

# Identifying Long-range Sources of Ozone Utilizing an Adjoint Method

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## ABSTRACT

It has been observed that local ozone concentrations can be impacted by both local emissions and by emissions that were transported from distant source regions. Thus, changes in ozone concentration in a particular region can only be understood by analyzing the precursor emission sources, such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and volatile organic compounds (VOC), over multiple regions. In this study, the primary sources of ozone concentration in seven receptor regions within North and Central America were quantitatively described by employing the GEOS-Chem model and its adjoint. The model results across all regions showed that the mean contribution of natural emissions to ozone concentration was 57% less than the contribution of anthropogenic emissions. It was also observed that local emissions have a larger contribution (at least 60%) to ozone concentrations than long-range transport in all observed regions except for eastern Canada. Further results show that peak ozone concentration and transport between regions in the model mostly occur during the spring and summer months. The exception to this trend was seen in Mexico, which had its largest ozone concentration and intake of transported emissions during Northern Hemisphere winter. Overall, this study concludes that ozone concentration and transport depend on a number of factors including emission type, season and geographical location.

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## 1. Introduction

Ozone is a secondary air pollutant that has a wide range of effects on our environment from contributions to climate change to increased health problems. With higher surface ozone concentrations, these environmental problems continue to increase. The concentration of ozone in the atmosphere is heavily dependent on the emissions of ozone precursors, such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and volatile organic compounds (VOC). These emissions can be anthropogenic or natural and have been observed to be transported long-distances to impact communities outside of the origins. Though local emissions have the greatest impact on local ozone concentration, the ozone concentration cannot be completely understood without examining the long-range transportation as well.

Long-range transports of aerosols and ozone have been examined in previous studies. Park et al. (2004) used the GEOS-Chem model to study the transport of sulfate-nitrate-ammonium aerosols. To examine how much a source region contributed to concentrations of these aerosols, they turned off the emissions of source regions and subtracted that from the base model run. Though this research was focused on sulfate-nitrate-ammonium the same method can be used to model ozone transport. Their method was sufficient for large regions, but was too computational for observing smaller source regions.

Zhang et al. (2009) applied a receptor-oriented method using the GEOS-Chem and its adjoint model to examine the ozone transport to two receptors. This method allowed quantification of the Asian contribution to the two receptor regions in the United States. The receptor-oriented method was more computationally efficient in calculating how much transport comes from source-regions.

Long-range transport does not only happen between the Asian continent and the United States. West et al. (2009) used the MOZART-2 to identify how NO<sub>x</sub> emissions influenced ozone concentrations in nine world regions. NO<sub>x</sub> emissions were reduced by 10% within one of the regions to examine how this impacted the ozone concentrations in the other eight regions. This allowed the long-range transport to be quantified, but on quite a large scale.

The Hemispheric Transport of Air Pollution (HTAP) 2010 stated that North America, Europe, South and East Asia were the largest contributors to anthropogenic NO<sub>x</sub> emissions. It was also explained that North America was the largest per capita. (Cooper et al., 2010) To reduce global surface ozone concentrations, these large source regions would need to all reduce their own ozone concentrations. The problem is these regions are having smaller subsections within them that have different geographical locations and land-use that causes different ozone concentrations across the region.

