

Real-World Measurements of Exhaust and Evaporative Emissions in the Cassiar Tunnel Predicted by Chemical Mass Balance Modeling

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The chemical mass balance model has been used to separate non-methane hydrocarbon emission factors measured in the Cassiar tunnel study into exhaust and evaporative emission factors. The local gasoline composition has been used as a real-world surrogate profile for exhaust emissions and has been demonstrated to result in vastly improved model performance compared to the performance obtained with the use of an exhaust profile derived from dynamometer testing. Because of the approach used, the combustion and unburned gasoline components of exhaust emission gases could be estimated separately. Unburned gasoline was found to comprise $63.4 \pm 7.0\%$ of exhaust gases for light-duty vehicles operating in steady-state driving conditions in this study. On-road benzene emissions were found to split 71%/27%/2% between the combustion, unburned gasoline, and evaporative sources. Evaporative non-methane hydrocarbons were found to represent $10.3 \pm 0.8\%$ of the total on-road emission rate on average. The apportionment of total NMHC emission factors to exhaust and evaporative emission factors allowed a detailed comparison to exhaust and on-road evaporative emission factors predicted by the MOBILE4.1C and MOBILE5C models.

Introduction

Air pollution and its impact on human health continues to be a concern in many urban areas today. Despite many efforts to reduce precursor emissions that contribute to ozone formation, the problem still exists, largely because of misdirected ozone control strategies in the past (1). Photochemical modeling is generally used to establish relationships between precursor emissions and ozone formation (2). This modeling requires the use of detailed emission inventories, the errors and uncertainties of which are frequently blamed for poor model performance and previous failures to solve the ozone problem. Motor vehicles are known to account for significant fractions of the nitrogen oxide (NO_x), volatile organic compound (VOC), and carbon monoxide (CO) emissions in these inventories. For regional inventories, motor vehicle exhaust emissions are currently estimated by the product of the emission factor for a given pollutant (g/mi) and the estimated vehicle miles traveled (VMT) for a given vehicle type and set of driving conditions. The emission factor is considered to be much more uncertain than the VMT estimate and is generally a function of many variables. Emission factors for most emission inventories are currently estimated by motor vehicle emission factor models such as the U.S. EPA's MOBILE models and the EMFAC model in use in California. In Canada, the MOBILE model is used, but with modifications made to the base emission rates of vehicles to account for differences in emissions control technology between U.S. and Canadian vehicles in past years.

An early comparison of emission factors measured in a tunnel with those predicted by an emission factor model were made following the Van Nuys Tunnel study (3, 4). Tunnels are convenient for vehicle emission measurements because they represent a controlled environment in which vehicles, operating under "real-world" conditions, can be monitored and their pollutants concentrated in a flowing air mass. One of the early tunnel experiments performed during the Southern California Air Quality Study (SCAQMS) indicated that the EMFAC model was performing reasonably well for the prediction of NO_x emission factors but was underestimating VOC and CO emission factors to a significant extent, by a factor of 2-4 (3). Since then, several updates have been made to the emission factor models, and several other tunnel studies have been performed (5, 6). Some of these more recent studies indicate that the newer versions of the emission factor models are no longer underestimating to such a great extent and may in fact be overestimating under certain conditions.

One such study, the Cassiar Tunnel study (7), was performed on a section of highway in Vancouver, B. C., during the 1993 Lower Fraser Valley Oxidants Study. A previous publication has outlined the general findings of that study for NO_x , non-methane hydrocarbons (NMHC), and CO emission factors (6). In this paper, we extend those findings to further focus on NMHCs and to report real-world emission factors of deconvoluted exhaust and evaporative NMHC emissions and to compare them to emission factors calculated with the Canadian versions of

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the U.S. EPA MOBILE models, MOBILE4.1C and MOBILE5C. The total measured NMHC emission factors, given by the sum of over 100 speciated hydrocarbons, are deconvoluted through the use of the chemical mass balance (CMB) model (8).

The CMB model has recently been applied to other tunnel studies and to regional studies of VOC sources (9–14). In the model, each source is represented by a source profile that specifies the fractional contribution of each VOC species to the mass emissions from that source. In all these studies, motor vehicle exhaust is the most significant VOC source and is generally represented by profiles derived from dynamometer testing of vehicles. The limitation in the use of dynamometer-based profiles is that they are specific to the technology, age, and operating condition of the vehicle as well as the composition of the fuel used in the vehicle. Recent literature has provided information about the problems associated with the use of these profiles although few other options have been explored (13). In particular, one recent study found that the source allocation by the CMB model was very sensitive to the choice of fitting species and particularly to the relative abundances of combustion products in the exhaust gas profile such as acetylene and ethylene (13). The relative proportion of acetylene is highly dependent on the state of repair, the age, and the operation mode of the vehicle. The proportion of other light olefin species is also dependent on the fuel composition. Because of the uncertainties associated with the use of dynamometer-derived exhaust profiles, several recent publications have indicated the need for development and use of real-world exhaust profiles in similar CMB applications (9, 13, 15). The suggested options for this include the site-specific use of a linear combination of published exhaust profiles, derived from vehicles with different emissions control technology, or the use of roadside measured profiles. The former approach will still suffer from the fact that the composition of the fuel used in the emissions testing may still not match the composition found in the geographic area to which the CMB model is being applied. The latter option will result in a profile that is representative of the local gasoline composition but also includes on-road evaporative emissions.

