



Supplement of

Plume-based analysis of vehicle fleet air pollutant emissions and the contribution from high emitters

J. M. Wang et al.

Correspondence to: J. M. Wang (jonm.wang@utoronto.ca)

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Sampling and Instrument Details

The gas analyzers Thermo Scientific models 42i, 48C, and 410i were calibrated before and after the measurement campaign using certified gas mixtures (Linde Canada Ltd., Mississauga, Ontario, Canada) for carbon monoxide (630 ± 13 ppm), carbon dioxide (99700 ± 2000 ppm), and nitrogen oxide (79.6 ± 4 ppb); and a multi-gas calibrator (model 146i, Thermo Scientific, Waltham, MA). Negligible differences were observed between the pre- and postcampaign calibrations of the gas analyzers. The 48C CO analyzer was set to auto-zero every 12 hours to ensure quality assurance of the higher instrumental drift.

A six level calibration was run before and after the measurement period for the PTR-TOF-MS using two standard VOC mixtures made by the National Air Pollution Surveillance Network at Environment Canada (Ottawa, Ontario) based on U.S. EPA-TO15 for 159 non-polar VOCs and 40 independently chosen polar VOCs. Data was exported using PTR Viewer 3.1.0.20 and converted from counts per second normalized to H_3O+O^{18} to mass concentration using the corresponding 6-level calibration curve.

The PASS-3 absorption measurement was converted to a black carbon mass concentration by linear correlation with thermal-optical analysis (Lab OC-EC, Sunset Laboratories, Tigard, OR) integrated over 2 hour periods that made coinciding measurements over the measurement campaign. The calculated conversion value from absorption (Mm^{-1}) to ($\mu g/m^3$) was 0.31, 0.27, 0.26, and 0.27 for fall, winter, spring, and summer campaigns respectively and expected to be specific for this study conditions.

Automatic Plume Identification Method

Measurement data were processed and analyzed in Igor Pro 6.34. Figure S1 presents plume cases ranging from more ideal (left panel) to less ideal (right panel), with various corresponding measured pollutant plumes. In some cases, there is no corresponding pollutant measurement due to negligible emission from the source.



Figure S1: Time series of automatic plume identification results (a) of the CO₂ trace separated as plume (red) and non-plume (black), with the sticks indicating beginning (green) and end (blue) of plume, and the corresponding slope of CO₂ over 10 points. Measurement time series (b) with example plumes for different pollutants, illustrating pollutants which are or are not detected from the passing vehicle.

The data treatment for CO is described in Section 2.3 and is different for CO due to the lower time response of the instrument, which has a moving average of 60 seconds, compared to the other measurements with time responses of 0.5 - 1 Hz. The CO₂ trace in the lower panel of Figure S2 was averaged to 60 seconds to match the time response of the CO measurement and an emission factor is calculated using this averaged CO₂ trace. This plume would then be matched by the nearest plume identified using CO₂ at 1 Hz.



Figure S2: Time series including only CO and CO_2 from Figure S1 (middle panel) with the automatic identification calculated using the 1 Hz CO₂ signal and corresponding identification using 0.02 Hz CO₂ averaged signal to match with the CO trace. A blue dashed arrow indicates matching between the start times of two plumes in which CO is present.

Roadside versus Near-Road Inlet Gradient Comparison

Extending on the near-road EF gradient test, assuming that the pollutants and CO₂ are conserved within the plume and dilute similarly as they are transported from the tailpipe to the inlet, ideally there should be no correlation between the PN EFs and dilution ratio. A rough estimate of the dilution ratio from the gradient comparison calculated by assuming the output concentration of CO₂ from the vehicles at 140,000 ppmv (14%) yielded no correlation between dilution ratio and PN EFs (Figure S3). This was assumed to be the case in many previous carbon balance fuel-based EF studies and has also been shown by Jayaratne et al. (2005). Assuming the same output of CO₂, based on the average amount of CO₂ measured in plumes, the mean dilution

ratios from tailpipe to 3 m and 15 m were approximately 6000 and 10000 respectively. This indicates that although there may be roughly a 70% increase in dilution between 3 m and 15 m, a large amount of dilution occurs on the road right after the tailpipe. Despite the large amount of dilution occurs, the PN EF values were observed to be consistent between 3 m and 15 m (Figure S3) within each trial, following the assumption that the exhaust plume is relatively well conserved within the street canyon.



