

We thank Referee #2 for reviewing our manuscript. Our answers to the referee's comments are given below.

Referee comment

I am uncertain about the meaning of much of the analyses. One primary concern is that the analysis of background NO_x is incomplete or possibly in error. In this manuscript, NO_x is averaged over 8 h periods corresponding to the maximum daily average 8 hr. But NO_x and ozone do not have the same temporal behavior, so I don't think this average can be used to determine background NO_x. NO_x is usually greatest at very different times than ozone. Although NO_x is important to O₃, the two often anticorrelate. So this analysis could miss large NO_x values that occur earlier in the day.

Author response

This is the first attempt to resolve background NO_x in the HGB on the long term using surface data. Whether our background NO_x analyses are incomplete or possibly in error can be answered by comparing our background NO_x estimates to those from other studies. Unfortunately, there are no long-term studies on background NO_x. A two-week study (cited in our manuscript, Zhang et al., 2011), used modeling and surface observations to determine regional and local NO_x source contributions to O₃ in the HGB. The regional "upwind" NO_x contribution to daily average O₃ were estimated to 20-60 ppb, while those from neighbor states to 20-25ppb. However, these large estimates are not representative to the season scale and the time period we used in our analysis. A recent long-term study (Souri et al., 2016) report 1-h average daytime and nighttime NO₂ in the HGB in a range of 6-10 ppb, which is not directly comparable to our 1-h daytime background NO_x.

We agree that O₃ and NO_x do not have the same temporal behavior (see P5, L10-12 and P15, L29-31).

Regarding the use of the 8-h average NO_x corresponding to the MDA8 O₃ to estimate background NO_x, please see our statement on P15, L31. We could also look at Fig. 5 in the manuscript and compare the 8-h average background NO_x corresponding to MDA8 O₃ (Approaches A-C) with the adjusted hourly background NO_x unconstrained by 1-h peak O₃ (the hourly median approach). The background NO_x from the hourly median approach, averaged over 8 daytime hours for comparison, is lower by 1-2 ppb than the 8-h average background NO_x from mid-July to early September, when important local chemistry is expected. This observation supports our statement on P15, L31 and suggests that we likely overestimate background NO_x when the 8-h average NO_x corresponding to MDA8 O₃ is used in the analysis.

We also agree that O₃ and NO_x are anticorrelated if there is significant chemistry between them. However, our primary focus here was to find the opposite behavior in the extracted regional background O₃ and NO_x, which we see in Fig. 3 of the manuscript. For the local effects (inferred from PC2), we found that hourly local O₃ and NO_x are anticorrelated (Fig. 1, at the end of this author response), as expected from a chemical interaction (we did not show this figure since our primary focus was on the regional component).

Referee comment

NO_x is defined in the introduction to be the sum of NO and NO₂. But the monitoring NO_x reported here is from chemiluminescence detectors with a molybdenum converter that also detects PAN and some HNO₃. This limitation isn't critical for measurements in urban regions dominated by fresh emissions, but the contributions from PAN, HNO₃, and other oxidized reactive nitrogen compounds is likely substantial if background locations and times are considered. The meaning of monitoring NO_x has been discussed in many papers (e.g., Winer et al., Response of Commercial Chemiluminescent NONO, Analyzers to Other Nitrogen-Containing Compounds, ES&T, 1974), and it should be considered here. If monitoring NO_x is used to examine background levels, there needs to be considerably more examination of the data, and it may be impossible to use NO_x for this sort of analysis. For example, all of the trends in NO_x could be dominated by changes in partitioning between the NO_x oxidation products (PAN, organic nitrates, and HNO₃), rather than a reduction in NO_x. If the ratio of organic nitrogen to HNO₃ has changed in the background air (which is likely), then the monitoring NO_x instruments would likely respond in a way that would alter trends in NO_x.

Author response

Indeed the monitored total NO_x might account for other oxidation products, such as PAN and HNO₃. However, the majority of the sites used to derive background NO_x (constrained by MDA8 O₃) are urban sites or sites that are affected by fresh emissions; as the reviewer points out, the limitation of the method used to monitor total NO_x is not a problem for these sites. Therefore, conversion to PAN and HNO₃ might have a weak effect on the temporal trends in background NO_x in the HGB region.