In this study, we have explored a new approach for exhaust representation in the CMB model. Since exhaust emissions are known to contain significant quantities of unburned gasoline as well as combustion species (16–19), we suggest that the local gasoline composition can act as a surrogate for a real-world exhaust profile. The combustion component of the exhaust gases can then be estimated by the difference between the observed and the CMB-calculated emission factors for identified combustion species. This method relies on a good description of the local gasoline composition that comprises ~60% of the exhaust gas mixture as opposed to the reliance on “tracer” combustion species such as acetylene and ethylene in the conventional approach where a dynamometer test profile is used.

In this paper, this new methodology was tested and validated through comparison to the use of a conventional exhaust profile in the CMB model. Following this validation, the results for 16 individual tunnel runs are presented. As an additional benefit to the new approach, we were able to estimate on a run by run basis the percentage contribution of gasoline to the exhaust gases. These results are discussed and compared to recent dynamometer-based

TABLE 1

Details of Individual Runs in the Cassiar Tunnel Study

run	time	date	vehicles	temp (°C)
1	02:00–03:00	8/13/93	125	13.4
2	06:00–07:00	8/13/93	1678	13.3
3	10:00–11:00	8/13/93	1821	15.4
4	15:00–16:00	8/13/93	2502	17.0
5	09:00–10:00	8/14/93	1470	15.3
6	09:00–10:00	8/15/93	948	15.3
7	02:00–03:00	8/16/93	93	14.2
8	06:00–07:00	8/16/93	1622	14.6
9	08:00–09:00	8/16/93	1859	12.8
10	02:00–03:00	8/18/93	100	12.8
11	06:00–07:00	8/18/93	1650	15.3
12	08:00–09:00	8/18/93	2074	13.4
13	10:00–11:00	8/18/93	1769	19.4
14	12:00–13:00	8/18/93	1850	20.0
15	14:00–15:00	8/18/93	1977	21.3
16	16:00–17:00	8/18/93	2975	22.5

studies. The paper concludes with a detailed comparison of exhaust and evaporative emission factors determined by the experimental/CMB approach and by emission factor models.

Tunnel Experiment

The Cassiar Tunnel is an urban two-bore tunnel, 730 m in length, with two lanes of traffic per bore. It is situated on the Trans-Canada Highway in Vancouver, BC. Traffic is generally heavy during the day with an average speed of ~90 km/h and a high proportion of light-duty vehicles. The methodology used for the calculation of mobile source emission factors in tunnels has been described in detail by Pierson (20). The details for this particular study have been outlined previously (6, 7). Emission factors were measured for a total of 16 1-h runs in the northbound bore during August 13–18, 1993. Table 1 highlights the conditions encountered for each tunnel run in the study. The detailed gasoline compositions sold during the study period in the areas of Vancouver and Whatcom County, WA, were obtained from a gasoline sampling program conducted in the Lower Fraser Valley (LFV).

Pollutant sampling was performed at the entrance and exit of the tunnel to analyze for NO_x, CO, CO₂, methane, and NMHCs. A canister sampler was used to collect samples of NMHC (C₂–C₁₀) in electropolished stainless steel canisters. The canisters were analyzed by GC-MSD at Environment Canada's River Road Environmental Technology Centre. The analytical methodology has been outlined previously (21). In total, 102 hydrocarbons were quantified.

Emission Profiles

NMHC emission profiles for input to the CMB model were created for each tunnel run using the emission factor methodology outlined above. The CMB also requires an estimation of the uncertainty for each measurement value. This uncertainty, σ_i , was estimated as

$$\sigma_i = \sqrt{(E_i CV)^2 + (E_{DL})^2}$$

where CV is the coefficient of variation for the emission factor measurements, conservatively estimated to be about 20%, and E_{DL} is the emission factor detection limit, estimated to be about 0.1 mg/mi.

TABLE 2

Source Profiles (% NMHC) Used in CMB Model^a

HC	species	F1 ^b	F2 ^b	F3 ^b	Exh801 ^c	Vangas ^d	Vanvap ^e	Whagas ^f	Whavap ^g
2	ethylene	*			9.90	0.000	0.000	0.000	0.000
3	acetylene	*			2.78	0.000	0.000	0.000	0.000
7	isobutane	*	*	*	0.920	0.428	5.678	0.116	1.793
10	butane	*	*	*	6.440	2.222	19.92	1.861	19.48
15	isopentane	*	*	*	4.930	7.630	25.65	7.615	29.89
18	pentane	*	*	*	2.210	4.959	12.30	4.402	12.75
23	2,2-dimethylbutane	*	*	*	0.440	0.218	0.334	0.192	0.345
26	cyclopentane	*	*	*		0.477	0.724	0.522	0.925
27	2,3-dimethylbutane	*	*	*	0.810	1.089	1.216	1.080	1.410
29	2-methylpentane	*	*	*	1.910	3.816	3.829	2.483	2.910
31	3-methylpentane	*	*	*	1.370	2.449	2.197	2.161	2.265
33	hexane	*	*	*	0.920	3.200	2.269	2.720	2.252
40	methylcyclopentane	*	*	*	0.920	2.125	1.370	1.976	1.487
41	2,4-dimethylpentane	*	*	*	0.820	1.006	0.460	1.159	0.619
43	benzene	*			3.910	2.114	0.928	2.370	1.216
44	cyclohexane			*		0.354	0.160	0.554	0.293
47	3-methylhexane	*	*	*	0.000	1.652	0.466	1.415	0.466
49	2,2,4-trimethylpentane	*	*	*	2.910	1.298	0.293	3.800	1.002
51	heptane			*		1.032	0.214	0.901	0.218
55	methylcyclohexane			*		0.595	0.126	0.526	0.130
57	2,4-dimethylhexane			*		0.349	0.048	0.460	0.073
58	2,3,4-trimethylpentane			*		0.752	0.091	1.559	0.221
59	toluene	*	*	*	7.100	9.907	1.265	9.994	1.491
60	2-methylheptane			*		0.492	0.045	0.416	0.044
61	4-methylheptane			*		0.252	0.023	0.242	0.026
62	3-methylheptane			*		0.585	0.050	0.457	0.046
65	2,2,5-trimethylhexane			*		0.381	0.028	0.136	0.012
67	octane	*	*	*	0.440	0.446	0.027	0.365	0.026
73	ethylbenzene	*	*	*	0.790	1.643	0.068	1.861	0.090
74	<i>m/p</i> -xylene	*	*	*	3.320	7.214	0.267	7.548	0.326
76	<i>o</i> -xylene	*	*	*	2.220	2.775	0.079	2.851	0.095
78	nonane	*	*	*	0.310	0.122	0.002	0.149	0.003
81	<i>n</i> -propylbenzene			*		0.537	0.008	0.577	0.010
82	3-ethyltoluene	*	*	*	1.630	1.911	0.023	2.010	0.029
83	4-ethyltoluene	*	*	*	0.000	0.823	0.010	0.870	0.013
84	1,3,5-trimethylbenzene	*	*	*	0.000	1.067	0.011	1.073	0.013
85	2-ethyltoluene	*	*	*	0.280	0.724	0.007	0.746	0.009
92	1,2,3-trimethylbenzene			*		0.746	0.005	0.731	0.005