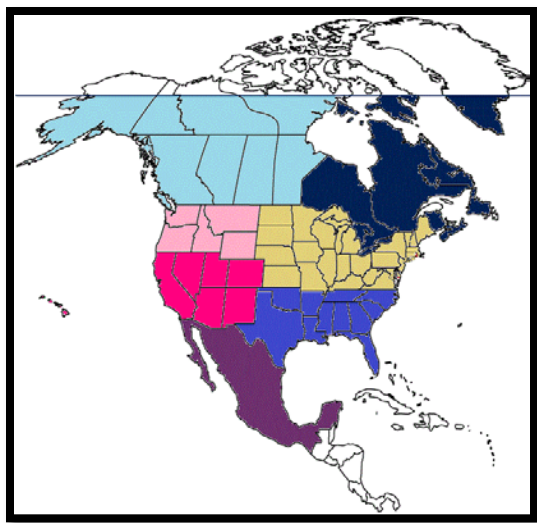
The objective of this research was to quantify the transport of ozone between seven regions in North America to understand the different ozone concentrations in North America. The GEOS-Chem and its adjoint were used to model the transport of NO<sub>x</sub>, CO, and VOCs using the receptor-oriented methods. The contribution of primary emissions to each receptor region was examined. The primary emissions are broken down into anthropogenic and natural emissions. How much anthropogenic emissions contributed to the receptor regions ozone concentration versus natural emissions was calculated. In Section 2, the GEOS-Chem model and

its adjoint will be explained along with the methodology. In Section 3, the results of the research will be presented and discussed.

## 2. Air Quality Model

The GEOS-Chem chemical transport model (Bey et al., 2001) is governed by NASA Goddard Earth Observing System Assimilated Meteorological data. The GEOS-5 dataset is on a  $2 \times 2.25$  horizontal grid and 47 vertical layers. Hemispheric Transport of Air Pollution (HTAP) 2010 emissions data was used in this study.

The GEOS-Chem adjoint (Henze et al., 2007) is a backward run of the model. It calculates  $\frac{\delta J}{\delta \epsilon}$  where  $J$  is concentration of the pollutant being examined and  $\epsilon$  is the change of the emissions. The adjoint method with the GEOS-Chem model began in 2003, but was not implemented with full chemistry simulations until 2005. We used the adjoint model to solve the inverse problem of the sources of surface ozone in North America.



**Figure 1:** The seven regions focused on during this study were the Northeast US (tan), Southeast US (light purple), Northwest US (salmon), Southwest US with Hawaii (hot pink), Eastern Canada (navy blue), Western Canada with Alaska (light blue), and Mexico (violet).

There were seven regions within North America focused on during this study. They were the Northeast United States, Southeast United States, Northwest United States, Southwest United States with Hawaii, East Canada, West Canada with Alaska and Mexico (Figure 1). These regions spanned different geographical locations, which have different seasons and climates. All the regions were examined for the year 2010.

To first examine the emission types that affect ozone concentrations, it was calculated how much anthropogenic versus natural emissions affect each of these regions. The anthropogenic emissions were then broken down into  $\text{NO}_x$ , CO, and VOC emissions to determine which of these impacted ozone concentrations the most.

The next elements examined were local versus long-range sources. HTAP Receptor Masks were used to separate the contribution the regions made on each other. This was then used to calculate the percent each region had on a specific region's ozone concentrations. The final element examined was the seasonality of ozone concentrations. This was based off the six month average of the daily one hour mean having the greatest values.

