emissions to formulate the detailed mechanism of evaporative emissions released into the atmosphere. The validation of new models was examined by comparing modeling results with the experimental results of DBL and RFL obtained in previous studies.[26,27] The annual evaporative emissions from DBL and RFL in Japan were evaluated, and future DBLs and RFLs in Japan were predicted. The theoretical models formulated in this study are universal in that they can be used to evaluate both the total amount of evaporation and the VOC composition from the breakthrough DBL and RFL, and they are expected to assist atmospheric scientists and policymakers in developing VOC management strategies in the future.

2. METHODS

2.1. Improvement of the Theoretical Model of Evaporation in Parking Events. A previous theoretical model used to evaluate the amount of evaporation from parked gasoline vehicles[26] is summarized as eq S1. Equation S1 was derived by assuming that gasoline is averagely composed of single components, which means that the features of individual components in gasoline are ignored despite the large differences in physical and chemical properties. This might introduce error into the model, such that a nonphysical empirical parameter is needed for the model to reproduce experimental results. Furthermore, the assumption of treating gasoline as a single component leads to the unpredictability of the composition of VOCs emitted into the atmosphere. To account for these problems, the following steps refer to the theoretical model of the previous study for PL emissions.[10] The time dependence of the ideal gas equation resulting from a diurnal temperature change inside a fuel tank is expressed as

$$\frac{dn_{tank}}{dt} = \frac{V_{tank}}{RT_{tank}}\frac{dP_{tank}}{dt} - \frac{V_{tank}P_{tank}}{RT_{tank}^2}\frac{dT_{tank}}{dt} \quad (1)$$

where n_{tank} is the molar number of the total gas inside the fuel tank (mol), V_{tank} is the tank vacant capacity (L), which is an official announcement capacity plus an additional 5 L.[10] R is the gas constant (=8.314 J/(K mol)), T_{tank} is the temperature inside the fuel tank (K), and P_{tank} is the total pressure inside the vacant area of the fuel tank (Pa). Since the difference of the vapor pressure inside fuel tank from the ambient pressure (101 kPa) is set to be lower than 5 kPa by the check valve for the targeted vehicles,[10] 106 kPa was applied to P_{tank} in this study. The first term on the right side of eq 1 represents the evaporation of gas due to the phase change between liquid and gas, whereas the second term represents the expansion of the gas phase due to an increase in temperature inside the fuel tank. The previous study[10] considered only the emission of vapor into the atmosphere due to the expansion of the gas phase (i.e., the second term on the right side of eq 1) and not that due to the phase change; this explains the underestimation of the emission of vapor to the atmosphere and why a fixed parameter was needed to reproduce experimental results. In the present study, the evaporation emitted into the atmosphere is expressed by adding the effect of the phase change between the liquid and gas as

$$\frac{dn_{out}}{dt} = \frac{V_{tank}P_{tank}}{RT_{tank}^2}\frac{dT_{tank}}{dt} + \kappa\frac{P_{tank}}{P_{air}}\frac{V_{tank}}{RT_{tank}}\frac{dP_{tank}}{dt} \quad (2)$$

where n_{out} is the molar number of all gas inside the fuel tank emitted into the atmosphere through the diurnal temperature change, P_{air} is the partial pressure of the air inside the fuel tank, and κ is a fixed parameter related to the limitation of mass transfer by convection of the gas phase inside the fuel tank ($\kappa <$ 1.0), as will be explained later. The first term on the right side of eq 2 represents the gas emission due to the expansion of the gas phase inside the fuel tank as a result of the temperature change, and the second term represents the emission due to the phase change from the liquid fuel to the gas phase. The vacant space of the fuel tank is filled by both air and the gasoline evaporative emission. The phase change from liquid to gas occurs only for gasoline, whereas the gas expansion occurs for both air and gasoline evaporative emission. Equation 2 is thus rewritten as

$$\frac{\mathrm{d}n_{\text{out}}}{\mathrm{d}t} = \frac{P_{\text{air}}}{P_{\text{tank}}}\frac{V_{\text{tank}}P_{\text{tank}}}{RT_{\text{tank}}^{2}}\frac{\mathrm{d}T_{\text{tank}}}{\mathrm{d}t} + \frac{P_{\text{evap}}}{P_{\text{tank}}}\left(\frac{V_{\text{tank}}P_{\text{tank}}}{RT_{\text{tank}}^{2}}\frac{\mathrm{d}T_{\text{tank}}}{\mathrm{d}t} + \kappa\frac{P_{\text{tank}}}{P_{\text{air}}}\frac{V_{\text{tank}}}{RT_{\text{tank}}}\frac{\mathrm{d}P_{\text{evap}}}{\mathrm{d}t}\right) \tag{3}$$

