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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong" *by* K. F. Ho et al.

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We sincerely appreciate the positive comments of the reviewer for helping us to improve the quality of our paper. Following the suggestions of the reviewer, we have revised the manuscript. We have structured this in the form of pasting the comments of the referees and responding directly below them.

Responses to Reviewer 2:

General comments: The paper presents emission factors of VOCs for mixed vehicles in a tunnel within Hong Kong. In my opinion this paper contains few interesting findings and little novelty in atmospheric chemistry and physics, although the data set provides the emission factors of many categories of VOCs. Nevertheless, I think the paper is

valuable for providing local emission profiles under certain circumstance (high emission factors of propane and butane related to emissions of LPG-fueled vehicles), and also helpful for estimating contributions of vehicular and non-vehicular emissions to ambient VOCs. In the present form, the paper only gives the emission factors of VOCs for "mixed vehicles" in a tunnel. The applicability and merits of this paper could be enhanced if authors can extend their study to derive emission factors for the three major vehicle types (diesel-, gasoline-, and LPG-fueled vehicles) in Hong Kong. With regard to ozone formation potential (OFP), the paper presents that the largest contributors to ozone production in Shing Mun Tunnel were ethene (23% of the measured VOC reactivity), propene (12%), and toluene (9%). However, no break-down knowledge was given for these compounds with high OFPs contributed from diesel-, gasoline-, or LPG-fueled vehicles. The result is of limited usefulness for estimating the degree of impact from the three major vehicle types on the environment, and thus providing little usefulness for making emission control strategies. Perhaps, the authors could try to derive individual emission factors for LPG-fueled, gasoline-fueled and diesel-fueled vehicles from the regression equations of EFs of individual VOC species with the change of the fractions of vehicle types in Table 3 under the conditions of fair to good correlations between them. Another approach that may be worth to try is to compare the emission factors of "mixed vehicles" in the tunnel with those of different type vehicles (diesel-, gasoline-, or LPG-fueled vehicles) from chassis dynamometer tests to estimate EFs of VOCs for individual types of vehicles running on road.

The concern of the reviewer regarding the contributions of vehicular emission factors for the three major vehicle types (diesel-, gasoline-, and LPG-fueled vehicles) is a critical comment in this study. As suggested by the reviewer, individual emission factors for diesel-, gasoline-, and LPG-fueled vehicles estimated by the regression equations of EFs of individual VOC species with the change of the fractions of vehicle types were performed (under the conditions of total emission factor >1 mg veh-1 km-1 and R > $\pm$0.4). Emission factors of LPG (4 species), gasoline-fueled vehicles (19 species) and diesel-fueled vehicles (20 species) were estimated. Moreover, the ozone formation potential (OFP) of diesel-, gasoline-, or LPG-fueled vehicles emission were calculated according to the estimated emission factors. The largest contributors to ozone production in Shing Mun Tunnel for diesel-, gasoline-, or LPG-fueled vehicles were ethene, toluene and n-butane, respectively.

Specific comments: Page 12651 Line 10: Was sampling time "one" or "two" hours? If it was two, the pressure in the 2-l canister would exceed 1 atm. Was the canister pressurized when sampling?

Sampling times was 1 hr in winter and 2 hr in summer. All canisters were pressurized during sampling. The statement will be revised to: Ambient volatile organic canister samplers (AVOCS) (Andersen Instruments Inc. Series 97-300, Smyrna, GA, USA) were used to collect whole air samples into pre-cleaned and pre-evacuated 2-l stainless steel canisters at a flow rate of 30 ml min^{-1} for 1 h in winter and 2 h in summer respectively. The canisters were pressurized when sampling.

Page 12651 Line 19: Emission profiles of motor cycles and private cars could be very different although they all use gasoline as fuel (Tsai et al., 2004). I think it's quite unsuitable to blend them together as the authors discuss the significance of different vehicle types to VOC emissions.

Authors understand the variations of emission profiles of vehicles with different fuels. We have carefully counted the traffic numbers and their classes during sampling events and also double-checked these records on video tapes. According to the Registration and Licensing of Vehicles by Fuel Type in March, 2004 released by Hong Kong Transport Department, 80% of minibus, 95% of light goods vehicles and 100% of big bus and heavy goods vehicles were diesel-fueled; 99% of motor cycle and private cars were gasoline-fueled; and, 99% of taxis were LPG-fueled. Our traffic counting was reported that the number of minibus and motor cycle contributed $\sim$4% and $\sim$2% of the total traffic flow respectively. With our assumptions, the classification uncertainty was only $\sim$1% which would not affect the overall picture of emission factors or profiles.

Page 12651 Line 20: Did all the light goods vehicles fueled by diesel in 2003 in Hong Kong?

With the same references shown above, 95% of the light goods vehicles were diesel-fueled in 2003 in Hong Kong.