^a Asterisk (*) indicates a fitting species. ^b Fitting species codes F1, F2, and F3 are defined here and used to describe different fits in Table 3.

^c Exh801a is derived from FTP tests on 46 in-use passenger vehicles, ref 26. ^d Vancouver gasoline composition profile. ^e Vancouver gasoline vapor composition profile. ^f Whatcom County gasoline composition profile. ^g Whatcom County gasoline vapor composition profile.

The emission factors were calculated for each species and run giving 16 NMHC emission factor distributions to be used in the CMB modeling. In addition to this, an extra distribution was created in an attempt to separate the effects of light-duty (primarily gasoline spark ignited) and heavy-duty vehicles (primarily diesel). This last emission distribution was created by performing a regression analysis on the emission factors for all of the 16 tunnel runs with the fraction of light-duty vehicles in each tunnel run as the independent variable. This methodology has been outlined in detail previously (22). The resultant light-duty emission profile is expected to have less contribution from diesel vehicles since the heavy-duty emission factors are excluded.

Source Profiles

The CMB model requires source profiles in addition to the measured receptor distributions (E_i). In this application, we wished to allocate total NMHC emissions to exhaust emissions and evaporative emissions. As mentioned previously, we used the gasoline composition profile as a surrogate for a real-world exhaust profile. The evaporative emissions were represented by a gasoline vapor profile.

Several organic source profiles were developed. Twenty-four gasoline samples were collected on both sides of the border in the LFV airshed during PACIFIC '93. Twelve were

from refiners in the Vancouver region, and 12 were samples collected from retail stations in Whatcom County, WA. The gasoline was sampled and analyzed for Reid vapor pressure (RVP) and detailed chemical composition by GC-MSD at the laboratories of Esso Petroleum Products in Sarnia, Ontario. Sales data by grade and by banner, obtained from a marketing survey, were used to calculate a sales weighted average gasoline composition for the Vancouver region and the Whatcom County region. The two profiles are labeled VANGAS and WHAGAS in Table 2. Since gasoline headspace samples were not taken, the gasoline vapor composition corresponding to the average gasoline for each side of the border was calculated from thermodynamic principles using Raoult's law by a method outlined previously (14). Excellent agreement has been observed recently between vapor profiles calculated in this manner and profiles of the vapor (headspace analysis) measured above the same gasoline sample (23, 24). The two gasoline vapor profiles were calculated at 20 °C and are listed as VANVAP and WHAVAP in Table 2.

Uncertainty estimates for each species in the gasoline and gasoline vapor profiles were calculated in the following manner. The gasoline samples were separated into the three grades: regular, midgrade, and premium. The standard deviation of the fraction of each species was then

calculated for each gasoline grade. These standard deviations were then propagated through to the final estimate of uncertainty for each species in the sales weighted average gasoline profiles and the corresponding vapor profiles. In this manner, the standard deviations include uncertainty from the analytical measurements as well as from variability in local gasoline composition.

A dynamometer-based exhaust profile was also used in the CMB analysis for comparison of the CMB performance using the conventional approach and the new surrogate approach outlined in this work. Profile Exh801a in Table 2 was derived from FTP tests of 46 in-use passenger vehicles for 1975–1982 model years (25). Profile Exh801a was recalculated by the California Air Resources Board from the original measurements to provide a more complete chemical break down. Propane/propene, benzene/cyclohexane, and toluene/2,3-dimethylhexane were not separately reported in the original work, so ratios of 3:22, 19:1, and 1:0 were derived from tunnel measurements (13) and used for these pairs of species, respectively. This modified exhaust profile has been used in several recent CMB modeling studies (9, 13, 14), and performance values have typically been better through its use compared to other exhaust profiles. All profiles are indicated in Table 2. For brevity, only those species used as fitting species in the model have been indicated in Table 2.

Application of the Chemical Mass Balance Model to Tunnel Runs

The chemical mass balance model (CMB) consists of a least-squares solution to a set of linear equations that express the measured receptor concentration of chemical species as a linear sum of products of the source profile fractions for the species and source contributions. The source profile fractions and the receptor concentrations, each with realistic uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions of each source to total measured NMHC as well as to individual NMHC concentrations. Standard uncertainties are calculated as well. Input data uncertainties are used to weight the relative importance of the input data to the model solution and to estimate uncertainties in the source contributions. Calculations were made using the U.S. EPA/DRI Version 7.0 of the CMB model (8).