where P_{evap} is the partial pressure of the evaporative emission inside the fuel tank. The first term on the right side of eq 3 corresponds to the emission of air from the fuel tank, whereas the second term on the right side of eq 3 corresponds to evaporative emission from the fuel tank to the atmosphere. The amount of gasoline evaporative emission from a parked gasoline vehicle due to a diurnal temperature change, $n_{\text{out,evap}}$, is therefore obtained from the second term on the right side of eq 3 as

$$\frac{\mathrm{d}n_{\text{out,evap}}}{\mathrm{d}t} = \frac{V_{\text{tank}}P_{\text{evap}}}{RT_{\text{tank}}^{2}}\frac{\mathrm{d}T_{\text{tank}}}{\mathrm{d}t} + \kappa\frac{P_{\text{evap}}}{P_{\text{air}}}\frac{V_{\text{tank}}}{RT_{\text{tank}}}\frac{\mathrm{d}P_{\text{evap}}}{\mathrm{d}t} \tag{4}$$

Equations 1 and 2 are formulated using a thermodynamics approach, so the rate of evaporation is unpredictable. The phase change may not be enough to spread throughout the vacant area of the fuel tank on a short timescale. The parameter κ is thus introduced to account for the insufficient information on the evaporation from the phase change dynamics. κ is further discussed in the next section. Note that the evaporation from the fuel tank occurs when T_{tank} increases with the passing of time. Therefore, from the afternoon to the following morning, during which time T_{tank} decreases, $\mathrm{d}n_{\text{out,evap}}/\mathrm{d}t$ is treated as zero. P_{evap} in eq 4 is evaluated using Raoult's law as

$$P_{\text{evap}} = \sum_{i} P_{\text{evap}}^{i} x_{\text{l},i} \tag{5}$$

where P_{evap}^{i} is the vapor pressure of gasoline component i and $x_{\text{l},i}$ is the molar fraction of gasoline component i in the liquid phase, which is obtained through the gas-chromatography flame ionization detector (GC-FID) analysis of gasoline on the commercial market and is further discussed in Section 2.3. P_{evap}^{i} is calculated using Antoine's equation or the Clausius–Clapeyron equation, the details of which are given in the Supporting Information (SI). Adopting numerical integration with a short time step ($\mathrm{d}t \approx \Delta t$) for eqs 4 and 5, the amount of evaporative emissions from the fuel tank is evaluated. Finally, the amount of each VOC in the evaporative emission is calculated as

$$n_{\text{evap,out}}^{i} = \frac{P_{\text{evap}}^{i}}{P_{\text{evap}}} n_{\text{evap,out}} \tag{6}$$

where $n_{\text{evap,out}}^{i}$ is the molar number of gasoline component i of the evaporative emission (mol).

2.2. Improvement of the Theoretical Model of Evaporative Emissions in Refueling Events. A previous study[27] formulated the RFL emission making the same assumption made for the previous DBL model (eq S1) that gasoline is averagely composed of individual components. Nevertheless, our previously proposed model[27] well fits the experimental results, but it is unclear whether the proposed model fits different experimental conditions. Furthermore, the proposed model can only be used to evaluate the total amount of evaporative emissions from the RFL, and no information about the VOC composition can be obtained. The mechanism of the RFL emission is simply that fuel gas inside the vacant space of the fuel tank is pushed upward and emitted during refueling, and the amount of evaporative emissions is equal to the refueling volume. Against this background, the RFL emission is expressed using the ideal gas equation as

$$n_{\text{r}} = \frac{P_{\text{evap}}V_{\text{refuel}}}{RT_{\text{tank}}} \tag{7}$$

where n_{r} is the molar number of the RFL emission (mol) and V_{refuel} is the volume of the refueled gasoline (L). P_{evap} is calculated using eq 5 and the gasoline composition of the evaporative emission is expressed using the ideal gas equation as

$$n_{\text{r}}^{i} = \frac{P_{\text{evap}}^{i}}{P_{\text{evap}}} n_{\text{r}} \tag{8}$$

where n_{r}^{i} is the molar number of gasoline component i of the refueling emission (mol).