Page 12656 Section 3.3: m,p-Xylene/ethylbenzene in different areas can be quite different. The authors can compare the ratio inside the tunnel with that outside the tunnel or in other nearby areas in HK to prove that VOCs inside the tunnel go through little photochemical processing. For the purpose stated in line 19-24 of page 12656, it's not suitable to compare with other far away areas, or even with other countries. In addition, propane/ethane is unsuitable to be employed for this purpose because of their relatively long lifetimes (around 40 days for ethane and 10 days for propane) and different emission sources.

As suggested by the reviewer, the propane/ethane ratios were deleted and the ratios of ethene/ethane and m,p-xylene/ethylbenzene inside the tunnel were compared with a nearby sampling location at Tsuen Wan.

Page 12657 Line 23: It's surprising that the correlation between isoprene and CO was poor in the tunnel, and the concentration of isoprene at the tunnel outlet was lower than the tunnel inlet in this study. It's very different from many other studies of anthropogenic isoprene sources (Reimann et al., 2000; Borbon et al., 2001; Barletta et al., 2002). The authors need to explain the possible causes for this.

Isoprene is mainly emitted from biogenic sources (e.g., vegetables). Authors had also done literature reviews on its formations. It is true that few researches reported fuel combustion is an emission source of isoprene. However, in many tunnel studies, the concentration of isoprene was found to be below detection limit (e.g., Staehelin et al., 1998; Hwa et al., 2002). In addition, Tsai et al. (2006) has found that isoprene was absent in diesel vehicular emission in Hong Kong. These prove the formation of isoprene from vehicle emission is uncertain. We believe that variations of fuel types used in different cities or countries can be explained the case.

Page 12658 Line 1-6: n-Pentane, i-pentane, 2,3-dimethylbutane, 2-methylpentane and toluene are also from exhaust of gasoline-fueled vehicles. Why is that the good correlations of these species can indicate the importance of running evaporative loss from gasoline-fueled vehicles? Moreover, n-nonane, n-decane and 1,2,4-trimethylbenzene are also emitted in part from gasoline-fueled vehicles. It could be just that the good correlation of most species from different type vehicles simply means that air in the tunnel was well mixed.

Authors agree that n-Pentane, i-pentane, 2,3-dimethylbutane, 2-methylpentane and toluene are emitted from the exhaust of gasoline-fueled vehicle and from the evaporative loss of gasoline-fueled vehicles. The statement has revised to: "n-pentane, i-pentane, 2,3-dimethylbutane, 2-methylpentane and toluene are the most abundant VOCs from the exhaust of gasoline-fueled vehicle or from the evaporative loss of gasoline vapor (Tsai et al., 2006). Strong correlations (R = 0.82 - 0.96) of these species indicated the importance of emissions from gasoline-fueled vehicles."

Page 12659 Line 23: Toluene and i-pentane are also from unburned gasoline in vehicular exhaust. Why are these two gases appropriate as tracers of gasoline evaporation in the tunnel? Additionally, in line 23-25, "their enhanced concentrations" compared with "what" to indicate the importance of running evaporative loss from gasoline-fueled vehicles?

Authors agree that toluene and i-pentane are emitted from the exhaust of gasoline-fueled vehicle and from the evaporative loss of gasoline-fueled vehicles. The statement has revised to: "Moreover, the abundances of toluene and i-pentane were high in Shing Mun Tunnel. These two gases are tracers of gasoline evaporation (Tsai et al., 2006). The high concentrations observed in tunnel indicated that the evaporative loss from gasoline-fueled vehicles may be one of the sources for toluene and i-pentane."

Page 12660 Line 20: "ethane" should be "ethene"

The mistake has been corrected in manuscript.

Page 12660 Line 23-35: "The unsaturated hydrocarbons contribute most to the potential ozone formation, at 56% but contribute to only 32% of ozone formation" This statement is confusing and needs to be rewritten.

The statement has revised to: The unsaturated hydrocarbons contribute 32% of potential ozone formation which is the most among the species.

Page 12660 Table 1: It would be better to show the standard deviation of traffic composition of Shing Mun Tunnel. Motorcycle and private car should be separated if their emission profiles were very different.

Table 1 has been added the information of detailed vehicle types (e.g., light and heavy goods vehicles), their numbers and standard derivations.

Reference:

Tsai, W. Y., Chan, L.Y., Blake, D. R., Chu. K.W., 2006. Vehicular fuel composition and atmospheric emissions in South China: Hong Kong, Macau, Guangzhou, and Zhuhai. Atmos. Chem. Phys., 6, 3281–3288.

Staehelin, J., Keller, C., Stahel, W., Schlapfer, K., Wunderli, S.,1998. Emission Factors from Road Traffic from a Tunnel Study (Gubrist Tunnel, Switzerland). Part III: Results of Organic Compounds, SO2 and Speciation of Organic Exhaust Emission. Atmospheric Environment 32, 6, 999-1009.

Hwa, M.Y., Hsieh, C.C., Wu, T.C., Chang, L.F.W., 2002. Real-world vehicle emissions and VOCs profile in the Taipei tunnel located at Taiwan Taipei area. Atmospheric Environment 36,1993-2002.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12645, 2009.