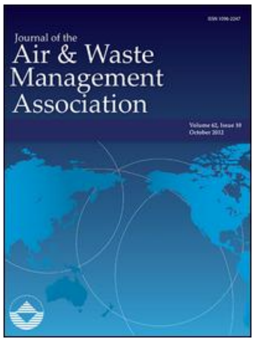

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Modeling cold soak evaporative vapor emissions from gasoline-powered automobiles using a newly developed method

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Modeling Cold Soak Evaporative Vapor Emissions from Gasoline-powered Automobiles Using a Newly Developed Method

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ABSTRACT

Volatile Organic Compounds (VOCs) evaporate and vent from a vehicle's fuel tank to its evaporative control system when the vehicle is both driven and parked. VOCs making it past the control system are emissions. Driving and parking activity, fuel volatility, and temperature strongly affect vapor generation and the effectiveness of control technologies, and the wide variability in these factors and the sensitivity of emissions to these factors make it difficult to estimate evaporative emissions at the macro level. Established modeling methods, such as COPERT and MOVES, estimate evaporative emissions by assuming a constant in-use canister condition and consequently contain critical uncertainty when real conditions deviate from that standard condition. In this study, we have developed a new method to model canister capacity as a representative variable, and estimate emissions for all parking events based on semi-empirical functions derived from real-world activity data and laboratory measurements. As compared to

chamber measurements collected during this study, the bias of the MOVES diurnal tank venting simulation ranges from -100% to 129%, while the bias for our method's simulation is 1.4% to 8.5%. Our modeling method is compared to the COPERT and MOVES models by estimating evaporative emissions from a Euro-3/4/5 and Tier-2 vehicle in Chicago and Guangzhou. Estimates using the COPERT and MOVES methods differ from our method by -56% to 120% and -100% to 25%, respectively. The study highlights the importance for continued modeling improvement of the anthropogenic evaporative emission inventory and for tightened regulatory standards.

Introduction

(1). Evaporative emission from vehicles is an important source of VOCs

Volatile Organic Carbons (VOCs) comprise one of the most important sets of precursors for criteria air pollutant ozone (O_3) and particulate matter (Carlton et al., 2009; Liu et al., 2016) with aerodynamic diameter less than or equal to 2.5μm ($PM_{2.5}$). Elevated concentrations of O_3 and $PM_{2.5}$ cause adverse health effects linked to higher risks of cardiovascular and lung cancer mortality (Anenberg et al., 2010; Buonocore et al., 2014). To control ground level concentrations of O_3 and $PM_{2.5}$, regulators have targeted VOC and NOx exhaust emissions, with large reductions from the light duty gasoline and diesel fleets (EPA, 2014b; Zhao et al., 2013). However, gasoline fueled vehicles can also release substantial amounts of VOCs through evaporative and refueling processes. Evaporative emissions are generated through the processes including running loss, hot soak, cold soak (also known as diurnal, resting, and parking), refueling, and permeation (EPA, 2014a). Aggressive regulation of all these emission processes has largely been limited to the United States and Canada, but China recently published similarly stringent control requirements for implementation in 2020 (ICCT, 2017; Mock, 2011). These regions maintain regulations controlling three or more days of parking with a hot soak, running loss, and refueling with aggressively low emission limits. However, regulations across the rest of the world are at 1980-1990s technology levels and only require control of 1-2 sequential parking events and a hot soak with only moderate emission limits. It is believed the reason for this regulatory gap is from the lack of quantitatively accurate estimation models or the lack of necessary inputs to effectively utilize existing models that are necessary to justify regulatory changes. The U.S. EPA reported that annual evaporative VOC emission inventories were ~50% higher than exhaust VOC inventories for the light duty fleet since 2005 (EPA, 2014a); A recent study (Hao Cai, 2013) demonstrated that the evaporative VOC emission rate (0.062 g/mile) is about 60% of the exhaust emission rate (0.108 g/mile) for 2010 model year passenger cars in the U.S.; Yamada et al. (Yamada, 2013) also suggested that cold soak emissions are about 25% of exhaust emissions from vehicles in Japan based on a chamber measurement study. Thus, it is likely that total evaporative emissions may contribute more VOCs than tailpipe emissions in areas where certain evaporative processes are left uncontrolled or where progress in improving standards has been slower than in the U.S.

(2). Coad soak emission and the vehicle on-board canister

Cold soak evaporative emissions are generated when the environmental temperature rises -- which causes gasoline's vapor pressure to increase and evaporation to occur inside the fuel tank -- and vented vapor escapes past the emissions control canister. Fig.1 presents the schematic diagram showing the vapor generation and canister control system, with glossary of relevant terms described in Table 1. This canister contains activated carbon that adsorbs incoming gasoline vapors, and the canister is regenerated using purge air when the vehicle is driven. The capacity of the canister going into the parking event relative to the amount of vapor generated in the tank during the parking event is primarily important in determining the level of emissions control. The three primary factors that affect cold soak emissions are vapor generation in the fuel tank, canister capacity, and purge flow rate across a range of driving and parking conditions. The mass of vapor generated in the fuel tank (TVG) and its generation rate are most greatly affected by fuel tank volume, gasoline Reid Vapor Pressure (RVP), the changing rate and extent of ambient air temperature, and the fill volume of the tank (Reddy R, 1989). Long parking duration, high temperatures, large fuel tanks with high open headspace, and high RVP favor vapor generation.Fuel tank geometry is also important, because the thank surface area affects the rate of heat uptake, and the height of the tank affects the rate of diffusive mass transfer when the vehicle is parked. Canister working capacity is the maximum amount of vapor that can be adsorbed and stored at a certain temperature and hydrocarbon concentration and desorbed with a fixed quantity of purge. Canister capacity is usually expressed as the butane working capacity (BWC) or as the gasoline working capacity (GWC). Car manufacturers generally design the canister GWC to accommodate the evaporative certification test with the highest vapor load. The effective GWC (EGWC) is a value less than or equal to GWC and describes the remaining capacity on the canister after vapors have been adsorbed by the canister. EGWC is reduced as the canister adsorbs vapors, and it increases or is maintained at maximum levels when purge is flowing through the canister (when the vehicle is being driven) and strips vapors off the activated carbon. The amount of TVG that adsorbs onto the canister during parking is called vapor load (VL), and the volume of clean air that is pulled through the canister during driving is termed as the purge volume (PV). Purge is the computer-controlled pull of air through the canister from the engine during vehicle operation. Automakers calibrate their vehicles' average purge rate generally in proportion to the canister capacity and inversely proportional to the duration of the drive cycle of the limiting evaporative certification test. The drive cycle is the required driving pattern, of certain speed and duration, established by the certification authority. During an evaporative certification test, vehicles are required to be driven through a drive cycle followed by a simulated diurnal evaporative test sequence to generate fuel tank vapors, and the resulting evaporative emission shall not exceed the limit established by the authorities.

Figure 1 here

Table 1 here.

(3). Difficulties to model coal soak emission and the motivation of this study

Because the above mentioned determining factors are always changing during driving and parking activities, quantifying inventories of cold soak emissions cannot be achieved by use of constant emission factors but requires estimation of the TVG, VL, PV, and EGWC, all of which are dynamic throughout each parking and driving event. Further complicating matters is that maximum EGWC can degrade with time by the buildup of heavy hydrocarbon components on the canister's activated carbon, and the extent of this degradation depends upon the properties of the activated carbon (Johnson and Williams, 1990; Williams and Clontz, 2001). Consequently, it is difficult to parameterize or explicitly quantify these factors because they are always changing.

Due to these difficulties, previous modeling efforts simplified the parameterization process. The European model COmputer Programme for calculating Emissions from Road Traffic (COPERT) assumes canisters are always fully-purged following a driving event and disregards the variations of vapor load (Mellios et al., 2009). COPERT applies vehicle-size-dependent and seasonal-dependent emission factors to estimate cold soak emission. Essentially, EGWC is assumed constant for small, medium, and large cars. Vapor load and daily emissions are also assumed constant for small, medium, and large vehicles with seasonal adjustments. The U.S. EPA's MOVES model better parameterizes in-use conditions by calculating the dynamics of TVG with ambient temperatures and applies a constant predefined Average Canister Capacity (ACC, calculated as the weighted averages of designed maximum canister capacities for vehicles across the fleet) to represent EGWC (EPA, 2014a). COPERT and MOVES are the most popular emissions and inventory models currently available, but the simplifying assumption of maximum canister capacity could over-predict the effectiveness of controls in-use, where drive times may be insufficient to fully purge the canister to this maximum GWC. The COPERT and MOVES models essentially assume that real-world driving is effectively the same as the certification drive, but in reality it is not. In our study, the EGWC of canister is calculated as a function of vapor load and purge. We developed a new method to account for the effect of in-use purge and vapor load on EGWC and to calculate cold soak emissions using semi-empirical functions derived from dynamometer and laboratory measurements with multiple fuel systems and typical vehicles representative of the U.S., European, and Asian markets. The correlation between the certification drive cycle and expected in-use purge rates and EGWC is also developed in this study, which enables the model to project how a regulatory drive cycle change could affect cold soak emissions as well.

Methodology

(1). The processes of cold soak parking emission and definition of steady-state conditions

This section briefly introduces the underlying physical processes affecting cold soak emissions and how they are modeled by our new method. Necessary introductions of the COPERT and MOVES methods are also described to point out assumptions in their makeup that are more properly addressed in our new method.

