

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

Anonymous Referee #2

Received and published: 4 June 2017

Review of Manuscript “Long-path measurements of pollutants and micrometeorology over Highway 401 in Toronto,” by Y. You, R.M. Staebler, S.G. Moussa, Y. Su, T. Munoz, C. Stroud, J. Zhang and M.D. Moran.

The paper presents a study by You et al. using open-path FTIR measurements to study traffic emissions across a large motorway located in an urban environment. These FTIR data are combined with a series of micrometeorological instruments to help identify / quantify a range of various air pollutants. Results are compared with in situ observations at a roadside monitoring station and also modelled using an air quality forecast model. Mixing ratios of NH₃, HCN and CO and other gases and vapours

C1

were observed, with elevated mixing ratios for NH₃. Diurnal and weekly variations are observed and discussed. The paper is generally well written and the English is good. Certain aspects of the paper are new (monitoring near such a large motorway) and may be worthy of publication, but in many regards the work lacks novelty. The greatest shortcoming of the paper, however, is that there appear to be serious flaws in the data or data analysis, particularly the FTIR spectral analysis. Indeed, it appears that the FTIR data were not analysed at all, but simply taken “as is” from the system, and the IR data appear to have large systematic errors. As a consequence we recommend that the paper be either rejected or reconsidered only after major revision whereby the authors completely reanalyse the IR data (or actually analyse for the first time!) using a more sophisticated and interactive approach. That the IR data or data analysis are fundamentally flawed will be discussed below.

With regards to novelty of the study, the crux of the paper is to collect FTIR measurements over an urban highway. Such works have been previously reported – see for example work by Bishop et al., Stremme et al., Colman et al., Grutter et al. and Chaney et al, as well as by other analytical methods (for example, the seminal paper by Stedman et al., the tunnel study by Popa et al and the newly released paper by Haugen et al.). That is to say, there exists significant literature regarding traffic emissions, and the present authors need to cite more of these studies, and also need to cite other studies that use open-path FTIR to measure similar compounds from other sources (for example, the several papers by Griffith et al., or the FTIR biomass burning studies using FTIR by Yokelson et al or the volcanic emission studies by Oppenheimer et al.). To add a more unique aspect to their study, we suggest that the authors i) emphasize more the aspect of monitoring near such a large motorway (e.g. perhaps there are atmospheric reactions / products only seen due to higher order rate constants requiring very high CO or O₃ levels?), and ii) present a more detailed analysis of the instrumental comparison, i.e. the “shoot-out” between the measurements collected from the FTIR and from the NAPS. However, the authors must beware that such comparison studies are tricky because even if the instruments do in fact agree (within the error bars), then

C2

it could mean that both are right or it still could potentially also mean that both are wrong as they have the same systemic errors. If the instruments do not agree then it could mean one instrument is right, the other is wrong, or even both are wrong! In the present case where the instrument values do not agree, the authors have largely chalked it up to a combination of a) the NAPS measuring as point source while the FTIR is measuring sources within a path, and b) wind variations dispersing the auto exhausts in different directions. Such generalities may be true, but do not provide much insight, except for raising the question as to whether the comparison as an “apples to oranges” point source v. path averaged measurement. If indeed the comparison is not valid, then what was the significance of doing the comparison, i.e. making the measurements? It seems the whole point of the study is to provide definitive gas phase measurements for certain species. However, at the end of the paper, it is unclear what are the reliable mixing ratios determined during the study. Are the FTIR values correct? Are the NAPS data correct? These authors suggest that both instruments are correct and that the difference in the mixing ratios is due only to wind inhomogeneity and/or different magnitudes of plume mixing. This is not really supported by the data, and does not provide much insight.