There is no evidence for the significance of PAN and HNO₃ in the long-term measured NO_x by TCEQ (5 seconds measurements averaged over 1 hour). We think that on the 1-h basis, loss of NO_x by conversion to PAN and HNO₃ might be important in dry and sunny conditions, since the lifetime of surface PAN against photolysis and chemical losses is about 3 h, while that of HNO₃ against dry deposition is around 14 h. However, on the 8-h average basis, the importance of NO_x conversion to PAN is reduced, because PAN has time to convert back to NO_x. Rapid wet deposition of HNO₃ during rainy days has the effects to reduce NO_x. Conversion of HNO₃ to particles can be assumed to be negligible during summer. Unfortunately, we cannot test the long-term effects of HNO₃ and PAN on measured NO_x because no coincident HNO₃, PAN and precipitation data are available. A future study might look on the long-term effect of NO_x conversion to PAN and HNO₃ using 1-h solar radiation to separate between dry and wet or cloudy periods. Coincident precipitation data are not available.

The monitored NO_x is the best metric that we could use for determining long-term background NO_x in the HGB region. Using chemiluminescence-based NO only, would have made the separation of the regional background from the local contribution even more difficult, since NO would be more an indicative of rapid chemistry. On the other hand, the NO₂ reported by TCEQ is calculated as the difference between total NO_x and NO. It is not really a measured value and also accounts for other oxidation products like the monitored total NO_x. Modeling and satellite-based NO₂ might be used in the future to test our data-driven background NO_x in the HGB region.

Therefore, we added the following on P4, L2:

"Public data, representing 1-h average of surface measurements of O₃, NO_x and meteorology (WD, WS and T), were downloaded from the Texas Air Monitoring and Information System website owned by TCEQ (see Data availability). The measurements were taken every five seconds and averaged over one hour. Note that, due to the measurement method (combined chemiluminescence detection-molybdenum conversion), the monitored total NO_x might include traces of other oxidation products (PAN, HNO₃, etc.)."

We also made the following revision on P16, L17:

"Background NO_x also declined in all approaches, with significant slopes (see Table 7). No other long-term background NO_x studies exist, making comparison impossible. Additionally, there is no long-term evidence on the effect of NO_x conversion to PAN and HNO₃ that could affect its temporal decline. Considering that the majority of the sites used to derive background NO_x are urban sites or sites that are affected by fresh emissions, we could assume that conversion to PAN and HNO₃ might have had a minor effect on the temporal trends in background NO_x."

Referee comment

The background NO_x value of 6.8 ppbv is surprisingly large, and it is inconsistent with the 2000 and 2006 intensive field studies that showed NO_x upwind of HGB was often <1 ppbv, and NO_y was a 1-4 ppbv (see for example the upwind or non-plume measurements shown in Daum, P. H., et al., A comparative study of O₃ formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study, *J. Geophys. Res.*, 108(D23), 4715, doi:10.1029/2003JD003552, 2003; Ryerson, T. B., et al. (2003), Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *J. Geophys. Res.*, 108(D8), 4249, doi:10.1029/2002JD003070; Neuman, J. A., et al., Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas, *J. Geophys. Res.*, 114, D00F08, doi:10.1029/2008JD011688). I don't know whether the discrepancy is an artifact of the data or the analysis, or both. But if background NO_x were truly 6.8 ppbv, then NO_x emission controls in HGB would need to be reconsidered. NO_x is short-lived, and it is possible that the NO_x measured at these monitoring stations is strongly influenced by local emissions. I recommend removing the analysis of background NO_x, or adding substantial discussion and examination of the NO_x data.

Author response

The two intensive field campaigns indeed show smaller NO_x mixing ratios upwind the HGB region. However, they focused on very short term (1-13 days) and did not capture multi-year, multi-months and intra-seasonal variations. Moreover, these low upwind or non-plume NO_x mixing ratios are measurements made from aircrafts that cannot be directly compared to background NO_x derived from ground monitoring data. For example, Ryerson et al. (2003) report low non-plume mixing ratios of airborne NO and NO₂ (<1 ppbv), measured downwind from relevant sources (power plants and petrochemical facilities), after 6 pm. Our daytime background NO_x is derived from surface measurements between 10 am and 6 pm, during May-October. Even if we ignore the different altitudes and periods of observations, the diurnal sampling is different between the two studies. Daum et al. (2003) reported low upwind NO_x mixing ratios (<1 – 5 ppb) from the morning flights over the southeast of Houston, but NO_x also reached 10 ppb over the city during that time. Neuman et al. (2009) measured in-plume NO_x during daytime (3-5 pm) ranging from 1 to 10 ppbv. Although our daytime background NO_x estimate falls within this range, a direct comparison is not possible due to inconsistent time-scales and altitudes of observations. It is possible that vertical mixing allows for significant dilution of surface NO_x, resulting in lower airborne mixing ratios, particularly during daytime, when the boundary layer is higher. Significant local chemistry near the surface may also contribute to reduced NO_x.

