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Comment on egusphere-2022-1154

Anonymous Referee #2

Referee comment on "Examining TROPOMI formaldehyde to nitrogen dioxide ratios in the Lake Michigan region: implications for ozone exceedances" by Juanito Jerrold Mariano Acdan et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-1154-RC2, 2023

Acdan et al., 2022 leveraged the satellite observations of HCHO and NO_2 columns retrieved from TROPOMI radiance and a ground-based monitoring station to contrast the underlying ozone regimes in a region undergoing high ozone exceedances in different episodes such as weekday vs. weekends and ozone exceedance days vs. seasonal averaged values. They observed higher NO_2 columns over Chicago during high ozone exceedances, but its dominantly VOC-sensitive regime did not change due to apparent enhancements in HCHO columns. They observed the typical weekday/weekend tendencies in the former ozone studies. The PAM measurements revealed higher FNRs than those of TROPOMI due to differences in sampling time and inherit column-to-surface discrepancies (Jin et al., 2017). Unfortunately, the scientific content of the paper is really thin; there are artifacts associated with HCHO retrievals; some assumptions about the thresholds were not well thought out; the paper does not inform about the driving factors of the PAMS vs. the satellite discrepancies, and the time period of the case study (during the lockdown) is poorly chosen. The paper also has repetitive analyzes, such as recycling the spatial distributions of HCHO and NO_2 in the shape of histograms that do not provide new content (they could have been presented in SI). The paper clearly does not reach the ACP standard; thus, I recommend rejection.

Major comments

HCHO artifact: Figures 4 and 10 show elevated HCHO concentrations over Lake Michigan that are nonsensical. The surface albedo treatment in the TROPOMI HCHO retrievals most likely causes this artifact. The atmosphere cannot work in that way such that we see a sharp contrast in a relatively spatially homogenous compound like HCHO between land and water. The transport pattern shown in the draft indicates an outflow originating from the lake to the surrounding areas, so the lake will not act as a reservoir to accommodate the transported HCHO. As a result, the statistics regarding HCHO and the ratio (such as the percentage of each underlying ozone regime) are unrealistic. If the authors disagree with me, they should scientifically prove that such elevated HCHO values can prevail over the lake. Do you see the same tendency using a CTM model over the same area (e.g., https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2022JD037042)? If yes, please break down the physiochemical processes to determine the major driver; I am very doubtful about the quality of TROPOMI HCHO over water especially lakes with complex surface albedo properties unresolved in 0.5x0.5° OMI albedo climatology used in TROPOMI HCHO retrieval.

J20 assumptions: The analysis heavily relies upon the thresholds defined in J20, whose application for this case study is questionable. Two central problems exist 1) J20 thresholds are not intended for understanding the sensitivity of PO3 to NOx and VOC but rather for understanding the sensitivity of maximum peak in ambient O3 concentrations to its precursors. Ambient O_3 levels can be largely impacted by physical processes such as dry deposition, transport, etc. These two sensitivities will not be the same. J20 thresholds are case-study specific and only applicable to their time period/location because the physical processes (i.e., transport, deposition, …) can vary greatly from time to time. 2) J20 focused on OMI data possessing significant dispersions in HCHO columns (De Smedt et al., 2021) as opposed to those of TROPOMI. The spatial representation between these two sensors is also different. As the retrieval algorithm is a major source of error in the ratio, the fuzziness in J20 thresholds was induced by the errors in OMI that are largely different from those in TROPOMI. The authors must have re-calibrated J20 thresholds by establishing the same relationship between max O_3 and TROPOMI HCHO and NO_2 columns over their region of interest. Also, please avoid mixing up different thresholds from different studies looking at different things. For example, Schroeder et al. 2017 focused on aircraft observations that are not necessarily applicable to the columnar ratio. J20 studied ambient ozone concentrations instead of PO3. Duncan et al. 2010 used a CTM realization subjective to assumptions made for chemical mechanisms and physical processes. Comparing these numbers is apple-to-orange.