Figure 2 here

Fig.2 describes the underlying processes of cold soak canister load and purge during a period of multiple parking and driving events. The initial in-use $EGWC_0$ equals the maximum theoretical $EGWC$. During the heat build (temperature increase) of the first parking event P_1, vapor generated in the fuel tank (TVG_1) vents into the canister and the amount of vapor adsorbed by the canister is VL_1. The canister loses part or all of its free capacity, and the rest of TVG_1 that is not adsorbed is vented as emissions per $Emis_1=TVG_1-VL_1$. In the consecutive driving D_1, fresh air is purged through the canister as PV_1, and this incrementally restores canister capacity by $\Delta EGWC_1$. For those parking events that experience not only a heat build but also a temperature decrease, the canister restores part of its capacity because air naturally flows back into the fuel tank as it cools (this back-purge process is not shown in Fig.1 because it may not exist for every parking event and the impact on canister capacity is much smaller than the impact from active purge during driving). In the consecutive parking event P_2, vapor generated is TVG_2, which loads onto the canister as VL_2 and generates $Emis_2$. In the next driving D_2, the canister again restores part of its capacity though purging and loses capacity during the next parking event P_3. The canister experiences this repetitive process of driving (air purging) and parking (vapor loading) over the lifetime of the vehicle. The activated carbon inside the canister would gradually become saturated if the canister was not purged sufficiently.

For any parking event P_n, emissions $Emis_n$ are determined by the initial capacity of the canister at the beginning of this event $EGWC_{n-1}$ and by the vapor generated TVG_n during this event. Due to the near infinite number of iterations of parking and driving combinations for a fleet of vehicles, modeling methods must all make assumptions to simplify and parameterize these underlying physical processes. The processes modeled by COPERT and MOVES are represented by grey and red dashed boxes in Fig.2, respectively. Neither method accounts for the variability in canister purge and introduce critical uncertainties in the estimation of emissions. To address the oversight in vapor load, purge, and related in-use canister capacity change by previous methods, yet maintain a reasonable number of computations, our new method defines a steady-state condition, derived from the parking and driving activity data as the weighted average parking and driving condition, to represent a more accurate in-use canister condition. "Steady state canister capacity" is the average, representative, purged canister condition for a given vehicle or vehicle population entering any parking event that takes into account vapor load and purge based on the average local driving distance and parking duration, certification standard, and monthly gasoline RVP and environmental conditions. It shall be noticed that in this study we applied the activity data collected from Florence as one example to demonstrate how our method works. Activity data is an input to our method.

As mentioned above, the canister's in-use capacity $EGWC_n$ for the $(n+1)^{th}$ parking event P_{n+1} is affected by regenerated capacity $\Delta EGWC_n$ from the driving process D_n and the canister's vapor load VL_n from the parking event P_n. So explicitly estimating the effective canister capacity going into a parking event P_n requires modeling the process as:

$$EGWC_n = EGWC_0 - \sum_{k=0}^{n-1} VL_k + \sum_{k=0}^{n-1} \Delta EGWC_k \quad (1)$$

This calculation involves a near infinite number of unknown variables $\Delta EGWC_k$ and VL_k, which makes explicit modeling unrealistic. Our method assumes that the series of fluctuating driving and parking events can be reasonably approximated by a repeating series of average driving and parking events. Thereupon, the canister should obtain a relatively stable range in *EGWC* resulting from steady vapor load (VL_{ss}) and steady purge activities. This steady state condition allows our method to estimate in-use $EGWC_n$ based on representative parking and driving events from specific driving activity data. In this study, we use the weighted-averages of real-world parking and driving activities data to derive the canister's status resulting from all previous parking ($P_{n-1}, P_{n-2}, P_{n-3}, \ldots, P_1$) and driving ($D_{n-1}, D_{n-2}, D_{n-3}, \ldots, D_1$) events when n approaches infinity. So, the in-use canister capacity at the beginning of any parking event can be modeled as:

$$EGWC_n = EGWC_{ss} - VL_{ss} - VL_{HS} + \Delta EGWC_{ss} \quad (2)$$

where $EGWC_{ss}$ is the steady-state canister capacity as:

$$lim_{n\to\infty} EGWC_n = EGWC_{ss} \qquad (3)$$

Thus:

$$\Delta EGWC_{ss} - VL_{ss} - VL_{HS} = 0 \qquad (4)$$

where $\Delta EGWC_{ss}$ is the regenerated capacity during steady-state driving, and VL_{HS} is the hot soak vapor load at the beginning of each steady-state parking event. Now the infinite unknown variables are simplified to four ($EGWC_{ss}$, $\Delta EGWC_{ss}$, VL_{ss}, VL_{HS}). It is important to emphasize that $EGWC_{ss}$ is not a constant parameter but is dynamic and calculated as a function of vapor purge and load with the method described in the next two sections. This derivation of $EGWC_{ss}$ differentiates our new method from the COPERT and MOVES methods and provides an improvement in estimating real-world conditions, particularly when average driving (distances, speeds, and durations), climatic, and fuel RVP conditions are significantly different from certification conditions. The derivation of steady-state conditions for this analysis is based upon real-world activity data including 999,062 driving events collected with on-board GPS systems for approximately 9,500 vehicles in Florence, Italy, with more details reported in Dong et al. (2015) and Martini et al. (2014). The steady-state driving time DT_{ss}, driving distance DD_{ss}, parking duration PT_{ss} are calculated as the weighted averages from the activity data, and the steady-state vapor load VL_{ss} is then calculated using Wade-Reddy's equation for the average tank volume of the fleet of vehicles and monthly RVP being analyzed. It is important to note that the activity data is an input required by the method. While it is optimal to use vehicle activity data specific to the city or region being investigated, these data are most often not available. In order to work around this limitation, the activity data could be scaled based on the local inputs of vehicle miles traveled (VMT) and driving speed which are more commonly available variables than the local driving and parking activity data. This scaling affects the steady-state condition in scale as well. If more local activity data are available, they can be substituted. The Wade-Reddy equation (Reddy, 1989) was developed as a semi-empirical function to calculate evaporative vapor generation as a function of vapor space, fuel vapor pressure, and temperature variations. This equation has been widely applied and adopted by the US EPA's models MOBILE and MOVES (US EPA, 2010; US EPA, 2012) to estimate vapor generation through cold soak.

(2). Estimating purge volume from driving activity and certification drive cycles

During an evaporative certification test, the canister is first saturated with 50% butane, then the vehicle is driven over a trace of speed versus time on a dynamometer to purge the canister. Currently there are three major different evaporative testing procedures (Liu et al., 2015): (1) the European drive cycle NEDC, (2) the U.S. EPA federal test U.S.48-hour, and (3) the California diurnal test U.S. 72-hour, with more details of the tests summarized in Table 2.The vehicle is then placed in a sealed housing for evaporative determination (SHED) for a hot soak test and diurnal emissions measurement. The SHED experiments performed in this study follow the relevant guidelines of the Code of Federal Regulations (CFR, 2002). The temperature within the SHED is varied to simulate steady-state or diurnal temperature fluctuations, and the concentration of VOCs emitted from the vehicle are monitored using a flame-ionized detector (FID). The mass of emissions from the vehicle is calculated from the concentration and the open volume within the SHED. The canister's designed volume of purge during the test drive cycle results in a certain, adequate *EGWC* that is generated from the canister originally saturated with butane. But real driving activity never exactly match and will many times be less favorable than test conditions, particularly in duration. The activity data showed an average drive time of 15.2 minutes. The shortest U.S. certification cycle is 30 minutes and the New European Driving Cycle (NEDC) is 60 minutes (EMEP/EEA, 2009),The COPERT and MOVES models effectively assume that EGWC is that which exists following the certification drive and entering the SHED test, but real-world activity data demonstrate this assumption is invalid COPERT and MOVES overestimate purge for the large majority of driving events.

Table 2 here.

Our method calculates the representative purge volume based upon a fleet's activity data. Purge volume (PV_{ss}) during a steady-state drive must be estimated in order to calculate $EGWC_{ss}$. To accomplish this, we used experimental measurements to derive a semi-empirical function (*Function1*) to calculate PV_{ss} from DT_{ss} $EGWC_0$ and the shortest drive cycle time of the certification test procedures (T_{cycle}). The experimental measurements involved five vehicles, representing typical passenger cars in the U.S., Europe and Asia, with detailed configurations of the vehicles summarized in Table 3. These typical passenger cars indicate that under a more developed regulatory standard (i.e. the U.S. standard), vehicles are equipped with relatively larger canisters with larger capacities to control evaporative vapor emission. Dynamometer driving tests – measuring vehicle speed, purge rate, and time – were performed on each vehicle by following the three drive cycles mentioned above.

Table 3 here

The measurements, shown in Fig.3, and the canister capacities shown above suggest that certification requirements have dominant impacts on vehicle calibration of purge rates and canister capacity. With the highest canister capacity and being certified to the U.S. Tier2 standard, Vehicles A and E showed the largest cumulative purge volume ($PV_{cumulative}$) across the three different sets of drive cycles. The three Euro-4 vehicles (Vehicle B, C, and D) had significantly lower canister capacity and were calibrated on the NEDC, which produced significantly lower *PV*, particularly at low speeds and idle. The measurement data shown in Fig.3 suggest that Euro-4 vehicles generate very little *PV* (<50L) in the first 15 minutes of driving (average real driving time), further indicating COPERT substantially overestimates EGWC for in the European fleet.

