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Ozone Formation Sensitivity to NOx and VOC Emissions in the LADCO Region

Technical Report

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EXECUTIVE SUMMARY

Ozone concentrations at surface monitors in parts of the LADCO region have consistently violated National Ambient Air Quality Standards (NAAQS) for O_3 over the last 40 years. As a result, many areas have been designated nonattainment of these standards. Emissions of the O_3 precursors, nitrogen oxides (NOx) and volatile organic compounds (VOC), have decreased dramatically since the 1990s. While these reductions have helped to decrease monitored O_3 concentrations, the O_3 concentration reductions have lagged behind the reductions in O_3 precursor emissions. Ozone is formed through complex, nonlinear reactions of NOx with VOC in the presence of sunlight. In order to develop the most effective O_3 control strategies, it is crucial to understand whether ozone formation is more sensitive to changes in NOx or VOC emissions.

This report applies a suite of analytical tools to air quality data in the Great Lakes region to determine whether ozone formation in the region is most sensitive to NOx- or VOC-emissions changes. This study also examines how the ozone-NOx-VOC chemistry has changed over the past decades. This study applied five new analyses to these problems. The first three approaches involved the use of molecular ratios as indicators of the ozone formation chemistry, with certain ranges of ratio values indicating NOx-sensitive, transitional, or VOC-sensitive ozone chemistry. The second two approaches used patterns in ozone concentrations to infer the ozone formation chemistry. All analyses focused on the ozone formation chemistry on high-ozone days. The five approaches are described below.

Ground-based formaldehyde-to-NO_2 (HCHO/NO_2) indicator ratios. This study examined these ratios at nine monitoring sites in the region over the last 30 years. The sparsity of ground-based HCHO/NO_2 data both spatially and temporally limits the usefulness of this ratio for determining O_3-NOx-VOC sensitivity in most parts of the LADCO region. Nevertheless, these measurements demonstrate that O_3 formation in the urban areas of the Great Lakes states has become less VOC-sensitive over the last few decades, with O_3 formation at these urban monitors shifting from primarily VOC-sensitive in the 1990s to primarily transitional in the 2010s. Ground-based

$HCHO/NO_2$ measurements may be especially useful in combination with other estimates of O_3 formation chemistry, such as from satellites, models, and spatial and temporal patterns in O_3 concentrations.

Satellite-based $HCHO/NO_2$ indicator ratios. This study applied these ratios to satellite data from 2018 and 2019. This analysis of TROPOMI satellite data finds the highest NO_2 columns in the Chicago area, followed by Detroit, with similar levels on days with O_3 exceeding the 2015 O_3 NAAQS and over the O_3 season as a whole. The highest HCHO columns were observed in the southern areas of the region, particularly St. Louis and Louisville on O_3 exceedance days in those areas. Application of ratio thresholds from Jin et al. (2020) to observed $HCHO/NO_2$ ratios estimated that O_3 formation chemistry in most nonattainment areas in the LADCO region was sensitive to NOx emissions. According to this analysis, all of the Western Michigan areas, Cleveland and St. Louis and almost all of the Wisconsin lakeshore, Louisville and Cincinnati were NOx-sensitive on O_3 exceedance days. Chicago and Detroit were the only areas with any VOC-sensitive areas, and the VOC-sensitive area was larger in Chicago than in Detroit. However, approximately half or more of the grid cells in these areas remained NOx-sensitive on exceedance days, primarily in the outlying parts of the nonattainment areas. These patterns are driven by a combination of high NO_2 columns in Chicago and Detroit from urban plumes and high HCHO columns from biogenic emissions in the southern areas. NO_2 emissions from coal-fired power plants also impacted the O_3-NOx-VOC sensitivity, particularly near the largest plants in the Ohio River Valley.

Model-based $HCHO/NO_2$ and hydrogen peroxide-to-nitric acid (H_2O_2/HNO_3) indicator ratios. This study examined modeling for the years 2016, 2020, and 2028 and is the only approach that directly predicted future changes in ozone. Results projected that concentrations of O_3 and precursor compounds will continue to decrease throughout the region. Analysis of model-derived ozone chemistry indicator ratios show that ozone formation is shifting away from VOC-sensitivity and towards more NOx-sensitivity throughout the region. The Chicago area is consistently the most VOC-sensitive area, and southern areas, particularly St. Louis, are the

most NOx-sensitive. The $HCHO/NO_2$ ratio suggests the presence of some areas of VOC sensitivity in all of the nonattainment areas in 2016, although the majority of the grid cells in most of the nonattainment areas are NOx-sensitive. In contrast, the H_2O_2/HNO_3 ratios suggest that at least 80 to 90% of the grid cells in all of the nonattainment areas were NOx-sensitive in 2016, with much smaller areas of VOC-sensitivity and transitional chemistry. The differences between the chemistry regime classifications based on the two indicator ratios may indicate an issue with the ratio threshold estimates, most likely for the H_2O_2/HNO_3 ratios.

Analysis of weekday-weekend differences in ozone concentrations. This study takes advantage of the difference in weekday-weekend NOx concentrations to examine how ozone responds to these NOx changes. This analysis of ozone-conducive days in the LADCO region shows that ozone concentrations have decreased in almost all areas over the past 20 years. As ozone has decreased, almost all areas have shifted towards more NOx-sensitive ozone formation. Ozone formation in southern areas (St. Louis, Louisville, and Cincinnati) was NOx-sensitive for most of this time period and became more so during this time. Ozone formation in Chicago and around Lake Michigan shifted from significantly VOC-sensitive to NOx-sensitive in most areas, and central Cleveland was the only VOC-sensitive part of the region in 2016-20. The reductions in ozone MDA8 concentrations appeared to have been driven by reductions in both NOx and VOC emissions. Importantly, reductions in reactive VOCs helped decrease ozone concentrations on ozone-conducive days even when ozone formation was heavily NOx-sensitive. This indicates that the greatest reductions in ozone will be achieved by a combination of NOx and VOC emissions.