2.3. Experimental Data from Previous Works and the Gasoline Composition Analysis Method. The validation of the proposed thermodynamics models for parking and refueling evaporation, eqs 4 and 7, is discussed in a later section using previously obtained experimental results of evaporative emissions.[26,27] This section summarizes the experiments conducted in the previous studies. Hata et al.[26] observed the behaviors of evaporative emissions in parking events for two categories of gasoline vehicles using a Sealed Housing for Evaporative Emission Determination unit. They conducted three experiments while varying the temperature, two while varying the fill of the fuel tank, and three while varying the Reid vapor pressure (RVP) for each vehicle. The experimental conditions are listed in Table 1 of ref 26 and Table S1. Yamada et al.[27] observed the behaviors of evaporative emissions in refueling events for six categories of gasoline vehicles and seven types of gasoline. They conducted experiments not only for pure gasoline but also for fuels containing 10% ethanol. Ethanol was thus included in the refueling model proposed in this study. The details of the experimental conditions for refueling emissions are given in Table S2.

The composition of hydrocarbons included in commercial gasoline in Japan is seasonally restricted to the assessment of evaporative emissions into the atmosphere; i.e., the RVP in the summer season is regulated to be lower than 65 kPa, whereas that in the winter season is regulated to be lower than 90 kPa.

To obtain the real-world trend of the composition of commercial gasoline, GC-FID analysis for 12 types of gasoline in each month from October 2016 to September 2017 was conducted. The GC-FID analysis was conducted by SVC Tokyo Company following Japanese Industrial Standard K2536-2, and the analysis results are listed in Tables S3−S14.

3. RESULTS AND DISCUSSION

3.1. Validation of Improved Models Using the Experimental Results of Evaporative Emissions.

3.1.1. Total Amount of Evaporation Obtained from Estimation Models of the Breakthrough DBL and RFL.

Figure 1 shows the validation of the proposed models by comparing the calculation of the amount of canister breakthrough emissions from DBL (DBLb) and RFL emissions with the experimental results obtained in the previous studies.[26,27] The calculation results of the previous models expressed by eq S1 are also plotted to compare the accuracies of these models with those of the proposed models expressed by eq 4. Figure 1a shows that the proposed model expressed by eq 4 well replicates the experimental results with $\kappa = 7.7/V_{\text{tank}}$ ($V_{\text{tank}} > 7.7$ L), where κ is a parameter related to the mixing ratio of evaporation from liquid gasoline to gas inside the fuel tank, as explained in Section 2.1. The value $\kappa = 7.7/V_{\text{tank}}$ indicates that the range of sufficient mixing of the evaporated gasoline with air in the tank within a short time is limited to 7.7 L. In the fuel tank, the liquid phase has a high heat capacity and is not easily affected by the outside temperature, whereas the gas phase has a low heat capacity and is greatly affected by the outside temperature. Therefore, the temperature of the liquid phase at the bottom of the tank tends to be slightly lower. As a result, the mixing of air and evaporation gas in the tank due to free convection driven by heat is less likely to occur in the tank. Meanwhile, the model proposed in this study assumes a perfect mixture in a short time. It is thus reasonable to introduce a coefficient, κ, to compensate for the effect of the evaporation term, which is particularly susceptible to mixing through convection. The previous model (eq S1) was derived assuming that the evaporation from DBLb due to a diurnal temperature change occurs only through the expansion of the fuel gas that already exists in the fuel tank, and evaporation resulting from the phase change between the liquid and gas due to the temperature change was not considered. This led to an underestimation relative to the experimental results, and the RVP term was substituted with the exponential form of eq S2 to compensate for the underestimation. Equation S2 has no physical basis and was simply derived as the best fitting functional form. Equation 4 was derived from time-dependent thermodynamics assuming a local equilibrium in short time steps, even though the detailed dynamics of evaporation can be described more exactly using computational fluid dynamics (CFD), because of the complex structure of the fuel tank and related parts. Nevertheless, the evaluation of evaporative emissions from DBLb using CFD may require much simulation resource and time and be too costly for the evaluation of VOC emissions in the field of environmental science. Equation 4 might therefore be considered a universal form of a simplified estimation model of DBLb. Despite this, the theoretical meaning of κ should be further evaluated in future work.