Figure 3 here

Fig. 3 also shows that the same vehicle purged at different rates when driven on different cycles, suggesting that vehicle speed can have an impact on purge rates. To account for this effect of certification drive cycle on a purge calibration response, the purge data were normalized by defining the drive cycle factor (*DCF*) as the ratio of purge rate (P_{rate}) for the drive cycle of interest with the purge rate over the NEDC as a reference condition:

$$DCF_{NEDC} = \frac{P_{rate,NEDC}}{P_{rate,NEDC}} = 1.0 \qquad (5)$$

$$DCF_{US\ 48-hr} = \frac{P_{rate,FTP75}}{P_{rate,NEDC}} = 0.84 \qquad (6)$$

$$DCF_{US\ 72-hr} = \frac{P_{rate,US\ 72-hr}}{P_{rate,NEDC}} = 0.58 \qquad (7)$$

where P_{rate} is derived for each type of drive cycle using measurement data as:

$$P_{rate} = \frac{PV_{cumulative}}{T_{cycle}} \quad (8)$$

Purge rates are calibrated in proportion to *EGWC* and in inverse proportion to T_{cycle}, and are a function of vehicle speed and idle per DCF.

(3). Estimating purge rate

Function1 was developed to estimate *PV* from purge rate as:

$$PV_n = \frac{C_1 \times DCF \times EGWC^{C_2}}{T_{cycle}^{C_3}} \times DT_n + C_4 \quad \textit{Function1} \quad (9)$$

where: $C_1 = 14215$, $C_2 = 0.25$, $C_3 = 2.3$, *and* C_4=-4.99 are the coefficients derived from the measurement data using least squares approach. For in-use applications, the $DCF_{US\ 48\text{-}hr}$ is applicable for most applications, although $DCF_{US72\text{-}hr}$ may be more representative if there is a high proportion of urban congestion. The performance of *Function1* as compared to the measurements is shown in Fig.4, and the correlation coefficient between simulation and measurement is 0.95. With this function, the steady-state purge volume PV_{ss} and the dynamic purge volume PV_n for any driving event D_n can be reasonably modeled using inputs from driving activity and certification conditions.

Figure 4 here

(4) Estimating in-use canister capacity from purge volume

With the estimation of *PV*, we derived another semi-empirical function (*Function2*) based on laboratory measurement to calculate *EGWC*. A 1L canister, filled with 11 BWC carbon pellets (BAX 1100), was loaded with 50% gasoline vapor (v/v) at 40 g/h until 2 gram breakthrough, and canister weight was monitored. The canister was purged using air at 22.7L/min up to 1200L, and canister weight was monitored. These load-purge cycles were repeated 25 times, and the data shown are for the 25th cycle. The function was derived as:

$$EGWC \quad = C_{aging} \times \frac{BWC}{11} \times (C_5 + C_6 \times ln(\frac{PV}{C_{volume}} + C_7)) \times V_{canister} \quad Function2 \quad (10)$$

where: C_{aging} is the capacity adjustment factor due to aging of the canister (assumed to be 93% when in-use standards are applied and 84% when not); *BWC* is the butane working capacity of the activated carbon; C_5 = -22.45, C_6 = 13.3, and C_7 = 5.49 are the constants derived based on least squares approach fitting, and $V_{canister}$ is the volume of the canister.

Figure 5 here

Fig.5 shows measured (black circles) canister capacity changes and *Function2* (blue curve) estimations, as a function of bed volumes of purge, defined as the purge volume divided by canister volume ($\frac{\mathrm{PV}}{\mathrm{C_{volume}}}$). It is important to note that the *PV* used in *Function2* is that relative from an initially saturated canister, which can be represented as point $A_{saturated}$, where both *PV* and *EGWC* are zero. Assuming the standard canister's maximum capacity is 70.2g (or any other value at the end of the curve) at 1200 bed volumes purge, point A_{purged} can be used to indicate the status of a fully purged (fully regenerated) canister. Excessive *PV* will not generate significantly more *EGWC* beyond A_{purged}, and unusually long drives would be required to reach 1200 bed volumes of purge. In-use, the canister *EGWC* will remain between a fully loaded ($A_{saturated}$) and a fully purged (A_{purged}) state across all normal operating conditions. Two points, A_{n-1} and A_n, are defined to represent the canister condition before and after driving event D_n, respectively. During in-use conditions, A_{n-1} will not usually equal $A_{saturated}$. Thus the purge volume PV_n generated during driving event D_n cannot be directly used in *Function2* to calculate $EGWC_n$. So $PV`_n$ is used to represent the state of the canister – in terms of *EGWC* on an equivalent purge volume basis – on the curve of *Function2*, then $PV`_n$ is equal to the actual PV_n only when the canister before this parking event is fully loaded (A_{n-1} equals to $A_{saturated}$). Since $PV`_n$ is unknown, our method seeks the solution of $EGWC_n$ based on the steady-state condition in which the canister load from A_n to A_{n-1} during the steady state parking event equals the negative of the amount purged from point A_{n-1} to A_n, and PV_{ss} is calculated using *Function1*. As mentioned in the beginning of this section, the steady-state condition represents the typical, representative purged and loaded canister condition resulting from infinite parking and driving activities, in which the vapor load during steady-state parking equals the absolute value of the regenerated canister capacity resulting from steady-state driving. Assuming there is near zero vapor emissions from the steady-state condition ($TVG_{ss} = VL_{ss}$), from equation (4) we have:

$$\Delta EGWC_{ss} = TVG_{ss} + VL_{HS} \qquad (11)$$

$EGWC_{n-1}$ and $EGWC_n$ is the canister capacity before and after driving event D_n respectively, so:

$$EGWC_n - EGWC_{n-1} = \Delta EGWC_{ss} < sub > \qquad (12)$$

$PV`_{n-1}$ and $PV`_n$ is the equivalent purge volume state of the canister before and after the driving event D_n, and the purge volume generated during driving event D_n is represented as:

$$\Delta PV = PV_n = PV`_n - PV`_{n-1} \qquad (13)$$

Under the steady-state condition, we have $PV_n = PV_{ss}$, so equation(13) is revised as:

$$\Delta PV = PV_{ss} \qquad (14)$$

Considering equations (11), (12) and (14) together, four unknown variables ($EGWC_n$, $EGWC_{n-1}$, $PV`_{n-1}$ and $PV`_n$) and two known variables ($\Delta EGWC_{ss}$ and PV_{ss}) exist. The value of TVG_{ss} can be calculated using Wade-Reddy's equation. In this study a hot soak vapor load VL_{HS} of 5.0g is used based on SHED measurements. Our method iterates on the curve of Function2 to find the solutions of $EGWC_n$, $EGWC_{n-1}$, $PV`_{n-1}$ and $PV`_n$ where equations (11) and (13) are satisfied simultaneously. These calculations are performed to calculate a unique $EGWC_{ss}$ for each month of the year, since vapor generation can differ significantly because of temperature and seasonal fuel RVP. This method also allows unique values of $EGWC_{ss}$ to be calculated for different certification conditions, regions, and driving patterns.

(5) Estimating of emissions from tank vapor generation and canister in-use capacity

Along with functions to determine *PV* and *EGWC*, a third semi-empirical function was also established to estimate cold soak emissions for a given amount of *TVG* based on a chamber measurement study. Canisters of various capacities were attached to fuel tanks of various volumes, and the combinations were placed in an environmental chamber. The temperature in the chamber was fluctuated between 72°F and 96°F, following the U.S. EPA's diurnal trace (EPA 40 CFR 86 Appendix II, Table 1), for a total of twelve days. Fuel tanks were filled to 40% of nominal volume with fresh fuel prior to each test. The initial capacity of the canister was measured. Twice each day, total mass of vapor vented from the fuel tank, mass of vapor adsorbed onto the canister, mass of vapor back-purged, and mass of emissions were measured. The canister was weighed on a laboratory balance twice daily, at minimum and peak temperatures, to establish vapor load and back-purge masses. Canister emissions were collected in a Tedlar bag at the time of daily peak temperature and measured using a flame ionization detector (FID) to establish mass of emissions. Total vapor generated from the fuel tank was calculated by adding the mass of emissions to the mass of vapor loaded onto the canister. The data were then compiled to correlate total vapor generated from the fuel tank with cumulative emissions over the twelve days for the various canister capacities. This laboratory study involved measurements for 14 different canister-fuel tank combinations and fuels with two different RVP to encompass typical in-use fuels and tank-canister configurations around the world, with the configurations summarized in Table 4. Tank volumes spanned across those of small to large light duty vehicles, and the canister capacities span across those expected as an outcome from any global regulation. In practice, canisters meeting pre-enhanced or Euro requirements are sized at a ratio of approximately 1 gram of GWC per liter of nominal fuel tank volume, and canisters meeting enhanced, Tier2, and Tier3 standards are sized at a ratio of approximately 2g/L of nominal fuel tank volume. While many of the test cases were at ratios close to these certifying ratios, the intention of the chamber experiment was to identify the relationship between vapor generation from the fuel tank, initial canister capacity, and emissions for a wide range of in-use conditions around the world. These conditions not only include existing fuel-tank/canister-capacity combinations, but also ones that could become practice in the future. Thus, some of the cases were at ratios lower or higher than seen in practice, so that the model would interpolate all results rather than extrapolate. For example, we designed some theoretical cases such as small fuel tank with large canister (case#2,#5,#12,#14) and large fuel tank with small canister (case#6) in order to get a wider range of vapor generation and emission measurements. As a result, the span of test conditions makes the developed relationship applicable to the myriad in-use conditions outside those of current certification conditions, where vapor generation rates can be higher than certification (from higher RVP fuels, higher temperature heat builds, lower tank fill levels, or where EGWC is lower than initial GWC) or can be lower than certification (from lower RVP fuels, lower temperature heat builds, or higher tank fill levels). Thus, these experimental data can be used to derive the semi-empirical function of emissions for both pre-enhanced/Euro or enhanced certified vehicles based on tank vapor generation and canister capacity.