Analysis of trends in ozone concentrations over space and time. This study examines how ozone changes with distance from city centers and over time in response to decreasing NOx (and VOC) concentrations in these two dimensions. This analysis demonstrates that ozone concentrations have decreased over the last 30 years throughout the LADCO region. The patterns of ozone reductions relative to the city centers and over time reveals patterns in ozone formation chemistry in these areas. In the southern areas of St. Louis, Louisville, and Cincinnati, areas of VOC-sensitivity or transitional chemistry in the city centers shifted to NOx-sensitivity by the

mid-2000s, and ozone has decreased steadily since then. The northern areas of Chicago, Detroit, and Cleveland had a dramatic drop in ozone concentrations accompanied by an apparent shift in ozone chemistry in the mid-2000s. All of these city centers appear to have had VOC-sensitive chemistry early in the study period. Detroit and Cleveland appear to have mostly shifted to NOx-sensitive chemistry, with decreasing ozone concentrations, although some areas of transitional chemistry may remain in the city centers. In contrast, most of the Chicago area appears to have chemistry that is shifting from VOC-sensitive to transitional, resulting in ozone concentrations that are increasing over time. These three northern areas also had larger reductions in ozone concentrations in outlying areas relative to the city centers. Ozone concentrations along the Lake Michigan shoreline have decreased the most at areas far downwind (north) of Chicago, while locations closer in to the city have decreased at a slower rate. These trends likely result from the lower amounts of ozone precursors in the relatively isolated over-lake plumes transported from the Chicago area northward. As ozone precursor emissions have decreased over time, the precursors in the plumes appear to be "used up" faster, resulting in decreasing concentrations in downwind portions of the plumes.

Each approach yielded somewhat different classifications for the different areas, with some approaches agreeing better than others. By evaluating and comparing the different approaches, LADCO determined our best estimate of the recent ozone formation chemistry in the different areas (Table ES.1). Most of the urban areas have transitional chemistry in their centers, but the only city that is clearly VOC-sensitive is Chicago. Chicago has a large area of VOC-sensitive chemistry, extending to roughly 60 km from the city center. However, ozone formation in this area appears to be shifting to transitional chemistry. The areas beyond the central part of Chicago appear to be on the NOx-sensitive side of transitional chemistry.

Ozone formation in all parts of the LADCO region has become less VOC-sensitive and more NOx-sensitive over the last 30 years. The central parts of most urban areas were VOC-sensitive in the early 1990s and shifted to transitional chemistry over the intervening 30 years. Ozone formation in the southern cities of Louisville and Cincinnati began as transitional, not

VOC-sensitive. The urban cores of these cities still appear to be transitional, although the extents of the transitional areas have shrunk as the surrounding NOx-sensitive areas have expanded. While Chicago has continued as VOC-sensitive, ozone formation in this city has also shifted towards transitional and NOx-sensitive.

Table ES.1. LADCO's best estimates of recent ozone formation chemistry regimes in the different LADCO nonattainment and maintenance areas.

Area	Recent ozone-NOx-VOC chemistry (best estimate)
St. Louis	NOx-sensitive with transitional chemistry downtown
Louisville	NOx-sensitive with possible transitional chemistry downtown
Cincinnati	NOx-sensitive with transitional chemistry downtown
Detroit	NOx-sensitive with transitional chemistry downtown and to northeast
Cleveland	NOx-sensitive with transitional chemistry downtown and along lakeshore
Chicago	VOC-sensitive/transitional in the central 60 km or so; transitional/NOx-sensitive beyond.
WI Lakeshore	NOx-sensitive with transitional chemistry in downtown Milwaukee & along the southern lakeshore
Western MI	NOx-sensitive

Considering the evidence from these studies, combined with that from other published or contracted work, the best approaches to determine the ozone formation sensitivity appear to be: ground-based HCHO/NO_2 ratios using ratio thresholds from Blanchard (2020), TROPOMI satellite HCHO/NO_2 ratios using thresholds from Jin et al. (2020), High-order Decoupled Direct Method (HDDM) modeling, and the analysis of ozone trends over space and time. While each of these approaches performed well, they all have their limitations. The TROPOMI analysis did not perform as well in all areas, over-predicting VOC sensitivity in some areas and underpredicting it in others. Ground-based HCHO/NO_2 ratios are only available at a small number of monitoring locations, located almost exclusively in city centers, limiting the usefulness of this approach.

HDDM modeling is not widely accessible since it requires a high performance computing system as well as extensive expertise and knowledge. In contrast, the ozone trends analysis only requires examination of trends in ozone concentrations; however, this analysis requires subjective judgements and interpretations of complex trends over space and time. Overall, we suggest the use of at least two different approaches in tandem to better understand ozone formation sensitivities.

1. Introduction

Ozone (O_3) is one of the main components of photochemical smog. Breathing O_3 pollution can cause serious health impacts, including difficulty breathing, inflammation of and damage to the airways, and aggravation of lung diseases such as asthma and emphysema. Ozone pollution also causes damage to vegetation and ecosystems. Because of these impacts, O_3 is one of six pollutants regulated by the U.S. Environmental Protection Agency (EPA) via the National Ambient Air Quality Standards (NAAQS) program.

1.1. Ozone in the LADCO region

Ozone concentrations at surface monitors in parts of the LADCO region have consistently violated O_3 NAAQS over the last 40 years. The monitors with the highest O_3 concentrations are often located tens to hundreds of miles downwind of major emissions source regions (Figure 1 and 2), indicating that long-range transport of emissions contributes to the elevated O_3 concentrations. Emissions of the O_3 precursors, nitrogen oxides (NO_x) and volatile organic compounds (VOC), have decreased dramatically since the 1990s, with emissions of anthropogenic sources of both precursors being cut in half from 2002 to 2014 alone. While these reductions have helped to decrease monitored O_3 concentrations, the O_3 concentration reductions have lagged behind the reductions in O_3 precursor emissions. As a result, many areas in the region have been designated as nonattainment for multiple O_3 standards (Figures 1 and 2).