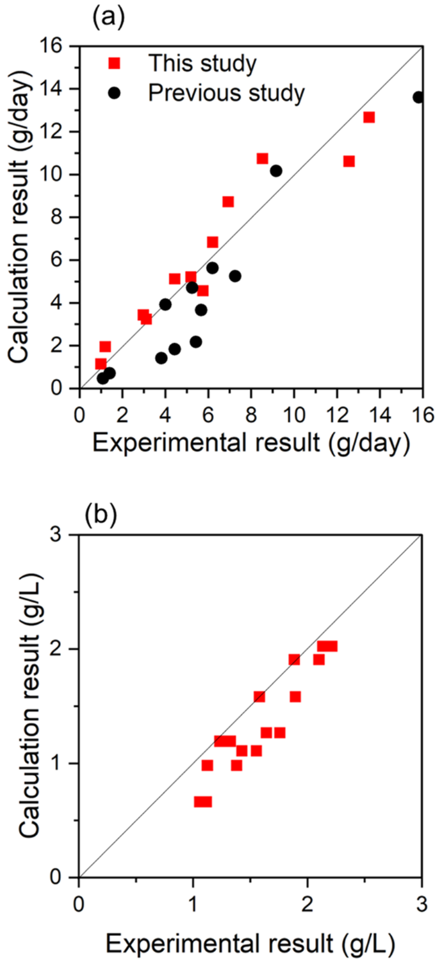

Figure 1. Model validations comparing calculation results with the experimental results of evaporative emissions[26,27] for (a) DBLb from parked vehicles obtained in this study (red) and the previous study[26] (black), and (b) RFL in the refueling process.

Figure 1b shows that the RFL calculated using eq 7 linearly replicates the previous experimental results with a determination coefficient, R^2, of 0.98. However, the calculation results are approximately 16% lower than the experimental results. In the refueling process, the refueling gasoline may splash, which may increase evaporation. Additionally, gasoline might adhere to the refueling hose and other related parts, again increasing evaporation. Another possibility is that there are differences between the temperatures of the fuel in the tank versus the dispensed fuel temperature. The RFL model of eq 7 does not include such additional evaporation as a physical factor, which may result in underestimation relative to the experimental results. The additional evaporations from gasoline splashing and adhering would depend on the structure of the fuel tank and refueling hose, and thus, the underestimation of eq 7 relative to the real refueling emission might be different for each vehicle or service station. Therefore, the underestimation of 16% might be applicable only to the results of the previous study, and the amount of evaporation due to the splashing and adhering of gasoline in the refueling process should be experimentally evaluated in future work.

3.1.2. Validation of the VOC Composition Obtained Using the Estimation Models of DBLb and RFL.

Figure 2 compares the VOC compositions of alkanes, *iso*-alkanes, alkenes, aromatics, and cycloalkanes having 3−12 carbons in the evaporative emissions between experimental results and