Our first time estimate of long-term 8-h average background NO_x (6.8 ppb) appears to be large compared to the hourly median approach, particularly from July to September (by 1-2 ppb). Indeed the monitoring sites are influenced by local emissions. They are also influenced by local chemistry as well as local and regional transport. By co-varying chemistry and meteorology, the PCA method could separate between the local and regional effects. We determined average regional background NO_x in the HGB region only from the component identified as being "regional". We acknowledge that by constraining the 8-h average NO_x and meteorology by the MDA8 O₃ might not be the best approach when local chemistry is important. Future studies should consider refining this estimate by analyzing the 8-h average NO_x, O₃ and meteorology that are not constrained by MDA8 O₃ and see how it compares to our estimate. Considering the above, it is not justified to remove our background NO_x analysis from the study.

Therefore, we propose to add the following on P1, L22 (Abstract):

“Average background O₃ is consistent with previous studies and between the approaches used in this study, although the approaches based on 8-h averages likely overestimate background O₃ compared to the hourly median approach by 7-9 ppb. Similarly, average background NO_x is consistent between approaches in this study (A-C), but overestimated compared to the hourly approach by 1ppb, on average. It is possible that we likely overestimate both background O₃ and NO_x when the 8-h average NO_x and meteorology coinciding with MDA8 O₃ are used in the analysis.”

Another addition would be on P17, L10 (Conclusions):

“Our estimates of 8-h based average background O₃ and NO_x are both slightly overestimated compared to the hourly median approach, likely due to constraining the 8-h average NO_x (and meteorology) by the MDA8 O₃. Future studies should consider refining these estimates by analyzing the 8-h average NO_x, O₃ and meteorology that are not constrained by MDA8 O₃.”

Consequently, we also modified the previous statement on P17, L10:

“To test the linearity of the temporal trends in background O₃ and NO_x and to continuously determine the effectiveness of control measures, and identify regulatory changes that need to be made, new studies should extend the trends in this study into future years. Additionally, wherever VOCs data are available, the extraction of background O₃ and NO_x should be constrained over that period by VOCs as well and possibly by solar radiation. The related temporal trends should be compared over that period with those estimated from this study to highlight the effect of including VOCs and an additional meteorological variable in the multivariate analysis.”

Referee comment

The use of MDA8 needs to be put into context, and the importance of MDA8 should be discussed. MDA8 is a regulatory construct. Is HGB in exceedance of the O₃ standard? What is the current O₃ standard (only the old standard is mentioned)? It would be helpful to indicate the NAAQS on the figures. The background fraction of total ozone discussed in section 3.7 also has me confused, and I think it misses the point of MDA8. The background MDA8 is important insofar as it contributes to the design value for the entire air basin. So background MDA8 should be compared with the largest MDA8 in the region to understand the effect of the background on compliance

with O₃ regulation. I don't see the point of comparing background MDA8 to an average of MDA8 from the same locations, as shown in figures S18-25. If the analysis finds sites and conditions that faithfully represent the background, then shouldn't the background MDA8 always equal the measured MDA8? Why are there so many points in the supplementary figures with the PCA-derived background O₃ greater than the measured O₃?

Author response

We agree that MDA8 O₃ is a regulatory concept and we acknowledge its importance, but it was not our goal to test if the MDA8 O₃ is in compliance or not. The goal of our study was to determine long-term regional background O₃ and NO_x in the HGB. We only used MDA8 O₃ to separate the regional contribution to it and to better quantify its temporal trend using long term measurements and a different analytical approach compared to previous studies. The current NAAQS standard for O₃ is 70 ppb and our average background O₃ represents about 64-67% of it.

In order to quantify the contribution of the regional component to MDA8 O₃ in the HGB, it is well justified to compare the average background O₃ with the season-scale MDA8 O₃ averaged from the sites used to determine the background. If we were only to compare the average background with a single site showing the highest MDA8 O₃ we would have biased the design value for the "entire air basin". Using the highest MDA8 O₃ to quantify regional contributions, would also bias the design value for the entire season.