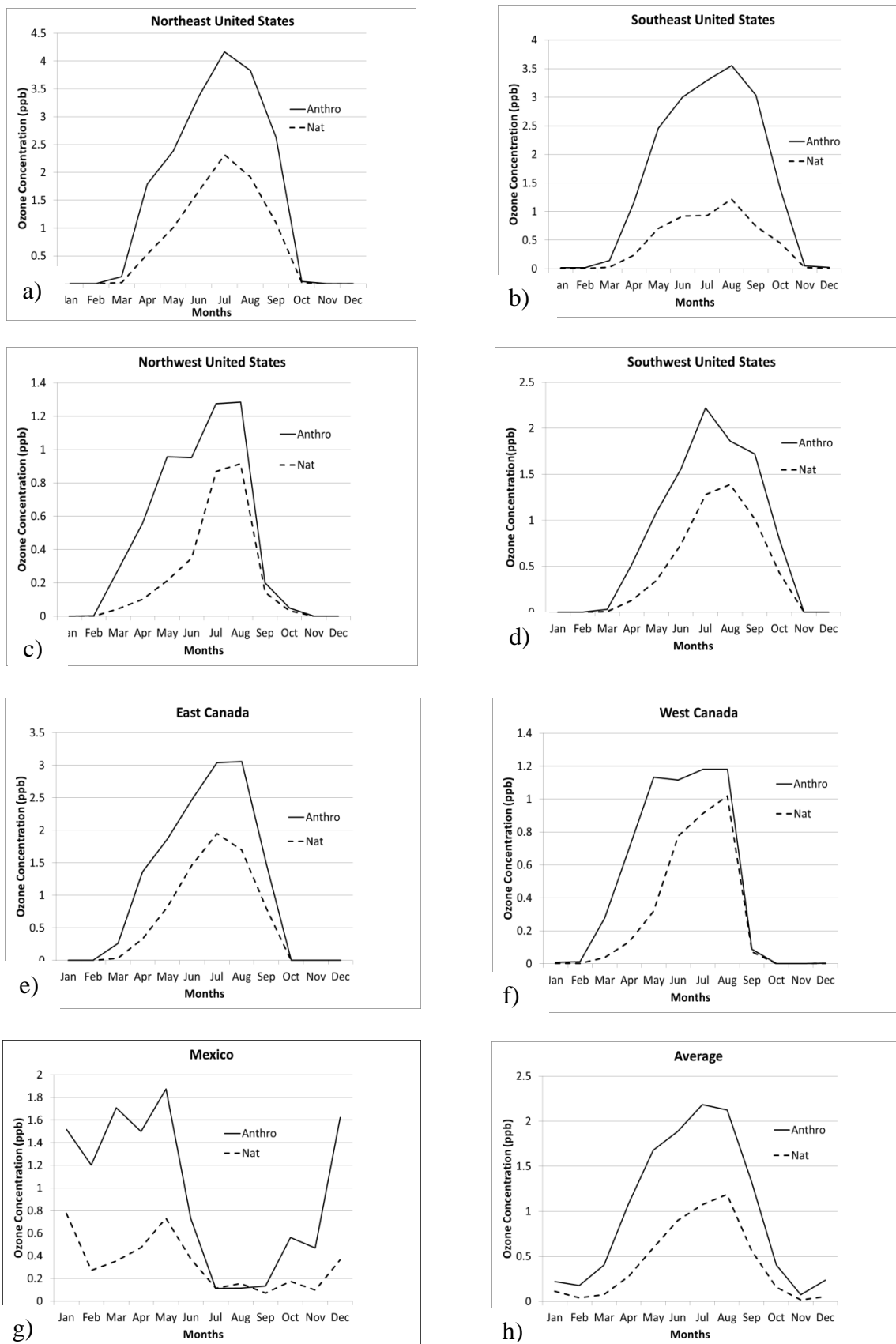


Figure 2: Time Series of anthropogenic (solid) vs natural (dashed) emissions to the six month mean of one hour maximum ozone concentration for each of the seven regions (a-g) and averaged over all regions (h).

### 3. Results and Discussion

The anthropogenic and the natural contribution to the six month mean of one hour maximum surface ozone concentration was calculated for each of the seven regions (Figure 2). On average, it was observed that natural emissions contributed 57% less than the anthropogenic emissions. Both anthropogenic and natural emissions were observed to peak within the same season for all regions. This suggested that there was a specific season more conducive to produce ozone.

The Southeast United States had the lowest natural contribution with natural emissions contributing 71% less than the anthropogenic contribution. The two regions with the highest natural contribution were the Southwest United States with Hawaii and Western Canada with Alaska with natural emissions contributing 45.6% and 45.5% less than anthropogenic contributions respectfully. Both of the regions are along the west coast and are downwind from the ocean, which might explain the higher natural contribution.