We believe (at least some of) the data as reported are not correct. In particular, looking at the CO plot in Figure 3, the trends for the two instruments follow one another in a nearly identical manner with overall very similar diurnal profiles. If the NAPS were as sensitive to wind direction as the authors purport, then its corresponding diurnal profile would not manifest the same diurnal trend as the FTIR: The NAPS profile would better reflect the wind direction dependence, yet the NAPS values never trend down as the FTIR values goes up (or vice versa). That is to say, at no time is there an obvious anti-correlation seen in the data. Furthermore, CO is a very well mixed gas and the NAPS instrument (Figure 1) is physically located in the middle of the FTIR optical path. Since the path for the FTIR includes both the highway and a stretch of land greater in length than the highway, the averaged CO mixing ratio obtain by FTIR over the entire path should be similar to the NAPS value, but possible lower due to mixing in cleaner

C3

adjacent air. Inspection of Figure 3 directly points to this – while the magnitudes and offsets differ (significantly!!), both the NAPS and FTIR data maxima and minima track each other very well, having the same diurnal patterns. However, the fact that the CO mixing ratio values (in terms of offset and amplitude) do not agree at a quantitative value suggest that either the data or data analysis is likely incorrect and it is in this regard we criticise the paper.

Specifically, if one observes the CO plot in Figure 3 focusing only on off hours (weekends and during the deep night-time hours), one can draw horizontal lines through the mixing ratio minima for the two methods. While this reviewer is limited to a pencil and paper for the analysis, for such lines “urban minimum baseline” mixing ratio we find the minimum value for the FTIR is ~ 380 ppb and for the NAPS data the off-hours minimum is ~ 190 ppb, almost exactly a factor of 2.0 difference for this “clean air” baseline. While one could argue that this is due to different dispersion / mixing, this is clearly not the case because: 1) the NAPS point source measurements are $\frac{1}{2}$ the FTIR values (always lower), and the FTIR values should be greater, representing increased dilution of CO, i.e. mixed with cleaner air further from the motorway, and 2) the overall diurnal variations track each other over the entire time interval. We suggest that the difference is likely due to either a systematic negative offset for the CO measurements via NAPS, or (more likely) a systematic large positive offset for the CO measurements with FTIR. It is unclear which of the two instruments is out of calibration, but we suggest the FTIR values are systematically offset and have the incorrect scaling factor, as nowhere in the paper is a calibration procedure reported. There are differences in the offsets for the other gases as well, but CO appears to have the highest. Furthermore, the mixing ratio range for CO from the FTIR is ca. 60% of the NAPS. Again, just by “eyeballing it” the data would appear to show a relative instrument response relation is of the order $Y_{FTIR} = (0.60) * Y_{NAPS} + 180$ ppb. Picking the EDT of 24/7-25/7 (CO from Figure 3), the minima and maxima values for the NAPS are ~ 220 and ~ 900 ppb, respectively, which is a range of ~ 680 ppb. While the minima and maxima values for the FTIR are ~ 400 and ~ 780 ppb, respectively, which is a range of ~ 380 ppb or 56% the dynamic

C4

range of the NAPS. Ozone has less of an offset, but the scaling factor is greater. Using the same EDT as above, the dynamic ranges for NAPS and FTIR are 48 and 20 ppb, respectively, which correspond to the FTIR being 42% the range of NAPS. Clearly, there is (are) a systematic flaw(s) present that biases the results by factors of 1.7 (CO) and 2.4 (ozone). Again, since the measurements do not agree, it is unclear what the mixing ratios are for CO and ozone at this certain location at this specific point in time.

Moreover, it is not clear if this scaling / offset artefact is just for CO and ozone or pertains to the analysis of other species as well? Plots of the spectra fit (with residual) are clearly warranted. There may be interferences in the spectra that are causing the offset and the lower dynamic range for CO, yet, there are no spectra in the paper for the readers to observe or evaluate. With no data to observe, we cannot say for certain, but we suggest that the FTIR data are the more suspect of the two instruments. In the paper, there are no explicit data evaluation plots that show what the classic least squares fit looks like relative to the measured spectrum as well as the associated residual plot. It would appear that there was minimal to none of the "hands on" analysis of the FTIR spectra, and as if the results of the Bruker FTIR software (OPS) were used without inspection or vetting. There may thus be miscalculations present that initially went unnoticed. FTIR spectral analysis of gaseous mixtures is not yet a fully automated procedure, but is an interactive process that is subtle and prone to mistakes, interferences, etc. There are several more sophisticated gas analysis programs that may be used to independently confirm or refute the results calculated by OPS, and actual evaluation of the spectra is required.