Table 4 here

Fig.6(a) shows the measurement of cumulative emission against cumulative TVG, which indicates that emission cannot be estimated from TVG only. Fig.6(b) shows the emission versus the ratio of $TVG/EGWC^{0.5}$, where the exponent of 0.5 was determined by a least squares approach to maximize the superimposition of the data. The ratio itself was chosen to normalize the data, since emissions can be expected to be proportional to the mass of vapor generated from the fuel tank and inversely proportional to the capacity of the canister.

Figure 6 here

Function3 was developed to calculate cold soak emission (*Emis*) as:

$$Emis = C_8 \times \left(\frac{TVG}{EGWC^{\ 0.5}}\right)^{C_9} + C_{10} \times \left(\frac{TVG}{EGWC^{\ 0.5}}\right) \times (1 - exp(C_{11} \times \left(\frac{TVG}{EGWC^{\ 0.5}}\right)^{C_{12}})) \quad \textit{Function3}$$

(15)

where $C_8 = 0.0334, C_9 = 1.84, C_{10} = 0.38, C_{11} = -2.41 \times 10^{-5}$, and $C_{12} = 3.58$ are constant coefficients for pre-enhanced/enhanced-evap/Euro3-6 vehicles derived using a least square approach fitting of the function. For Tier2/China6 and Tier3 vehicles, C_8 is 0.003 and 0 respectively, while the other coefficients remain the same. The relationship can be applied across any reasonable set of environmental conditions as well as a large range of regulatory technology responses in canister capacity and tank volume and gasoline RVP. Furthermore, the relationship applies to short as well as extended parking events and the influence of back-purge is imbedded within the results.

To demonstrate the importance of considering both *EGWC* and *TVG* for estimating emissions, the performance of *Function3* was compared with the MOVES method. The MOVES method applies the predefined ACC as constant *EGWC* for all parking events, and then utilizes a semi-empirical function (*FunctionM*) developed based on laboratory measurement collected from the CRC E77 study (Haskey and Liberaty, 2004; 2008) to calculate emissions from *TVG* as:

$$Emis = \frac{-(B \times TVG + E) + \sqrt{(B \times TVG + E)^2 - 4 \times C \times (A \times TVG^2 + D \times TVG + F)}}{2 \times 1.15} \quad \textit{FunctionM} \qquad (16)$$

where A, B, C, D, E, F are constants that vary with vehicle categories – pre-enhanced, enhanced, and Tier2 (EPA, 2011). To compare the performance of *Function3* and *FunctionM*, simulations were validated with the measurement data from our laboratory study, as shown in Fig.7.

Figure 7 here

The simulations are compared with measurements for different cases separately to reveal the functions' performances for typical pre-enhanced and enhanced vehicles. The correlation between measurement and simulation is 0.46 for the *FunctionM*, and 0.99 for *Function3*. Compared to measurement, deviation of the MOVES simulation is -100%, 79.9%, and 129% for *TVG* less than 50g, between 50-100g, and higher than 100g, respectively, while the deviation of our method is 1.4%, 8.5%, and 2.0% respectively. In fact, *FunctionM* calculates negative emission when *TVG* is less than 50g, but it is reset as zero emission in the MOVES model (EPA, 2011). Our chamber measurements found that even small vapor loads onto canisters with excessive *EGWC* still generated small levels of emissions. This validation suggests that the MOVES method may underestimate cold soak emission for typical short parking events (<2days, TVG<50g) and is not applicable for estimating the emissions from long parking events (>5days, TVG>100g) and/or those with high vapor generation rates.

Results and Discussion

Our method is compared with the COPERT and MOVES methods in a case study by estimating cold soak emissions for two types of vehicles – pre-enhanced and Tier2 – with the temperature profiles and monthly fuel RVP typical of Chicago and Guangzhou. Pre-enhanced and Tier2 vehicles have large differences in canister capacity and purge rates, and most of the world's current in-use vehicles are being certified to levels equivalent to one of these two standards. Euro 3-5 vehicles in COPERT are assumed comparable to pre-enhanced vehicles in MOVES – relative to evaporative emissions control. As many of the megacities in Europe, Asia, and North America are located in the 10ºN-45ºN latitudes with subtropical or temperate climate conditions, Chicago and Guangzhou are selected as being representative for climate conditions across most of the mid-latitude urban areas in the Northern Hemisphere, where vehicle populations are concentrated. These two cities are selected as examples also because of their different regulatory standards on evaporative emissions. It is important to notice that our method can be applied under any climate condition and for any city or location with the local inputs. Detailed configurations of the simulated vehicle, fuel, canister, and temperature characteristics and other parameters used in the analysis are summarized in Table 2. The COPERT method uses predefined emission factors (EFs) categorized in terms of engine size, seasonal temperature range, and canister size. The COPERT EFs are expressed as grams per procedure (parking event). In this study, EFs for Euro-4 certified passenger cars with 1.4-2.0L engine size and large canisters were selected to estimate cold soak emissions. The COPERT model is designed for use in Europe, so it does not define EFs for Tier2 vehicles. Tier 2 technology package levels are excessive for the Euro 3-5 standards, and this type of vehicle does not exist in Europe. So simulations with COPERT were only performed for pre-enhanced/Euro-4 vehicles. On the other hand, the similarity between pre-enhanced and Euro 3-5 evaporative control technology allows MOVES to model Euro 3-5 vehicles effectively.

Table 5 here

Figure 8 here

To better demonstrate the differences between the constant canister capacity and the in-use dynamic canister capacity, Fig.8 shows the ACC and $EGWC_{ss}$, along with TVG from one-day and five-days parking events. The predefined ACC values used by MOVES are represented with flat red lines in Fig.8 since the values are the same for all vehicles falling into the same category, regardless of variation in seasonal temperature and RVP. The $EGWC_{ss}$ calculated by our method is 19-21%(14.5-16.3g) and 25-29%(38-45g) of the MOVES ACC for pre-enhanced and Tier2 vehicles, respectively, as shown in Fig.8, suggesting that real in-use canister capacity is significantly lower than the fully purged state. For pre-enhanced and Tier2 vehicles, the ACC value is 72.8g and 150.7g respectively, while $EGWC_{ss}$ is less than 20g and around 40g respectively with slight monthly variation due to changes in temperature and RVP. Fig.8 suggests that one-day TVG is usually under the in-use canister capacity while the five-day TVG can be substantially higher than that, especially for pre-enhanced vehicles, indicating large amounts of cold soak emissions for the those vehicles. The maximum amount of TVG for a one-day parking event was estimated as 34g and 37g for pre-enhanced and Tier 2 vehicles, respectively, in October in Guangzhou. Differences in TVG were due to different tank volumes specified by MOVES as being representative for pre-enhanced and Tier 2 vehicles.

Figure 9 here

Fig.9 shows the simulation comparison of one-day parking event cold soak emissions between COPERT and our method. Overall estimation from the COPERT method is 120% and 4% higher than estimation from our method for Chicago and Guangzhou respectively. Our simulation shows distinct seasonal variation of cold soak emissions while COPERT shows only discrete seasonal variation. Both pre-enhanced and Tier2 vehicles have higher emissions in the warmer months with peak emissions occurring in June in Chicago. Guangzhou has the highest emissions in October due to the combined effects of temperature and fuel RVP. Simulations from COPERT suggest similar seasonal variation for pre-enhanced vehicles in Chicago as compared to our simulation, but COPERT could not reproduce the monthly emission changes in Guangzhou. The COPERT method uses four emission factors for four different temperature ranges to represent seasonal variations as shown in Table 5, so areas such as Guangzhou with relatively small monthly temperature changes was supplied with only two emission factors for all twelve months, despite the fact that vehicles shall have a larger variation of TVG due to the combined effects from temperature and RVP. Simulation with our method suggests that pre-enhanced vehicles generally have ~15 times more cold soak emissions as compared to Tier2 vehicles in both Chicago and Guangzhou, indicating the dominant impact of the certification standard on evaporative emissions. Advanced certification requires higher canister capacity and higher purge rates, which lead to lower evaporative emissions.

