Improvement of the theoretical model for evaluating evaporative emissions in parking and refueling events of gasoline fleets based on thermodynamics

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Text S1 *Mechanism of evaporation from a fuel tank and vapor reduction technologies*

Figure S1 shows an overview of a fuel system. Evaporative emissions from the breakthrough of diurnal breathing loss (DBLb) and refueling loss (RFL) originate from gasoline gas due to fuel evaporation inside the fuel tank. DBLb occurs when the pressure inside the fuel tank reaches the limit of the check valve and the evaporation is released to the outside. A canister is set between the check valve and atmosphere to trap evaporation from DBLb, but DBLb is directly emitted to the atmosphere when the canister loses its adsorption capacity in a long-time parking event. RFL occurs when refueling is conducted through a port. During refueling, gasoline gas inside the fuel tank is pushed out through the refueling port and directly emitted to the atmosphere; this is the mechanism of RFL.

Figure S1: Overview of the fuel system and evaporative emissions from the breakthrough of DBL and RFL.
To prevent RFL emission, two emission reduction technologies, so-called Stage II and onboard refueling vapor recovery (ORVR) technologies, have been introduced worldwide (mainly in developed countries including the United States, United Kingdom, countries in the European Union, South Korea, and China). Note that ORVR has only been introduced in California, United States. Japan introduced Stage II technology in 2019, but the rollout of this technology is still in process, and many service stations are still large emission sources of VOC in Japan. Stage II technology evacuates evaporative emissions using an evacuator attached to the refueling nozzle. The evacuated vapors are returned to the storeroom of the gasoline fuel at the service station. ORVR is a method of capturing evaporative emissions in the refueling process using a large canister attached to the vehicles. The adsorbed gas is sent to the engine system to burn out in driving.
Text S2  Theoretical models of evaluating gasoline evaporation from the breakthrough of DBL and RFL proposed in previous studies

Theoretical models to calculate the evaporative emissions from DBLb and RFL were formulated in previous studies using empirical and physical methods, as reviewed by Romagnuolo et al.\textsuperscript{3} We formulated models of DBL\textsuperscript{4} and RFL\textsuperscript{5} in our previous works. According to Hata et al.\textsuperscript{4}, DBLb is emitted to the atmosphere through the expansion of evaporative gas inside a fuel tank in response to a diurnal temperature change in a parking event, and the total evaporation, $\Delta w_{\text{tank}}$ (g/day), is calculated as

$$
\Delta w_{\text{tank}} = \frac{M V_{\text{tank}} P_{\text{exp}}}{\Delta H} \left[ \exp \left\{ \frac{\Delta H}{R} \left( \frac{1}{T_r} - \frac{1}{T_{t+1}} \right) \right\} - \exp \left\{ \frac{\Delta H}{R} \left( \frac{1}{T_r} - \frac{1}{T_t} \right) \right\} \right], \quad (S1)
$$

where $M$ is the molecular weight (g/mol), $V_{\text{tank}}$ is the volume of the empty fuel tank (L), $P_{\text{exp}}$ is a parameter related to the Reid vapor pressure (kPa), $\Delta H$ is the gasoline evaporation enthalpy (J/mol), $R$ is the gas constant (8.314 J/(K mol)), $T_r$ is the temperature in the definition of the Reid vapor pressure (311 K), and $T_t$ is the environmental temperature at time $t$ (K). $P_{\text{exp}}$ has one regression parameter and is expressed as

$$
P_{\text{exp}} = P_r e^{a P_r}, \quad (S2)
$$

where $P_r$ is the Reid vapor pressure (kPa) and $a$ is a regression parameter to be fitted to the experimental results. The previous study\textsuperscript{4} did not concretely explain why the exponential form of vapor pressure in Equation (S2) is suitable for the prediction of the amount of evaporative emissions from the fuel tank. Furthermore, equation (S1) treats gasoline evaporation as a single component and cannot be used to predict the VOC composition in evaporative emission, which
is needed for the evaluation of ozone and PM$_{2.5}$ concentrations using the chemical transport model. According to Yamada et al.$^5$, the RFL emission to the atmosphere is generated by the expansion of evaporative gas inside the fuel tank during the filling of the fuel tank with gasoline, and the total evaporation, $\Delta w_{\text{refuel}}$ (g/day), is calculated as

