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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 would like to express our appreciation to the reviewers for providing us with valuable comments. We have revised our manuscript by fully taking the reviewer's comments into account. We have structured this in the form of pasting the comments of the referees and responding directly below them.

Responses to Reviewer 1:

1. The introduction part mentioned more about the source profiles, the reviewer thinks that the literature review for emission factors will have to be added. The evaluation of the advantage/disadvantage of chasis-dynamometer and tunnel experiment needs to be re-summarized. And the paragraph of line 10-20 on page 12649 read strange, how

this paragraph fits into the introduction section?

Authors agree for the suggestions from reviewer. We have reorganized and changed the introduction part as follow:

"Vehicular emissions are a major source of volatile organic compounds (VOCs) in the urban areas throughout the Pearl River Delta Region in China. The VOCs (e.g. benzene and 1,3-butadiene) emitted from vehicles directly influence human health due to their toxicity as well as are precursors for the formation of ozone and other photooxidants in ambient air (Finlayson-Pitts and Pitts, 1986). VOCs also play an important role in the formation of ground-level ozone and photochemical oxidants associated with urban smog (Monod et al., 2001). Photochemical smog is now an everyday occurrence in many urban areas throughout the world. Smog is a mixture of secondary pollutants such as ozone, nitrogen dioxide, nitric acid, aldehydes and other organic compounds, formed from photochemical reactions between nitrogen oxides and hydrocarbons. There are two widely used methods to determine vehicular emission profiles: chassis dynamometer tests and direct measurements in roadway tunnels. These two types of measurements strongly vary with many factors, such as vehicular engine types (e.g., gasoline fueled and diesel fueled engines) and engine operating conditions (e.g., cruising, idling, and transient modes) (Kaiser et al., 1992; Heeb et al., 1999, 2000; Tsai et al., 2003). With the chassis dynamometer tests, operating conditions and fuel compositions can be adjusted and controlled, thus it has ability to examine vehicular emissions under different driving or loading settings and to effectively evaluate exhaust control technologies (Ning et al., 2008). Moreover, it is an ideal tool to distinguish between exhaust and evaporative emissions at a well-regulating environment (Liu et al., 2008). The drawbacks of chassis dynamometer test are expensive and time consuming in set-up. In addition, it cannot reflect the emissions from a real world traffic environment where a composite of different on-road vehicles are being operated. For these reasons, another approach of roadway tunnel measurement has been developed and applied to determine vehicular emissions in the past decade (e.g., Pierson

et al., 1990; Haszpra and Szilagyi, 1994; Gertler et al., 1996; Duffy and Nelson, 1996; Mugica et al., 1998; Stemmler et al., 2005; Chiang et al., 2007). It directly determines vehicular emission profiles and rates at a complicated on-road condition which mixes with emissions from vehicle tailpipes, unconsumed gasoline, and vehicle evaporative emissions. The result obtained is thus more representative and accurate in estimation of emissions from a large number of vehicles to the local urban areas (Lonneman et al., 1986). The roadway tunnel measurements have several assumptions and limitations, including no cold start emissions, bias in fleet distributions, resistance caused by tunnel walls, and speed limits inside the tunnels. Many tunnel studies reported the emission factors of individual and total VOCs. Stemmler et al. (1995) measured the emissions of CO, SO2, NOx and 26 individual VOCs including alkanes and aromatic hydrocarbon in Gubrist tunnel in Switzerland in 1993. The emission factors of the total hydrocarbons are 426.5 and 432.5 mg km-1 for all vehicles and light duty vehicles, respectively. In 2002, they have done a monitoring at the same location and found that the emission factors of particular VOCs were sufficiently lower than the values obtained in 1993 (Stemmler et al., 2005). For instance, the emission factors of benzene and toluene decreased from 13.69 to 2.7 mg km-1 and 26.27 to 6.4 mg km-1, respectively. The figures indicate that the efficient technology of modern car fleets with respect to VOCs emissions. In Taiwan, research also reported that paraffins and aromatics are the main VOCs groups in the tunnel (Chiang et al., 2007). The emission factors of total non-methane hydrocarbon (NMHC) were 440-1500 mg km-1 (Chiang et al., 2007; Haw et al., 2002; Hsu et al.,2001). Hong Kong is a densely populated city. According to the Hong Kong Transportation Department, there were 532,872 licensed vehicles in December 2004. Several ambient studies have recently been completed indicating vehicular emissions are the most important source for VOCs in Hong Kong (Lee et al., 2001; Ho and Lee, 2002; Guo et al., 2004). Diesel, gasoline, and LPG are the main fuels used by vehicles in Hong Kong. In 2004, gasoline fueled vehicles accounted for 70.4% of the total licensed vehicles, while diesel and LPG fueled vehicles accounted for 24.5% and 3.5%, respectively (Hong Kong Transport Department, 2004). Vehicular