Furthermore, while authors did correct the raw mixing ratios for temperature and pressure, it appears that the temperature/pressure corrections need to be processed on the reference spectra as well, prior to the fitting. In other words, each reference spectrum (from HITRAN or PNNL) need to be scaled to the correct temperature/pressure then used for quantification. For example, the high resolution reference spectra need to be deresolved to the same resolution of the measured spectra, which in this case is 0.5

C5

cm-1. In the paper, it was not evident if the HITRAN or PNNL reference data were correctly fit to the instrument parameters and instrument lineshape (ILS). It is critical to create the same (instrumental) lineshape and resolution for the fit. Reference spectra may be deresolved using a Gaussian, Lorentzian or Voigt profile, and after deresolving them it is a good idea to check the FWHM to confirm the resolution.

Finally, it appears that one or both instruments were used without any calibration. In order for the scientific community to have confidence in the values obtained, it is important that the instrument(s) undergo some sort of on-site calibration. For the FTIR a wavenumber calibration is necessary and e.g. uses a small gas cells containing NH₃ are used for this purpose; other compounds such as H₂O, CO or CO₂ can also be used. For both IR wavelength and intensity values, the authors are suggested to see e.g. the EPA TO-16 for protocol and procedures. Also to this end, the authors should see the following manuscripts list below, particularly, the many papers of Griffith, Yokelson, Lindenmaier, Burling, Strong, and others where one interactively evaluates and inspects the micro windows associated with specific molecule detection. This is still an involved procedure and there are many papers in the field.

In light of all the calibration issues, we cannot recommend the paper be published as is – while we believe that it affects the ability to quantise all the species, there are too many lingering questions about the reported values, e.g. is the CO mixing ratio 200 ppb, or 400 ppb?

Some (of several) relevant references are listed below.

Bishop, G. A., McLaren, S. E., Stedman, D. H., Pierson, W. R., Zweidinger, R. B., & Ray, W. D. (1996). Method comparisons of vehicle emissions measurements in the Fort McHenry and Tuscarora Mountain Tunnels. *Atmospheric Environment*, 30(12), 2307-2316.

Burling, I. R., Yokelson, R. J., Griffith, D. W., Johnson, T. J., Veres, P., Roberts, J. M., ... & Hao, W. M. (2010). Laboratory measurements of trace gas emissions from

C6

biomass burning of fuel types from the southeastern and southwestern United States. *Atmospheric Chemistry and Physics*, 10(22), 11115-11130.

Chaney, Lucian W. "The remote measurement of traffic generated carbon monoxide." *Journal of the Air Pollution Control Association* 33.3 (1983): 220-222.

Coleman, Marc D., Simon Render, Chris Dimopoulos, Adam Lilley, Rod A. Robinson, Thomas OM Smith, Richard Camm, and Rupert Standring. "Testing equivalency of an alternative method based on portable FTIR to the European Standard Reference Methods for monitoring emissions to air of CO, NO_x, SO₂, HCl, and H₂O." *Journal of the Air & Waste Management Association* 65, no. 8 (2015): 1011-1019.

Goode, J. G., Yokelson, R. J., Susott, R. A., & Ward, D. E. (1999). Trace gas emissions from laboratory biomass fires measured by open-path Fourier transform infrared spectroscopy: Fires in grass and surface fuels. *Journal of Geophysical Research: Atmospheres*, 104, 21237.