$$\Delta w_{\text{refuel}} = \frac{P_r M V_{\text{tank}}}{R} \exp \left( \frac{\Delta H}{R} \left( \frac{1}{T_r} - \frac{1}{T_{\text{tank}}} \right) \right), \quad (S3)$$

where $T_{\text{tank}}$ is the temperature in the fuel tank during refueling (K). Equation (S3), unlike equation (S1), has no unspecified fitting parameter, but it also assumes that gasoline is a single component and thus cannot be used to evaluate the VOC composition of evaporation. To account for the above deficiencies, more precise and affordable equations for evaluating the amount and composition of evaporative emissions from DBLb and RFL were formulated in the present study.
Text S3 Calculation of vapor pressure for each component from liquid gasoline

The new models for DBLb and RFL, expressed as eqs. (4) and (7) in the main article, require the vapor pressure of component \(i\), \(P_{\text{evap}}^i\), to calculate both the total amount and composition ratio of evaporations. In this study, \(P_{\text{evap}}^i\) was evaluated using the same methodology reported in a previous study for puff loss emissions\(^6\). This section provide a brief summary of the method. \(P_{\text{evap}}^i\) is calculated using Antoine’s equation, which formulates vapor pressure, \(P_{\text{evap}}^i\), with three regression parameters (Antoine parameters), \(A^i\), \(B^i\), and \(C^i\):

\[
\log_{10}P_{\text{evap}}^i = A^i - \frac{B^i}{T + C^i}.
\]  

(S4)

Here, the parameters were obtained from the *NIST Chemistry Webbook*\(^7\), which holds a wide variety of thermodynamic parameters obtained from the experimental results of previous studies. Antoine’s parameters were not available for some species, in which case the Clausius–Clapeyron formula was applied instead:

\[
P_{\text{evap}}^i = P_r^i \exp\left\{\frac{\Delta H}{R} \left(\frac{1}{T_r} - \frac{1}{T}\right)\right\},
\]  

(S5)

where \(P_r^i\) is the Reid vapor pressure of component \(i\) (kPa). The evaluated components were divided into five categories of the component type (alkanes, alkene, cycloalkanes, aromatics, and others including ethanol and ethyl-tertiary-butyl-ether (ETBE)) having 3 to 13 carbons. Further details are provided in both the main article and supplementary materials of the previous study\(^6\).
Table S1. Fuel composition in previous studies of Hata et al. (2018) and Yamada et al. (2018). All values in the table except RVP are expressed as a percentage of weight.

| Label in this study | F1 | F2 | F3 | F4 | E10 |
|---------------------|----|----|----|----|-----|
| Label in Yamada et al. (2018) | - | F3 | F5 | F6 | FE10 |
| RVP (kPa)           | 57<sup>a</sup> | 68<sup>a</sup> | 80<sup>a</sup> | 85<sup>a</sup> | 65  |
| Alkanes             | 9.5 | 14.6 | 15.6 | 13.7 | 11.4 |
| Iso-alkanes         | 40.2 | 37.9 | 30.7 | 35.7 | 24.2 |
| Alkenes             | 17.2 | 1.5 | 13.4 | 16.2 | 11.8 |
| Cycloalkanes        | 5.1 | 1.8 | 8.3 | 7.2 | 6.2 |
| Aromatics           | 28 | 43.9 | 27.5 | 23 | 36.1 |
| ETBE                | - | - | 4.1 | 3.8 | 0.4 |
| Ethanol             | - | - | - | - | 9.1 |