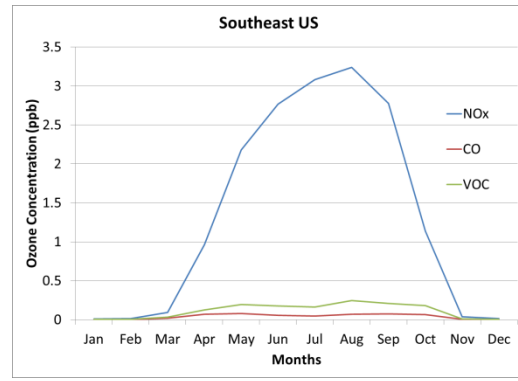
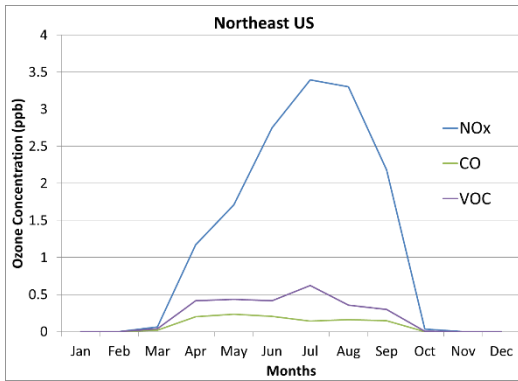
The anthropogenic NO<sub>x</sub>, CO, and VOC contribution to the six month mean was also examined to identify which anthropogenic emission contributed most to ozone concentration (Figure 3). When looking at all regions, NO<sub>x</sub> emissions were the highest contributor ranging from 76-90%. As a whole this was followed by VOCs ranging from 7-15%, and finally CO ranging from 2.5-8.5%.

The region with the highest NO<sub>x</sub> contribution was the Southeast United States with 90% and the region with the lowest NO<sub>x</sub> was Eastern Canada with 76%. For CO the region with the highest contribution was Eastern Canada with 9 % and the lowest was the Southeast United States with 2.5%. Finally for VOCs the highest contributor was Eastern Canada with 15% and the lowest was Western Canada with 6.8%.

It makes since that Eastern Canada had the lowest NO<sub>x</sub> emission contribution, but the largest CO and VOC concentration. This suggested that Eastern Canada produces the least NO<sub>x</sub> emissions and the most CO and VOC emissions, but it could also be due long-range sources for NO<sub>x</sub>, CO, or VOCs.

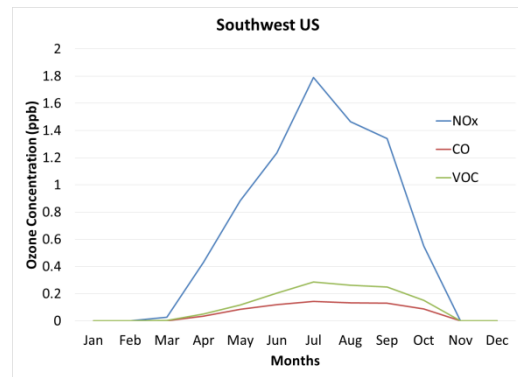
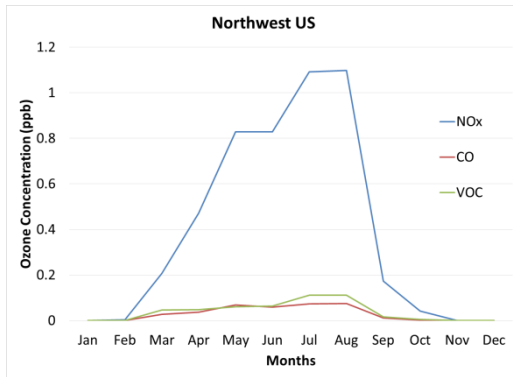
Long-range refers to species that are transported into the receptor. In this study, local emissions (emissions that come from the receptor region) generally accounted for 60-90% of the local ozone concentrations (Figure 4). The region with the highest local contribution was found to be Mexico with 90%. The lowest region was Eastern Canada with local emissions only accounting for 34%, which was outside the general range.

