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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elucidating real-world vehicle emission factors from mobile measurements over a large metropolitan region: a focus on isocyanic acid, hydrogen cyanide, and black carbon" *by* Sumi N. Wren et al.

Anonymous Referee #1

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General Comments: The paper by Wren et al. focuses on quantifying HNCO, HCN and BC emission factors using mobile summer and wintertime measurements conducted over 9 days (in July 2015) and 8 days (in Jan 2016), respectively in the Greater Toronto Area.

In general, the paper is well written and the work and results are quite interesting and will improve current understanding of concerning the traffic emission source of HNCO and HCN to the atmosphere. I recommend publication in ACP after the following comments have been addressed.

Comments: Abstract: Line 20-23: "Our results demonstrate that although biomass burning is a dominant source of both air toxics on a national scale, vehicular emissions play an increasingly important role at a local scale, especially in heavily-trafficked urban areas." This statement is not really a new scientific result but rather something that is expected to hold generically, so am not sure you need it in the abstract in the absence of quantitative information concerning the national and local scale emissions here.

Introduction: line 6-9: "However, it is not established if these species are directly responsible for negative outcomes associated with TRAP, or if they act in tandem with, or as proxies for, other compounds in the pollutant mixture (Brook et al.,2007;Mauderly and Samet, 2009;Dominici et al., 2010)." Please clarify: I don't think there is doubt about direct health impact of CO and NO. Page 4; Line1: While Roberts et al. did indeed calculate the concentration exposure of documented concern, they relied on Wang et al. for the toxicological basis so it makes sense to also cite Wang et al. 2007. Citation: Wang, Z., et al., 2007. Protein carbamylation links inflammation, smoking, uremia and atherogenesis. Nat. Med. 13 (10), 1176–1184.

Page 6; Line 1-2: The description of the algorithm for excluding self-sampling could be given in a few lines here and the reader can be referred to the supplement for details as this is an important issue. Section 2.1.2and Section 2.1.3: The technical description of the PTR-TOF-MS and HR-TOF-CIMS is too sketchy in the main manuscript and warrant some more description. The supplement does have the details so atleast the operational parameters (Townsend ratio, humidity dependent sensitivity reported as a range and correction magnitude, detection limits and number of samples below detection limit) can be added here in 3-4 lines.

Comment and suggestion: The PTR-TOF-MS can also measure HNCO and it would be very useful for readers to know how the HR-TOF-CIMS using the iodide ionization method measurements and the PTR-TOF-MS measurements of HNCO compare? As reported by Kumar et al., 2018 in Scientific Reports, which the authors cite in another context, some of the amide and amine precursors of HNCO can also be detected us-

ing the PTR-TOF-MS. This data would provide more insights and help improve the subsequent discussion of HNCO sources and in my view should be included in the revised manuscript. 2.1.4. High-sensitivity laser-induced incandescence (HS-LII) for Black Carbon: What is known about its performance Vs the traditional BC measurement devices like an aethalometer? Are there inter-comparisons that are available in the literature?

Considering that the emission factors reported in this study are much lower than many other studies for HCN, it is important to discuss the possibility of systematic "biases" intrinsic to the techniques that may have been used to quantify HNCO, HCN and BC in other studies to avoid pinning down the contribution of such effects on other factors and ambient variability alone.

Page 7; Line 21: How much would the results change if instead of 2nd percentile one used 5th or 10 th percentile? It important to provide the range of final values resulting from such choices. Page 7 ; Line 31: Please include the r values for these correlations. Page 8; Lines 16-17: In the daytime the photochemical transformation of NO does pose a problem for such analysis. How much time would have typically elapsed between emission from the tail pipe and its sampling and measurement. What were the ozone mixing ratio in summer and winter? How often did it rain during the sampling days? Page 9; Line 2: Why are toluene and C2- benzenes missing from the winter campaign list? Page 9; Line 9: Wasn't it a suburban site influenced strongly by open agricultural BB fires? Page 9; Line 14: Is it possible to construct a 9 to 17 hours diurnal variation plot from the composite data for HNCO and HCN. This would throw light on the photochemical source strength for HNCO? Page 9; Line 16: "The HCN mixing ratios measured in this study are two orders of magnitude lower than the mean HCN mixing ratios of 3.45 $\pm$ 3.43 ppbv. The standard deviation does not reflect ambient variability for a dataset that is normally distributed. Can the authors clarify?

Page 10; Lines 16-19: What is the HNCO lifetime in the atmospheric environment of Toronto? Actually unless there is strong wet scavenging it can be quite long lived since

it reacts very slowly with hydroxyl radicals, if at all.

Secondly it is not clear to me as to why there should be less BB in winter. In most places, BB emissions and resultant pollutant concentrations peak during winter due to increased emission (people burn more BB to keep warm in winter if they do not have access to cleaner energy sources) and there is suppressed mixing due to the lower boundary layer in winter. So the authors should clarify and improve this discussion.

Page 12; Lines 5-8: Looking at the road sampling sites which are located near the coast, what could be the effect of humid sea-land breezes during the day on the measured emission factors, as CO2 and other more soluble gases like HNCO could experience different dilution/removal effects. Can these effects of the sea-land breeze be completely ignored? Page 14; Lines 305: Was the HNCO measurement technique identical in all these studies? Please clarify.

Conclusions: This section is very well written and some of the quantitative findings reported here can be put in the abstract which currently has scope for improvement. Figure 2: BKG instead of BCK in the Figure caption?

Supplement: Page 2: The molecular formula of tricholorobenzene is incorrect. Should be C6 instead of C3 in the molecular formula. Also given the low mixing rations observed after background correction, the authors should explain the magnitude and methodology for the sensitivity corrections owing to changing humidity of sample air in more detail.

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