The CMB model was used to estimate evaporative and exhaust source contributions to observed NMHC emission factor profiles in the tunnel. The Vancouver gasoline profile was used to represent the exhaust source, while the corresponding vapor profile was used to represent on-road evaporative emissions. A caveat to this method is that on-road evaporative emissions, as they are defined in the MOBILE models, may include some emissions that are not the same in composition as a gasoline vapor in equilibrium with the liquid. For on-road evaporative emissions, we expect these contributions to be small. The use of a gasoline profile to represent exhaust emissions is new in this CMB application. Previous studies using different methods have shown that unburned fuel represents a significant component of exhaust NMHC for various fuels (16) and is estimated to be 50–65% for gasoline used in current technology vehicles (18). The other contribution to exhaust NMHC is from combustion species such as acetylene, ethylene, olefins, and benzene. While some of these species such as acetylene and ethylene are key tracers for auto-

mobile exhaust, our approach here has been to eliminate all combustion species from the analysis by not using them as fitting species in the CMB model. The tradeoff in this approach is to obtain much better model performance by relying on a very good description of the ca. 60% gasoline present in exhaust as opposed to relying on the generic combustion tracers.

The disadvantage to this approach is that the CMB calculated emission factor does not account for the mass of emitted combustion species in exhaust. It only accounts for on-road evaporative emissions and the unburned fuel component of exhaust. This was overcome by allocating the excess measured mass for identified combustion species (above that calculated by the CMB model) to the combustion source. This is valid since the emission factor methodology used in the tunnel experiment ensures that the total mass of NMHC originates from vehicles operating in the tunnel. The combustion component for selected species was therefore calculated external to the model as the difference between the experimental emission factor and the CMB calculated emission factor. The sum of these differences over all species defined to be combustion species has been labeled the combustion component in this study and is largely derived from the low molecular weight olefins and benzene. The true exhaust source can then be calculated as the sum of the gasoline component and the combustion component.

To test and validate this approach, numerous fits were performed on several of the Cassiar emission distributions using different combinations of source profiles and fitting species. The results for model simulations performed with one emission factor distribution, the average light-duty vehicle profile obtained by least squares regression, are shown in Table 3. For each model simulation, Table 3 indicates the number and type of fitting species used, performance measures, and the different source contributions (in units of g/mi). Four performance measures are indicated. R^2 represents the goodness of fit between calculated and measured emission factors, indicating the fraction of the variance in the measured factors that is explained by the variance in the calculated factors. The reduced χ^2 value is equal to the weighted sum of squares of the differences between measured and calculated concentrations for the fitting species. Lower values indicate a better fit. Values of χ less than 1.0 indicate a very good fit to the measured data by the source profiles (27). The percent mass recovery (MASS) is the percent ratio of total NMHC calculated by the model vs the measured value. Values close to 100% indicate that the sources used for modeling adequately account for all the measured mass. The last measure included, collinearity (COL), indicates the presence or absence (Y/N) of similarity/uncertainty clusters in the fit as indicated by the model output (28). These clusters result from collinearity between source profiles or excessive uncertainty in the source and receptor profiles and indicate that resolution of the source contributions may not be adequate.

The first five fits in Table 3 were performed with a preliminary set of files containing 33 species intended to be used for conventional CMB modeling with an exhaust source profile. The last two fits were done with an expanded set of files containing 84 species. To be consistent in our comparisons, none of the fitting species in the model simulations included olefins greater than two carbon atoms, any species with greater than nine carbon atoms, and several

TABLE 3

Summary of CMB Model Performance for Fitting the LDV Emissions Profile with Various Source Profile Combinations

	N_f^a	R^2	χ	MASS ^b (%)	COL ^c	Exh801 (g/mi)	Vangas (g/mi)	Vanvap (g/mi)	Whagas (g/mi)	Whavap (g/mi)	Combustion ^d (g/mi)
1	26 (F1)	0.62	3.68	61.3 ± 9.2	N	0.251 ± 0.029		0.102 ± 0.026			
2	26 (F1)	0.84	1.32	70.0 ± 9.0	Y	0.061 ± 0.045	0.285 ± 0.043	0.057 ± 0.026			
3	23 (F2)	0.63	3.55	58.3 ± 9.0	N	0.224 ± 0.030		0.111 ± 0.026			
4	23 (F2)	0.97	0.21	65.9 ± 8.9	Y	-0.016 ± 0.050	0.329 ± 0.045	0.066 ± 0.027			
5	23 (F2)	0.97	0.21	66.6 ± 8.6	N		0.319 ± 0.033	0.065 ± 0.026			
6	35 (F3)	0.97	0.24	107.9 ± 13.5	N		0.318 ± 0.026	0.066 ± 0.025			0.238 ± 0.029
7	35 (F3)	0.93	0.45	111.0 ± 14.0	N				0.329 ± 0.029	0.065 ± 0.027	0.246 ± 0.029

^a N_f is the number of fitting species. The fitting species used are indicated by the code in parentheses; cross reference to Table 2. ^b Mass recovery (MASS) for simulations 1–5 only account for mass allocated by the model. For simulations 6 and 7, mass recovery is redefined to include mass allocated by the model as well as the "Combustion" component; (gasoline + vapor + combustion)/(total measured NMHC) where gasoline is either Vangas or Whagas and vapor is either Vanvap or Whavap. ^c Presence or absence of similarity/uncertainty clusters in model fit. ^d Combustion represents the sum of (measured – calculated) emission rates for species defined as combustion species.

