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Interactive comment on "The use of tunnel concentration profile data to determine the ratio of NO_2/NO_x directly emitted from vehicles" *by* X. Yao et al.

X. Yao et al.

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1. This paper describes experiments undertaken in two road tunnels in Hong Kong that were aimed at determining the NO2/NOx ratio directly emitted from vehicles. Measurements were made using a mobile laboratory. There is currently increased interest in the ratio of NO2/NOx in vehicle exhausts because of the influence that modern pollution control technologies have e.g. use of oxidation catalysts on new diesel cars/vans and continuously regenerating traps on heavy vehicles such as buses or trucks. My major criticism of this paper is the limited nature of any new findings. Similar work in tunnels has already been reported e.g. Kurtenbach et al. (2001). On this basis, even though the paper is within the scope of ACP, I find the lack of any substantive conclusions an

important weakness and would therefore find it difficult to support its publication. I also have some more specific concerns with the work and these are outlined below.

Response: Kurtenbach et al. (AE, 35 (20), 3385-3394, 2001) did not report or discuss primary NO2/NOX ratio emitted directly from vehicles. They investigated emissions and heterogeneous formation of HONO in a road traffic tunnel. The tunnel study as reported in this paper (ACPD-2005-0344) or by the authors in a previous publication (Yao et al., AS&T, 2005) is along the entire length of the tunnel, i.e., the concentration profiles of air pollutants are measured, whereas, in conventional tunnel studies, selected points (usually at or near the entrance and exit, e.g., Kurtenbach et al. AE, 35 (20), 3385-3394, 2001) are used. The two are very much different. As pointed out in our study, one of the most critical issues in reporting vehicular NO2/NOX ratios is secondary reactions, in particular reactions with ozone; true vehicular NO2/NOX ratio should be, as the name implies, measured without such secondary reactions. The vehicle primary NO2/NOX ratio based on measurements in open air or at the end zones of tunnels cannot and will not alleviate secondary reaction interference. Our MAP temporal, spatial data, obtained inside long tunnels where solar irradiation is absent, show that, indeed, there is very little ozone in the mid-section of the tunnel. It is therefore expected that the NO2/NOX ratio thus measured is much smaller that reported in open air and tunnel end zones. This is further supported by our open air and tunnel end zone measurements having NO2/NOX ratio similar to that reported in the literature. Furthermore, the integrity of the data is exemplified by the quality of the concentration profiles measured; they agree with many model studies in the literature except for the end zones where intrusion and dilution from sources external to the tunnels exit. We believe our study is original, novel and important to this field.

Specific comments 2. A more detailed description of the road vehicle characteristics is required. For example, are the passenger cars gasoline-powered? How is a truck defined? What are the typical ages and technologies used in these vehicles? The charactertics of the speed of these vehicles is also important; we are only told that the

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speed limit is 70 kph.

Response: More information on on-road vehicles in Hong Kong including vehicle speed is in the revised version.

3. On pg. 3 some of the advantages of the tunnel environment are considered. In the context of the current work some of the characteristics of the tunnel probably complicate the analysis. In particular, the forced input of "fresh" ambient air containing ozone ensures that O3-NO reaction remain important in this environment. A more balanced description of the advantages and complexities is required.

Response: We agree that O3 complicates the measurements of the NO/NO2 ratio from emissions. That is the very reason why we believe that measurements in the tunnel, more specifically, along the whole length of the tunnels, not in open areas, are important. Fresh ambient air carried into the tunnel by ventilation can influence the concentrations of NO, NO2 and O3 in the tunnel. We agree that the reaction of O3 with NO can occur inside the tunnels and this reaction is one of the four sources of NO2 discussed in this paper. In addition, we provided both NO2 and (NO2+O3) concentration profiles for the discussion of the role of possible reactions of NO with free radicals (HO2, RO2, etc.) in the transformation of NO to NO2 and to isolate the contribution by the reaction of O3 with NO. The fact that any possible secondary reactions remain important in this environment as pointed out by the reviewer, only substantiates the message that is being delivered in this paper, i.e., should we be able to completely remove these reactions, the ratio would be even lower.

4. Pg. 4/5 Some information on the sampling technique is required. Did the mobile lab follow other traffic through the tunnel? If so, to what extent would the concentrations be affected by the vehicle in front of the lab e.g. a diesel truck or a gasoline car. A more thorough description of the sampling approach is required that supports the aims of the work. Are the samples representative of the entire vehicle fleet using the tunnel?