As of early July 2022, 9 areas in the LADCO region were designated nonattainment for the 2015 O_3 NAAQS (Figures 1.1 and 1.2). Six of these areas border Lake Michigan and three are urban areas in other parts of the LADCO region. Six other areas were originally designated nonattainment for the 2015 O_3 NAAQS but have since been redesignated to maintenance status (Figure 1.1). Seven areas have been redesignated to maintenance status for the 2008 O_3 NAAQS, including the Chicago area. Nonattainment area designations require the states to develop plans for how to bring the areas into attainment. As these attainment plans should include an

evaluation of different control strategies for NOx and VOC emissions, it is important for states to understand the factors driving O_3 formation in this region.

The highest O_3 concentrations in the region have consistently been around Lake Michigan (Figure 1.1) along the Wisconsin and Michigan lakeshores. Ozone concentrations are high in this area due to complex lake-driven meteorology that adds to regional pollution transported into the area (e.g., Dye et al., 1995; Stanier et al., 2021). Conceptually, on days that are conducive to high O_3 concentrations morning land-to-lake breezes blow emissions of O_3 precursors from urban and industrial areas, such as Chicago, Milwaukee, Gary and other areas, over the lake where they concentrate and react in a shallow boundary layer to form O_3 in high concentrations. Prevailing southerly or southwesterly winds move this polluted air northwards towards Wisconsin and/or Michigan, and midday or afternoon lake-to-land breezes ("lake breezes") move this air onshore. These pollutant air masses have the largest impacts along the coast of Lake Michigan, as indicated by the high concentrations seen by the surface O_3 monitors that are located nearest the lakeshore. Ozone in the air masses is diluted or degraded as the air masses move inland, lowering O_3 concentrations (Cleary et al., 2022). Similar lake-driven factors impact O_3 formation in Cleveland and Detroit. The MOOSE field campaign of 2021 and 2022 in Southeast Michigan studied the role of the lake breeze on O_3 concentrations in Detroit.

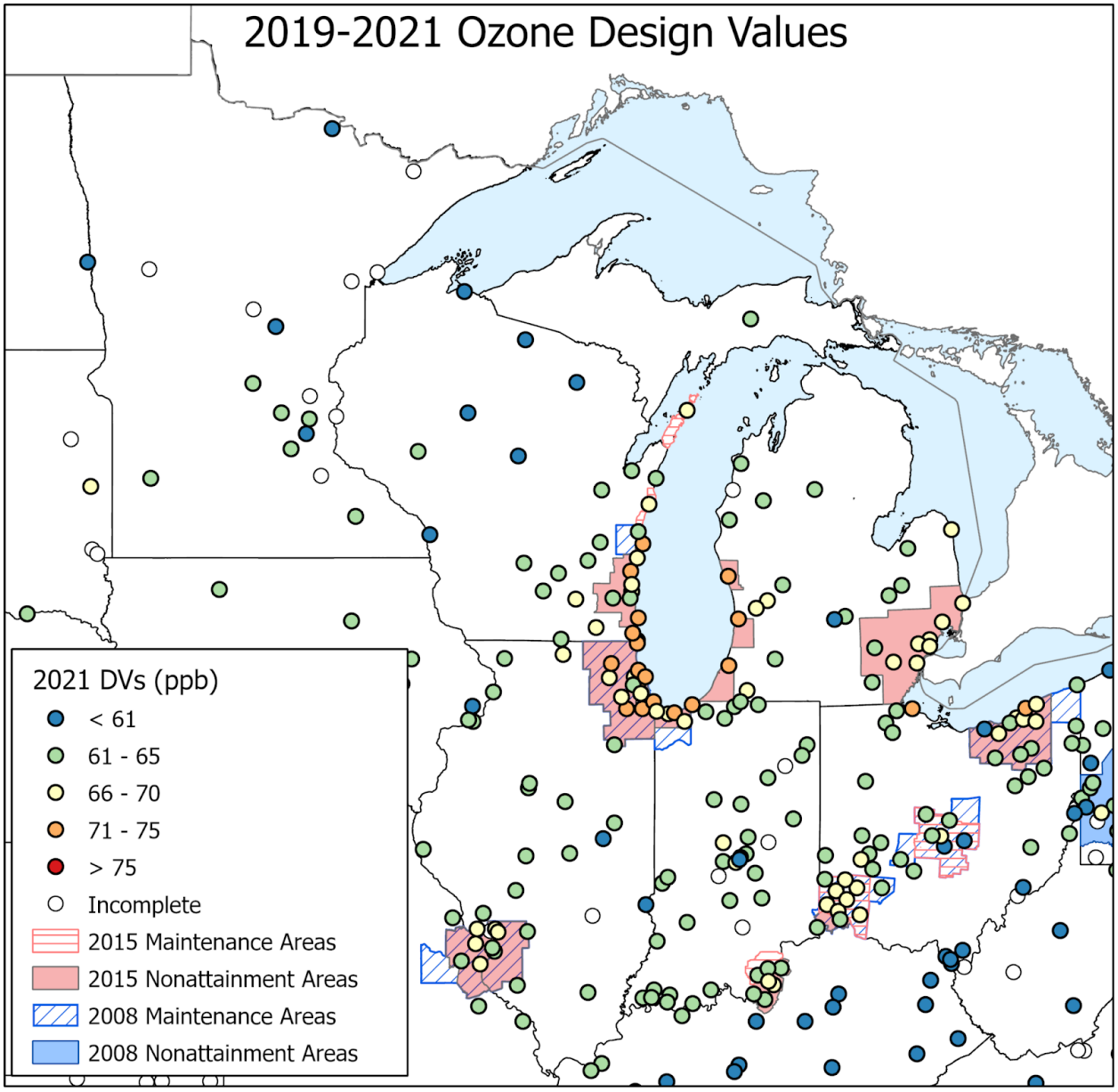

Figure 1.1. 2019-2021 ozone design values for the entire LADCO region. Nonattainment and maintenance areas for the 2008 and 2015 ozone NAAQS are shown for comparison. Where the two nonattainment areas overlap, the area appears purple.

