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Atmospheric Measurement Techniques Discussions

Interactive comment on "Interference from alkenes in chemiluminescent NO_x measurements" *by* Mohammed S. Alam et al.

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We would like to thank the reviewer for their comments and suggestions, and for taking the time to review our manuscript.

"The authors present a study of NO and NO2 measurements made in the presence of a series of alkenes in the EUPHORE atmospheric simulation chamber. Measurements of NO and NO2 were made using four instruments based on detection of chemiluminescence of excited NO2* formed by the reaction of NO with O3 generated within the instrument. This technique enables the direct measurement of NO, but measurements of NO2 require conversion of NO2 to NO, followed by measurement of the resulting NO which represents the sum of NO and NO2 concentrations and gives the concentration

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of NO2 from the difference between the sum of NO and NO2 and the measurement of NO alone. Two of the instruments used in this study use catalytic conversion of NO2 to NO using a heated Mo catalyst, while the other two instruments employ photolytic conversion using a blue LED.

The authors outline a number of potential interferences in NOx measurements that can affect instruments based on detection of chemiluminescence, and primarily focus on potential chemical interferences resulting from detection of chemiluminescence from species other than NO2*. Given the importance of accurate NOx measurements for air quality, the results of this study are potentially significant. The experimental procedures seem robust, the paper is well-written and within the scope of the journal, and will be of interest to the wider atmospheric chemistry community. However, there are a number of areas which should be improved in the manuscript prior to publication.

In general, the discussion of the observed effects is somewhat limited and the manuscript would benefit from expanding the possible causes of the interference and providing some recommendations for future experiments to identify and eliminate interferences as far as possible. Several species are mentioned as being potentially responsible for the chemiluminscence interference, including excited HCHO, vibrationally excited OH and electronically excited OH. Some discussion of the filters used in the NOx instruments is given, but it would be informative, where possible, to give the emission spectra of possible interfering species, NO2*, and the filters used in the instruments employed in this study. Are there significant differences between filters in different instruments? Could future work using alternative filters rule out interferences from these species? Could emission spectra of the chemiluminescence interferences be measured in future experiments?"

RESPONSE: Some recommendations for future experiments to identify and eliminate interferences have been added to the conclusion in lines 396 – 400. "Further research to explore these impacts, and other parameters (e.g. H2O abundance), is urgently needed. The chemiluminescence from monoterpene ozonolysis should also be inves-

tigated to identify emission spectra of possible interfering species; given the varying OH yields and energetics from the ozonolysis of different alkenes, the intensity of emission are likely to vary. A combination of selective long-pass filters and detector characteristics can then be exploited within chemiluminescence NOx monitors to eliminate such interferences with similar emission spectra to NO2*."

The long-pass filters used in the chemiluminescence NOx monitors in this study are not reported in their respective user manuals, but typically block light below ca. 600 nm, while typical PMT response characteristics are between 400 – 950 nm. Any chemiluminescence signal in the 600 – 950 nm wavelength range can therefore cause a potential interference. This has been added to the text in lines 235 – 238. The emission wavelengths of potential interferents: excited HCHO, vibrationally excited OH and electronically excited OH have been given also in the introduction (lines 140 – 143) as requested by referee #2.

"Some discussion of the kinetics of ozone-alkene reactions is given in comparison to the observed interferences, which indicates that more rapid ozone-alkene reactions are more likely to result in interferences. Consideration of the energetics of the ozone-alkene reactions investigated, combined with modelling of the chemistry involved, might be more insightful and could help to identify whether production of excited species is likely, and which species with appropriate emission spectra might be present in sufficient concentration to produce significant interferences."

RESPONSE: We agree that this would be interesting to study, however, modelling the chemistry involved to predict whether the responsible excited species would be present in concentrations likely to cause significant interferences would be out of the scope of this study. Modelling these types of experiments to predict excited species and their emission spectra would be a potential further study. Further research that is needed has been added to the manuscript in lines 396 – 400: "The chemiluminescence from monoterpene ozonolysis should also be investigated to identify emission spectra of possible interfering species; given the varying OH yields and energetics from the

ozonolysis of different alkenes, their intensity of emission are likely to vary. A combination of selective long-pass filters and detector characteristics can then be exploited within chemiluminescence NOx monitors to eliminate such interferences with similar emission spectra to NO2*."