MDA8 O₃ at each of the "background" sites does not always equal background MDA8, unless those sites are remote, rural or relatively clean sites. The 5-10 sites used to extract background O₃ from MDA8 O₃ are all within Harris County, except for Conroe Relocated. We do not think that a single site should be decisive about the design value in the "entire air basin" and for the entire season, particularly if that single site is subjected to unexpected local emissions (i.e., wildfires).

There are several instances (all below 35 ppb) of PCA-derived background O₃ greater than average measured O₃ for the hourly median approach only (Fig. S18). This is also the case for background NO_x in Fig. S19. The reason could be the intra-seasonal variation, spring versus summer/fall. We explained that for NO_x at the end of section 3.7.

Referee comment

Some of the language is imprecise, and I had to read the sentences many times to distinguish the literal meaning from the authors' likely intent. For example, pg 2 line 14 states that "no study has yet to quantify the regional contributions to direct O₃ precursors themselves: : :". I'm not sure what this means. Zhang et al, and many other papers, examines background O₃ precursors, and is already referenced. The second sentence of the abstract states that ozone dependence on VOC:NO_x ratio makes ozone difficult to control locally. I think the whole point of this paper is that large background contributions, rather than the VOC:NO_x, may make local ozone control challenging. I don't understand page 3, line 1 that says "Meteorological controls : : : are reflected by a more significant decline .. in the east than in the west". Cooper et al explain this difference by changes in Asian emissions and biomass burning, not changes in meteorology. I don't understand page9, line 19: why does NO_x increase with windspeed? The last paragraph of the conclusion is not supported by the manuscript. Rather than emphasize work that needs to be performed, the authors should focus on their most important findings.

Author response

For clarity, we rephrased P2, L14-16 as:

"No long-term study exists that quantifies the regional contributions to direct O₃ precursors themselves, such as nitrogen oxides (NO_x = nitrogen dioxide (NO₂) + nitric oxide (NO)). Our goal is to better characterize the trends in regional background O₃ and NO_x in the HGB region on the decadal scale. "

Regarding the ozone dependence on VOC/NO_x ratio, we rephrased line 2-3 in the Abstract:

"Because of its dependence on the volatile organic compounds (VOCs) to nitrogen oxides (NO_x) ratio, ground-level O₃ is difficult to control locally, where many sources of these precursors contribute to its mixing ratio."

to read:

"Local precursor emissions, such as volatile organic compounds (VOCs) and nitrogen oxides (NO_x), together with their chemistry contribute to the O₃ and NO_x mixing ratios in the HGB region."

P3, L1: It is our interpretation at the scale of US. We did not say that meteorology changes, we did imply that the meteorological controls are different in the west than in the east and they are reflected into a differential decline of O₃ at the scale of the US. For clarity, we rephrase this line on page 3:

“Meteorological controls on the scale of the US also may play a role in the differential decline during recent decades of summer surface O₃ observed in the east, southeast and midwest (Cooper et al., 2012; Hudman et al., 2009) than in the west (Cooper et al., 2012). There are different meteorological controls in the west (i.e., thermal inversion and orographic lifting, Langford et al., 2010), which can either increase O₃ locally or transport O₃ up in the free troposphere and towards east. Additionally, the pollution transport from Asia contributes to a higher O₃ in the western US compared to the eastern US (Cooper et al., 2012).

P9, L19: Fig. S6e shows that at wind speeds > 4 m s⁻¹, the PC2-NO_x scores are positive (suggesting an increase in NO_x). This is the case for October. During this month, winds were from SE (Fig. S6d). Together the two wind variables say that some regional NO_x is also included in the second component during this month, on the 1-h basis.

P17, L10: Our study opens the paths for new research. Therefore, it is important to point out how future studies should be focused. The last paragraph is the most appropriate for this purpose. However, we modified the conclusions (see our answers above related to P17, L10).

Referee comment

The results reported here can be made more valuable by further synthesizing the findings. There are 25 figures in the Supplementary section, and it is hard to distinguish one from the next. The first 6 tables are very dense, showing many PCA loadings for many different sites. I don't think many readers will be able to use all these tables of numbers and all the figures in the Supplementary. This paper examines many topics, and most points are supported by a scatter plot and the associated statistics obtained from a linear least squares fit. It is challenging to appreciate the important findings, as they are obscured by an abundance of data and statistics. An in-depth consideration of a single topic, such as the decadal change in wind direction and its effect on background ozone, would be a more powerful contribution to the literature.