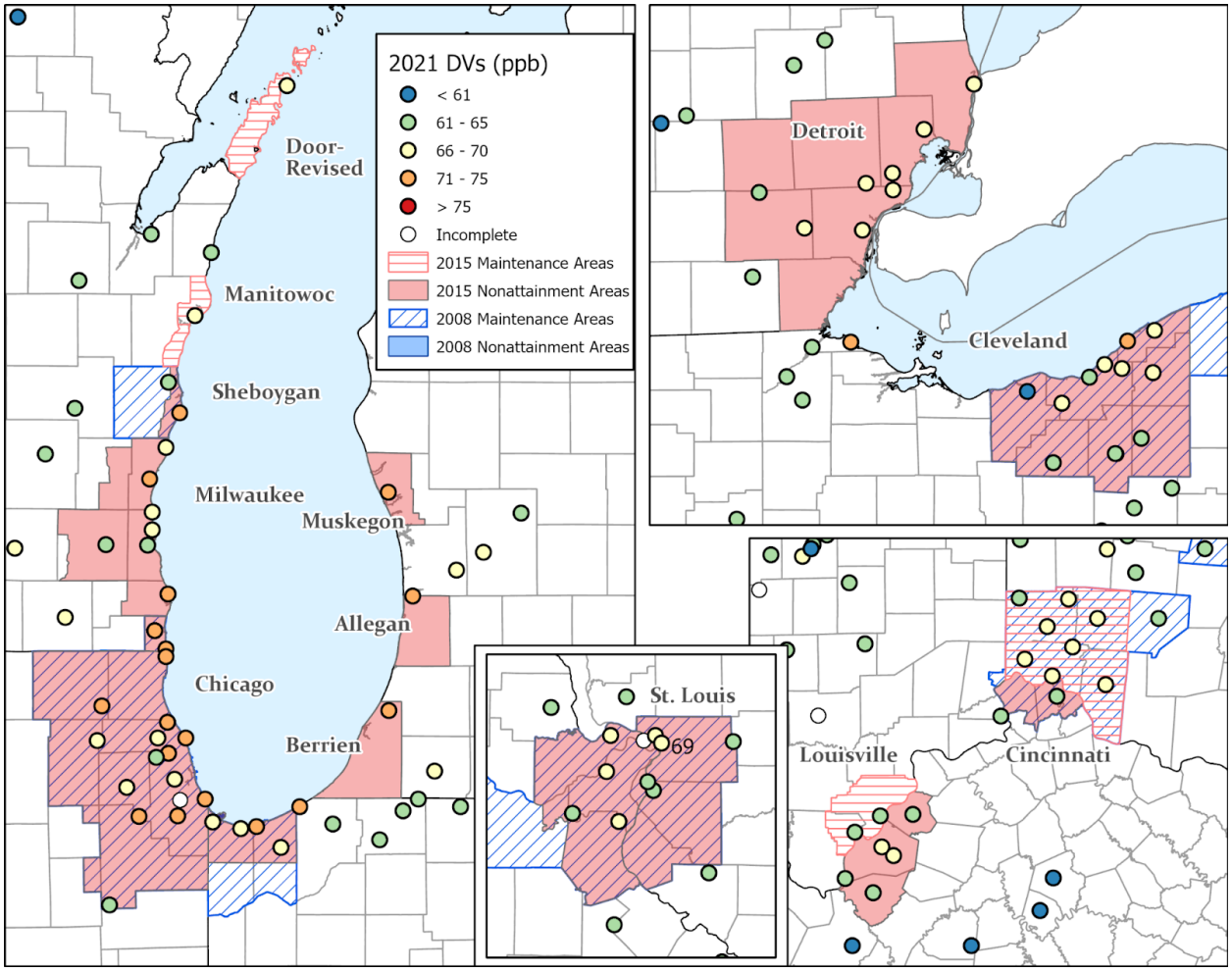

Figure 1.2. 2019-2021 ozone design values for the nonattainment and maintenance areas (labeled) in the LADCO region. Note that the Indiana and Ohio portions of the Louisville and Cincinnati areas have been redesignated to maintenance whereas the Kentucky portions have not. The nonattainment status of areas is given as of July 2022.

1.2. Ozone formation chemistry (Ozone-NOx-VOC sensitivity)

Ozone is formed through complex, nonlinear reactions of NOx with VOC in the presence of sunlight (Sillman, 1999; Pusede and Cohen, 2012). The term "ozone-NOx-VOC sensitivity" is a shorthand term describing whether O_3 formation in an area is responsive to changes in NOx emissions ("NOx-sensitive"), VOC emissions ("VOC sensitive"), or both ("transitional"). Under NOx-sensitive conditions, reductions in NOx will lead to much larger decreases in O_3 than would a similar reduction in VOCs; under these conditions, reductions in VOC emissions may have little

to no impact on O_3 formation. Under VOC-sensitive conditions, also known as "NOx-saturated" conditions, O_3 concentrations are more responsive to changes in VOC emissions. The situation with NOx emissions under VOC-sensitivity conditions is complex because reductions in NOx emissions may actually increase O_3 formation. These O_3 increases could occur via a reduction in the process known as "NOx titration", which occurs when fresh nitric oxide reacts with O_3 to form NO_2. Reductions in NOx emissions, particularly in urban areas, could reduce the amount of NOx titration that occurs, leading to increases in O_3 in these urban areas.[1] This reaction is reversed as the air mass travels downwind to reform the O_3. Under "transitional" conditions, O_3 concentrations are responsive to changes in both NOx and VOCs. In order to develop the most effective O_3 control strategies, it is crucial to understand the ozone-NOx-VOC sensitivity.

