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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-path measurements of pollutants and micrometeorology over Highway 401 in Toronto" *by* Yuan You et al.

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Comments from anonymous reviewer 3.

Long-path measurements of pollutants over a highway in Toronto Yuan You et al.

Summary The paper presents measurements of CO, O3, NH3, HCHO, HCN, CH3OH made by an open path FTIR over highway 401 in Toronto, ON for a 15 day period in July (year was not given). Long path measurements of some compounds were compared to a co-located near road air quality monitoring site and to results from a chemical transport model. Data from a co-located scintillometer was used as input

for a dispersion model (WindTrax) to calculate emission rates from vehicles given the measured pollutant concentrations.

General Comments The authors have useful data to show on roadside levels of NH3 and HCN and potential impact of vehicle emissions as a source of these compounds. For me that is the principle value of this paper. The basic analysis of the data to show the level of agreement between open path (OP) and fixed point measurements is also useful. In general the paper is well written and organized and the figures are clear. I think the analysis of the data is some cases has been stretched to the limit of credibility; in particular the comparison of weekday / weekend effects from such a limited data set. The authors should put their 15 days worth of data into context using the longer record of data from the near road site. A significant part of the paper was calculating CO, NH3, NO, and CH3OH emission factors using the WindTrax dispersion model. This is a free online particle dispersion model but I do not have the expertise to comment on the technical merits of this model and thus this portion of the analysis. A major input to the model is the "background" concentration and I thought choices made for NH3 and CO need better explaining. The authors show that the vehicle emission values they calculate agree reasonably well with ranges reported by others. Emission values reported for methanol are hard to believe as this compound has large sources from other things and is not a major emission that I know of from vehicles. The methanol results merit more discussion and highlights that meteorological variability may induce correlations between compounds that get interpreted as being source driven.

I have identified in the minor comments things that were unclear, some issues I had with the analysis, and a section in the introduction that could be removed. I think if the authors could revise the paper to address some of these issues few issues I have this paper would be it pretty good shape for publication.

Minor Comments P3. It the interest of brevity, the section on page 3 describing how PBL dynamics can impact surface concentration of pollutants is probably unnecessary for the readership of this journal. I found this introductory material unnecessary and I

think it adds to manuscript bloat.

P3. "... first direct comparison of this kind..." It would be good to check the publication of M. Grutter at Centro de Ciencias de la Atmósfera, UNAM, Ciudad Universitaria, Mexio City. He also uses OP FTIR and there had been some big field international air quality field experiments in Mexico City over the last 15 years that would have likely produced opportunities for OP FTIR / fixed point measurement comparisons. I know he has done this for formaldehyde.

P4. Experimental section should list dates of the study period.

P8. It is not clear why the GEM-MACH model results for CO was averaged over 3 hours (1 hour period on each side of the h1-hr period of interest) to get a running average to compare with the 1-hr averages of the data?

P8. WindTrax. The discussion didn't make clear how the concentration at the measurement site was apportioned to the source area (highway lanes) of interest. Wouldn't the back trajectory model need a high resolution emission model to determine what mass of CO measured at the site was from the emission area of interest? This needs to be clarified for the reader who hasn't used WindTrax . Why is this model needed for equation (9) if the denominator is being determined by another model (the bLS model)? I found this section confusing.

Figure 2. I can't tell the difference between the line for z/L and the line for u*.

Fig 4. This is a nice figure but it isn't clear from the text what is actually plotted – the image looks smoothed to color code difference ranges rather than being a collection of individual data points.

P11. Ambient temperature. It is well known that traffic emission of CO can be influenced by temperature but this is primarily due to start emissions when catalytic converters are still cold (< 200 C). Vehicle running emissions of CO are not strongly influenced by ambient temperature. This section has an odd reference "Choi pdf" accessed

from the internet. It would be better to cite an actual EPA report on MOVES temperature parameterization of vehicle emissions. One suggested reference is "MOVES2010 Highway Vehicle Temperature, Humidity, Air Conditioning, and Inspection and Maintenance Adjustments", EPA-420-R-10-027.

P12. Why was a background value of 256 ppbv used for CO – what is the reasoning for this as a "background" values for the airshed or for upwind of the FTIR beam? Do you get the same value for a CO vs NOx regressions? Air entering the urban airshed or crossing the highway will contain NH3 and CO – shouldn't these background values be subtracted from both to reveal increase due to local traffic emissions? This background value is an important number as it is later used in the WindTrax calculations so it deserves better definition.

P14. It is more common in the literature to report CO vs NOx regressions and to discuss CO-to-NOx molar ratios (cf. the papers by D.D. Parrish or Wallace et al Atmos Environ. 2012). A ratio of $\sim$ 5 would be expected for running emissions at your site. I think it would be better to show Figure 10 in the traditional way (NOx vs CO) so that your slopes could be compared with the literature and vehicle emission inventory.

P14. The analysis of the weekend / weekday comparison of ozone is perhaps more than what the data can support. There were only 2 weekend periods. Is this really enough data to statistically demonstrate that weekends have different ozone production rates that weekdays? Isn't the production and accumulation of ozone in the airshed also affected by meteorology (irradiance, dispersion)? How were these factors accounted for? You state poor statistics in explaining HCHO patterns. The week day / weekend difference of vehicle emission on ozone production is interesting but you do not have a statistically relevant difference with 15 days of data. This should be recognized in this section. I would recommend you can place the campaign data into context with ozone data from the NAPS site for a multi-year summer period.

P15. If the gas phase mechanism in the GEM-MACH model does not explicitly rep-

resent HCHO then it shouldn't be portrayed as HCHO in Figure 6, that is somewhat misleading if one doesn't read the fine print. What other compounds are included with HCHO, methacrolein and methyl vinyl ketone? If this is the case then it I suggest leaving out the model data in Fig 6 for "HCHO".

P15. The HCN section is very brief. Any idea why it is so variable; most data appear below DL of instrument except for 3 days at the end of the campaign. If HCN is from vehicle exhaust why isn't it elevated when CO was elevated? It is hard to tell from the figure, but it doesn't seem to follow CO.

P15. I don't understand the reasoning behind the statement " ...flat on weekends, indicating that a large component of CH3OH may have come from traffic emissions". Methanol doesn't co-vary with CO from examination of the figures. I find it hard to believe all CH3OH in an urban area is due to vehicles. What are other sources of methanol? As far as I know methanol is not included as a compound in vehicle emission inventories by the US EPA but perhaps this is different in Canada? Trees emit methanol. You would probably measure similar levels of methanol outside of the Toronto urban area as a result. Are there other urban sources of methanol that are relevant, solvent use for example?

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