Figure S3: Scatter plot of calculated PN EFs from both 3 m (red) and 15 m (black) against dilution ratio determined by CO₂.

Repeated Drive-By Vehicle Tests and PN EF comparison

In order to test the capture efficiency and accuracy of the measurements at the near-road site, a 2013 Ford Focus gasoline direct injection passenger vehicle was driven by the site testing four drive states; idle, cruise, acceleration, and braking. A total of 25 passes were made for each respective drive state, where a capture efficiency was calculated based on the number of passes where a plume was identified by CO₂ and met quality assurance measures for a successful capture in contrast to an unsuccessful capture from no observable change in the pollutant signals. At 15m, the capture efficiencies were highest for idling in line with the inlet (52%) compared to acceleration and braking (44%), and cruise (42%). Coincident measurements made at the roadside (3 m) had a higher average capture efficiency of 71%. This indicates that there was a 25% decrease in capture efficiency at 15 m, likely as a result of plumes missing the sample inlet or diluting pollutant concentrations below the sensitivity of the instrument.

Sensitivity Analysis of Mean EFs

The number of individual plume measurements required to accurately estimate the fleet mean EFs was tested with a sensitivity analysis using random subsampling of the dataset was conducted. This was done by decreasing the fraction of the data used to calculate the mean (Figure S4) with 100% being 103,000 plumes to 95, 75, 50, 25, 10, 5, 1, 0.5, and 0.1%. With a random subsampling with a 10% fraction of the data, the mean EFs deviated at most 6%. However, with 1% and 0.1%, the deviation in mean EFs were upwards of 19% and 87%, respectively. Although the objective of this analysis was to evaluate the fleet mean EF, it also shows that the variability of EFs across the fleet population can be estimated with >10% or >10,000 plumes for these pollutant measurements.



Figure S4: The mean EF for each pollutant in units of per kg of fuel and error bars indicating 95% confidence interval as a function of the randomized fraction of data included in calculating the mean.

A sensitivity analysis was conducted on the effects of changing various criteria thresholds (i.e. minimum plume time and CO_2 response, shifting start and end times of the plumes). The analysis of these results are discussed in the main text in Section 2.3.

Table S1: Percent differences relative to the plume criteria of >10 second and >5 ppmv used in the EF method. The left section of the table are differences based on the mean EFs, which include BT EFs, whereas the right section is for above threshold (AT) EFs only. Indicated in red of the column headers are criteria thresholds that would never be considered, but are simply tests of each extreme.