Figure 10 here

The MOVES method calculates vapor generation for parking events up to only five successive days, so emission simulations were limited to this duration. Our method allows for modeling of any vehicle type up to about twelve days of parking. Fig.10 shows the estimations of cumulative cold soak emissions for a 5-day parking event using COPERT, MOVES, and our method. The MOVES predefined ACC is 72.8g and 150.7g for pre-enhanced and Tier2 vehicles respectively, while $EGWC_{ss}$ calculated by our method is only 19-21%(14.5-16.3g) and 25-29%(38-45g) of the ACC (comparison of $EGWC_{ss}$ and ACC shown in Fig.8), indicating that MOVES significantly overestimates *EGWC* for the driving activity considered in this study. For a pre-enhanced vehicle in Chicago, cold soak emissions simulated by all three methods have consistent seasonal variations. Vapor emissions are relatively high in the summer and low in the winter because of the overall impacts of temperature changes and RVP on *TVG*. Our method identifies a more pronounced level of monthly variation as compared to the other two methods. Our method estimated that the highest emissions are found in June (11.9g/event), more than 20 times higher than the lowest emissions in December (0.5g/event). COPERT and MOVES simulated annual average cold soak emissions for pre-enhanced vehicles in Chicago at levels 56% and 33% less than our method, respectively, mainly due to the unreasonable overestimations of *EGWC*. For pre-enhanced vehicles in Guangzhou, estimations from COPERT appear to greatly underestimate emissions, particularly in winter months, because it applies seasonal adjusted EFs as mentioned before (also see Table S2 for the COPERT EFs). Areas such as Guangzhou utilize high RVP winter fuels, but the temperature remains high. This causes relatively high winter, spring, and fall vapor generation rates and the accompanying high emissions. The MOVES method predicts unreasonably high emissions in Oct. and Nov. as compared to Sep. and Dec. For Oct., it predicts 92.3g emissions out of 145g *TVG* using a canister with 72.8g ACC, because the MOVES *FunctionM* becomes too sensitive to offer a stable estimation when *TVG* is higher than 100g as discussed earlier in last section. For the Tier2 vehicle in Chicago, MOVES predicts all zero emissions for TVG<50g due to the overestimated ACC and the inaccurate assumption that small vapor loads in a canister with high remaining EGWC do not generate emissions. The estimations of Tier2 emissions in Guangzhou are generally consistent between MOVES and our method with a 56% difference, except for the zero emissions simulated by the MOVES method during cool months (Jan.-Apr.).

Summary

In this study, cold soak evaporative emissions from gasoline-fueled automobiles are estimated using a newly developed method. The most important innovation is dynamically estimating the in-use canister capacity based on activity data and functions to estimate purge volumes, derived from laboratory measurements, instead of assuming a constant fully purged canister state as used in previous modeling attempts. A steady-state condition of the canister is derived by using the weighted averages of real-world parking and driving activity data to represent the typical vapor load and purge that a canister can be expected to experience before entering any in-use parking event. Semi-empirical functions were derived from laboratory measurements to model: (1) purge volume as a function of canister capacity, certification drive cycle, and typical in-use drive time, (2) canister capacity as a function of vapor load and purge volume, and (3) vapor emissions as a function of effective canister capacity and tank vapor generation. Our vapor emission function was compared with the MOVES semi-empirical function against laboratory measurement, and the MOVES function showed substantially larger bias. The in-use canister capacity calculated with our method is only 19-21% and 25-29% of the MOVES predefined ACC for pre-enhanced and Tier2 vehicles, respectively. Vehicle driving activity data show that most driving events are 25-50% of the duration of certification drives, suggesting the assumption of a fully purged canister, found exiting the certification drive, is not valid. The case study over Chicago and

Guangzhou shows that the MOVES estimation of emissions was 37% lower and 25% higher than the estimation using our method, respectively, and 100% lower and 56% lower than our method for Tier2 vehicles, respectively. The COPERT method under-predicted the emissions for pre-enhanced vehicles by an average of 56% as compared to our method, due to using predefined emission factors.

The results from this study have important policy implications regarding the current estimation of evaporative emission inventories around the globe and future regulation of these pollutants. COPERT and MOVES are the two models commonly used now to quantify official estimates of evaporative emission in Europe and the U.S., respectively. This study reveals, however, that significant uncertainties are associated with both of the established models, and even more uncertainty will exist when modeling vehicles in regions outside those in which the models were calibrated. The U.S. has the most complete anthropogenic emission inventory and the most stringent automotive emissions standards in the world, but this study shows that the MOVES evaporative emission inventory may still underestimate. Even more uncertainty exists in the inventories modeled using COPERT. These uncertainties can mislead regulators in their understanding of VOC sources and inventories, and cause regulatory agencies to avoid developing sufficient evaporative standards and test procedures that could help them meet air quality and public health targets. This model, that uses readily available inputs, can be used by the many environmental agencies that currently do not have access to accurate inventory models. Estimating the contribution of evaporative emissions toward the total anthropogenic inventory is recommended, as it will benefit the understanding of urban air pollution sources and the potential for future emission control and its cost-benefit as well. This study also suggests that the evaporative standards and testing procedures should be updated in Europe, Asia and other regions that currently follow the European or equivalent certification standards to generate higher canister capacities and purge rates and result in significantly lower emissions.

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Table 1. Glossary of Terms

Acronyms	Terms [units]	Descriptions
ACC	Average Canister Capacity [g]	A variable defined by the MOVES that presents the average in-use capacity of the canisters
BWC	Butane Working Capacity [g]	A measure of the capacity of the canister filled with activated carbon to adsorb and desorb butane from the intake air
Canister	Canister Size [Liter]	The vehicle onboard charcoal (active carbon)-filled canister is used to absorb fuel vapor that would otherwise vent out to the atmosphere. Vapors trapped by the canister are released back into the engine through the purge valve and then burned.
COPERT	COmputer Programme for calculating Emissions from	Model used by European Environment Agency to estimate emissions from

	Road Traffic	transport
DC	Drive Cycle	A drive (or driving) cycle is a series of data points representing the speed of a vehicle versus time. Drive cycles are configured by the regulation agencies to assess the fuel consumptions and emission tests of vehicles.
EGWC	Effective Gasoline Working Capacity [g]	The real in-use capacity of the canister.
Enhanced	-	The evaporative emission regulation defined by U.S. EPA with phase-in beginning in 1996
GWC	Gasoline Working Capacity [g]	A measure of the capacity of the canister filled with activated carbon to adsorb and evaporative vapor from the intake air
Hot soak	-	Vapor loss when engine and exhaust heat dissipation to the fuel tank after the

		engine is turned off
MOVES	MOtor Vehicle Emission Simulator	Model used by U.S. EPA to estimate emissions from transport
NEDC	New European Driving Cycle	NEDC was implemented in Europe as the testing procedure to assess the emission levels and fuel economy in passenger cars.
Pre-enhanced	-	The 1982 U.S. EPA evaporative emission regulation
PV	Purge Volume [Liter]	The amount of fresh air pulled through the canister during driving.
RVP	Reid Vapor Pressure [psi]	A measure of the volatility of gasoline
SHED	Sealed Housing for Evaporative Determination	A sealed housing facility used to measure evaporative emission from the gasoline-fueled vehicles.

SS	Steady State	In this study, we define the "steady state canister capacity" as the average, representative, purged canister condition for a given vehicle or vehicle population entering any parking event that takes into account vapor load and purge based on the average local driving distance and parking duration, certification standard, and monthly gasoline RVP and environmental conditions.
Tier2	-	The evaporative emission regulation defined by U.S. EPA with phase-in beginning in 2004
TVG	Tank Vapor Generation [Liter]	Evaporative vapors generated inside the fuel tank
VL	Vapor Load [g]	The amount of evaporative vapors that adsorbs onto the canister

VKT/VMT	Vehicle Kilometers/Miles Travelled [km/year, miles/year]	Annual kilometer/mileage travelled by the vehicle

Table 2. Testing Procedures

Test Procedure	Drive Time	Drive Distance	Average Speed
NEDC	60 min	33.021 km	33.63 km/h
U.S. 48-hour	31 min	17.806 km	34.19 km/h
U.S. 72-hour	97 min	45.645 km	27.11 km/h

Table 3. Detailed Information for Vehicles Used in Purge Rate Test

Vehicle	Main Market	Canister Volume (L)	Designed Capacity (g)	Certification Standard
Vehicle A	U.S.	2.0	140	U.S. Tier2
Vehicle B	Europe, China	0.7	38.5	Euro-4 (C-4)
Vehicle C	China	0.9	49.5	Euro-4 (C-4)
Vehicle D	Europe	0.95	52.25	Euro-4 (C-4)
Vehicle E	U.S.	2.1	147	U.S. Tier2

Table 4. Canister, tank, and fuel configurations for measuring cumulative emission.

Case# Config.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
EGWC (g)	103	137	65	137	164	65	164	267	103	137	137	164	164	267
Tank Volume (L)	51	51	66	66	66	80	80	80	51	51	66	66	80	80
Fuel RVP (kPa)	62	62	62	62	62	62	62	62	69	69	69	69	69	69

Table 5. Configurations of vehicle, temperature, and fuel for simulations

Vehicle Configuration			**Temperature (ºC) & Fuel RVP (psi) Configuration**								
	Pre-enhanced	**Tier2**		**Chicago**				**Guangzhou**			
Inputs for all methods				T_{min}	T_{max}	RVP	EF#	T_{min}	T_{max}	RVP	EF#
Tank volume	70.4L	76.8L	Jan.	-8	-1	14.9	0.04	10	18	12.8	0.08
Tank fill	40%	40%	Feb.	-6	2	14.9	0.04	12	19	12.8	0.08
Inputs for MOVES only			Mar.	-1	8	14.9	0.04	15	22	12.8	0.08
ACC	72.8g	150.7g	Apr.	6	15	13.5	0.05	20	16	11.6	0.16
$A_{Backpurge}$	24%	24%	May	11	21	9.0	0.08	23	30	10.4	0.16

Inputs for COPERT only			Jun.	17	27	9.0	0.08	25	32	9.4	0.16
Proc./day	5.8	-	Jul.	20	29	9.0	0.16	26	34	9.4	0.16
Canister type	Large	-	Aug.	19	28	9.0	0.16	26	33	9.4	0.16
Engine size	1.4-2.0L	-	Sep.	14	24	9.0	0.08	24	32	11.0	0.16
Inputs for our method only			Oct.	8	17	11.5	0.08	21	30	12.8	0.16
PT_{ss}	7h	7h	Nov.	2	9	13.5	0.05	16	26	12.8	0.08
DT_{ss}	15.8m	15.8m	Dec.	-5	2	14.9	0.04	11	21	12.8	0.08

[#]EFs selected here are corresponding to gasoline passenger cars with 1.4-2.0L engine size equipped with larger size canister and are used for the COPERT method only

Implications:

The COPERT and MOVES methodologies contain large uncertainty for estimating evaporative emission, while our new modeling method is developed based on chamber measurements to estimate evaporative emission and can properly address those uncertainties. Modeling results suggest urgent need to complete emission inventory with evaporative emission, and also indicated that tightening evaporative emission regulation standard is urgent especially for warm areas.