Response: In tunnels, MAP always follows other vehicles. The key issue is the dis-

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tance between MAP and the vehicles ahead. Yao et al. (AST, 2005, cited in ACPD-2005-0344) reported that when MAP is 5-30 m behind a vehicle, localized emissions from the vehicle in front is measured as shown by the high-time-resolution (1s) 50 nm concentration profile measured by Engine Exhaust Particle Sizer (EEPS) onboard of MAP in the tunnel. Peaks due to emissions from the vehicle in front of MAP are observed. The figure plotting concentration profile of 50 nm particles in localized plumes in Tai Lam Tunnel (southbound), 11 October 2004 can be found at http://www.ust.hk/~webiesd/AEPapers/Yaoacpd_2005_0344.pdf (Figure 1). Yao et al. (AST, 2005) also found, for distances $>$30 m, the measurements reflected the average emission of the vehicles using that particular section of the tunnel and were not just the vehicle directly ahead. Every effort was made to keep MAP at least 30 m from the vehicle in the front in this study. The manuscript has been revised accordingly. In addition, our measured NOx concentration profiles along the tunnels are consistent with the simulated concentration profiles in tunnel by Chang and Rudy (AST, 24, 672-676, 1990). Theoretically, the important thing in estimating direct vehicular NO2/NOX ratio is the absence of secondary reactions triggered by oxidants such as ozone. It is, therefore paramount to find a site where ozone does not exist and there are plenty of vehicles moving around. We are not that interested in reporting the definitive NO2/NOX ratio because there are so many operational factors that can impact this value, we merely wanted to demonstrate that measuring NO2/NOX ratio directly emitted from vehicles has a lot of problems when ozone is present.

5. References have been made to the mobile lab used. It would be useful to have a brief description of the methods used to measure NO, NO2 and ozone.

Response: Done.

6. By only considering the lowest NO2/NOx ratio as being that related to direct emissions of NO2 is inadequate. With measurements of O3, the total oxidant (OX = O3+NO2) would provide a more robust approach to calculating the faction of NOx that is in the form of NO2 (as applied by Clapp and Jenkin, 2001).

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Response: We used NO2/NOx ratio instead of NOx and OX because our data suggest that the latter may not be applicable in vehicular plumes, the center of this study. Clapp and Jenkin (2001) interpreted the intercept of the (NO2+O3) and NOx correlation equation to be regional background and the slope to be local contribution. The intercept should not be negative if the interpretation is to have any realistic meaning.

We plot the NO2 vs. NOx open air data in Figure 5 in the manuscript (where R2 is 0.63 (NOx <300ppb) and 0.15 (NOx 300ppb) in daytime, and 0.65 (NOx <300ppb) and 0.27 (NOx 300ppb) in nighttime). For the same datasets, the correlation coefficients (R2) between OX and NOx, were 0.3 (NOx <300ppb) and 0.2 (NOx 300ppb) in daytime, and 0.60 (NOx <300ppb) and 0.27 (NOx 300ppb) in nighttime. In general, they are worse than that of NO2 and NOx. Recall that NOx >300 ppb is used to demarcate between vehicular and ambient plumes. In daytime for NOx <300 ppb (i.e., not in vehicular plume) the intercept is positive, while for the nighttime data, the intercept for NOx >300 ppb (i.e., vehicular plume) is negative (even though it can be positive in other cases). This suggests that Clapp and Jenkin's interpretation may not be suitable for vehicular plumes. Figures plotting the Ox vs. NOx can be found at http://www.ust.hk/~webiesd/AEPapers/Yaoacpd_2005_0344.pdf (Figure 2a, 2b)

7. Pg. 10. The simple chemical model used is probably too simple. A consideration of OX would provide more insight. The model also implicitly assumes the NO2/NOx ratio from vehicle emissions is 2 %. The correlations shown in Fig. 5 suggest the ratio could be higher. This could be achieved by plotting NOx vs. OX and use the slope as the NO2/NOx emission ratio estimate. For NOx > 300 ppb (with presumably little O3 availability) the slope in Fig 5a is approximately 13 % suggesting a ratio of 2 % is too low.

Response: Our response to the OX issue is the same as that for Comment 6. The data shown in Figure 5a are open air data and contain transformed NO2, therefore, the ratio would be higher (15%) as pointed out by the reviewer. In a reactor with simulated

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vehicle exhaust, Cariappa et al. (Combust. Sci. Technol. 100, 355-361, 1994) and Shi and Harrison, (AE 31, 3853-3866, 1997) observed transformed NO2 due to secondary reactions.

8. Section 4 (summary) should present the conclusions of the work. In this section one would expect to see something written on the new findings, their implications, how they compare with previous work etc.

Response: Done in the revision.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12723, 2005.