PAMS's loneliness: The authors briefly showed the contrast between the columnar observations and the surface ones in Section 3.1. They came to the conclusion that various thresholds should be used to segregate chemical conditions using satellite vs. surface observations because they saw a large offset in the PAMS FNRs. This argument is oblivious to the fact that these two datasets look at two different areas, one at the surface layer and the other one within columns, so even if we assumed a universal threshold, the underlying chemical regime would be totally different between those two regions. See Jin et al., 2017 who carefully studied the column-to-surface conversion for different areas/times. The authors could have potentially applied a conversion factor to look at the same layer. Moreover, this section is fully detached from the rest of the study. How did PAMS data look like for the weekday/weekend and ozone exceedances days/normal warm days, i.e., the rest of the paper? What can we really learn from this point measurement that TROPOMI cannot offer? Just showing the ratio difference between the surface and the column is not new; it has been carefully studied in more detail by Jin et al., 2017 and Schroeder et al., 2017 with more suitable tools and data.

Covid-19 time period and re-gridding: The study aimed to diagnose the chemical conditions for emission regulations; I wonder why the authors chose the covid-19 period when there were unusual disruptions in the emissions. What we can potentially learn from these ratios may not be applicable for a regular year. Also, an important advantage of using TROPOMI lies in its high spatial resolution. It is disappointing that the authors picked a 12x12 km^2 resolution for their analysis, while TROPOMI offers more spatial variance within this grid.

The inability to explain the differences in concentrations: One of the potentially interesting tendencies observed from TROPOMI NO_2 is the larger NO_2 concentrations over Chicago in high ozone exceedances. This certainly deserves a more thorough discussion using EPA surface monitoring network, bottom/top-down emissions, or available CTMs. Another possible explanation that could have been easily vetted was to study the fraction of the number of weekdays/weekends for this episode. In terms of HCHO, the authors could use parametrized isoprene emissions (e.g., MEGAN) to potentially single out the biogenic contributions. There are also well-established studies performing a temperature-dependency adjustment to minimize the meteorological effect (e.g., Shen et al., 2019). Explaining tendencies adds value to the paper, not mapping out the data.

Repeatability: The manuscript repeats the same tendencies observed from spatial distribution maps by plotting histograms which can be moved to the SI. You can briefly mention whether the differences are statistically significant in one or two sentences. This task could also be better executed by taking a different part of the distribution, like what was done beautifully by Lin et al., 2015 (https://www.nature.com/articles/ncomms8105). In general, two things can degrade the quality of a paper: i) repeating what other people have already done and ii) repeating the same results with a different presentation (aka fillers). There are many aspects pertaining to the analysis that deserves deeper analysis. More in-depth studies can be found related to this region's ratio and chemistry (e.g., Abdi-Oskouei et al.).

Specific Comments:

L50. You mentioned two regimes, but you will define three ones.

L53. HO2 needs to be accounted too.

L54. What type of non-linear chemistry? Please elaborate.

Line 54-55. The definition of NOx-sensitive or VOC-sensitive regimes is irrelevant to the availability of free oxygen atoms. In NOx-sensitive conditions, PO3 is reduced due to decreased [NO][RO2] and [NO][HO2] because all terms are reduced. [RO2] and [HO2] are efficiently removed in NOx-sensitive conditions, yielding H2O2. In rich NOx regions, so much NOx is available that terminates OH/HO2 cycling (the ROx cycle) through NO2+OH. You need to involve the ROx-HOx cycle in this paragraph. It may also be advantageous to talk about OPEs (how much O3 is produced per NOx molecule), which vary from NOx-sensitive (high OPE) to VOC-sensitive (low OPEs) conditions.

L55-60. Jin and Holloway, 2015 are not the founders of chemical condition labels. Please use a better reference, such as Sillman et al., 2002 or Duncan et al., 2011.

L61-62. But didn’t he conclude that H2O2/HNO3 was the most viable indicator fully describing the HOx-ROx cycle?

L62. HCHO is not a proxy for VOC concentrations. It is a proxy for VOC reactivity.

L68. We shouldn’t rule out the importance of H2O2/HNO3.

L67. But NOy can provide information on how transported NOx from far areas can affect local PO3. I don’t think it’s necessarily a weakness.