Freshly emitted pollutant plumes typically start off as more VOC-sensitive and become more NOx-sensitive as the plume ages (Sillman, 1999). This change in chemistry occurs in relatively isolated plumes transported over water bodies, such as the Great Lakes (e.g., Vermeuel et al., 2019), as well as those transported over land. As a result, O_3 formation tends to be the most VOC-sensitive in urban areas with large amounts of fresh NOx emissions and more NOx-sensitive in more rural areas with lower levels of fresh emissions (Sillman, 1999).

As NOx emissions and VOC emissions have decreased over the last several decades as a result of a number of regulatory control programs, the ozone-NOx-VOC chemistry around the country has changed. Ozone formation has generally shifted away from VOC sensitivity and towards NOx sensitivity. The areas of VOC sensitivity within urban areas have shrunk in extent, moving inwards towards the city centers, as the surrounding NOx-sensitive areas have expanded (Pusede and Cohen, 2012; Jin et al., 2020; Koplitz et al., 2022). Ozone formation in the U.S. is generally considered to be NOx-sensitive, and most recent control programs (e.g., the Revised Cross State Air Pollution Rule Update and the proposed Clean Trucks Rule) have focused on reducing NOx emissions. However, the ozone-NOx-VOC sensitivity may vary dramatically from

[1] In addition to titration, the reaction rate of NO with RO_2 radicals to form O_3 also impacts ozone responses under high-NOx conditions. This reaction rate peaks at intermediate levels of NOx and slows at higher levels of NOx, such that ozone is formed more slowly at high NOx concentrations. The net impact of these two factors is similar, so we consider them together in this discussion.

location to location, such that different areas would most benefit from a different combination of emissions control programs.

1.3. Recent studies of ozone-NOx-VOC sensitivity in the LADCO region

A number of recent studies have investigated the ozone-NOx-VOC sensitivity of ozone formation in the LADCO region. Much of this work has focused on the Lake Michigan area as it is the area in the region with the highest O_3 concentrations.

In 2020, LADCO and the Wisconsin Department of Natural Resources (WDNR) awarded two contracts to perform analyses to determine the sensitivity of O_3 formation in Chicago and along Wisconsin's Lake Michigan shoreline to changes in NOx and VOC concentrations. The principal focus of this work was on the current ozone-NOx-VOC sensitivity in this area, including the spatial variability of such sensitivity. The work also described how this sensitivity has changed over time. This work relied upon already existing ground-based and remote sensing (e.g., TROPOMI) datasets, including observation-based methods. These studies also applied complementary modeling analyses using a generalized additive model (GAM) and a chemical box model. Full reports of this work are available on the LADCO webpage.[2] One component of this study expanded the analysis of ozone-NOx-VOC sensitivity in air parcels transported over Lake Michigan from Vermeuel et al. (2019) to additional days.

These studies found that O_3 formation in the Chicago area is VOC-sensitive and NOx-inhibited during the O_3 season as a whole and on exceedance days. Ozone formation in air masses transported northward from Chicago on high-O_3 concentration days begins as more VOC-sensitive and becomes more NOx-sensitive as air parcels travel northward over Lake

[2] Charles L. Blanchard (September 30, 2020) Final Report: Observation-Based Analyses of the Sensitivity of Ozone Formation in the Lake Michigan Region to NOx and VOC Emissions. [link].
Acdan et al. (September 30, 2020) Final Report: Observation-Based Analyses of the Sensitivity of Ozone Formation in the Lake Michigan Region to NOx and VOC Emissions. [link].

Michigan (Acdan et al., 2020). As a result, O_3 formation at downwind sites along the Wisconsin and Michigan lakeshores is less VOC-sensitive than in the Chicago area, although the studies disagreed about whether O_3 formation in these areas was NOx-sensitive or transitional. The GAM analysis suggests that O_3 formation is responsive to both NOx and VOC (e.g., transitional) on high-O_3 concentration days along most of the Wisconsin and Michigan lakeshores during recent years (Blanchard 2020). Formaldehyde to nitrogen dioxide ($HCHO/NO_2$) ratios from the TROPOMI satellite suggest that O_3 formation in 2018 and 2019 was NOx-sensitive in the Lake Michigan region outside of Chicago on O_3 NAAQS exceedance days. Ozone formation became increasingly NOx-responsive over time as ambient NOx concentrations decreased.

Another study used a photochemical grid model to study ozone-NOx-VOC sensitivity in the Lake Michigan region (Abdi-Oskouei et al., in revision). This study used four different emissions inventories with varying amounts of NOx and VOC emissions to investigate O_3 chemistry regimes on high-O_3 concentration days during the 2017 Lake Michigan Ozone Study (LMOS 2017). This work focused on coastal monitoring sites and on the region of high-O_3 concentrations over the lake. This modeling study found that most of the Lake Michigan region was sensitive to both NOx and VOC emissions, with greater sensitivity to NOx emissions (e.g., NOx-sensitive). Central Chicago was a mix of NOx-suppressed (VOC-sensitive) and transitional in the early afternoon, and the VOC-sensitive area may extend up to 85 km over Lake Michigan downwind of Chicago. Other areas with high NOx emissions around the lake had smaller pockets of VOC-sensitive O_3 formation, however, most of the Lake Michigan area was NOx-sensitive.

