

Interactive comment on “Effectiveness of replacing catalytic converters in LPG-fueled vehicles in Hong Kong” by X. P. Lyu et al.

Anonymous Referee #2

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General comments This paper provides information on the impact of the replacement of catalytic converters in vehicles fuelled by LPG in Hong Kong. The policy was based on the need to maintain the effectiveness of the catalysts; it was extensive and conducted over a period of several months over 2013 – 2014. The paper reports roadside and background measurements of VOCs, NO_x, O₃ and CO and a set of analyses to investigate the effectiveness of the programme. The measurements and analysis are of considerable interest and of relevance to the development of effective urban air quality policies. The reduction in LPG-related VOCs was substantial over only a 9 month period. The paper, however, has a number of deficiencies related either to the clarity of the presentation or to the methodologies used in the analysis and interpretation.

Specific comments

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1. More information should be given to aid the understanding of the general situation in Hong Kong and the basis of this intervention programme. (a) A brief review of the regional physico-chemical processes and atmospheric transport and their extent in influencing air quality in Hong Kong. There have been several such studies and a brief discussion would be helpful. (b) A tabulation of typical VOC concentrations at the roadside and background sites – at present it is difficult to assess the importance of the LPG-related VOCs – a number of values are given for the fractional contribution to the total atmospheric VOC burden, but real data on all significant VOCs measured, perhaps with the pseudo first order rate constant for OH removal (i.e. $k_{OH} + \text{VOC}[\text{VOC}]$), would be of value.

2. Regional processes are excluded from the analysis on the basis of the propane / CO ratio at the main roadside site. The atmospheric lifetimes of the LPG VOCs are considerable (For $[\text{OH}] \sim 106 \text{ cm}^{-3}$ and rate constants of $1\text{-}3 \times 10^{-12} \text{ molecule cm}^{-3} \text{ s}^{-1}$ the lifetime is $\sim 100 \text{ h}$) Even for a windspeed of 2 m s^{-1} , ozone will be generated from such gases over $\sim 1000 \text{ km}$. So while the roadside concentrations of the VOCs are arguably dominated by local sources, chemistry and ozone production are necessarily regional, although titration and the establishment of the NO_x/O_3 stationary state are local. Since much of the emphasis of the paper is on ozone formation, some discussion of the area over which the new controls operate, and reference to previous Eulerian / Lagrangian analyses of ozone formation in the Hong Kong region, would be of value. Note that on p35949, line 27, the authors refer to the O_3 calculation as being “purely local”.

3. The arguments deriving from the PMF analysis, that NO_x concentrations can be ascribed to emissions from gasoline vehicles is unconvincing. Diesel Euro5 NO_x emissions are still substantial and the controls on gasoline vehicles would have to be very weak if they were to dominate. This problem emphasises the need for more data – we are not told about the magnitude of the total VOC concentrations in the four factor areas, nor about the numbers and types of vehicles in the gasoline, LPG and diesel

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categories.

4. The method of establishing VOC concentration from primary processes, discussed in section 2.3.1-3, which are then used extensively in the rest of the paper, is questionable. The background concentrations are subtracted to determine the base case, and the LPG-related concentrations, presumably based on the PMF analysis, are subtracted to form a set of scenarios. We need to be given information on what these sets of concentrations are.

5. These concentration sets are then used in box models of the local processes, using the detailed chemistry from the MCM. Is this approach justifiable? The chemistry occurring is unable to distinguish between the sources of the species present in the atmosphere. LPG VOCs are affected by the background concentrations, and those derived from other sources. Subtracting out species concentrations is highly questionable.

6. I presume that this approach is responsible for the rather strange results of the HOx calculations that are given: a. The calculated [OH] and especially [HO₂] are very low. A rationale is given, but it is highly qualitative. b. What is meant by “net O₃ photolysis”, which is found to consume OH. I presume this arises from the subtraction method used and clearly demonstrates the problems such an approach generates. The production and destruction rates are, I presume, calculated from the ambient concentrations multiplied by the rate constant or J value. O₃ photolysis as a sink is nonsensical.

7. The HOx calculations are, in principle, of value in assessing the influence of the replacement strategy on the photochemistry but the approach must be revised. The calculations must be conducted with the full ambient concentrations, rather than using the subtraction approach. One way to examine the effects of the replacement programme would then be to compare total rates and concentrations (of ozone, HOx etc) before and during the programme. Of course ambient conditions can change, presenting comparison problems. The best way would be to conduct a proper sensitivity

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analysis, examining the sensitivity of specific objectives, e.g. the ozone formation rate or [OH] on the concentration of LPG VOCs and NO_x, under conditions prior to and during the replacement process.

8. It would also be useful to see a more complete analysis of production and destruction, with separate analyses for OH and HO₂. I presume that Figure 11 refers to the overall HO_x radical formation and removal rates and this is why OH + VOC reactions do not figure in Figure 11. It explains why overall production and destruction rates do not balance, the differences relating to other radical formation / destruction. This partial analysis leaves more questions than it answers. Either this table should relate to total radical formation and destruction – a substantial problem in a region with a complex VOC species range. This would allow assessment of the total initiation and termination rates for the reaction system. Or it should concentrate on OH and HO₂, as at present, but reporting their total production and removal rates, including the propagation reactions (e.g. reaction with VOCs). Such an analysis is straightforward with the MCM. It would provide a much more useful analysis of the impact of the LPG reductions than does the present analysis, whose objective is obscure.

Technical / typographical comments 35942; 16: change since to over the. 21: initiate rather than initialize. Also elsewhere in the paper. 23. Reword – the LPG vehicles weren't replaced with catalytic converters – the converters on them were replaced. 35943, 8. Insert the before South 12. Insert A before marine 35945, 20 et seq. There is confusion of emissions / formation and concentrations. The wording should be changed. Concentrations indicate emissions or formation, but aren't synonymous – they have different units. 35946, 18: omit the before fresh 35949, 14: omit in the (or omit the whole phrase and change to the concentrations of some species in the free troposphere 35950, equation (9). The dash before free troposphere looks like a minus sign – I couldn't understand what was going on. Make identical to that on line 7 or change to RIR(weighted concentrations). 35956, 22. The current use of "well" is clumsy and rather colloquial. ? Change well to accurately. 20,21. What is meant by

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“background O₃reaction”? 35959, 25 change to “constitutes the major source of ..” Figure 4. Explain the variability during Jun-Aug 2013 – the variations exceed the subsequent downward trend. Define x.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 35939, 2015.

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