species that were suspected to have chromatographic interference. The first fit shown uses two source profiles, the conventional exhaust profile and a vapor profile. Twenty-six fitting species were used (Table 2), including the combustion species: acetylene, ethylene, and benzene. The performance measures are reasonably poor for this fit ($R^2 = 0.62$, $\chi = 3.68$, MASS = 61.3%, $N_f = 26$). The second fit, still using combustion fitting species, indicates that a better fit can be obtained by inclusion of the local gasoline profile. The gasoline source is dominant over the exhaust source, and the combustion species, still retained as fitting species, are greatly underpredicted. The retention of these combustion species are likely responsible for the still reasonably poor R^2 value (0.84). The next two fits (3 and 4) were performed with the same source profiles as the first two but with the combustion species (acetylene, ethylene and benzene) not included as fitting species. This does not significantly improve the fit performed with the exhaust and vapor profile (3 compared to 1) but does significantly improve the fit that includes the extra gasoline source profile (4 compared to 2). The improvement in this fit is understandable since the combustion species are not present in the gasoline profile. The fifth fit, performed with just the gasoline and vapor profiles, resulted in an excellent fit.

This good CMB performance made it clear that the gasoline composition could be used successfully as a surrogate for gasoline exhaust. With this fact established, expanded source and receptor files were then created containing 84 common species. From this list of 84 species, fitting species selection was performed in the following way. As a base, all species were selected. Then all potential combustion species were removed including ethane, acetylene, ethylene, propane, other olefins, and benzene. Several species with chromatographic interferences were then removed (2-methylhexane/2,3-dimethylpentane; 2,5-dimethylhexane/2,2,3-trimethylpentane) along with all species that had greater than nine carbon atoms because of potential interference from diesel emissions. This process left 35 fitting species. It is noted that toluene, which has been identified as a potential combustion species (17), was retained as a fitting species in this study since initial simulations indicated that most of the toluene mass (~90–93%) could be accounted for by the exhaust and evaporative components. This was well within the error observed for other noncombustion species. Subsequent sensitivity simulations showed that the exclusion of toluene as a fitting species has a very minor effect on the results. The fit using the VANGAS and VANVAP source profiles with 35 fitting

species is shown on line 6 of Table 3. The performance measures are excellent ($R^2 = 0.97$, $\chi = 0.24$, MASS = 107.9%, $N_f = 35$). A revised definition of mass recovery has been used for fits 6 and 7 to include the mass of combustion species calculated external to the model. The calculated and measured fitting species emission factors for fit 6 are shown in Figure 1.

The improved CMB performance using gasoline composition as a surrogate for exhaust arises from the fact that exhaust contains significant quantities of unburned gasoline. Additionally, the gasoline composition profile used in the model was specific to the region and time in which the Cassiar study was performed. Intrinsically, the Exh801a profile also contains gasoline composition information, but the gasoline composition used in those dynamometer tests is likely different from that available in the LFV, Table 2. We may therefore expect that gasoline profiles that are not specific to the region will give poorer model performance. To test this theory, an extra fit was done (fit 7 in Table 3) in which the Whatcom County gasoline and vapor source profiles were used. This is a unique test for the modeling approach outlined here since the two gasoline pools are present in the same LFV airshed, and yet intermixing is limited due to the presence of an international border. The Canadian gasoline is expected to dominate in the Cassiar Tunnel. While the source contributions are similar to those obtained with the base fit (fit 6), the performance measures are deteriorated ($R^2 = 0.93$, $\chi = 0.45$, MASS = 111%, $N_f = 35$). It is expected that differences in fuel composition between the two areas and the dominance of Canadian fuel in the Vancouver market (and hence the Cassiar tunnel) are responsible for the differences in model performance. Some of the differences in fuel composition between the two areas can be identified in Table 2.

It is worth noting that the CMB performance obtained with the use of the Exh801a dynamometer-based profile can be improved by deselecting fitting species that show large deviations between measured and calculated emission factors. This approach suffers from the fact that it is somewhat arbitrary, although it is probably equivalent to an approach in which one deselects species for which the compositions differ significantly, between the LFV gasoline and the gasoline used in the dynamometer tests.

With the previous results and discussion taken as a validation of the methodology for using gasoline composition as surrogate for exhaust emissions, each tunnel run was then fit using the VANGAS and VANVAP profiles and

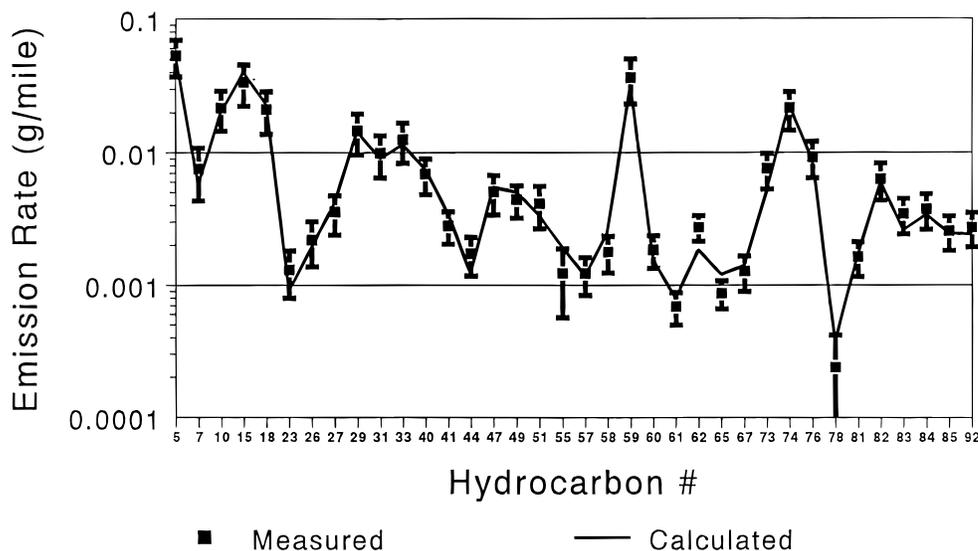


FIGURE 1. Comparison of measured and CMB-calculated emission factors for the average light-duty emission distribution. The CMB fit was performed with two profiles; the local gasoline composition and its calculated vapor composition. See LDV in Table 3 for further details.