<sup>a</sup>: Taken from Hata et al. (2018)
Table S2. Experimental conditions for RFL in a previous study.  

| Label          | EEH | E2H | E3H | E4H | EEL | E2L | E3L | E4L | BEH | B2H | B3H | B4H | BEL | B2L | B3L | B4L |
|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Car           | E   | E   | E   | E   | E   | E   | E   | E   | B   | B   | B   | B   | B   | B   | B   | B   |
| Fuel          | E10 | F2  | F3  | F4  | E10 | F2  | F3  | F4  | E10 | F2  | F3  | F4  | E10 | F2  | F3  | F4  |
| Temp. (K)     | 35  | 35  | 35  | 35  | 20  | 20  | 20  | 20  | 35  | 35  | 35  | 35  | 35  | 20  | 20  | 20  |
| Refuel vol. (L)| 50.3 | 50.0 | 50.3 | 32.1 | 50.3 | 50.1 | 50.3 | 50.5 | 22.4 | 22.3 | 22.5 | 23.9 | 22.4 | 20.6 | 22.5 | 24.5 |
Table S3. Composition of gasoline surveyed in January. All values in the table are expressed as a percentage of weight. This gasoline contains 4.50% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.026   | -           | 0.003   | 0            | -         |
| 4             | 3.004   | 2.896       | 1.675   | 0            | -         |
| 5             | 4.075   | 8.89        | 4.826   | 0.605        | -         |
| 6             | 3.653   | 9.833       | 3.306   | 2.073        | 0.665     |
| 7             | 1.771   | 7.141       | 2.477   | 2.18         | 9.377     |
| 8             | 0.814   | 3.031       | 0.894   | 1.416        | 5.294     |
| 9             | 0.203   | 1.907       | 0.428   | 0.604        | 6.426     |
| 10            | 0.112   | 0.989       | 0.183   | 0.142        | 2.455     |
| 11            | 0.057   | 0.654       | 0.048   | 0            | 0.612     |
| 12            | 0.03    | 0.179       | 0.023   | 0            | 0.171     |
| 13            | 0.009   | 0.043       | 0       | 0            | 0         |
Table S4. Composition of gasoline surveyed in February. All values in the table are expressed as a percentage of weight. This gasoline contains 5.27% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.04    | -           | 0.00    | 0.00         | -         |
| 4             | 4.29    | 2.37        | 1.69    | 0.00         | -         |
| 5             | 3.89    | 8.02        | 5.47    | 0.57         | -         |
| 6             | 3.75    | 10.20       | 3.70    | 2.16         | 0.63      |
| 7             | 1.55    | 7.64        | 2.70    | 2.14         | 7.41      |
| 8             | 0.68    | 2.82        | 1.12    | 1.62         | 5.12      |
| 9             | 0.19    | 1.98        | 0.52    | 0.62         | 5.72      |
| 10            | 0.12    | 1.06        | 0.27    | 0.13         | 2.42      |
| 11            | 0.06    | 0.61        | 0.07    | 0.00         | 0.59      |
| 12            | 0.03    | 0.16        | 0.02    | 0.00         | 0.16      |
| 13            | 0.01    | 0.04        | 0.00    | 0.00         | 0.00      |
Table S5. Composition of gasoline surveyed in March. All values in the table are expressed as a percentage of weight. This gasoline contains 5.01% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.04    | -           | 0.00    | 0.00         | -         |
| 4             | 3.88    | 2.74        | 1.26    | 0.00         | -         |
| 5             | 4.46    | 7.91        | 5.07    | 0.69         | -         |
| 6             | 3.96    | 10.30       | 3.49    | 2.54         | 0.68      |
| 7             | 1.73    | 7.57        | 2.71    | 2.29         | 6.99      |
| 8             | 0.57    | 2.66        | 1.12    | 1.58         | 4.34      |
| 9             | 0.16    | 1.95        | 0.48    | 0.63         | 6.09      |
| 10            | 0.11    | 1.07        | 0.23    | 0.19         | 2.81      |
| 11            | 0.08    | 0.70        | 0.13    | 0.00         | 0.84      |
| 12            | 0.04    | 0.25        | 0.03    | 0.00         | 0.25      |
| 13            | 0.01    | 0.07        | 0.00    | 0.00         | 0.00      |
Table S6. Composition of gasoline surveyed in April. All values in the table are expressed as a percentage of weight. This gasoline contains 5.80% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.05    | -           | 0.00    | 0.00         | -         |