Author response

Regarding the tables, we reduced them to four, thus keeping only the tables containing the loadings because they were so important for interpreting the meaning of the principal components. Therefore, we propose to remove Tables 1 and 4 as they appeared in the manuscript and replace the current Table 3 by that containing the loadings for Approach A.

By just focusing on a single topic as suggested “wind direction and its effect on background ozone, would be a more powerful contribution to the literature” we would limit our study to what others did. We wanted to look at the data in different ways to improve the estimation of regional background O₃ in the HGB region on the longest term possible and to assess its trends. To estimate regional background NO_x it was important to analyze O₃ and NO_x simultaneously. We added one more level of complexity by simultaneously analyzing chemistry and meteorology. These are not different topics. In this context, we found it important to report all the relevant statistics that provide support to the figures and to our analysis and interpretation.

References

- Daum, P. H., Kleinman, L. I., Springston, S. R., Nunnermacker, L. J., Lee, Y.-N., Weinstein-Lloyd, J., Zheng, J., Berkowits, C. M.: A comparative study of O₃ formation in the Houston urban and industrial plumes during the 2000 Texas Air Quality Study, *J. Geophys. Res.*, 108, D23, 4715, doi:10.1029/2003JD003552, 2003.
- Langford, A. O., Senff, C. J., Alvares, R. J., Banta, R. M. and Hardesty, R. M.: Long - range transport of ozone from the Los Angeles Basin: A case study, *J. Geophys. Res.*, 37, doi:10.1029/2010GL042507, 2010.
- Neuman, J. A., Nowak, J. B., Zheng, W., Flocke, F., Ryerson, T. B., Trainer, M., Holloway, J. S., Parrish, D. D., Frost, G. J., Peischl, J., Atlas, E. L., Bahreini, R., Wollny, A. G., Fehsenfeld, F. C.: Relationship between photochemical ozone production and NO_x oxidation in Houston, Texas, *J. Geophys. Res.*, 114, doi:10.1029/2008JD011688, 2009.

Ryerson, T. B., Trainer, M., Angevine, V. M., Brock, C. A., Dissly, R. W., Fehsenfeld, F. C., Frost, G. J., Goldan, P. D., Holloway, J. S., Hübler, G., Jakoubek, R. O., Kuster, W.C., Neuman, J. A., Nicks, D. K., Parrish, D. D., Roberts, J. M., Sueper, D. T.: Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *J. Geophys. Res.*, 108(D8), 4249, doi:10.1029/2002JD003070, 2003.

Figures

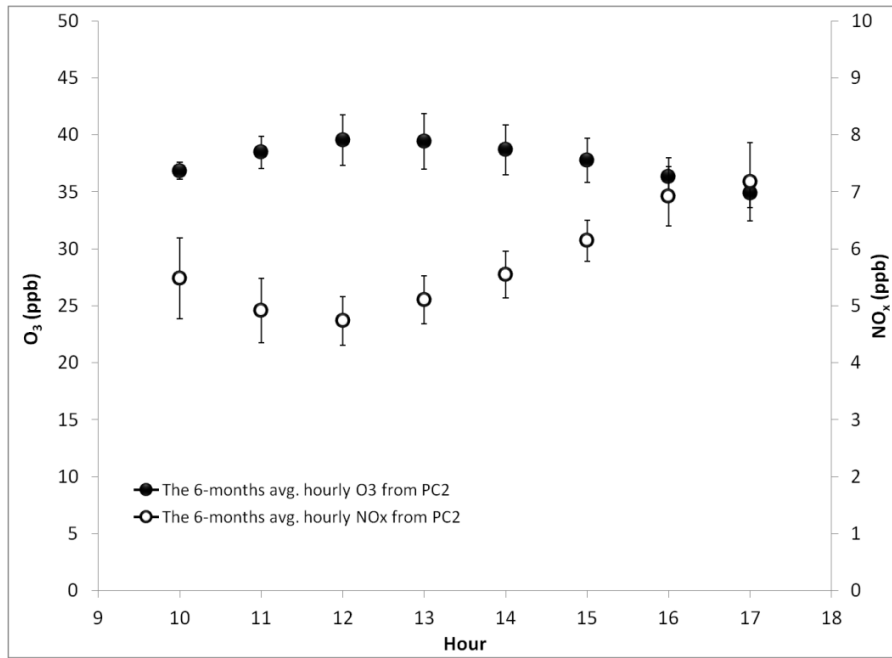


Figure 1: The season averaged hourly local O₃ and NO_x. Error bars represent the 95% confidence interval for the mean.