"Minor comments are given below." "Lines 54-55: This sentence appears to be incomplete." RESPONSE: Amended. Line 37 – added "because"

"Line 128: Are the 212 monitoring sites in the UK, EU or a wider area?" RESPONSE: "In the UK" added to Line 101.

"Line 154: Are the CO2 mixing ratios in the chamber elevated significantly above ambient levels such that interferences could result in the chamber?" RESPONSE: The CO2 mixing ratios within the chamber are not elevated significantly above ambient, and are therefore unlikely to affect the interference results. The manuscript remains unchanged.

"Lines 175-178: Please provide further details of the previous work. What alkenes were investigated? What were the conditions? Were emission spectra reported? If so, what were the emission wavelengths? Do the previous studies give any further details on which species might have been responsible for the observed chemiluminescence?" RESPONSE: This information has been added into the text. See line 139 – 142. "Chemiluminescence from the ozonolysis of 14 short chain alkene species at total pressures of 2 – 10 Torr was first reported by Pitts et al. (1972). Excited HCHO, vibrationally excited OH and electronically excited OH in the wavelengths 350 – 520 nm, 700 – 1100 nm and 306 nm, respectively, were the identified chemiluminescent species (Finlayson et al., 1974); and indeed has been used to perform field measurements of both ozone and alkenes (e.g. Velasco et al., 2007; Hills and Zimmerman, 1990)."

Added reference to line 594-595: "Pitts Jr, J.N., Kummer, W.A., Steer, R.P., and Finlayson, B.J.: The chemiluminescent reactions of ozone with olefins and organic sul-

phides, Advances in Chemistry, 113, 10, 246-254, 1972."

"Line 199: Were the sampling lines all of similar length?" RESPONSE: Yes. This is added into the manuscript. Line 156

"Line 203: What were the concentration ranges over which calibrations were performed?" RESPONSE: The calibration range has been included into the text: "(in the range 0 – 100 ppb)". Line 160

"Line 280: Can the relationship between the level of interference and the alkene + ozone reaction rate be quantified in any way? Does a plot of the level of interference against rate of reaction reveal any general trend?" RESPONSE: This is explained in detail in the discussion section. The relationship between the level of interference and k(alkene+o3) has been described in the "interference magnitude: kinetic and structural effects" section and the use of the kinetic interference potential (KIP). The manuscript remains unchanged.

"Lines 295-296: What are the differences in conditions between instruments?" RESPONSE: The main differences between the instruments are the different pressures within the reaction chambers and the different NO to NO2 conversion technologies. This is explained in line 241 – 244 and 159 – 161, respectively. The manuscript remains unchanged.

"Line 332: Is CH2OO the only possible Criegee intermediate produced? What other species/Criegee intermediates are produced?" RESPONSE: Myrcene contains three C=C bonds, two of which are terminal bonds, while limonene possesses two C=C bonds, one of which is terminal. This information is given in Table 4. Ozonolysis of terminal C=C bonds will lead to a CH2OO CI (the simplest of CIs), while the ozonolysis of internal C=C bonds will results in different CI structures (dependent upon the alkene). Each CI resulting from an internal C=C bond (of a different alkene) will not only be different in structure but will also have different yields depending on the energetics of the reaction. This discussion is not in the scope of the study and is not the primary

focus of the paper – the manuscript remains unchanged.

The possible CI formed from limonene and myrcene ozonolysis can be found in the following studies: (1) Deng, P., Wang, L. and Wang, L., 2018. Mechanism of gas-phase ozonolysis of β-myrcene in the atmosphere. The Journal of Physical Chemistry A, 122(11), pp.3013-3020. (2) Baptista, L., Pfeifer, R., da Silva, E.C. and Arbilla, G., 2011. Kinetics and thermodynamics of limonene ozonolysis. The Journal of Physical Chemistry A, 115(40), pp.10911-10919.

"Line 364: Is there any likely effect of the age of the catalyst?" RESPONSE: To the authors knowledge there are no known effects of the age of the Mo catalyst in the NOx monitors, so this is unlikely to cause any deviation in the results presented. The largest interference observed were from the photolytic convertor NOx monitors (AQD and Eco Physics) which are not catalysts. The manuscript remains unchanged.

"Line 496: Remove the comma at the end of the line." RESPONSE: Amended. Line 417

"Table 2: Values and uncertainties should be given to the same number of significant figures." RESPONSE: Amended. All values have been amended to 3sf. See Tables 2 and 3.

"Figures 1, 2, & 3: Panels B & D should be labelled as NO2 on the y-axes." RESPONSE: Amended.

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