| 4             | 4.52    | 2.01        | 0.89    | 0.00         | -         |
| 5             | 3.65    | 7.16        | 5.15    | 0.68         | -         |
| 6             | 4.01    | 8.83        | 3.70    | 2.35         | 0.58      |
| 7             | 1.80    | 8.45        | 2.27    | 2.25         | 6.56      |
| 8             | 0.62    | 2.91        | 2.62    | 1.21         | 4.14      |
| 9             | 0.19    | 1.67        | 0.62    | 0.77         | 6.62      |
| 10            | 0.13    | 1.13        | 0.25    | 0.19         | 3.25      |
| 11            | 0.08    | 0.61        | 0.19    | 0.06         | 1.29      |
| 12            | 0.05    | 0.09        | 0.07    | 0.00         | 0.31      |
| 13            | 0.02    | 0.05        | 0.00    | 0.00         | 0.00      |
Table S7. Composition of gasoline surveyed in May. All values in the table are expressed as a percentage of weight. This gasoline contains 6.10% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.01    | -           | 0.00    | 0.00         | -         |
| 4             | 1.82    | 0.55        | 0.69    | 0.00         | -         |
| 5             | 5.44    | 8.24        | 4.77    | 0.74         | -         |
| 6             | 4.25    | 8.88        | 3.40    | 2.14         | 0.73      |
| 7             | 1.55    | 6.34        | 2.37    | 2.13         | 10.16     |
| 8             | 0.63    | 3.07        | 1.39    | 1.17         | 4.48      |
| 9             | 0.17    | 1.58        | 0.58    | 0.73         | 8.61      |
| 10            | 0.11    | 1.03        | 0.27    | 0.17         | 3.12      |
| 11            | 0.08    | 0.50        | 0.17    | 0.05         | 1.12      |
| 12            | 0.04    | 0.08        | 0.06    | 0.00         | 0.27      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S8. Composition of gasoline surveyed in June. All values in the table are expressed as a percentage of weight. This gasoline contains 6.55% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.01    | -           | 0.00    | 0.00         | -         |
| 4             | 1.93    | 0.74        | 0.62    | 0.00         | -         |
| 5             | 5.08    | 7.18        | 3.98    | 0.57         | -         |
| 6             | 4.17    | 7.91        | 3.02    | 2.17         | 0.69      |
| 7             | 1.87    | 6.23        | 2.38    | 2.17         | 11.10     |
| 8             | 0.89    | 3.17        | 1.43    | 1.21         | 5.31      |
| 9             | 0.23    | 1.65        | 0.61    | 0.78         | 9.05      |
| 10            | 0.11    | 0.98        | 0.28    | 0.17         | 3.13      |
| 11            | 0.07    | 0.51        | 0.18    | 0.05         | 1.15      |
| 12            | 0.05    | 0.08        | 0.05    | 0.00         | 0.27      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S9. Composition of gasoline surveyed in July. All values in the table are expressed as a percentage of weight. This gasoline contains 6.65% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.02    | -           | 0.00    | 0.00         | -         |
| 4             | 1.71    | 0.78        | 0.59    | 0.00         | -         |
| 5             | 4.90    | 7.96        | 3.19    | 0.41         | -         |
| 6             | 4.20    | 10.06       | 2.65    | 2.14         | 0.56      |
| 7             | 1.44    | 6.89        | 2.34    | 1.97         | 9.28      |
| 8             | 0.63    | 3.09        | 1.78    | 1.09         | 7.83      |
| 9             | 0.17    | 1.57        | 0.61    | 0.73         | 6.97      |
| 10            | 0.11    | 1.01        | 0.27    | 0.18         | 3.24      |
| 11            | 0.07    | 0.65        | 0.24    | 0.07         | 1.25      |
| 12            | 0.05    | 0.08        | 0.06    | 0.00         | 0.30      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S10. Composition of gasoline surveyed in August. All values in the table are expressed as a percentage of weight. This gasoline contains 6.21% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.01    | -           | 0.00    | 0.00         | -         |