	Mean EFs							AT EFs Only								
	Change minimum CO ₂ average response				Change minimum plume time			Shifting the start and end plume times (PT)								
					14 sec @	6 sec @	30 sec @	1 sec @								
	2ppmv	4ppmv	8ppmv	10ppmv	8 ppmv	2 ppmv	0 ppmv	0 ppmv	PT -2	PT -5	PT +2	PT +5	PT -2	PT -5	PT +2	PT +5
NO	-0.5%	-0.3%	1.7%	1.9%	1.7%	-0.5%	-6.0%	-0.4%	1.5%	3.4%	1.5%	5.7%	1.6%	2.8%	1.2%	3.6%
NO ₂	-5.7%	-2.0%	3.2%	4.0%	3.3%	-5.7%	14.2%	-6.3%	-0.5%	-0.4%	3.1%	10.6%	-0.2%	-0.6%	1.9%	5.4%
NO _x	-3.6%	-1.3%	2.6%	3.2%	2.6%	-3.6%	6.8%	-3.9%	0.3%	1.1%	2.5%	8.7%	0.6%	1.0%	2.2%	6.0%
CO	-10.1%	-3.3%	4.8%	8.3%	4.8%	-10.2%	37.7%	-11.5%	3.0%	8.1%	-3.0%	-0.3%	-1.2%	-4.7%	0.3%	1.0%
PN	1.1%	0.7%	-3.1%	-5.4%	-3.1%	1.0%	-0.6%	0.9%	-0.4%	-2.0%	1.9%	6.9%	0.7%	0.2%	1.1%	4.0%
BC	0.5%	0.2%	-1.5%	-3.3%	-1.5%	0.5%	4.9%	0.0%	0.2%	2.3%	2.7%	18.1%	0.8%	3.4%	1.9%	5.9%
CH ₃ OH	3.9%	1.6%	-2.5%	-3.8%	-2.6%	3.9%	-4.7%	4.0%	-0.5%	-1.1%	4.8%	10.5%	-0.5%	-1.3%	4.6%	9.4%
C ₆ H ₆	-4.1%	-1.3%	-7.1%	-8.2%	-7.1%	-4.1%	5.0%	-4.5%	-10.0%	-14.0%	3.9%	17.9%	-7.8%	-10.2%	1.6%	6.2%
C ₇ H ₈	1.1%	0.4%	-2.6%	-5.0%	-2.6%	1.0%	0.0%	1.2%	-3.1%	-4.8%	4.6%	15.2%	-2.2%	-4.1%	3.2%	8.6%
C ₈ H ₁₀	1.0%	0.5%	-4.1%	-7.0%	-4.0%	0.9%	0.9%	1.1%	-3.1%	-5.7%	5.0%	14.9%	-1.9%	-3.8%	3.5%	9.0%
PAH	-4.9%	-1.6%	3.5%	3.4%	3.6%	-5.0%	9.7%	-5.7%	-1.0%	0.2%	3.8%	12.4%	0.7%	2.5%	1.3%	3.4%

Individual EF Analysis

Individual plumes were selected from the measurement time series based on large magnitude pollutant plumes from the measurement period. These plumes did necessarily originated from high or heavy emitters as dilution can also play a critical role in the measured concentrations at the inlet. The selection basis used was visually obvious plumes in comparison with other plumes from the period based on high levels of any one or multiple pollutants. These short time interval periods were then verified as having no truck influence (cars only) or having one or more trucks passing (cars and trucks) using video recordings of the passing fleet. Of the 152 heavy emitter plumes randomly chosen, 62 were cars and 88 were truck-influenced periods. Although the truck influenced-periods are more difficult to distinguish whether it is the truck or a poorly-tuned car that may be emitting higher levels of pollutants, the expected lag time was typically matched to the passing truck.

A subset of 75 plumes were selected randomly from the individual plume analysis and EFs were calculated using two techniques. The automated technique has been described in Section 2.3. The manual technique identified plumes on a visual basis from the time series data. The plume was then background subtracted by selecting a minimum point from the plume period, manually integrated and an EF was calculated in a similar manner as the automated technique. On average, the mean percent difference between manual and automatic methods was 8% and within acceptable limits given the differences in the two methods (Table S2).

Major deviations of the EF values (17% for BC) was most influenced by noisier measurement signals, which resulted in the baseline determination for background subtraction. Additionally, effective sensitivities were determined for the instrument in order to eliminate the effect of noise on lower EF values. Testing this on some of the manually calculated BC EFs resulted in a decrease in mean percent different by a factor of two. Other deviations between the two methods were the result of the plume identification differences, where although both methods were consistent in start times, the length of the plume was highly subjective in the manual method.

Pollutant	Mean Percent				
	Difference (%)				
NO _x	6.9%				
CO	8.0%				
PN	7.1%				
BC	16.9%				
CH ₃ OH	9.7%				
C ₆ H ₆	8.6%				
C7H8	7.2%				
C ₈ H ₁₀	6.5%				

Table S2: Mean percent difference of calculated EFs using manual and automatic techniques.

