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Interactive comment on "Regional background O_3 and NO_x in the Houston-Galveston- Brazoria (TX) region: A decadal-scale perspective" *by* Loredana G. Suciu et al.

Anonymous Referee #2

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The manuscript "Regional background O3 and NOx in the Houston-Galveston-Brazoria (TX) region: A decadal-scale perspective" by Suciu et al. determines the composition of air coming in to the region using a principal component analysis of O3 and NOx monitoring data. The results for background O3 presented here are consistent with previous studies that used similar data and analysis. New contributions include consideration of long-term changes in meteorology and in background NOx. The manuscript is well-organized has been edited carefully.

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

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ozone. 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 anti-correlate. So this analysis could miss large NOx values that occur earlier in the day.

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 NO-NO, 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.

The background NOx value of 6.8 ppbv is surprisingly large, and it is inconsistent with the 2000 and 2006 intensive field studies that showed NOx upwind of HGB was often <1 ppbv, and NOy 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 NOx on tropospheric ozone formation in Houston, Texas, J. Geophys. Res., 108(D8), 4249, doi:10.1029/2002JD003070; Neuman, J. A., et al., Relationship between photochem-

ical ozone production and NOx 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 NOx were truly 6.8 ppbv, then NOx emission controls in HGB would need to be reconsidered. NOx is short-lived, and it is possible that the NOx measured at these monitoring stations is strongly influenced by local emissions. I recommend removing the analysis of background NOx, or adding substantial discussion and examination of the NOx data.

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?

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.

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.

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