Eastern Canada was the only region in this study where local emissions did not contribute the most to ozone concentration (Figure 4e). The main contributor was the Northeast United States with the contribution of 50%. The Northeast includes many major cities including New York, Chicago and Cleveland, which would produce more anthropogenic emissions. Eastern Canada doesn't have as many major cities as the Northeast within its region to allow for the high local contribution. It was also downwind from the Northeast allowing for easier transport.



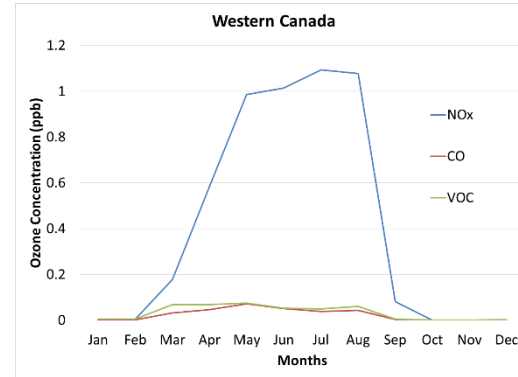
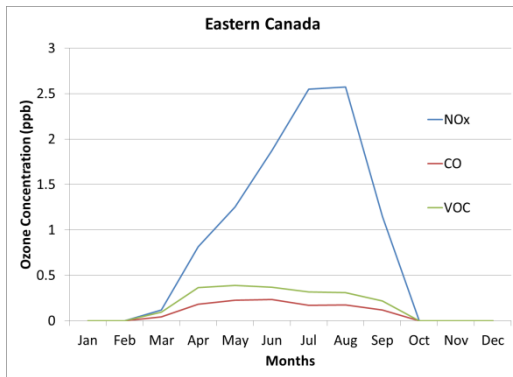
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b)



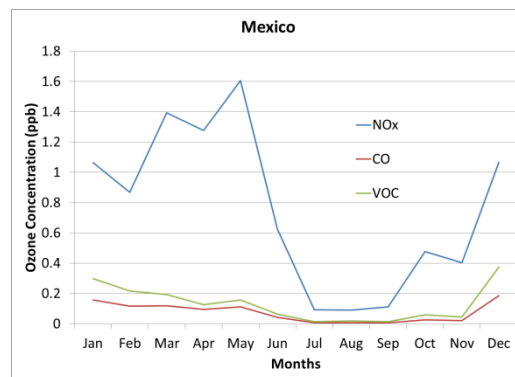
c)

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e)

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g)