Pollutant EF Distributions

The mean AT EFs described in Figure 3 (main text) are dependent on the effective sensitivity of the measurement methods used for each respective pollutant. These AT EF values are not representative of the entire fleet, but rather the subsection of the fleet with detectable emissions of the specific pollutant. This becomes especially important in a plume-by-plume analysis, where selectively identifying plumes based on measurably higher pollutant levels may preferentially target heavier emitting vehicles. Time-integrated sampling is only limited by the detection limits of the measurement technique because all emissions are inherently captured by each sample. However, proper inclusion of BT values is crucial in plume-by-plume analysis, where in order to represent the entire detectable fleet, a representative sample that includes BT plumes needs to be taken into consideration, as done in this study. A considerable difference is observed when comparing fleet mean EFs with mean EFs calculated only using AT EFs (Table S3). In particular, pollutants with a high percentage of BT EFs including BC, CO, and BTEX EFs are nearly half of their respective mean AT EF values.

Pollutant	Fleet Mean EFs ^a	Mean AT EFs ^b	Geometric	EF Unit	BT EFs ^c
	±95% CI	±95% CI	Mean AT EFs		
NO _x	$2.29 - 2.33 \pm 0.02$	2.97 ± 0.02	2.11	g kg-fuel ⁻¹	23 %
CO	$10.0 - 10.3 \pm 0.2$	39.9 ± 0.6	29.6	g kg-fuel ⁻¹	75 %
PN	$7.53 - 7.57^{\circ} \pm 0.11$	11.0 ± 1.6	6.11	# 10 ¹⁴ kg-fuel ⁻¹	30 %
BC ^e	$35 - 55 \pm 1$	106 ± 3	143	mg kg-fuel ⁻¹	66 %
CH ₃ OH	$1.70 - 1.71 \pm 0.08$	2.94 ± 0.15	1.16	g kg-fuel ⁻¹	40 %
C ₆ H ₆	$50 - 52 \pm 1$	101 ± 1	82	mg kg-fuel ⁻¹	49 %
C ₇ H ₈	$143-148\pm 6$	315 ± 13	189	mg kg-fuel ⁻¹	54 %
C_8H_{10}	$129 - 135 \pm 2$	301 ± 5	221	mg kg-fuel ⁻¹	55 %

 Table S3: Fleet-average emission factors from detectable plumes in fuel-burned units

^a Mean EFs for all identified plumes including BT EFs as zero and calculated with the operational detection limit, ^b mean EFs with all BT EFs removed respective to each pollutant, ^c percentage of EFs treated as BT and given a zero value, ^d range for fleet mean PN EFs is small due to the low operational detection limit of the CPC, ^eBC EFs from the PASS-3 only had 75% data coverage due to automatic zeroing of the instrument.

Assuming in-use mean fuel consumption rates of 10.6 L/100 km for LDVs and 30.9 L/100 km for HDVs and a 97% and 3% fleet make-up of the two respective vehicle types (StatsCan, 2010), a weighted arithmetic fleet mean fuel consumption rate can be used to convert the per kg fuel burned EFs into per km units (Table S4).

Pollutant	Fleet Mean $EFs^b \pm 95\%$ CI	EF Unit
NO _x	$0.188 - 0.192 \pm 0.001$	g km ⁻¹
СО	$0.823 \ -0.846 \pm 0.011$	g km ⁻¹
PN	$6.19 - 6.22 \pm 0.10$	$\# 10^{13} \text{ km}^{-1}$
BC ^e	$2.9 - 4.5 \pm 0.1$	mg km ⁻¹
CH ₃ OH	$0.140 - 0.141 \pm 0.007$	g km ⁻¹
C ₆ H ₆	$4.11 - 4.29 \pm 0.04$	mg km ⁻¹
C ₇ H ₈	$11.8 - 12.2 \pm 0.5$	mg km ⁻¹
C_8H_{10}	$10.6 - 11.1 \pm 0.2$	mg km ⁻¹