Figure 1. Schematic diagram of the vehicle onboard carbon canister load and purge process.

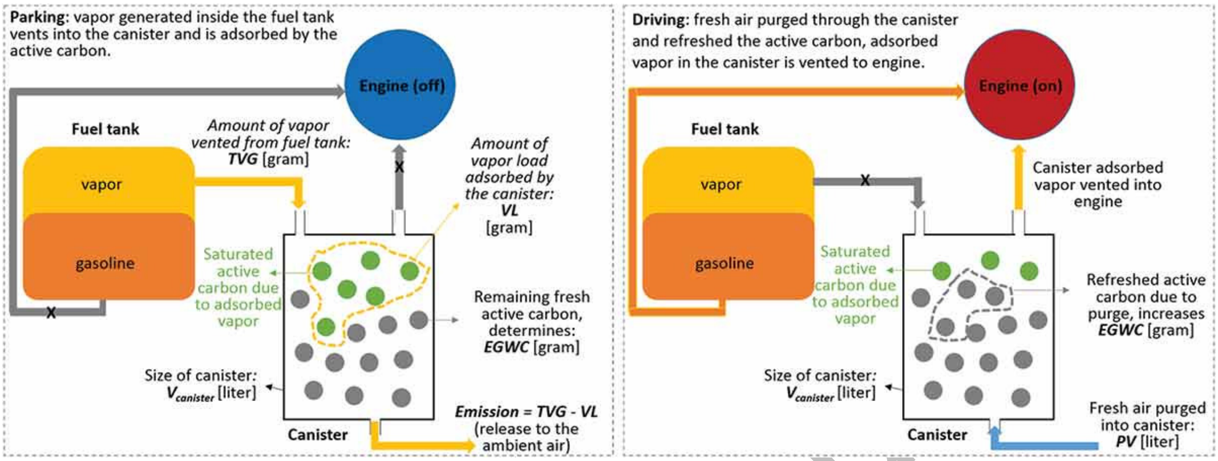

Figure 2. Underlying physical processes modeled by the COPERT, MOVES and our model.

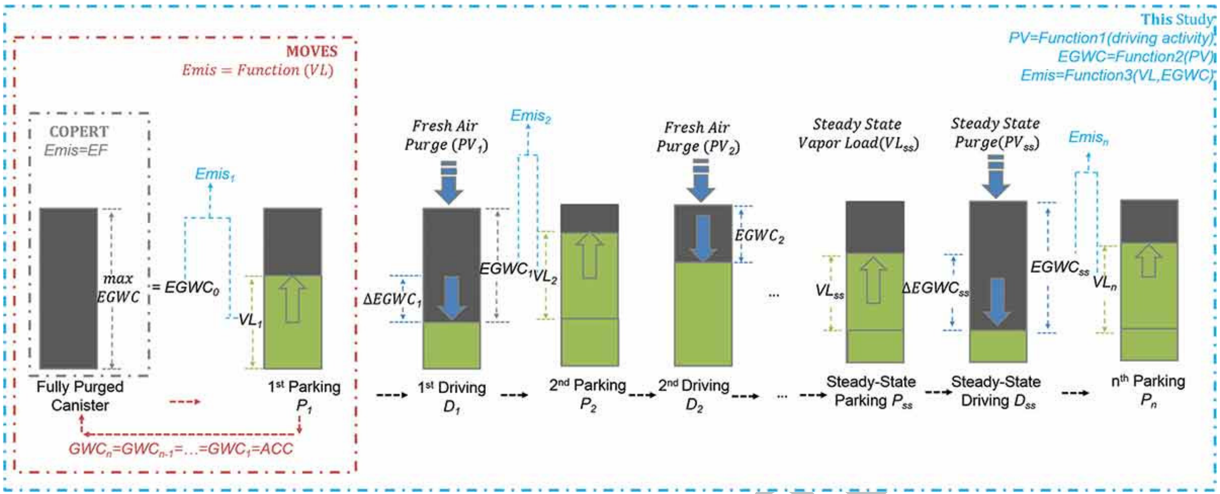

Figure 3. Driving speed (grey dash lines) and cumulative purge volumes of five different vehicles (red for Vehicle A, green for Vehicle B, purple for Vehicle C, blue for Vehicle D, and orange for Vehicle E) under the (a) NEDC, (b) US 48-hr, and (c) US 72-hour testing procedures.

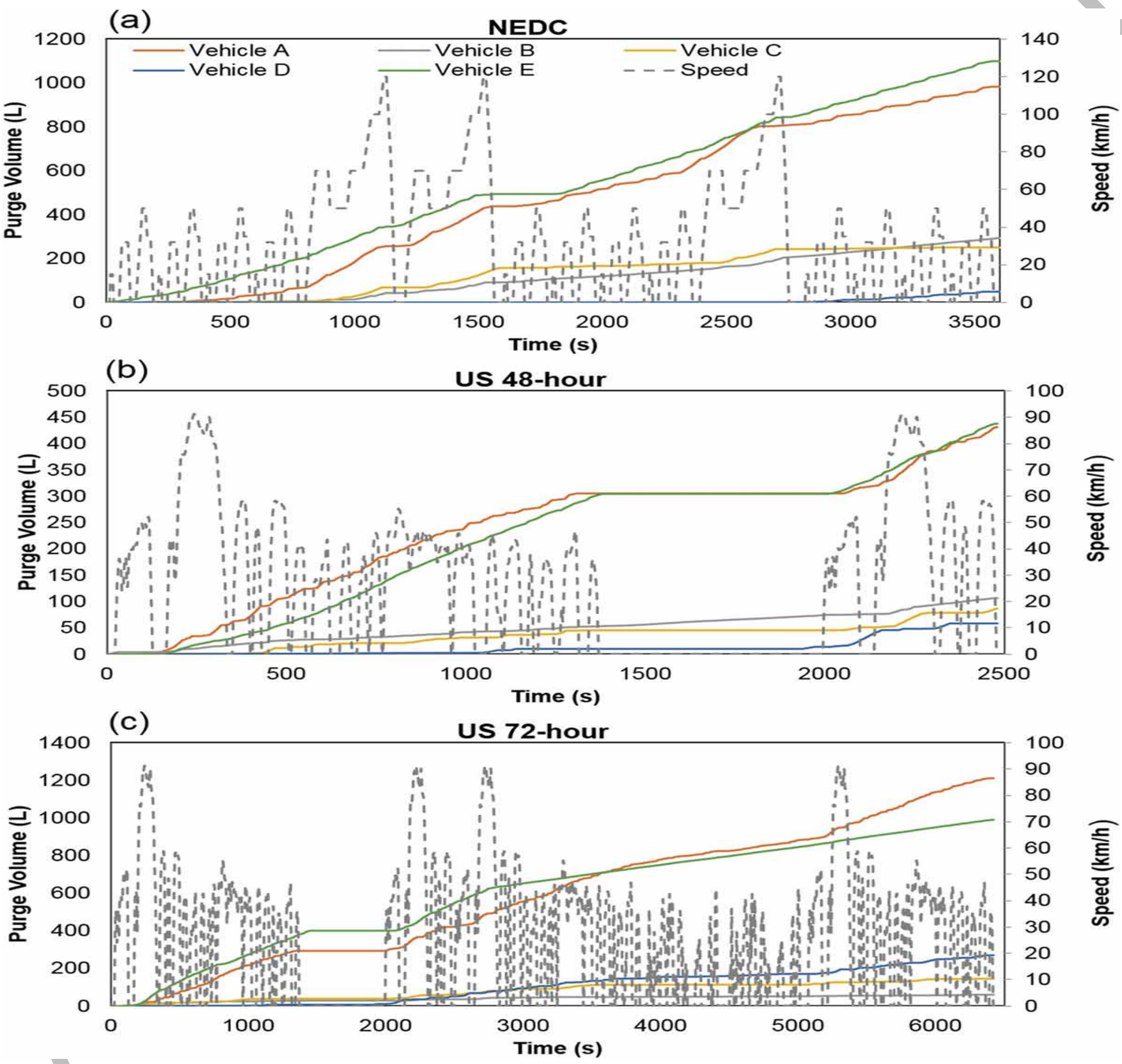

Figure 4. Comparison of simulated and measured cumulative purge volumes of five different vehicles (red for Vehicle A, green for Vehicle B, purple for Vehicle C, blue for Vehicle D, and orange for Vehicle E).