L79-81. What do you mean by avoiding? They ignored the critical fact that PO3 is equal to O3. O3 can easily get impacted by meteorology and dry deposition, which are not informed by the ratio. Please rewrite this part.

Table1. These thresholds do not define the regimes you defined earlier. They are not directly related to PO3. What is the definition of VOC-sensitive from an ambient O3 concentration perspective? You should carefully describe the assumption J20 made and its major limitations.

L85. This time period is during the lockdown. How informative is the case study for a normal year?

L101. Why do you need both versions?

L115. Errors in AMFs also contribute to the total error.

L 120. What assumption did they make to say that? The surface albedo and aerosol effects can vary between 340 and 440 nm.

L121. The correlated term should be “-2cov(HCHO, NO2)/(HCHO×NO2)”. So if HCHO and NO2 retrievals are positively correlated, they will only reduce the total relative errors when either NO2 or HCHO values are low. The correlated term will likely be small in polluted areas where HCHO and NO2 are elevated.

L128. I am not sure if I agree with the discussion about SNR. SNR has a specific definition related to the instrument specifications and the observed radiance. HCHO retrieval is inherently inferior because its optical depth (despite being higher than NO2) is located in the UV range where Rayleigh scattering and O3 absorption prevail, resulting in a less robust spectral fitting.

L135. The detection limit is sensor/retrieval specific; those studies are not applicable. Why not use TROPOMI studies? De Smedt et al. 2021 say 3×10^{15} molec.cm^{-2} for TROPOMI, which is an improvement of a factor of 2 compared to OMI.

L135. Also, I am unsure if I agree that the SNR is the same between OMI and TROPOMI. What does the literature say? When comparing SNRs, we should account for the footprint, so you have to normalize it by pixel size.

L154. Why do you degrade TROPOMI spatial variance by upscaling it to 12x12 km^2 when it provides higher spatial information?

L174. What are the weights? The spatial response function?

Section 2.2. Please provide the errors associated with PAM measurements. Also, because TROPOMI captures one snapshot, can we rely on monthly-averaged samples from in-situ measurements? Large diurnal variability is associated with HCHO and NO2, which is not resolved in PAMS.

L258. Those thresholds are not necessarily related to satellites. So I don’t think you should put all of them in one basket.

L289. Some hypotheses based on previous works?

L311. Does an increase in biogenic VOC always lead to higher O3? I think you are trying to say here about the relationship between O3 and increased temperature. See Figure 8 at https://pubs.acs.org/doi/full/10.1021/cr5006815. You shouldn’t rule out the effect of RO2NO2. Can you show the 2m air temperature difference too?

L365. This is a generic tendency you will observe in any city worldwide. As NOx dilutes far from the sources, the chemical condition becomes less VOC-sensitive.

L409. I don’t understand the connection between HCHO and thermal gradients. Why don’t we look into air temperature from a model?

L410-414. If this is true, why is HCHO larger over the lake than the land? See my major comment.

Figure 8. I’m surprised by the KS test saying that the distributions of NO2 are statistically different. How many times have the tests been done? Are they done on the total distribution or a specific part of it? Please see the analysis nicely done at https://www.nature.com/articles/ncomms8105. I really don’t see them being too different.

Figure8. What do we learn from these histograms that were not presented in the previous plots? I feel like the authors repeat the same tendencies. It really doesn’t add new information.

L465. This is too speculative, given the HCHO artifact. Also, how sure are we that isoprene emissions behave similarly in two episodes?

L563. What do you mean by saying that ozone production occurs throughout the day? There is no production at nighttime.

Last paragraph in conclusion: Please always provide aspects that your analysis has focused on. Your study did not quantify the temporal representation errors to gauge the importance of TROPOMI vs. GEO satellites. This paragraph is just a filler with no relevance to the results.

Editorial Comments:

L33. Longer than what?

L116. Please use the right symbol for times instead of x.

L117. Molec. is better over mol. Please remake all figures and apply this to the text. Mol can be wrongly interpreted as mole.

Appendixes could be moved to SI.