| 4             | 0.68    | 0.75        | 1.37    | 0.00         | -         |
| 5             | 4.21    | 8.57        | 4.99    | 0.43         | -         |
| 6             | 4.28    | 10.60       | 3.97    | 2.50         | 0.70      |
| 7             | 1.20    | 7.04        | 2.42    | 2.21         | 5.45      |
| 8             | 0.62    | 2.93        | 3.06    | 1.32         | 6.43      |
| 9             | 0.19    | 1.78        | 0.71    | 0.85         | 5.99      |
| 10            | 0.13    | 1.21        | 0.32    | 0.21         | 3.49      |
| 11            | 0.09    | 0.62        | 0.20    | 0.07         | 1.37      |
| 12            | 0.06    | 0.09        | 0.07    | 0.00         | 0.35      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S11. Composition of gasoline surveyed in September. All values in the table are expressed as a percentage of weight. This gasoline contains 6.24% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.01    | -           | 0.00    | 0.00         | -         |
| 4             | 1.32    | 0.54        | 0.70    | 0.00         | -         |
| 5             | 4.41    | 8.54        | 5.24    | 0.63         | -         |
| 6             | 4.27    | 10.66       | 3.81    | 2.47         | 0.63      |
| 7             | 1.39    | 7.49        | 2.23    | 2.08         | 7.87      |
| 8             | 0.61    | 2.89        | 2.67    | 1.20         | 5.48      |
| 9             | 0.17    | 1.62        | 0.60    | 0.77         | 6.07      |
| 10            | 0.12    | 1.07        | 0.28    | 0.18         | 3.02      |
| 11            | 0.08    | 0.59        | 0.17    | 0.07         | 1.12      |
| 12            | 0.04    | 0.08        | 0.06    | 0.00         | 0.27      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S12. Composition of gasoline surveyed in October. All values in the table are expressed as a percentage of weight. This gasoline contains 4.55% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.02    | -           | 0.00    | 0.00         | -         |
| 4             | 1.47    | 0.69        | 0.93    | 0.00         | -         |
| 5             | 4.85    | 8.64        | 4.40    | 0.52         | -         |
| 6             | 3.14    | 9.53        | 3.00    | 1.89         | 0.63      |
| 7             | 1.76    | 6.35        | 2.14    | 2.13         | 11.55     |
| 8             | 0.79    | 4.13        | 2.36    | 1.27         | 5.09      |
| 9             | 0.22    | 1.72        | 0.68    | 0.80         | 7.09      |
| 10            | 0.14    | 1.05        | 0.30    | 0.21         | 3.43      |
| 11            | 0.09    | 0.40        | 0.24    | 0.06         | 1.10      |
| 12            | 0.05    | 0.08        | 0.05    | 0.00         | 0.28      |
| 13            | 0.02    | 0.02        | 0.00    | 0.00         | 0.00      |
Table S13. Composition of gasoline surveyed in November. All values in the table are expressed as a percentage of weight. This gasoline contains 4.65% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.04    | -           | 0.00    | 0.00         | -         |
| 4             | 3.30    | 2.76        | 1.26    | 0.00         | -         |
| 5             | 4.23    | 7.26        | 4.58    | 0.68         | -         |
| 6             | 4.19    | 9.35        | 3.19    | 2.35         | 0.72      |
| 7             | 1.48    | 6.60        | 1.93    | 2.20         | 10.07     |
| 8             | 0.77    | 3.10        | 2.33    | 1.26         | 4.34      |
| 9             | 0.20    | 1.69        | 0.56    | 0.80         | 7.27      |
| 10            | 0.11    | 0.99        | 0.25    | 0.16         | 3.11      |
| 11            | 0.07    | 0.31        | 0.15    | 0.05         | 1.09      |
| 12            | 0.04    | 0.07        | 0.05    | 0.00         | 0.25      |
| 13            | 0.02    | 0.01        | 0.00    | 0.00         | 0.00      |
Table S14. Composition of gasoline surveyed in December. All values in the table are expressed as a percentage of weight. This gasoline contains 5.04% ETBE in addition to the ingredients listed in the table.