performance affects fuel consumption and emissions in part because it would affect the combustion efficiency and evaporative emissions from the fuel system. On the contrary, Turrio-Baldassarri et al. (2004) reported that synthesis and application of different types of fuels, modifications of engine designs, and improving emission control and catalytic technologies cause variations in emissions. In Pearl River Delta Region, only researches (e.g., Guo et al., 2007; Chan et al., 2006; Barletta et al., 2005; Ho et al., 2004; Lee et al., 2002) reported the urban levels of VOCs. To our best knowledge, there are only limited measurement-based VOC emission profiles available in Hong Kong. This is a pilot study to determine local VOC emission profiles from vehicular exhaust. Air samples were collected in the heavy usage tunnel during winter and summer in 2003. The project also developed a reliable monitoring program to determine the emission factors of VOCs. The emission factors were estimated by measuring the concentration differences between the tunnel inlet and outlet, the traffic rates, and the tunnel ventilation flux during sampling periods. The in-depth understanding provides important information for management of Hong Kong air quality."

2. The method section had also some problems, the reviewer wonders why the position of VOCs sampling sites were selected: 686 m from the entrance, and 350 meters from the exit? Secondly, the authors really need to clarify how to distinguish the gasoline, diesel fuel and LPG powered vehicles from such a tunnel experiment? One cannot tell from either traffic counting or video recording? I would accept if the authors state the categories of motor cycle, cars, vans and buses. I personally think this is an important issue, and will affect the discussion section. And finally, the 5 pairs of samples in summer seem to be so limited for a reliable estimation of emission factors, the authors merged these data with the ones in winter time?

The positions of VOCs sampling sites were chosen due to restriction and limitation of tunnel area. There provide sufficient spaces for setting up other sampling instruments (e.g., hi-vol samplers for collection of aerosol filter samples). However, the selection of positions would not affect our emission factor calculation. The emission rate equation

we used calculates the extra amount of a target pollutant accumulated between outlet sampling point and the inlet sampling point over the sampling time. It is independent whether substantial vehicular emission has occurred or not at the selected inlet location. There are many other studies with the inlet position >100 m (Fraser et al., 1998; Winfors et al., 2001; Colberg et al., 2005; Kristensson et al., 2004; Chang et al., 2004) Authors have carefully counted the traffic numbers and their classes during sampling events and also double-checked these records on video tapes. We have revised Table 1 and added the information of detailed vehicle types (e.g., light and heavy goods vehicles), their numbers and standard derivations. We have categorized motor cycle and private car into gasoline-fueled, taxis into LPG-fueled, and minibus, big bus, light and heavy goods vehicle into diesel-fueled vehicle. 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 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. Authors have actually collected more than five pairs of air samples in summer but few were invalid due to sampler or instrument faults. From the results of valid samples, they showed no statistical differences in emission profiles and factors between summer and winter samples. We have thus combined the samples into calculation. Statements have been added to clarify the case in manuscript.