A study by U.S. EPA combined a weekday-weekend analysis with higher-order decoupled direct method (HDDM) sensitivity modeling to study the ozone-NOx-VOC sensitivity around the U.S. (Koplitz et al., 2022). This study focused in greater detail on a number of locations, including Chicago and Detroit. This study found that by 2016, almost all of the U.S. was NOx-sensitive on O_3 NAAQS exceedance days. However, small pockets of transitional and VOC-sensitive chemistry lingered in a number of urban areas. The HDDM modeling found that central Chicago (Cook County) had a patchwork of transitional and VOC-sensitive grid cells near the lakeshore,

whereas the inland edges of the county were NOx-sensitive. A portion of Lake Michigan near Chicago had a mix of VOC-sensitive and transitional chemistry. Areas of transitional chemistry extended up through the southern Wisconsin and northwestern Indiana lakeshores and included downtown Milwaukee and a few other pockets. However, the rest of the region was NOx-sensitive. The HDDM model determined that almost all of the Detroit region was NOx-sensitive, with a few transitional grid cells. It also found some transitional chemistry along the lakeshore in Cleveland and near Toledo, OH, where there was one VOC-sensitive grid cell. The weekday-weekend analysis generally agreed with the HDDM analysis, although it projected that most Chicago area monitors were transitional or NOx-sensitive.[3] These results are generally consistent with those from Abdi-Askouei et al. (in revision).

LADCO recently hired researchers at Georgia Tech to apply a modeled HDDM analysis to the nonattainment areas in the LADCO region (Odman and Hu, 2022). This analysis found that ozone formation in 2016 was more responsive to NOx controls in most of the nonattainment areas, including St. Louis, Louisville, Cincinnati, Cleveland, Detroit, all three western Michigan sites, and coastal monitors in Chicago, although VOC controls were also beneficial in the coastal Chicago area. Both NOx and VOC controls were effective along the Wisconsin lakeshore, from the Milwaukee area up to Door County, and at the far northern and inland monitors in Chicago. Overall, this analysis agreed well with the HDDM analysis in Koplitz et al. (2022). However, Odman and Hu (2022) found somewhat less VOC sensitivity in the Chicago area and less NOx sensitivity along the Wisconsin lakeshore than did the Koplitz et al. (2022) analysis.

[3] Note however that this weekday-weekend analysis examined only single years (2007 or 2016), did not control for meteorological differences between weekdays and weekends, which can be significant, and focused on all days rather than just high-ozone days. All of these factors are likely to make it more difficult to see chemistry-driven trends in the data.

1.4. LADCO O_3 Chemistry Analysis

For this study, LADCO conducted an analysis of O_3 chemistry using a wide range of tools to determine the ozone-NOx-VOC sensitivity across the entire LADCO region, with a focus on the ozone nonattainment areas. This analysis expands some tools previously applied to the Lake Michigan area to other parts of the region; these tools include analysis of molecular indicator ratios from the TROPOMI satellite and from ground monitors. We also apply additional tools to nonattainment areas around the region, including analyses of O_3 chemistry indicator ratios from photochemical modeling and a thorough weekday-weekend analysis using meteorologically-adjusted data for O_3-conducive days. We also examine trends in high O_3 values over space (measured as distance from city centers) and over time for insight into how O_3 chemistry regimes have changed in the nonattainment areas over time. We also develop temporal trends in ozone-NOx-VOC sensitivity via several of the other analyses.

All of the analyses of ozone-NOx-VOC sensitivity require assumptions, and the different analyses can produce somewhat contradictory results. Accordingly, it is important to examine the question of O_3 formation sensitivity from as many angles as possible in order to close in on the "true" chemical regime that produces high O_3 concentrations in each area. By applying five new analyses to all nonattainment areas in the LADCO region, this analysis helps close the gaps in our understanding of which O_3 precursors states should aim to control to most effectively lower O_3 concentrations and bring their nonattainment areas back into attainment of the NAAQS.

2. Insights from Ozone Formation Sensitivity Indicator Ratios

2.1 Introduction

Molecular indicator ratios have been widely used to determine ozone-NOx-VOC sensitivity. Most frequently, chemical compounds involved in O_3 chemistry are used as indicators of the history of O_3 formation to that point (Sillman, 1995). These molecules may be species that are formed as secondary species during O_3 formation (e.g., formaldehyde, hydrogen peroxide, or nitric acid) or primary pollutants involved in O_3 formation (such as NO_2). Often, one species in a ratio is linked to VOCs (e.g., HCHO or H_2O_2) and the other species is linked to NOx (e.g., NO_2 or HNO_3), and their relationship to each other via the ratio provides insight into the relative availability and reactivity of VOCs versus NOx. The application of these ratios is discussed in greater detail in Sillman (2022) and Blanchard (2020).

In recent years, the most widely applied ratio has been the formaldehyde-to-NO_2 ratio ($HCHO/NO_2$) (e.g., Tonnesen and Dennis, 2000; Duncan et al., 2010; Jin et al., 2020). This ratio is especially useful because both formaldehyde and NO_2 are monitored as part of state monitoring networks, although both monitors are sparse. In addition, both species are detected by satellites such as the Ozone Monitoring Instrument (OMI), the TROPospheric Monitoring Instrument (TROPOMI), and the soon-to-be-launched Tropospheric Emissions: Monitoring of Pollution (TEMPO) instrument. Satellite retrievals allow the determination of $HCHO/NO_2$ ratios on a daily basis across the country, including at locations far distant from ground monitoring stations. The use of satellite-based $HCHO/NO_2$ ratios is complicated by the need for complex data processing algorithms to prepare the data and the fact that satellites do not measure ground-level air quality. Assumptions also must be made to identify the ratio values that separate different O_3 chemistry regimes. In addition, indicator ratios are valid only for the hours from noon to sunset (Sillman, 1995).

HCHO is a short-lived oxidation product formed from the reaction of a wide variety of VOCs, and its production is roughly proportional to the summed reactions of all of these VOCs with the OH radical (Sillman, 1995; Duncan et al., 2010). NO_2 is an O_3 precursor, directly involved in the formation of O_3. The $HCHO/NO_2$ ratio is essentially a reactivity-weighted measure of the VOC/NOx ratio and as such theoretically reflects the relative availability of NOx and total VOC reactivity to the OH radical (Sillman, 1995; Jin et al., 2020).