| Carbon number | Alkanes | Iso-alkanes | Alkenes | Cycloalkanes | Aromatics |
|---------------|---------|-------------|---------|--------------|-----------|
| 3             | 0.04    | -           | 0       | 0            | -         |
| 4             | 3.49    | 2.65        | 1.58    | 0            | -         |
| 5             | 3.68    | 8.49        | 5.01    | 0.64         | -         |
| 6             | 3.89    | 9.86        | 3.46    | 2.04         | 0.62      |
| 7             | 1.67    | 7.42        | 2.63    | 2.09         | 7.6       |
| 8             | 0.35    | 3.17        | 0.93    | 2.04         | 4.35      |
| 9             | 0.18    | 1.93        | 0.39    | 0.58         | 6.84      |
| 10            | 0.11    | 0.95        | 0.19    | 0.15         | 3.07      |
| 11            | 0.07    | 0.73        | 0.05    | 0            | 0.95      |
| 12            | 0.04    | 0.23        | 0.03    | 0            | 0.31      |
| 13            | 0.01    | 0.07        | 0       | 0            | 0         |
Figure S2. Model validations comparing calculation results with the experimental results of the VOC composition for DBLb from parked vehicles. The left side presents experimental values from a previous study\(^4\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 300–305 K, vehicle W (minicar), and fuel F1 and (b) a temperature of 302–307 K, vehicle W (minicar), and fuel F1. The detailed conditions for each experiment and fuel are presented in Table 1 of Hata et al. (2018)\(^4\) and Table S1.
Figure S3. Model validations comparing calculation results with the experimental results of the VOC composition for DBLb from parked vehicles. The left side presents experimental values from a previous study$^4$ and the right side presents calculations made in this study. The conditions are (a) a temperature of 293–308 K, vehicle W (minicar), and fuel F2 and (b) a temperature of 293–308 K, vehicle W (minicar), and fuel F3. The detailed conditions for each experiment and fuel are presented in Table 1 of Hata et al. (2018)$^4$ and Table S1.
Figure S4. Model validations comparing calculation results with the experimental results of the VOC composition for DBLb from parked vehicles. The left side represents experimental values from a previous study\(^4\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 300–305 K, vehicle E (van), and fuel F1 and (b) a temperature of 302–307 K, vehicle E (van), and fuel F1. The detailed conditions for each experiment and fuel are presented in Table 1 of Hata et al. (2018)\(^4\) and Table S1.
Figure S5. Model validations comparing calculation results with the experimental results of the VOC composition for DBLb from parked vehicles. The left side presents experimental values from a previous study\(^4\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 293–308 K, vehicle E (van), and fuel F1 and (b) a temperature of 293–308 K, vehicle E (van), fuel F1, and a tank filling rate of 20%. The detailed conditions for each experiment and fuel are shown in Table 1 of Hata et al. (2018)\(^4\) and Table S1.
Figure S6. Model validations comparing calculation results with the experimental results of VOC composition for RFL in the refueling process. The left side presents experimental values from a previous study and the right side presents calculations made in this study. The conditions are (a) a temperature of 293 K, vehicle B (compact car), and fuel E10 and (b) a temperature of 308 K, vehicle E (van), and fuel F3. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S7. 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 from a previous study$^5$ and the right side presents calculations made in this study. The conditions are (a) a temperature of 293 K, vehicle E (van), and fuel F2 and (b) a temperature of 293 K, vehicle B (compact car), and fuel F2. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S8. 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 from a previous study\(^5\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 293 K, vehicle E (van), and fuel F3 and (b) a temperature of 293 K, vehicle B (compact car), and fuel F3. The detailed conditions for each experiment and fuel are shown in Tables S1 and S2.
Figure S9. 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 from a previous study\(^5\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 293 K, vehicle E (van), and fuel F3 and (b) a temperature of 293 K, vehicle B (compact car), and fuel F3. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S10. 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 from a previous study\textsuperscript{5} and the right side presents calculations made in this study. The conditions are (a) a temperature of 308 K, vehicle Car E (van), and fuel E10 and (b) a temperature of 308 K, vehicle B (compact car), and fuel E10. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S11. 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 from a previous study\(^5\) and the right side presents calculations made in this study. The conditions are (a) a temperature of 308 K, vehicle E (van), and fuel F2 and (b) a temperature of 308 K, vehicle B (compact car), and fuel F2. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S12. 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 from a previous study$^5$ and the right side presents calculations made in this study. The conditions are (a) a temperature of 308 K, vehicle E (van), and fuel F4 and (b) a temperature of 308 K, vehicle B (compact car), and fuel F4. The detailed conditions for each experiment and fuel are presented in Tables S1 and S2.
Figure S13: Sensitivity of DBLb emissions from parked vehicles to the average temperature and daily temperature change for (a) summer-type gasoline (in August) and (b) winter-type gasoline (in December).
Figure S14. Sensitivity of VOC components from DBLb to the average temperature and temperature change on a day for summer-type gasoline in August.
Figure S15. Sensitivity to of components from DBLb to the average temperature and temperature change on a day for winter-type gasoline in February.
Text S4 Calculations of monthly emissions of DBLb and RFL