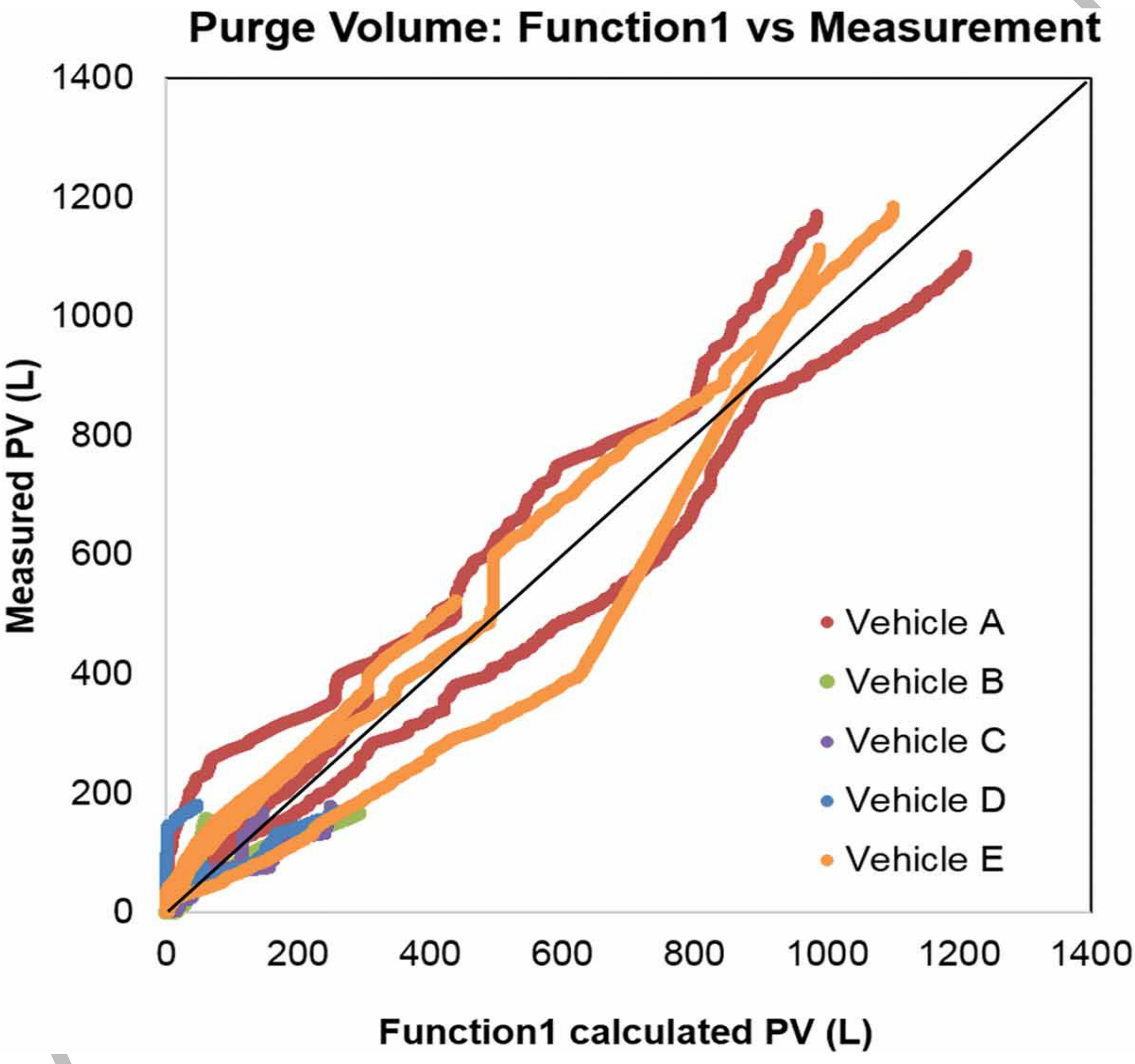

Figure 5. Relationship between PV and canister EGWC.

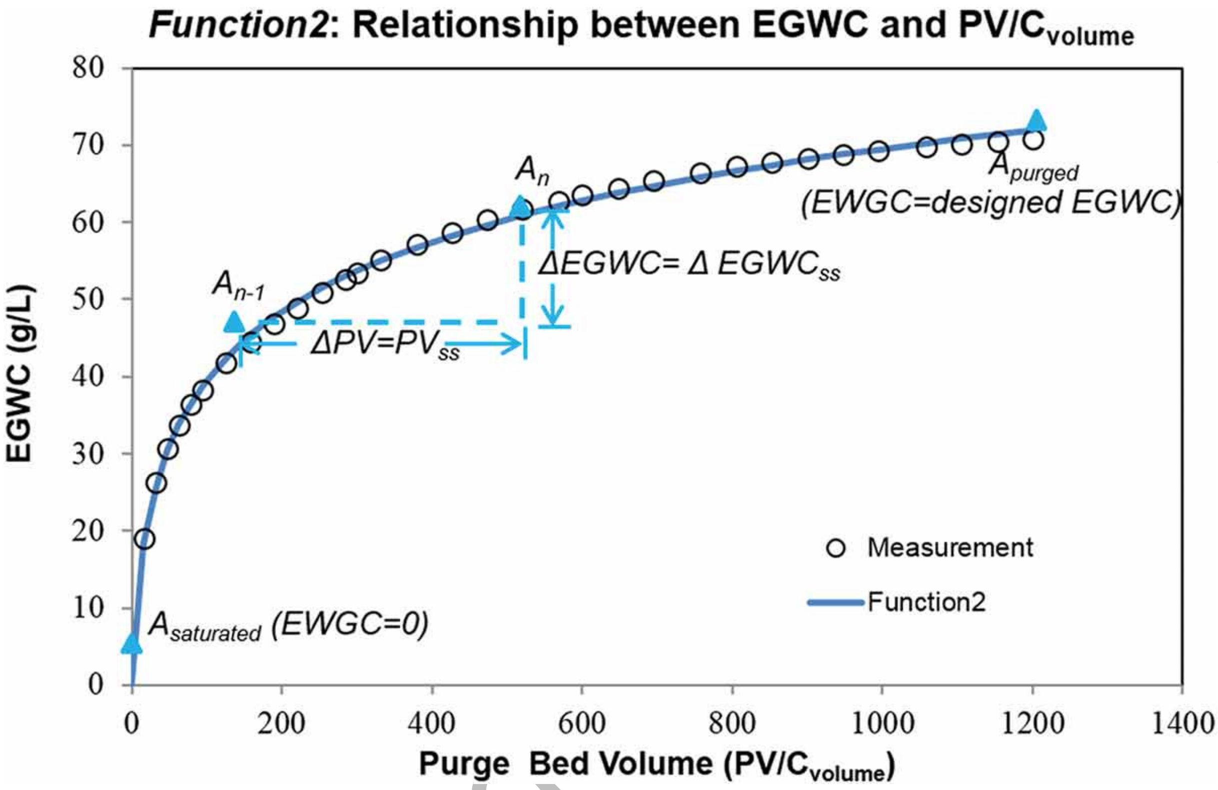

Figure 6. (a) Measurement of emission against TVG; (b). Relationship between TVG, EGWC, and Emission

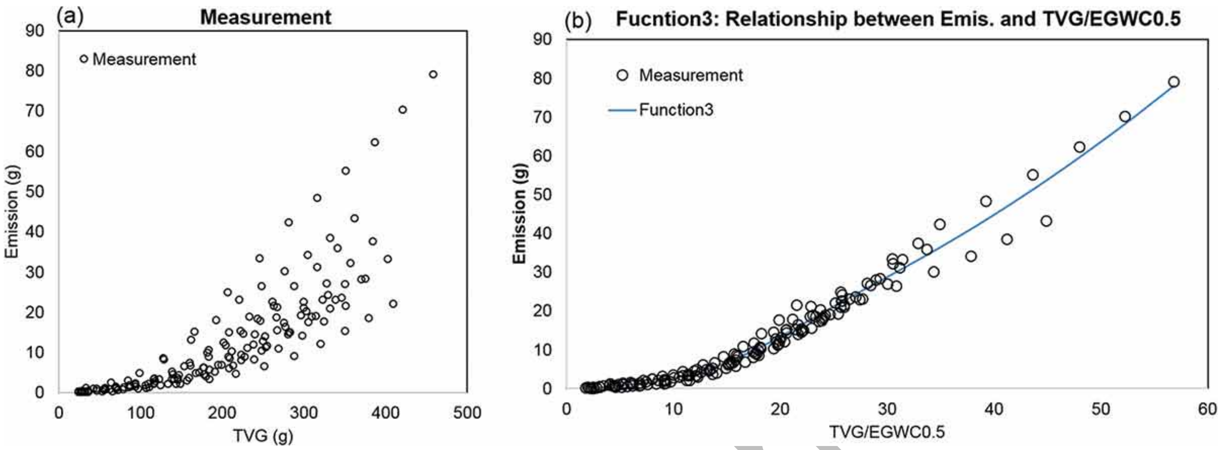

Figure 7. Evaluations of cold soak cumulative emissions with laboratory measurement (black cross) for simulations from the MOVES *FunctionM* (red circles) and our method *Function3* (blue circles) for (a) pre-enhanced and (b-g) enhanced/Tier1 vehicles.