The ratio of hydrogen peroxide-to-nitric acid (H_2O_2/HNO_3) is more directly linked to the amount of O_3 formation under VOC- versus NOx-sensitive conditions than does that $HCHO/NO_2$ ratio (Sillman, 1995; Tonnesen and Dennis, 2000). This is because both H_2O_2 and HNO_3 are formed via the same reactions that form O_3, in the reactions that terminate the O_3 cycle (Vermeuel et al., 2019). H_2O_2 is formed when there are excess VOCs (e.g., under NOx-sensitive conditions), and HNO_3 is formed when there is excess NOx (e.g., under VOC-sensitive conditions). Accordingly, the ratio $HCHO/HNO_3$ gives a fairly direct ratio of the relative importance of O_3 formation under NOx- and VOC-sensitive conditions. However, it is much harder to measure H_2O_2 and HNO_3 in the environment, and these measurements are rarely made. Additionally, these compounds are not measured from satellites, so approaches using this ratio have most frequently relied upon modeled concentrations. A further limitation is that photochemical models may not always accurately capture the concentrations of these two compounds.

Applications of indicator ratios to determine the O_3-NOx-VOC sensitivity most frequently use thresholds that separate NOx-sensitive from transitional chemistry, and transitional from VOC-sensitive chemistry. The use of indicator ratio thresholds allows the application of the calculated ratios for identifying the O_3-NOx-VOC sensitivity at particular times and locations. The value of the ratio thresholds greatly impacts the interpretation of the O_3 formation chemistry.

Acdan (2021) effectively demonstrated the impact of ratio thresholds in interpretation of TROPOMI satellite-derived $HCHO/NO_2$ ratios. He found that application of two commonly applied ratios yielded dramatically different interpretations of O_3 formation sensitivity in the

Lake Michigan region (Figure 2.1). Use of thresholds from Duncan et al. (2010) suggests that almost all of the region is NOx-sensitive, and only a small portion of downtown Chicago is transitional. In contrast, use of thresholds from Jin et al. (2020) indicates that O_3 formation in all of central Chicago is VOC-sensitive, surrounded by an area of transitional chemistry.

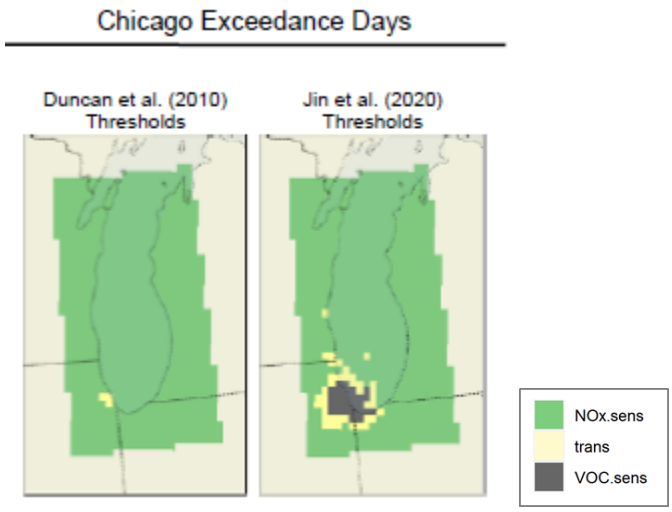

Figure 2.1. Comparison of ozone chemistry regimes determined from the same TROPOMI-derived HCHO/NO2 ratios by applying ratio thresholds from (left) Duncan et al. (2010) and (right) Jin et al. (2020). From Acdan (2021).

Different approaches to measuring the $HCHO/NO_2$ ratio result in different observed ratios (Table 2.1). For example, most ground monitors measure 24-hour average HCHO concentrations. Because there is generally more NO_2 and less HCHO overnight, this means that 24-hour average ratios will tend to be lower than afternoon ratios. Relatedly, the TROPOMI satellite passes over in the early afternoon, when $HCHO/NO_2$ ratios are at their highest, which will make these measurements still higher than 24-hour average measurements. In addition, satellites measure the total column amounts of pollutants; HCHO tends to be higher in the column relative to NO_2, which tends to be enhanced near the surface. This difference in distribution will further increase satellite-derived ratios compared with ground-based ratios. Finally, most ground-based measurements of NO_2 have been biased high, measuring other nitrogen compounds in addition to NO_2. While many sites have switched to a "true NO_2" measurement in recent years, most

ground-based NO_2 measurements have this bias, which will further decrease ground-based monitoring ratios. As a result of these different factors, the ratios determined from 24-hour average ground-based monitoring will be substantially lower than those from 1-hour modeling estimates of surface ratios (Table 2.1). Both of these ratios will in turn be lower than observations from TROPOMI or other satellites. As a result, one needs to apply different ratio thresholds to the different types of $HCHO/NO_2$ ratios. Acdan (2021) suggested that ratio thresholds from Jin et al. (2020) were most appropriate for interpretation of satellite-derived $HCHO/NO_2$ ratios, whereas the thresholds from Duncan et al. (2010) were most appropriate for ground-based ratios from monitoring and models (Table 2.1). Blanchard (2020) suggested that a third set of ratio thresholds was most appropriate for ratios based on 24-hour averages of ground-based HCHO and NO_2 monitoring.

Table 2.1. Comparison of the differences in the $HCHO/NO_2$ ratios determined from 24-hour average monitored data, 1-hour average modeling, and polar-orbiting satellites (passing over at midday). The ratio thresholds we selected as most appropriate are listed at the bottom of the table. Down and up arrows indicate whether that factor will decrease or increase the $HCHO/NO_2$ ratio.