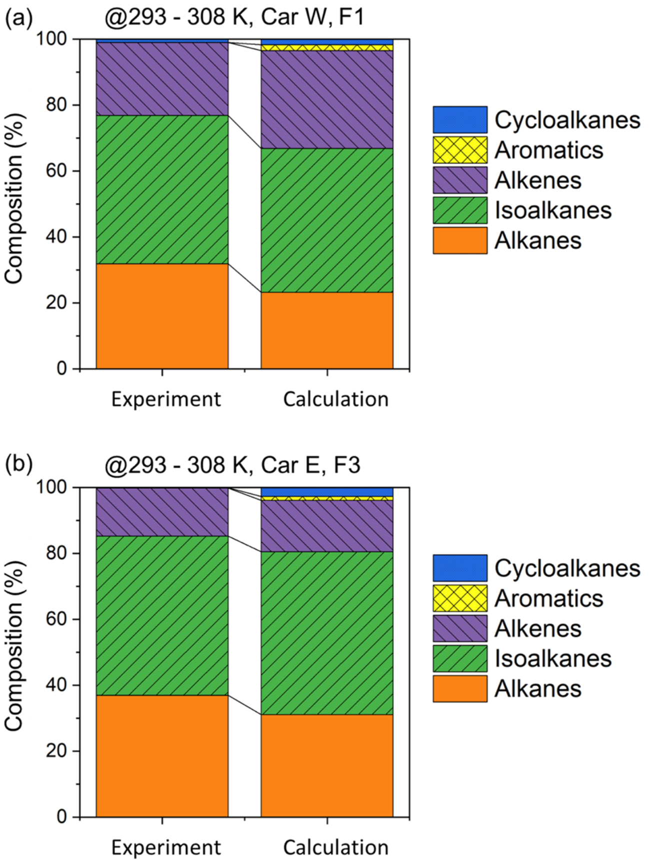

Figure 2. Model validations comparing calculation results with the experimental results of the VOC composition for DBLb from parked vehicles. The left side presents experimental values obtained in a previous study,[26] whereas the right side presents calculations made in this study. The conditions are (a) a temperature of 293−308 K, vehicle W (minicar), and fuel F1 and (b) a temperature of 293−308 K, vehicle E (van), and fuel F3. The detailed conditions for each experiment and fuel are given in Table 1 of ref 26 and Table S1.

calculation results obtained using eq 6 for DBLb. The figure shows that the overall estimation results well replicate the experimental results for DBLb, although there are differences. In particular, the ratio of alkane components obtained using eq 6 seems lower than the experimental result. Under the experimental conditions, breakthrough emission occurred after the saturation of a carbon canister, but there were transition periods between before and after the saturation of the canister. In these periods, a fraction of the potential emissions trapped by the canister and the remainder was emitted into the atmosphere. Activated carbon better absorbs alkenes than alkanes and aromatics,[28] and alkenes might therefore be trapped efficiently in the canister in the transition periods. Meanwhile, eq 6 only considers the partial pressure of gasoline component i after the breakthrough of the carbon canister, leading to the overestimation of alkenes due to the transition period. Figure 3 compares the VOC composition of alkanes, alkenes, mono-aromatics, and ethanol having 3 to 12 carbons in the evaporative emissions between experimental results and calculation results obtained using eq 8 for the RFL. The VOC composition estimated using eq 8 well replicates the experimental results for E10 fuel under an environmental temperature of 308 K. The small difference between the estimation and experiment might be due to the analytical errors of both evaporative emissions and fuel compositions.

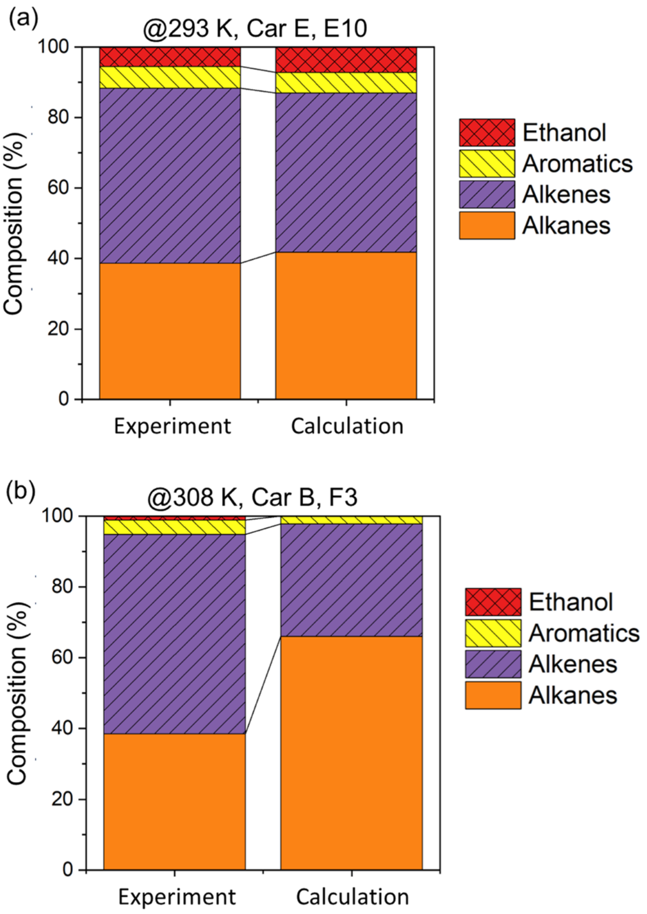

Figure 3. Model validations comparing calculation results with the experimental results of the VOC composition for RFL in the refueling process. The left side presents experimental values obtained in a previous study,[27] whereas the right side presents calculations made in this study. The conditions are (a) a temperature of 293 K, vehicle E, and fuel E10 and (b) a temperature of 308 K, vehicle B (compact car), and fuel F3. The detailed conditions for each experiment and fuel are given in Tables S1 and S2.