TABLE 4
Emission Rates Apportioned by CMB Model for 16 Tunnel Runs and Averages

run	R^2	χ	MASS (%) ^a	LFVGAS (g/mi)	LFVVAP (g/mi)	combustion ^b (g/mi)	vapor ^c (%)	gasoline in exhaust ^d (%)
1	0.59	5.60	73.2 ± 8.5	0.846 ± 0.054	-0.073 ± 0.019	0.561 ± 0.052	-5.4 ± -1.5	60.1 ± 5.0
2	0.95	0.62	106.1 ± 12.0	0.413 ± 0.025	0.046 ± 0.016	0.280 ± 0.025	6.2 ± 2.1	59.6 ± 4.7
3	0.94	0.73	110.2 ± 12.6	0.297 ± 0.019	0.135 ± 0.023	0.211 ± 0.020	21.0 ± 3.8	59.6 ± 4.7
4	0.96	0.47	110.3 ± 12.4	0.277 ± 0.017	0.039 ± 0.012	0.176 ± 0.015	8.0 ± 2.4	61.2 ± 4.8
5	0.96	0.52	107.8 ± 12.2	0.218 ± 0.013	0.021 ± 0.008	0.149 ± 0.013	5.4 ± 2.0	59.5 ± 4.8
6	0.95	0.54	110.2 ± 12.4	0.244 ± 0.015	0.020 ± 0.008	0.147 ± 0.013	4.9 ± 2.0	62.5 ± 4.9
7	0.91	1.11	99.0 ± 11.4	0.157 ± 0.011	0.062 ± 0.011	0.268 ± 0.023	12.7 ± 2.4	36.9 ± 3.3
8	0.94	0.77	105.5 ± 11.9	0.338 ± 0.021	0.048 ± 0.014	0.260 ± 0.023	7.4 ± 2.2	56.5 ± 4.6
9	0.95	0.65	107.9 ± 12.1	0.530 ± 0.032	0.059 ± 0.019	0.329 ± 0.029	6.4 ± 2.1	61.7 ± 4.8
10	0.78	3.02	94.5 ± 10.8	0.185 ± 0.014	0.077 ± 0.016	0.252 ± 0.019	15.0 ± 3.2	42.4 ± 3.9
11	0.95	0.58	110.7 ± 12.6	0.457 ± 0.029	0.135 ± 0.027	0.252 ± 0.023	16.0 ± 3.3	64.4 ± 5.2
12	0.95	0.59	109.5 ± 12.4	0.468 ± 0.029	0.080 ± 0.021	0.292 ± 0.026	9.5 ± 2.6	61.6 ± 4.9
13	0.96	0.49	109.0 ± 12.3	0.271 ± 0.017	0.055 ± 0.014	0.196 ± 0.017	10.5 ± 2.7	58.0 ± 4.7
14	0.96	0.48	108.7 ± 12.3	0.214 ± 0.014	0.046 ± 0.011	0.160 ± 0.014	10.9 ± 2.7	57.2 ± 4.7
15	0.97	0.37	107.8 ± 12.3	0.177 ± 0.012	0.038 ± 0.009	0.140 ± 0.012	10.7 ± 2.7	55.9 ± 4.7
16	0.97	0.40	108.3 ± 12.3	0.445 ± 0.028	0.117 ± 0.026	0.337 ± 0.029	13.0 ± 2.9	56.9 ± 4.6
AVG ^e	0.953	0.581	108.3 ± 3.5	0.344 ± 0.006	0.068 ± 0.005	0.235 ± 0.006	10.3 ± 0.8	59.1 ± 1.4
LDV ^f	0.97	0.24	107.9 ± 13.5	0.318 ± 0.026	0.066 ± 0.025	0.238 ± 0.029	10.5 ± 4.1	57.2 ± 6.2

^a Mass recovery in this application is defined as the percentage ratio of (LFVGAS + LFVVAP + combustion)/total measured NMHC. ^b Combustion represents the sum of (measured - calculated) emission rates for all combustion species not used as fitting species. ^c Vapor percentage is the percentage ratio of the CMB predicted evaporative emission rate to the total emission rate, LFVGAS + LFVVAP + combustion. ^d Percentage gasoline in exhaust is given by the percentage ratio of LFVGAS/(LFVGAS + combustion). ^e AVG is the vehicle-weighted average values for all 16 tunnel runs. ^f LDV is the light-duty vehicle NMHC distribution obtained by vehicle-weighted regression of 16 runs.

35 fitting species (F3 in Table 2). The CMB results are shown in Table 4 for the 16 tunnel runs and the light-duty vehicle emission factor distribution. In addition, a vehicle-weighted average of 13 valid tunnel runs (AVG) has been calculated. This line (AVG), like the LDV results, is characteristic of the overall study. There is reasonable agreement between the results listed for AVG, obtained from averaging the CMB results from each tunnel run, and LDV, obtained from the CMB results for an average distribution of all tunnel runs. The agreement between these two simulations gives further confidence that the CMB modeling for the individual runs is not affected in a significant way by diesel emissions, since the LDV emission factor profile, through correlation, is dominated by gasoline vehicles.