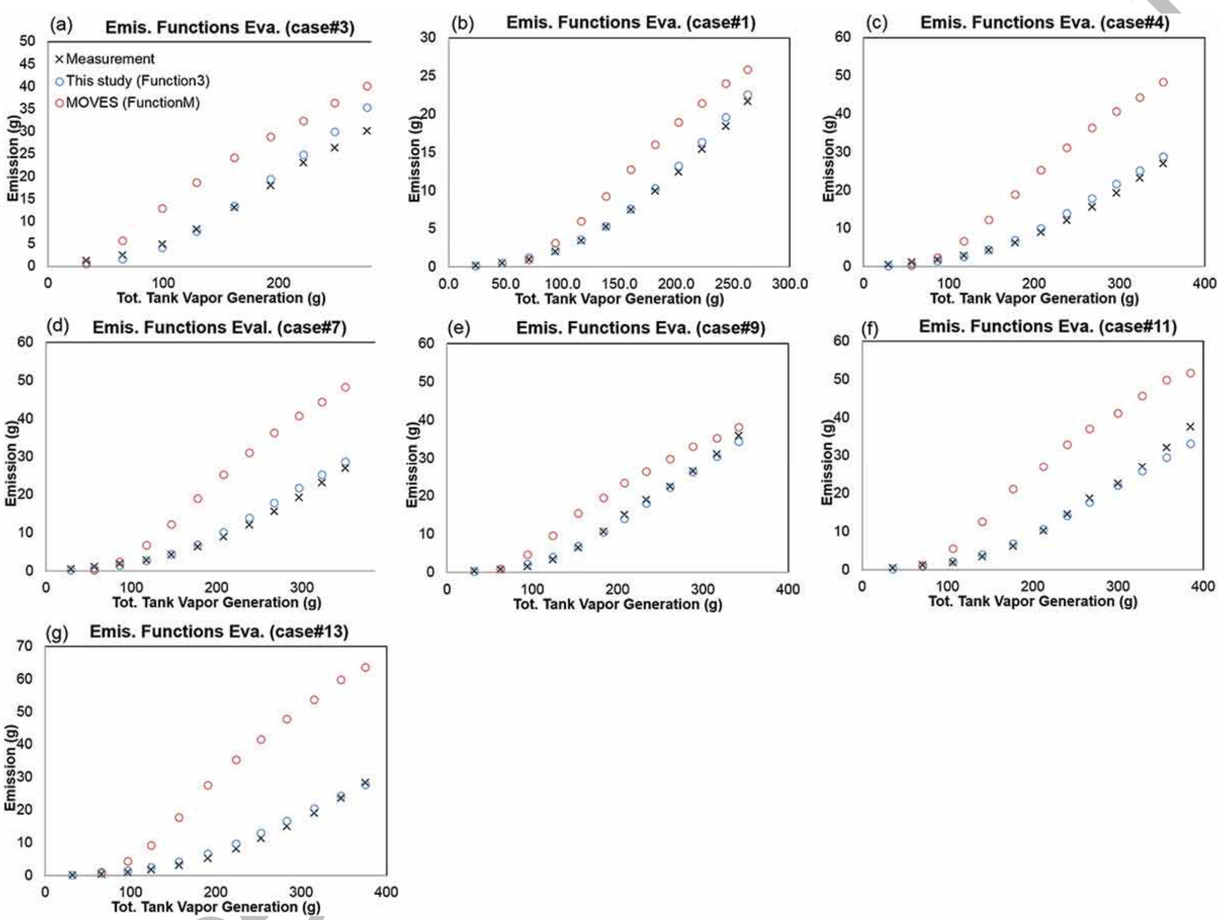

Figure 8. Comparison of the EGWC$_{ss}$ calculated by this study (blue lines) and the MOVES predefined ACC (red lines), and TVG from 5-days (green triangles) parking events for (a) pre-enhanced certified vehicle at Chicago, (2) pre-enhanced certified vehicle at Guangzhou, (c) Tier2 vehicle at Chicago, and (d) Tier2 vehicle at Guangzhou.

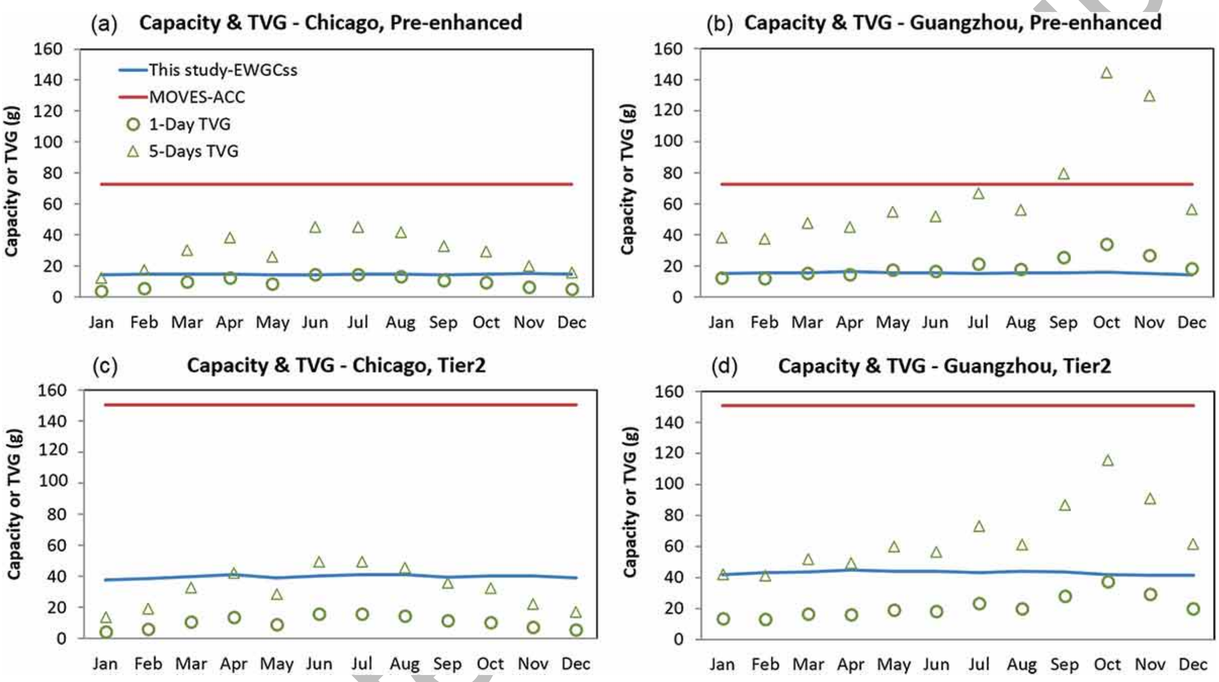

Figure 9. Comparison of simulated one-day parking cold soak emission from COPERT (grey bars) and our new method (blue bars) for pre-enhanced certified vehicles (upper panels) and Tier 2 vehicles (lower panels) in Chicago (left panels) and Guangzhou (right panels). The MOVES estimated cold soak emissions for one-day parking events for both pre-enhanced and Tier 2 vehicles are zero, so the MOVES estimates are not shown.

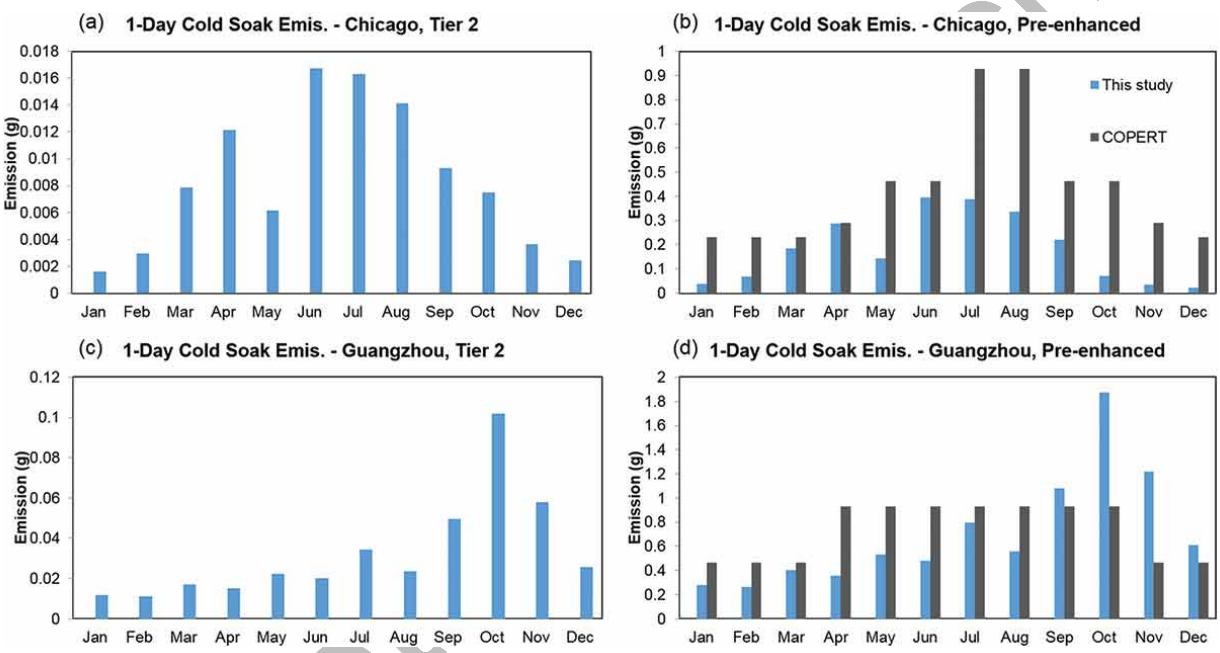

Figure 10. Comparison of simulated 5-day cold soak emissions from the MOVES (red bars), COPERT (grey bars) and our new method (blue bars) for (a) pre-enhanced certified vehicle at Chicago, (b) pre-enhanced certified vehicle at Guangzhou, (c) Tier2 vehicle at Chicago, and (d) Tier2 vehicle at Guangzhou.