Meanwhile, the experimental and calculation results for fuel F3 under an environmental temperature of 293 K did not match well, with the calculated ratio of alkanes being more than 1.5 times the experimental result. This trend is more pronounced for fuels F2 and F3 in Figures S6−S12. The rationale for this discrepancy is not known, but a possible reason is error in the sampling and the GC-FID analysis of the gasoline composition. To further validate the proposed models for DBLb and RFL, additional analyses of the composition of evaporative emissions were conducted. In the additional experiments, evaporation was directly induced by bubbling gasoline and sampled the evaporation by a stainless canister, and then injected into a GC-FID. Figure S18 shows the results of additional analyses, and the proposed model well replicated the experimental results of evaporation from summer- and winter-grade gasoline. It is concluded that the estimation models of eqs S4 and S5 well replicate the experimental results despite differences occurring due to error in the analytical method of the experiments.

3.2. Sensitivity of Environmental Parameters in the Estimation Model of DBLb.

While the RFL is determined by the absolute temperature inside the fuel tank, the mechanism of DBLb is more complex because DBLb occurs owing to an hour-to-hour change in the ambient temperature. There are two pathways of DBLb emission: the expansion of evaporation due to the temperature change and the emission from the direct phase change from liquid to gas. While the expansion of gasoline vapor is due to the temperature change, the phase change from liquid to gas is a function of absolute temperature, and thus, both the diurnal temperature change and absolute temperature are important factors affecting the amount of DBLb emission. To clarify the effects of the temperature change and absolute temperature on the DBLb emission, Figure S13 shows the sensitivity of the DBLb emission from Japanese summer-grade and winter-grade gasoline to the two temperature parameters, where the average temperature on a day was used for the absolute temperature to allow easy comparison. The calculation used the gasoline composition and temperature for February and August listed in Tables S4 and S10. According to Figure S13, the DBLb emission is sensitive to both average temperature and temperature change, while average temperature shows higher sensitivity than temperature change. The average temperature and temperature change on a day tend to be higher in spring and autumn in Japan, and it is presumed that there are higher emissions of DBLb in these seasons. The amount of DBLb from the winter-grade gasoline seems to be approximately 3 times that of the summer-grade gasoline because of the higher volatility of the winter-grade gasoline adopted for better engine startup performance in the cold seasons. Figures S14 and S15 show the sensitivity of the VOC components from DBLb to the average temperature and temperature change. The behavior of the emission is the same as that of the total emission of DBLb. *Iso*-alkanes, alkenes, and *n*-alkanes are highly sensitive to the temperature parameters because they are the major components of the gasoline fuel.

3.3. Estimation of the Total Amount of Evaporative Emission from DBLb and RFL Throughout Japan.

The total evaporative emissions from DBLb and RFL throughout Japan in 2015 were evaluated using the estimation models expressed by eqs 4, 7, S4, and S5. The evaluations were made using diurnal atmospheric temperature changes for 47 prefectures provided by the Japan Meteorological Agency.[29] The number of gasoline vehicles in each prefecture was obtained from the Japan Automobile Inspection and Registration Information Association.[30] The frequency of canister breakthrough was proposed based on the parking frequency in Japan.[23] The refueling amount was obtained from the total gasoline use per year (L/y).[31] The results of GC-FID analysis for the fuel composition in each month from October 2016 to September 2017 mentioned in Section 2.3 were applied as the initial parameters of the model evaluation. The gasoline composition is almost the same each year because the composition and physical properties of gasoline sold in Japan were specified by the government in 2012. Therefore, although the gasoline composition data are for the year 2016−2017, the emission estimates were made using meteorological data for the year 2015 to allow for easy comparison with previous studies.[10,23] Monthly emissions of DBLb and RFL throughout Japan can be calculated using eqs S6 and S7. Though PL is not included in the RFL in this study, the results of PL estimation is shown in Figure S16 for the purpose of reference.