In general, the performance of the model is very good for most of the model simulations in Table 4. Three simulations show poor performance (1, 7, and 10) with low values of R^2 , high values of χ^2 , and depressed values of

mass percent. Not coincidentally, these runs have the lowest vehicle counts (~100/h) and highest diesel counts resulting in less statistical confidence. It is also noted that run 1 had suspected sampling problems. The three runs were considered to be invalid for further analysis and were not included in the average results listed as AVG. Mass recovery values are somewhat higher than 100%. The vehicle-weighted average for all the runs is 108.3% while that for the LDV profile is 107.9%. This slightly high mass recovery stems from the fact that the gasoline profiles were derived from 319 calibrated and uncalibrated NMHC GC peaks while the emission measurements were derived from only 102 calibrated NMHCs. The 102 calibrated NMHCs are expected to represent a significant portion of the C_2-C_{12} mass whereas the 319 peaks are likely to represent closer to 100% of the mass. It was found that a subset of the total 319 GC peaks, namely, the 102 hydrocarbons measured in the tunnel, account for 81% of the gasoline mass. Thus the total mass allocated to the LFVGAS source by the CMB

model reflects 23% more mass than was measured. Our theoretical mass % should therefore be about 112% for an average tunnel run where 57% of the mass is allocated to gasoline. This is close to the average value for mass recovery of 108% in Table 4.

Contribution of Gasoline to Exhaust Emissions

Total exhaust emissions rates are given by the sum of the gasoline component and the combustion component. The contribution of gasoline to the total exhaust is defined as the percent ratio: $\text{LFVGAS}/(\text{LFVGAS} + \text{COMBUSTION})$ and is indicated in Table 4 for all runs. For the 13 valid runs, this value ranges from 56 to 64% with a vehicle-weighted average of $59.1 \pm 1.4\%$ and a light-duty vehicle value of $57.2 \pm 6.2\%$. These values assume that all combustion species evolve from gasoline combustion. It is known that this value is impacted by the presence of propane vehicles operating in the tunnel since propane is one of the combustion species. NMHC emissions from propane vehicles are composed of about 60% propane (28). A full analysis of the effect of propane vehicles in the tunnel study is currently being completed in order to quantify propane emissions from vehicles in the LFV. For the purposes here, we have done a sensitivity test using the LDV emission factor distribution and included an extra source profile derived from recent measurements (28) to represent propane vehicle emissions. This sensitivity test indicated that the inclusion of a propane profile had little impact on the LFVGAS and LFVAP source contributions but reduced the COMBUSTION contribution slightly because of the allocation of significant propane and some light olefins to the propane vehicles source. The test also indicated that the percentage contribution of gasoline to light-duty gasoline vehicle exhaust NMHC was increased to $63.4 \pm 7.0\%$ as compared to the original estimate of $57.2 \pm 6.2\%$. This was largely the result of a large fraction of the propane emissions being allocated to propane vehicles.

The average level of unburned gasoline in exhaust determined in this study, 63.4%, is in general agreement with that determined in dynamometer-based measurements (18). Another study of three new vehicles found the range of unburned gasoline in composite engine-out and composite tailpipe emissions to be 50–55% and 35–55%, respectively, the difference being attributable to the effect of the catalyst (17). In that study, the level of gasoline was determined for each bag of the Federal Test Procedure (FTP) Urban Dynamometer Driving Schedule (UDDS), and it was found that the level of gasoline in engine-out emissions was much less sensitive to the emissions mode (bag 1, bag 2, or bag 3) compared to the tailpipe emissions. This difference was also attributable to the effect of a fully functioning catalyst. For tailpipe emissions, the level of unburned gasoline was lowest for the hot stabilized portion (bag 2) of the UDDS, 5–25%, in these relatively new vehicles. It is expected that the type of driving in this portion of the UDDS would be most similar to the driving encountered in the Cassiar Tunnel, and yet, we have observed much higher levels of unburned gasoline. The more recent publication (18) also observed sustained levels of unburned gasoline in the bag 2 portion of the UDDS (~60%) in agreement with our measurements here. The differences observed with the study that showed low levels of gasoline in bag 2 and this study may be attributable to differences in catalyst type, engine repair, or emissions control system.

It also may indicate that catalysts are not functioning well in real-world vehicles.

Of general interest in CMB modeling is the ability to specify the contribution of each source to observed levels of individual hydrocarbons. A complete analysis is not presented here, although it is useful to examine the results for benzene, a major component of gasoline, and a known combustion species. The presence of benzene in exhaust is largely attributed to the dealkylation of other substituted aromatics during the combustion process (16). The separation of exhaust into combustion and gasoline components allows us to determine these two contributions separately. For the light-duty vehicle profile CMB simulation (LDV in Table 4), it was found that the total on-road benzene emission factor could be apportioned to combustion (exhaust), gasoline (exhaust), and evaporative emissions to the levels of $70.8 \pm 38.3\%$, $26.7 \pm 9.9\%$, and $2.4 \pm 0.9\%$, respectively. The fact that ~71% of on-road benzene comes from the combustion process is interesting since it indicates that efforts to lower human exposure to ambient levels of benzene cannot be confined to the elimination of benzene in gasoline alone. The effort has to be combined with a lowering of aromatics in the fuel at the same time.

Evaluation of Exhaust and Evaporative Emission Factors

One of the objectives of the Cassiar Tunnel study was to compare experimental emission factors with those calculated by current on-road emission factor models. In Canada, the most current model used in the calculation of emission factors for inventory development is MOBILE5C (30), an adaptation of the U.S. EPA Model MOBILE5a, while the previous version used was MOBILE4.1C (31). The Canadian versions of the model have been modified to take into account differences in Canadian and U.S. regulated emission control technology that existed for vehicles of model year 1981–1987. Because of less stringent emission standards in Canada during that period, fleets of vehicles from those model years have higher emission factors compared to those in the United States.