Table S4: Fleet-average emission factors from detectable plumes in distance units^a

^a Assumed fuel densities of 725 kg m-³ (https://www.ic.gc.ca/eic/site/mc-mc.nsf/eng/lm00129.html) for commercial unleaded gasoline and diesel 836 kg m-³ (https://www.ic.gc.ca/eic/site/mc-mc.nsf/eng/lm00127.html), ^b mean EFs for all identified plumes including BT EFs as zero and calculated with the operational detection limit.

Pollutant EFs were found to be log normally distributed, with most pollutants having one mode (Figure S5). It is important to note that the BT or zero/effective sensitivity value EFs (Eq. 3) are excluded from these distributions but are included as percentages in Table S2. Some of the pollutant EFs were limited less by the measurement limit of detection, as there is an apparent decrease in the distribution at lower EF levels. However, in the distribution of certain pollutant EFs such as BC, CO, and VOCs a truncated distribution is apparent, most likely associated with poorer sensitivities. This is most apparent in the EF distribution of BC, where the mode is close to zero, thus making it difficult to determine whether this is the true mode or if it is below the detection limit of the PASS-3.



Figure S5: Emission factor distributions for pollutants NO_x, BC, PN, CO, CH₃OH, C₆H₆, C₇H₈, and C₈H₁₀.

The distribution for NO_x is the only pollutant to have two modes, at 0.6 g kg-fuel⁻¹ and 2.2 g kg-fuel⁻¹. The two modes represent averaged influences from NO and NO₂ dominated plumes respectively (Figure S6), although direct interpretation of these species is kept simple within the text by focusing on NO_x EFs only.



Figure S6: Emission factor distribution for NO and NO₂.

The stacked plot (Figure S7), similar to the Figure 2 in the text, used the operational detection limit rather than zero values to represent the BTs in order to provide a more conservative value for the percent contribution of emissions from higher EF emitters. Although the distributions of the contributions remain similar to those shown in Figure 4 of the text, one noticeable change is in the distribution for BC, which is much lower. This is the result of a relatively higher defined detection limit compared to the other pollutant measurements as a result of noise from the PASS-3, which shifts the distribution towards the BT EFs for BC. It is unexpected that a large proportion of the fleet would emit significant amounts of BC, thus these BT EFs should be closer to zero. In addition to the higher BT EF values as result of using the detection limit for calculation, the sheer number of BT EFs of BC further inflates the lower portion of the distribution. Thus, this figure was included in the supporting information as reference and not included in the text.



Figure S7: Stacked bar plot showing the contribution of heavy emitters in percentage based on the top 5, 10, and 25% of detectable plumes used to calculate EFs and operational detection limit to calculate BTs.

Ontario's Emissions Testing Program

Vehicle emissions in southern Ontario are regulated by the provincial government through "Drive Clean", an emissions testing program for in-use vehicles similar to the U.S. EPA. For LDVs, emissions testing of in-use vehicles is equivalent of U.S. EPA Tier 1 standards, and are conducted for vehicles older than 7 years. Certain exemptions apply including vehicles manufactured before 1988, hybrid vehicles and motorcycles, and geographical locations outside of the Windsor-Ottawa corridor. Gasoline vehicles undergo mandatory testing on a dynamometer for CO, NO_x, and hydrocarbon emissions every two years. Additionally, light-duty diesel vehicles are also tested using a visible smoke test for exhaust opacity, a measure for particulate matter in the vehicle exhaust. For HDVs, the program is modelled after U.S. EPA 2004 and 2007 HDV emissions standards based on model year, however only an exhaust opacity test is conducted for PM emissions. Since January 2013, the Drive Clean program began solely using the on-board diagnostic for post-1997 LDVs to infer emissions quality (MoE, 2010; McCarter, 2012).

References

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