Figure 4 presents the results of the evaluation of the monthly DBLb and RFL in Tokyo and the estimation results obtained using previous models. The amount of DBLb obtained using the model proposed in this study is lower than that obtained using the previous model except in the summer months from June to September. As mentioned in Section 3.2, the previous model includes a fitting parameter for an exponential form of the RVP and thus overestimates under a high-RVP condition at higher temperatures. The model proposed in this study eliminates this overestimation through the use of thermodynamics, which decreases the estimated DBLb amount in cooler seasons under higher RVP conditions. DBLb emissions are higher in March, April, and May because of the higher temperature under high-RVP fuel conditions. The total yearly evaporation from DBLb was estimated to be 8800 ± 1200 t/y, which is approximately 1.3% of VOC emissions from stationary sources in Japan in 2015.[32] The error was evaluated by the variance of average temperature in each month. Though Dong et al.[33] suggested that the estimation of DBLb emissions under the assumption of constant in-use canister conditions contains critical uncertainty, the present study used the assumption of a constant fully purged canister state because of the lack of the in-use canister capacity based on the activity data. Figure 4b shows that the monthly RFL emission is higher in summer because of the high temperature but the difference between seasons is negligible compared with that of DBLb. The total evaporation from RFL was estimated to be 73,300 ± 1300 t/y, which corresponds to approximately 11% of VOC emissions

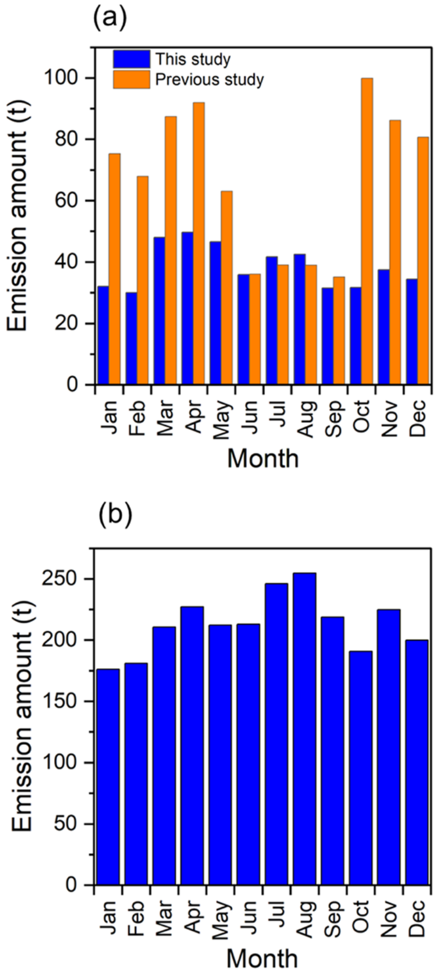

Figure 4. Total evaporative emissions estimated using the proposed models in this and previous study[26] for (a) DBLb from parked vehicles and the proposed moel in this study for (b) RFL in the refueling process in Tokyo in 2015. Values are listed in Table S15.

from stationary sources in Japan in 2015. The error of RFL was calculated by the same method as DBLb. The amount of RFL was also evaluated by the model proposed by EPA,[34] resulted in 60,000 t/year which is 20% lower than the result from the model proposed in this study. The total DBLb and RFL thus reach 12% of total VOC emissions from stationary sources. Apart from the DBLb and RFL, there are other processes of evaporation from the gasoline fleet outside the scope of this study, and thus, the total amount of gasoline evaporative emissions may exceed 15% of all emission sources of VOC, indicating the strong effect of evaporative emissions on the atmospheric environment.

Finally, future DBLb and RFL emissions are estimated assuming that all gasoline vehicles sold in Japan will be ZEVs from 2035. Two scenarios are considered in this study. In the first scenario, the sales of all vehicles between 2020 and 2035 are assumed to be the same as those of the current situation in which ZEVs account for 0.6%[35] of vehicles sold. In the second scenario, half of the vehicles sold between 2020 and 2035 are assumed to be ZEVs, and half are assumed to be fuel-based vehicles (i.e., gasoline, diesel, and hybrid vehicles). Annual gasoline vehicle sales from 2017 to 2020 in Japan range from 2.5 to 2.9 million, while ZEVs account for only 0.6−0.9% of gasoline vehicle sales. Therefore, in the estimation, it is assumed that there is no change in vehicle sales, and the ratio of ZEVs in vehicle sales is assumed to be constant at the 2020 value until 2035. It is assumed that there is no evaporative emission from ZEVs. The average service life of vehicles is set at 13.51 years.[36] The percentage of cars sold in year t_0 that continue to be used in year t, $y_{t_0,t}$ (%), is