Griffith D.W.T. and I.M. Jamie, "FTIR Spectrometry in atmospheric and trace gas analysis in *Encyclopedia of Analytical Chemistry – Applications, Theory and Instrumentation*," R.A. Meyers, Ed. John Wiley and Sons, Ltd. Chichester, (2000).

Griffith, David WT, et al. "FTIR remote sensing of biomass burning emissions of CO₂, CO, CH₄, CH₂O, NO, NO₂, NH₃, and N₂O." *Global biomass burning. Atmospheric, climatic, and biospheric implications*. 1991.

Griffith, David WT, and Bo Galle. "Flux measurements of NH₃, N₂O and CO₂ using dual beam FTIR spectroscopy and the flux–gradient technique." *Atmospheric Environment* 34.7 (2000): 1087-1098.

Grutter, M., Flores, E., Basaldud, R., & Ruiz-Suárez, L. G. (2003). Open-path FTIR spectroscopic studies of the trace gases over Mexico City. *ATMOSPHERIC AND OCEANIC OPTICS C/C OF OPTIKA ATMOSFERI I OKEANA*, 16(3), 232-236.

Haugen, Molly J., and Gary A. Bishop. "Repeat Fuel Specific Emission Measurements

C7

on Two California Heavy-Duty Truck Fleets." *Environmental Science & Technology* 51.7 (2017): 4100-4107.

Horrocks, L., Burton, M., Francis, P., & Oppenheimer, C. (1999). Stable gas plume composition measured by OP-FTIR spectroscopy at Masaya Volcano, Nicaragua, 1998-1999. *Geophysical Research Letters*, 26(23), 3497-3500.

Johnson, T. J.; Profeta, L. T.; Sams, R. L.; Griffith, D. W.; Yokelson, R. L., An infrared spectral database for detection of gases emitted by biomass burning. *Vibrational Spectroscopy* 2010, 53 (1), 97-102.

Lindenmaier, R., Batchelor, R. L., Strong, K., Fast, H., Goutail, F., Kolonjari, F., ... & Walker, K. A. (2010). An evaluation of infrared microwindows for ozone retrievals using the Eureka Bruker 125HR Fourier transform spectrometer. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 111(4), 569-585.

Oppenheimer, C., & Kyle, P. R. (2008). Probing the magma plumbing of Erebus volcano, Antarctica, by open-path FTIR spectroscopy of gas emissions. *Journal of Volcanology and Geothermal Research*, 177(3), 743-754.

Popa, Maria Elena, et al. "Vehicle emissions of greenhouse gases and related tracers from a tunnel study: CO: CO₂, N₂O: CO₂, CH₄: CO₂, O₂: CO₂ ratios, and the stable isotopes ¹³C and ¹⁸O in CO₂ and CO." *Atmospheric Chemistry and Physics* 14.4 (2014): 2105-2123.

Stremme, W., Grutter, M., Rivera, C., Bezanilla, A., Garcia, A. R., Ortega, I., ... & Hannigan, J. W. (2013). Top-down estimation of carbon monoxide emissions from the Mexico Megacity based on FTIR measurements from ground and space. *Atmospheric Chemistry and Physics*, 13(3), 1357-1376.

Stedman, Donald H. "Automobile carbon monoxide emission." *Environmental Science & Technology* 23.2 (1989): 147-149

Yokelson, R. J.; Karl, T.; Artaxo, P.; Blake, D. R.; Christian, T. J.; Griffith, D. W.; Guen-

C8

ther, A.; Hao, W. M., The Tropical Forest and Fire Emissions Experiment: overview and airborne fire emission factor measurements. *Atmos. Chem. Phys.* 2007, 7 (19), 5175-5196.

Yokelson, R. J.; Christian, T. J.; Karl, T.; Guenther, A., The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data. *Atmos. Chem. and Phys.* 2008, 8 (13), 3509-3527.

