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Atmospheric Measurement Techniques Discussions

Interactive comment on "Long-term NO_x measurements in the remote marine tropical troposphere" *by* Simone T. Andersen et al.

Anonymous Referee #2

Received and published: 18 January 2021

Nitrogen oxides have an important role in the atmosphere regulating the key atmospheric oxidants O3 and OH. There are few long-term measurements of nitrogen oxides in the background atmosphere. This is one of a few papers that combine a detailed description of a measurement technique with multi-year observations of nitrogen oxides in the background atmosphere and it presents unique observations. After some issues are addressed, the paper merits publication in Atmospheric Measurement Techniques.

The aspect of the paper that requires additional detail, in the reviewers opinion, is the need to explicitly address the effect of humidity on the observations. The authors note that humidity affects the quenching of excited nitrogen dioxide and hence the instrument calibration. They do not explicitly note that humidity affects the background (zero) signal in these measurements via wall reactions associated with ozone that cause light

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emissions in the reaction cell. This signal decreases at higher humidity. The point is that without a robust examination of the role of humidity, the uncertainty of the observations is most probably underestimated.

Lines 163-166 describes gas phase reactions and reactions in the photolytic convertor but not the ozone-surface reactions in the reaction chamber that makes up the majority of the zero minus thermionic noise signal. Prior studies have identified the role of water vapor in modifying the rates these surface reactions leading to the NO detection artifact. This needs correction. Line 392-393 While addressing humidity, the comment does not deal with it in any depth.

The authors dry their sample air with a Nafion dryer and use dry zero air for diluting their calibration gas. Two questions:

1. Is the absolute humidity in the reaction cell the same in calibration and measurement modes?

2. If not, what effect does this have on the calibration?

With regard to ambient measurements:

1. what variation in efficiency of water removal occurs on short and long time scales with the Nafion dryer in the course of ambient monitoring?

2. What effect will the associated variations in humidity in the reaction cell have on ambient measurements?

3. Are there tests of the NO and NO2 transmission of the Nafion dryer?

Minor Issues 1. The paper, Berkes et al. (2018) AMT covers related material from a different perspective. Including discussion of the Berkes paper would strengthen the current paper.

2. Abstract line 19. It would be appropriate to introduce NO detection before NO2 conversion.

3. Units. From line 57 onwards. pptV is not a SI unit. I suggest the authors consider including text something like the following: The appropriate SI unit is mole fraction, picomole/mole. It is assumed that under tropospheric conditions at the low mole fractions discussed, that NO and NO2 behave as ideal gases and therefore mole fraction is equivalent to volumetric mixing ratio. Volumetric mixing ratio is commonly used in the literature and the appropriate range here is represented by ppt, 10-12 mixing ratio by volume and ppt is used here. (Use of pptV is generally discouraged, see IUPAC review of units in atmospheric chemistry.)

4. Given the magnitude of the uncertainties and sd's recorded throughout the paper, the data in ppt could be rounded to one decimal place (0.1 ppt).

5. Line 126-130. Is the flow in the inlet laminar or turbulent? What is the transmission efficiency of the inlet line plus filter for NO and NO2?

6. Line 280-300. The discussion lacks mention of the role of humidity in artifacts. This needs additional discussion as identified above.

7. Line 281-283 The first sentence is unclear and requires revision.

8. Line 293 the word ordinarily may not be the best choice for this description.

9. Line 330-339 Were the convertors cleaned during the course of the observations? What was the cleaning procedure? What was the effect of cleaning on the conversion efficiency and the NO2 artifact?

10. Line 344 The two "believed" are really "assumed"? The authors should state the consequences for data interpretation if the assumptions are wrong as well as when they are correct. This section could be clearer if expressed as a set of simple equations.

11. Line 379 Wind direction does not appear to be correctly specified.

12. Line 507 A more general overview sentence would make a better introduction to the Conclusion section.

13. Table 1, the reviewer finds the caption, headers and footnote confusing. Please clarify.

14. Figure 7, please clarify: is the fitted red line a weighted least square fit, a reduced major axis regression or something else?

Supplementary Information

1. Line 48-89. The use of the term photo-stationary state appears inconsistent with the definition of photo-stationary state by IUPAC (please modify) see https://goldbook.iupac.org/terms/view/P04654 A steady state reached by a reacting chemical system when light has been absorbed by at least one of the components. At this state the rates of formation and disappearance are equal for each of the transient molecular entities formed.

2. Line numbers cease at line 121. For subsequent text check spelling, define relative uncertainty and indicate that relative uncertainty is being used in the evaluations.

3. Figure S2 Please include dimensions.

References The following references need completion/correction.

Bell, S.

Buhr, M.P.

Drummond, J.W.

Gilge, S.

The following is probably the correct reference and web location for the reference Galbally (2019) cited in the paper.

Galbally, I.E. (2020). Nitrogen Oxides (NO, NO2, NOy) measurements at Cape Grim: A technical manual. In 'Baseline Atmospheric Program (Australia): Technical Series'. (eds. S.J. Cleland, N. Derek and P.B. Krummel). Bureau of Meteorology and CSIRO

Oceans and Atmosphere: Melbourne Australia, v, 111p. https://doi.org/10.25919/dt6y-3q53

The following reference is relevant and should be included in the background and discussion:

Florian Berkes, Norbert Houben, Ulrich Bundke, Harald Franke, Hans-Werner Pätz, Franz Rohrer, Andreas Wahner, and Andreas Petzold. The IAGOS NOx instrument – design, operation and first results from deployment aboard passenger aircraft. Atmos. Meas. Tech., 11, 3737–3757, https://doi.org/10.5194/amt-11-3737-2018, 2018

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