In a previous publication, a comparison was made between emission factors of NO_x , total NMHC, and CO measured in the Cassiar Tunnel and those calculated with the two Canadian MOBILE models (6). In this work, apportionment of total NMHCs to exhaust and evaporative emissions allows a more detailed comparison of NMHC emission factors. The methodology used for calculating emission factors in this study using the two MOBILE models has been outlined previously (6, 7). Briefly, the approach used was to collect sufficient data so that each tunnel run could be modeled separately with hourly specific information. The model input for each run included the local gasoline RVP, local by model year diesel fractions, and hourly average speeds, temperatures, and by model year vehicle distributions. The MOBILE model calculates average or model year-specific emissions factors for eight vehicle classes. The video tapes for each run were used to separate the observed vehicles into the eight vehicle classifications. These counts along with the emission factors for each vehicle type and model year were then used to calculate a vehicle-weighted average emission factor for each tunnel run.

The MOBILE models give a breakdown of NMHC emission factors by mode including exhaust, running loss,

TABLE 5

Comparison of MOBILE and Experimental/CMB-Derived Emission Factors

	Mobile4.1C	Mobile5C	CMB	ratio	
				M4.1C/CMB	M5C/CMB
exhaust (g/mi)	0.406	0.711	0.575 ± 0.064	<i>0.71 ± 0.08</i>	1.24 ± 0.14
running loss (g/mi)	0.019	0.033	NA	NA	NA
resting loss (g/mi)	0.066	0.042	NA	NA	NA
on-road evap (g/mi)	0.085	0.075	0.068 ± 0.013	1.25 ± 0.24	1.10 ± 0.21
tot (g/mi)	0.491	0.786	0.643 ± 0.065	<i>0.76 ± 0.08</i>	1.22 ± 0.12
evaporative (%)	17.9	10.1	10.3 ± 0.8	<i>1.74 ± 0.14</i>	0.98 ± 0.08

resting loss, diurnal, and hot soak emissions. By definition, diurnal and hot soak emissions are not on-road emissions and were not evaluated in this study. Running loss emissions are defined as evaporative emissions occurring while the vehicle is being driven, and they arise from emissions from various engine components, the vehicle fuel tank, and inadequate purging of the evaporative control canister. Resting loss emissions are another form of evaporative emission, defined as vapors permeating parts of the emission control system, migrating out of the carbon canister, and evaporating liquid fuel leaks. Contrary to running loss emissions, resting loss emissions may occur 24 h a day. From this definition, it is clear that resting loss emissions are not necessarily distinct from other types of evaporative emissions either in definition or in measurement. While the name may imply that resting loss emissions occur off-road when the vehicle is at rest, recent guidance has suggested that the intention in the MOBILE models is that these emissions occur on-road as well as off-road (32). From the above discussion, it is clear that there may be some ambiguity over the chemical composition of the on-road evaporative emissions. It is expected that emissions from the fuel tank and evaporative canister will be similar in chemical composition to gasoline vapor as would emissions from the escape or permeation of gasoline vapors from parts of the engine. Some "evaporative" emissions may be similar in composition to unburned gasoline, namely, any fuel leakage or crankcase emissions. One might expect that on-road fuel leakage is smaller than off-road leakage simply due to time of contact considerations. It is also noted that current estimates of crankcase emissions from light-duty vehicles in the MOBILE models are also very small. With these considerations, we have taken the approach in the comparison to be presented here, that on-road evaporative emissions are most similar in composition to gasoline vapor. For comparison purposes, the MOBILE model predicted equivalent of on-road evaporative emissions has been taken to be the sum of running loss and resting loss emissions. We acknowledge the possibility for misidentification of some small component of gasoline exhaust to be those on-road evaporative emissions that are similar in composition to unburned gasoline.

Thirteen runs were included for comparison of emission factors, namely, those that were considered valid through good performance indicators with the CMB model (all runs excluding 1, 7, and 10). Vehicle-weighted emission factors (13 run average) were calculated for each of the two MOBILE models and the experimental/CMB combination (Table 5). Table 5 shows both absolute emission factors and the relative proportion of evaporative emissions. Also shown are calculated ratios of the magnitude of the MOBILE model over/underprediction based upon the measurements in this study. Differences between the experimental and

MOBILE values are indicated by ratios different from 1.0. Uncertainties are not included in the MOBILE models. The uncertainties in the experimental/CMB combination are those calculated by the CMB model and propagated through the calculation of a vehicle-weighted average result. For absolute emission factors, the uncertainties include the propagation of the 50% uncertainty in emission factors for each tunnel run due to experimental uncertainties mentioned previously. Those values that are statistically different from 1.0 at the 95% confidence level are italicized in the table.

The table indicates that MOBILE5C overestimates exhaust, on-road evaporative, and total NMHC by +24, +10, and +22%, respectively, with the associated uncertainties while the MOBILE4.1C percentages are -29, +25, and -24%, respectively. The underestimation of exhaust and total NMHCs by the MOBILE4.1C model are significant. The exhaust/evaporative percentages predicted by the CMB modeling are less affected by experimental uncertainty. These indicate that the MOBILE5C model underpredicts the evaporative percentage by 2% while the MOBILE4.1C model overpredicts this ratio by 74% in a statistically significant manner. It is clear that this overprediction of the evaporative ratio by MOBILE4.1C is largely due to an underestimation of exhaust emissions.

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