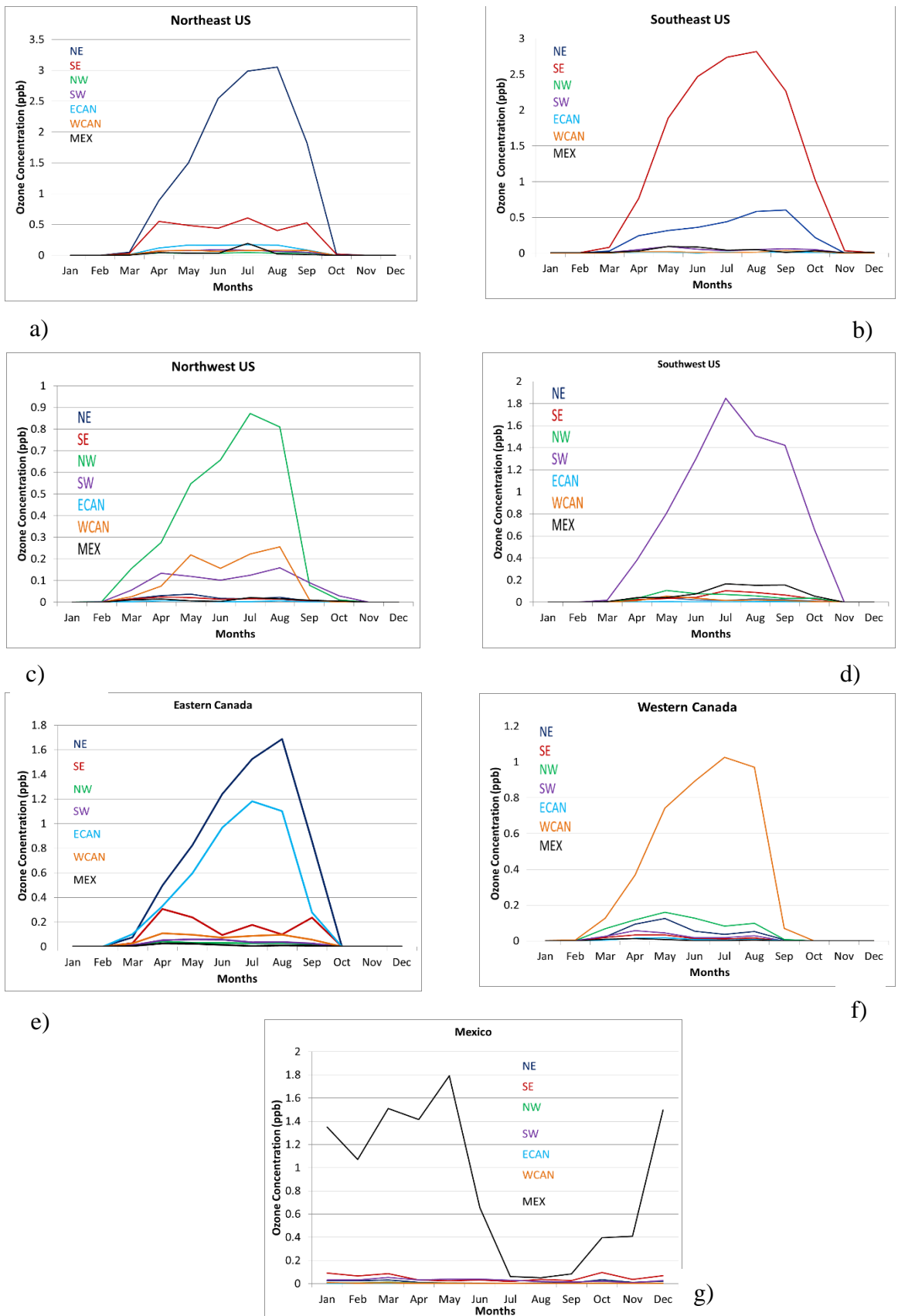


Figure 4: Time series of source regions anthropogenic contribution to receptor's (a-g) six month mean of the one hour maximum surface ozone concentration.

Seasons also can contribute to how much ozone is produced. An ozone season is where

the six month average of the daily one hour maximum ozone was the greatest. In this study it was found that the main ozone season was the spring and summer months. This was most likely due to the extended hours of sunlight during these months allowing for more production of ozone. The exception to this finding was Mexico.

Mexico's ozone season was found to be during the winter months (Figure 4g). This was thought to be due to Mexico being more equatorward and having extended hours of sunlight throughout the year, which lead to the belief that Mexico's ozone concentration holds a more constant concentration throughout the year. Further research would need to be done to verify Mexico's generally constant ozone concentration throughout the year.

#### **4. Conclusions**

This study demonstrated that anthropogenic NO<sub>x</sub> emissions had the greatest impact on ozone concentrations in North America. It also was shown that overall local emissions contribute more than long-range sources to local ozone concentrations. The exception to this was Eastern Canada, where the Northeast contributed 50% to the ozone concentrations compared to Eastern Canada's 34%. Finally it was shown that the spring and summer months are the main ozone season for all regions except Mexico. These findings can have impacts on the policies being created to lower surface ozone concentrations.

Regulations are being developed for states to control their own ozone by the EPA, who only considers "long-range" influences to be 1%. This study found long-range influences to be 10-40% and 66% for Eastern Canada. These results show that the regulations cannot be based on 1% of long-range transport. With states being held solely responsible to lower their own ozone concentrations, the concentrations will be lowered but not as low as expected if the long-range sources that contribute 10-40% are not also reduced.



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