Monthly DBLb and RFL emissions for the whole of Japan can be calculated as

Monthly emission of DBLb = \[ \sum_j F_b(T_{\text{max},j,\text{month}}, T_{\text{min},j,\text{month}}, N_j, D_b) \] (S6)

Monthly emission of RFL = \[ \sum_k F_R(T_{\text{ave},j,\text{month}}, V_{R,j,\text{month}}) \] (S7)

Monthly emission of PL = \[ \sum_k F_P(T_{\text{ave},j,\text{month}}, V_{R,j,\text{month}}) \] (S8)

where \( F_b(T_{\text{max},j,\text{month}}, T_{\text{min},j,\text{month}}, N_k, D_b) \) is a function used to calculate the monthly DBLb emission with four variables and \( F_R(T_{\text{ave},j,\text{month}}, V_{R,j,\text{month}}) \) is a function used to calculate the monthly RFL emission with two variables. \( F_P(T_{\text{ave},j,\text{month}}, V_{R,j,\text{month}}) \) is a function used to calculate the monthly puff loss emission with two variables.\(^6\) \( T_{\text{max},j,\text{month}} \) is the monthly average of the highest temperature on a day in prefecture \( j \), \( T_{\text{min},j,\text{month}} \) is the monthly average of the lowest temperature on a day in prefecture \( j \), \( N_j \) is the number of vehicles in prefecture \( j \), \( D_b \) is the average number of days that breakthrough occurs in a month, \( T_{\text{ave},j,\text{month}} \) is the monthly average temperature in each prefecture, and \( V_{R,j,\text{month}} \) is the refueling volume in a month in prefecture \( j \). In the function \( F_R \) and \( F_P \), temperature in the fuel tank is calculated by MOVES equation.\(^8\)
Table S15. Estimated evaporative emission from DBLb and RFL in Tokyo, 2015.

