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

Author response

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

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

Regarding the use of the 8-h average NOx corresponding to the MDA8 O3 to estimate background NOx, please see our statement on P15, L31. We could also look at Fig. 5 in the manuscript and compare the 8-h average background NOx corresponding to MDA8 O3 (Approaches A-C) with the adjusted hourly background NOx unconstrained by 1-h peak O3 (the hourly median approach). The background NOx from the hourly median approach, averaged over 8 daytime hours for comparison, is lower by 1-2 ppb than the 8-h average background NOx 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 NOx when the 8-h average NOx corresponding to MDA8 O3 is used in the analysis.

We also agree that O3 and NOx 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 NOx, which we see in Fig. 3 of the manuscript. For the local effects (inferred from PC2), we found that hourly local O3 and NOx 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

NOx is defined in the introduction to be the sum of NO and NO2. But the monitoring NOx 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 NOx 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 NOx is used to examine background levels, there needs to be considerably more examination of the data, and it may be impossible to use NOx for this sort of analysis. For example, all of the trends in NOx could be dominated by changes in partitioning between the NOx oxidation products (PAN, organic nitrates, and HNO3), rather than a reduction in NOx. If the ratio of organic nitrogen to HNO3 has changed in the background air (which is likely), then the monitoring NOx instruments would likely respond in a way that would alter trends in NOx.
Author response

Indeed the monitored total NO\textsubscript{x} might account for other oxidation products, such as PAN and HNO\textsubscript{3}. However, the majority of the sites used to derive background NO\textsubscript{x} (constrained by MDA8 O\textsubscript{3}) 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\textsubscript{x} is not a problem for these sites. Therefore, conversion to PAN and HNO\textsubscript{3} might have a weak effect on the temporal trends in background NO\textsubscript{x} in the HGB region.

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

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

Therefore, we added the following on P4, L2:

"Public data, representing 1-h average of surface measurements of O\textsubscript{3}, NO\textsubscript{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\textsubscript{x} might include traces of other oxidation products (PAN, HNO\textsubscript{3}, etc.)."

We also made the following revision on P16, L12:

"Background NO\textsubscript{x} also declined in all approaches, with significant slopes (see Table 7). No other long-term background NO\textsubscript{x} studies exist, making comparison impossible. Additionally, there is no long-term evidence on the effect of NO\textsubscript{x} conversion to PAN and HNO\textsubscript{3} that could affect its temporal decline. Considering that the majority of the sites used to derive background NO\textsubscript{x} are urban sites or sites that are affected by fresh emissions, we could assume that conversion to PAN and HNO\textsubscript{3} might have had a minor effect on the temporal trends in background NO\textsubscript{x}."

Referee comment

The background NO\textsubscript{x} value of 6.8 ppbv is surprisingly large, and it is inconsistent with the 2000 and 2006 intensive field studies that showed NO\textsubscript{x} upwind of HGB was often <1 ppbv, and NO\textsubscript{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 O\textsubscript{3} 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\textsubscript{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\textsubscript{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\textsubscript{x} were truly 6.8 ppbv, then NO\textsubscript{x} emission controls in HGB would need to be reconsidered. NO\textsubscript{x} is short-lived, and it is possible that the NO\textsubscript{x} measured at these monitoring stations is strongly influenced by local emissions. I recommend removing the analysis of background NO\textsubscript{x}, or adding substantial discussion and examination of the NO\textsubscript{x} data.
The two intensive field campaigns indeed show smaller NO₂ 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 NO₂ mixing ratios are measurements made from aircrafts that cannot be directly compared to background NO₂ 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 NO₂ 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 NO₂ mixing ratios (<1 – 5 ppb) from the morning flights over the southeast of Houston, but NO₂ also reached 10 ppb over the city during that time. Neuman et al. (2009) measured in-plume NO₂ during daytime (3-5 pm) ranging from 1 to 10 ppbv. Although our daytime background NO₂ 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 NO₂, 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 NO₂.

Our first time estimate of long-term 8-h average background NO₂ (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 NO₂ in the HGB region only from the component identified as being "regional". We acknowledge that by constraining the 8-h average NO₂ 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 NO₂, 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 NO₂ 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 NO₂ compared to the hourly median approach by 7-9 ppb. Similarly, average background NO₂ is consistent between approaches in this study (A-C), but overestimated compared to the hourly approach by 1 ppb, on average. It is possible that we likely overestimate both background O₃ and NO₂ when the 8-h average NO₂ 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 NO₂ are both slightly overestimated compared to the hourly median approach, likely due to constraining the 8-h average NO₂ (and meteorology) by the MDA8 O₃. Future studies should consider refining these estimates by analyzing the 8-h average NO₂, 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 NO₂ 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 NO₂ 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 NOx 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 NOx in Fig. S19. The reason could be the intra-seasonal variation, spring versus summer/fall. We explained that for NOx 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:NOx ratio makes ozone difficult to control locally. I think the whole point of this paper is that large background contributions, rather than the VOC:NOx, 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 NOx 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 (NOx = nitrogen dioxide (NO2) + nitric oxide (NO)). Our goal is to better characterize the trends in regional background O3 and NOx in the HGB region on the decadal scale.”

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

“Because of its dependence on the volatile organic compounds (VOCs) to nitrogen oxides (NOx) 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 (NOx), together with their chemistry contribute to the O3 and NOx 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. S6 shows that at wind speeds > 4 m s⁻¹, the PC2 NOₓ scores are positive (suggesting an increase in NOₓ). This is the case for October. During this month, winds were from SE (Fig. S6d). Together the two wind variables say that some regional NOₓ 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 NOₓ it was important to analyze O₃ and NOₓ 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


Figures

![Graph showing season-averaged hourly local O₃ and NOₓ](image)

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