$$y_{t_0,t} = 100 \times \exp\left\{\frac{-(t - t_0)}{13.51}\right\} \tag{9}$$

As an example, for cars sold in 2020, $y_{2020,15}$% will continue to be used in 2035, whereas $(100 - y_{2020,15})$% will be scrapped. Estimates of DBLb and RFL emissions for 2015 are used for the 2020 emission estimates. Because the number of passenger cars in Japan increased by 2% in five years from 2015 to 2020 and the sales ratio of ZEVs is expected to be 0.6% in 2020, the estimated DBLb emissions in 2015 are corrected and 8,900 t/y is set as the estimated DBLb emissions in 2020. The refueling amount decreased by approximately 15% between 2018 and 2020[37] presumably owing to the strong effect of COVID-19. This can be inferred from the fact that there is a difference of less than 3% in the refueling amount from 2015 to 2018.[37] Therefore, in the future estimation, assuming that the refueling amount would have decreased by 1% per year in the past 5 years without the COVID-19 impact, a 5% lower value relative to estimated RFL emissions in 2015, 69,700 t/y, is used as the value for 2020 when there is no impact of COVID-19. In the future estimation, the usage conditions of vehicles were assumed to be the same as today. The total emissions of DBLb and RFL in 2020 is estimated to be 78,600 t/y. The results of future evaporative emissions are presented in Figure 5. The total emissions of DBLb and RFL are less than half the current level by 2045 in the first scenario and by 2040 in the second scenario. On the basis of these results, when VOC emissions from stationary sources are estimated exponentially from the emissions of the past 10 years, as shown in Figure S17, the fuel evaporative emission is expected to continue to be more than 5% of Japanese VOC emissions from stationary sources and greatly affect the atmospheric environment until after 2045 even if vehicle sales are heavily regulated as a ban on gasoline vehicle sales that is implemented from 2035.[1]

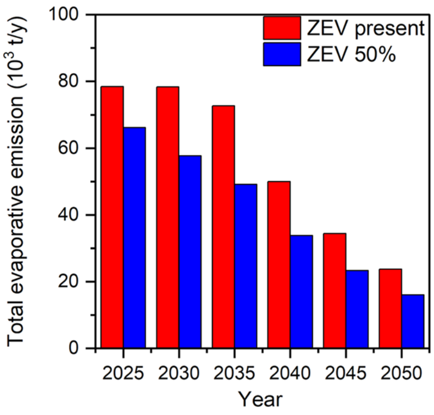

Figure 5. Estimates of the total evaporative emissions of DBLb and RFL in Japan. ZEV present refers to a scenario in which all vehicle sales until 2035 are the same as those in the current situation, with ZEVs accounting for 0.6% of vehicle sales, and ZEV 50% refers to a scenario in which half of the vehicles sold are gasoline vehicles and half are ZEVs until 2035. In both scenarios, all vehicles sold after 2035 are assumed to be ZEVs. Values are listed in Table S16.

4. CONCLUSIONS

Estimation models to calculate canister breakthrough emissions from diurnal breathing loss (DBLb) and emissions from refueling loss (RFL) were improved based on thermodynamics. The new models enable the evaluation of the amount of evaporative emissions and VOC compositions by applying the initial conditions of environmental temperature and the information about the hydrocarbon ratio of gasoline fuel. The validation of the proposed models was examined by comparing them to the experimental results of DBLb and RFL in the previous studies, and the proposed models well replicated the experimental results. Total amounts of evaporative emissions from DBLb and RFL in Japan in 2015 and the future until 2050 were estimated assuming that the sale of gasoline vehicles in Japan will be banned from 2035 and ZEVs will be introduced at the same time. The evaporative emissions from DBLb and RFL in 2015 correspond to 12% of that from whole stationary sources in Japan. The results of future analysis suggested that the evaporative emissions will be halved in 2045, indicating that the effects will continue in the long run even after the introduction of ZEVs in the Japanese market. Evaporative emissions from gasoline vehicles remain a major issue related to air pollution, and the findings of this study will contribute to both policymaking and the improvement of atmospheric modeling.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02715.

Additional information and results of calculations and experiments (PDF)

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Notes

The authors declare no competing financial interest.

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