| Month | January | February | March | April | May | June |
|-------|---------|----------|-------|-------|-----|------|
| DBLb (t) | 32.0 | 30.0 | 48.0 | 49.7 | 46.6 | 35.9 |
| RFL (t)  | 176.0 | 181.1 | 210.4 | 227.0 | 212.1 | 212.9 |

| Month | July | August | September | October | November | December |
|-------|------|--------|-----------|---------|----------|----------|
| DBLb (t) | 41.7 | 42.5 | 31.5 | 31.7 | 37.4 | 34.4 |
| RFL (t)  | 245.9 | 254.6 | 218.8 | 190.8 | 224.7 | 199.8 |
Figure S16: Estimates of total evaporative emissions of DBLb, DBLp, RFL and PL in Japan. Emission of DBLb and RFL were calculated by this study model, PL was calculated by the model of previous study, DBLp was calculated by MOVES2014 equation. 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. The dotted line shows the total emissions of DBLb, DBLp, RFL and PL in 2020. Values are listed in Table S17.
Figure S17. Prediction of the VOC emission from Japanese stationary sources. The regression equation for prediction is $W = 776,100 \, e^{-0.021(Y - 2009)}$, where $W$ is the emission amount and $Y$ is the year. The VOC emissions inventory from 2010 to 2020 was cited from Official report of VOC emissions from stationary sources in Japan, 2021.\(^9\)
Table S16. Estimates of future DBLb, DBLp, RFL and PL emissions in Japan. Emissions of DBLb and RFL were calculated by the proposed study models, PL was calculated by the model reported by Hata et al. (2020)\(^6\), DBLp was calculated by MOVES2014 equation.\(^8\) ZEV present refers to the 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. ZEV 50% refers to the 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.

|            | 2020  | 2025  | 2030  | 2035  | 2040  | 2045  | 2050  |
|------------|-------|-------|-------|-------|-------|-------|-------|
|            | DBLb (t) | DBLp (t) | RFL (t) | PL (t) | Total (t) |
| ZEV present|       |       |       |       |         |       |
|            | 8900  | 4100  | 69700 | 5100  | 87800  |
|            | 8883  | 4092  | 69567 | 5090  | 87633  |
|            | 8872  | 4087  | 69477 | 5084  | 87520  |
|            | 8225  | 3789  | 64414 | 4713  | 81141  |
|            | 5660  | 2607  | 44323 | 3243  | 55833  |
|            | 3899  | 1796  | 30534 | 2234  | 38464  |
|            | 2688  | 1238  | 21052 | 1540  | 26519  |
| ZEV 50%    |       |       |       |       |         |       |
|            | 8900  | 4100  | 69700 | 5100  | 87800  |
|            | 7488  | 3450  | 58644 | 4291  | 73873  |
|            | 6532  | 3009  | 51155 | 3743  | 64439  |
|            | 5559  | 2561  | 43534 | 3185  | 54839  |
|            | 3825  | 1762  | 29956 | 2192  | 37735  |
|            | 2635  | 1214  | 20637 | 1510  | 25996  |
|            | 1817  | 837   | 14228 | 1041  | 17923  |
Figure S18. Comparison of the additional experiments and the results of model calculation for (a) summer grade gasoline (RVP = 58.9 kPa), and (b) winter grade gasoline (RVP = 77.3 kPa). The comparisons were conducted only for C4 and C5 VOCs because of the analytical limitations (less sensitivity of FID to C6 and larger VOCs). The temperature of liquid gasoline was set to 298 K using a water bath.
Table S17. Specifications of vehicles used in previous and this study.

|                   | W     | E     |
|-------------------|-------|-------|
| **Name**          | **W** | **E** |
| **Manufacture**   | Suzuki| Honda |
| **Category**      | Minicar| Mini van|
| Tank capacity (L) | 27    | 70    |
| Canister volume (L)| 0.3  | 0.9   |
| Displacement (L)  | 0.65  | 2.99  |
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