3. As to The results and discussion section, I had arguments as following: (1)I think the reader want to know from the results shown in table 2 which species could be attributed to vehicular emissions. Therefore I would suggest to make several groups in table 2 by the differences between inlet and outlet, to indicate clearly that some species had evident emissions from vehicles, some species were likely from vehicular emission, and some species were definitely not from vehicles. The paragraph in line 5-20 on page

12655needs to be re-wording with a focus on VOCs species; (2) The emission factors obtained from this study need to be compared with the ongoing vehicular emission standards in Hong Kong. The comparison in table 5 does not make much sense without indication of the emission standards of vehicles, and typical vehicle types running in those tunnels; (3)The correlation analysis is interesting, but one has to aware that within the tunnel, the correlation could not support the conclusion of the same source origin, like benzene and CO, and fuel evaporation and exhaust, as they are all vehicle related, and therefore could show correlation, but they are from different source origins. (4)The Ozone formation potential calculation is not necessary for this manuscript, it makes more sense when comparing with other sources.

(1) Authors agree the grouping scheme for the VOC species. Table 2 has been modified and updated in manuscript. Statements have been added to the Section 3.2 which described the contribution of NMHC species. The average concentrations and standard deviations of targeted VOCs and their classes determined in the tunnel are shown in Table 2. The average total NMHC concentration at the inlet and outlet of the tunnel were 81,000 pptv and 120,000 pptv, respectively. Among the 107 NMHC, ethene was the most abundant, ranging from 16000-25000 pptv. Ethyne and toluene was the next two most abundant NMHC. Interestingly, propane is the fourth most abundant at the tunnel inlet while n-butane is the fourth most abundant at the outlet. This is thought to be the influence of emissions arising from LPG vehicles (see Sect. 3.3). Unsaturated and saturated hydrocarbons are the two largest species which contributed 45.9% and 35.1%, respectively, of the total NMHC generated by vehicles in the tunnel. Less contribution (17.3%) was found for aromatics. Halocarbon contributed <0.1% of the total NMHC. It has been reported that concentrations of individual VOCs in tunnels were typically 10 times higher than those of the same species measured in fresh air at the ventilation intake (Kirchstetter et al., 1996) or outside the tunnel (Mugica et al., 1998). In this study, the individual VOCs in the tunnel were generally 5–10 times higher than those in ambient air in Hong Kong (Guo et al., 2007). For other NMHC species, although OCS emissions make up only a small fraction of the total sulfur emitted into

the atmosphere compared to SO2, its relative inertness in the troposphere, OCS is transported to the stratosphere where it is photodissociated and oxidized to SO2 and ultimately sulfate particles. Anthropogenic sources of COS arise from the combustion of biomass and fossil fuel. Emission of OCS from vehicles is one of such example (Fried et al., 1992). The average concentrations of OCS at the inlet and outlet of the tunnel were 970 pptv and 1200 pptv, respectively, which is higher than that of free troposphere (510 ppt) (Carroll, 1985) and similar to that in Beijing city (1340 ppt) (Mu et al., 2002).

(2) There is no any vehicular emissions standard of individual and total VOCs in Hong Kong. This pilot study provides useful profiles and data for the Government and other relative authorities. It may assist legalization or regulation for controlling of VOCs emission from vehicles in Hong Kong. The information of typical vehicles types involved in the tunnel studies have been added in the comparison table (Table 5).

(3) Authors agree with the idea of reviewer and the correlation analysis between individual VOC species (e.g. benzene) and CO was deleted.

(4) Authors disagree that the ozone formation potential calculation is not necessary. Many tunnel or motor vehicles studies (e.g., Sagebiel et al., 1996; Staehelin et al., 1998) have also reported the calculations. Vehicular emission is one of the largest sources of VOCs in urban areas. And the VOCs are important precursors of ozone formation. The calculation can provide information to readers how significant of the possible ozone formation from vehicular emissions in Hong Kong.

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