Yokelson, R. J., Burling, I. R., Gilman, J. B., Warneke, C., Stockwell, C. E., Gouw, J. D., ... & Kuster, W. C. (2013). Coupling field and laboratory measurements to estimate the emission factors of identified and unidentified trace gases for prescribed fires. *Atmospheric Chemistry and Physics*, 13(1), 89-116.

Other Suggestions Abstract Pg. 1, sent.21: In previous studies, emission factors have units of g kg⁻¹, here the emission factors have units of g km⁻¹. Please explicitly define the emission factor that you are estimating somewhere in the manuscript. Introduction

Pg. 1 sent 29: There are more pollutants associated with motor vehicles that are not listed here. (Please see Review Article)

Pg. 2 sent 40: change "of" to "in"

Pg. 2 sent 60: change "spectrometry" to "spectroscopy"

Pg. 3 sent 65: remove "however" from the sentence.

Pg. 3 sent 85-86: remove "which were" from the sentence

Pg. 3 sent 87-88: please state what NAPS measures

Pg. 3 sent 89: change "in-situ" to "in situ"

Pg. 3 sent 95: the objectives have already been done (paper by Griffith et al. and Yokelson et al.). Experimental

Pg. 4 sent 104: The Globar temperature between 1200 and 1500°C is its varying state,

C9

however, it will not be in its varying state during the measurements.

Pg. 4 sent 105: This is called a bistatic configuration.

Pg. 4 sent 116: Please add a reference to the end of this sentence. For example: Akagi, S.; Yokelson, R. J.; Burling, I.; Meinardi, S.; Simpson, I.; Blake, D. R.; McMeeking, G.; Sullivan, A.; Lee, T.; Kreidenweis, S., Measurements of reactive trace gases and variable O₃ formation rates in some South Carolina biomass burning plumes. *Atmos. Chem. and Phys.* 2013, 13 (3), 1141-1165.

Pg. 4 sent 119: Please add references to the previous studies that used absorption features in spectral window for analysis.

Pg. 4 sent 122: Please add reference for the HITRAN database

Pg. 4 sent 123: Please add reference for the PNNL database

Pg. 5 sent 126: How were these values adjusted for temperature/pressure? The reference spectra need to be adjusted to the correct temperature/pressure and used in the fitting process. From this sentence, it appears that the reference spectra were not corrected, but instead the reference spectra were used as is to calculate the mixing ratios, which were then adjusted for temperature/pressure.

Pg. 5 sent 131: cite PNNL and HITRAN databases.

Pg. 5 sent 135: This is a huge uncertainty for greenhouse gases. For example, is the CO₂ 400? Or 440 ppm?

Pg. 5 sent 146: sensible heat flux... what is this?

Pg. 7 sent 174: does this make a difference?

Pg. 7 NAPS measurements: please provide type of analysers used at the NAPS station. Results and Discussion

Pg. 9 sent 225: the measurement are off and so what is the point of the study?

C10

Pg. 9 sentence 244 add references to this sentence.

Pg. 9 sentence 247 “generally agree with each other, but with a significant offset. . .”
what does this mean? The language used here is vague and does not tell us anything.

Pg. 10 paragraph 1/looking at figure 3: CO from FTIR has an offset of 390 ppb and the
NAPS has an offset of 190 ppb?

Pg. 12 sent. 320-321: Please cite the studies that you are referring to here. Throughout
the paper whenever referring to studies, please cite them.

Pg. 12 sent. 331: Fig 6 should be Fig 5?

Pg. 13 sent 364: Here you are not comparing the FTIR results (due to water interfer-
ence) to the model, yet FTIR is mentioned here.

Pg. 13 sent 369: remove “and a” from the sentence.

Pg. 17 sent. 471: Here it states the differences, and the range is large, yet you state
that it “within the range of estimates”. Cite some of those ranges to support your claim.

Pg. 18 sent. 498: change “are in range” to “in the range”

Pg. 18 sent. 499: change “of” to “the”

Pg. 19 sent. 529: change “comparable” to “compare”

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-328>,
2017.