Factor	Monitored data	Model results	Satellite observations	Explanation
Averaging period	↓ (24-hr)	-- (1-hr)	-- (short)	Nighttime has less HCHO & more NO_2
Timing	↓ (24-hr)	[depends on which hours used]	↑ (~1:30 pm)	Ratios are highest in the daytime
Column versus ground-level	↓ (ground)	↓ (ground)	↑ (column)	Ground-level has more NO_2, column has more HCHO
NO_2 measurement biases	↓	NA	NA	Older NO_2 measurement methods biased high (not "true NO_2")
Net results:	**Lowest ratios**	**Intermediate ratios**	**Highest ratios**	
Best thresholds:	**<0.3 = VOC-sens. >1 = NOx-sens. (Blanchard, 2020)**	**<1 = VOC-sens. >2 = NOx-sens. (Duncan et al., 2010)**	**<3.2 = VOC-sens. >4.1 = NOx-sens. (Jin et al., 2020)**	

In this report, we have applied $HCHO/NO_2$ ratio thresholds from Blanchard (2020) to 24-hour ground-based monitoring data, thresholds from Duncan et al. (2010) to 1-hour modeling results, and thresholds from Jin et al. (2020) to TROPOMI satellite results. In addition, we applied ratio thresholds from Sillman (2022) to the 1-hour modeled H_2O_2/HNO_3 results. The Sillman thresholds define areas with ratios less than 0.25 as VOC-sensitive and areas with ratios greater than 0.35 as NOx-sensitive. Areas with ratios between 0.25 and 0.35 are defined as transitional.

2.2. Ground-Based Indicator Ratios: Formaldehyde-to-NO_2 ($HCHO/NO_2$) Ratio

2.2.1. Introduction

Analysis of $HCHO/NO_2$ ratios from ground-based monitoring could appear to be the most straightforward approach to determining the ozone-NOx-VOC chemistry of a location. This analysis has the significant advantage over other types of indicator ratios as being based on direct measurements of the chemical conditions of the atmosphere near the earth's surface. Surface monitoring-based ratios don't require complex computer models or algorithms to calculate. However, ground-based measurements of both HCHO and NO_2 are quite sparse and not always measured at the same locations, so our ability to calculate $HCHO/NO_2$ ratios is extremely limited.

From 1991 through 2021, only nine sites in the LADCO region had $HCHO/NO_2$ records (Table 2.2). In addition, as discussed above, most HCHO measurements are 24-hour averages, so the $HCHO/NO_2$ ratios are 24-hour averages. Ozone formation indicator ratios are intended for application to air quality data during the afternoon hours, when O_3 formation is at its peak (Sillman, 2022). As a result, these ratios may not accurately reflect the O_3 chemistry regime during hours of peak O_3 concentrations. Despite these limitations $HCHO/NO_2$ ratios still provide insight into O_3 formation sensitivity around the monitoring locations, particularly when coupled with other types of analyses.

In this section, we present methods and results from the calculation of $HCHO/NO_2$ ratios at all monitors in the LADCO region with available data for the years 1991 through 2021. We applied ratio thresholds from Blanchard (2020) to determine the O_3-NOx-VOC sensitivity of O_3 formation at these monitors and how this sensitivity has changed over time.

2.2.2. Methods

Raw HCHO and NO_2 data for the years 1991 through 2021 were downloaded from EPA's Air Quality System (AQS; https://aqs.epa.gov/aqs/). Hourly HCHO data for Northbrook, IL from 2003 through 2009 and HCHO data from Gary IITRI, IN prior to 2009 were dropped because of apparent data quality issues.[4] All data were averaged to create 24-hour averages, with a data completeness requirement of 75% complete for each day. All replicate monitors at a site were then averaged to give one daily value for each pollutant. $HCHO/NO_2$ ratios were filtered to select only days with maximum daily 8-hour average O_3 concentrations (MDA8) greater than 60 ppb. Data were grouped into six different bins based on the year, and data were analyzed based on these bins.

NO_2 was primarily measured using chemiluminescence, which is the federal reference method (FRM) for NO_2. Chemilumiscence is non-specific for NO_2, meaning that it also detects some amount of higher oxides of nitrogen as NO_2, such that measurements made using this method overestimate the actual concentrations of NO_2. Beginning in 2010, some monitoring agencies began using photolytic chemiluminescence to detect NO_2. This detection method is more specific to NO_2 than the FRM but is still an indirect measurement. Since 2015, agencies have been deploying "direct NO_2" instruments that use cavity attenuated phase shift spectroscopy (CAPS, another FEM) to measure "true NO_2" in the atmosphere. NO_2 concentrations measured by CAPS will be lower than those measured by the other methods and are believed to be more representative of actual NO_2 concentrations. In 2020, approximately a third of the NO_2 monitors in the LADCO region measured NO_2 by CAPS. The footnote to Table 1 lists which monitors used

[4] 24-average HCHO data was available at Northbrook for these years, so $HCHO/NO_2$ ratios are still available.

which methods. Because of the limited NO_2 measurements available, indirect and "true" NO_2 measurements are combined in this analysis, which introduces some additional uncertainty to the HCHO/NO_2 ratios.

2.2.3. Results and discussion

Only nine monitors in the LADCO region had both HCHO and NO_2 measurements during the years 1991 through 2021 (Table 2.2). These included four monitors in the Chicago area, two in Milwaukee, and one each in Detroit, Grand Rapids (near the Western Michigan nonattainment areas), and St. Louis. None of these monitors measured both HCHO and NO_2 for the entire period of interest. The HCHO/NO_2 records at five of the sites include gaps, during which monitoring ceased for anywhere from one year (at the Milwaukee sites) to over a decade at the Detroit and Grand Rapids sites. Several of the records stopped in 2016, when EPA changed the requirements for their Photochemical Assessment Monitoring Stations (PAMS) network. Additional monitors began operating in 2021 as part of the PAMS network redesign. There were also some apparent data quality issues, particularly with the HCHO measurements, that required elimination of some years of data at some monitors.

Most of the HCHO monitors measured 24-hour average values, so all data has been averaged to 24-hour averages. As noted previously, the use of 24-hour averages biases the HCHO/NO_2 ratios low because there is less HCHO and more NO_2 during the nighttime than during the daytime, when O_3 is produced. In addition, most of the NO_2 methods did not measure "true NO_2", as discussed in the Methods section.. These and the other factors discussed in the Introduction result in lower surface monitoring-based HCHO/NO_2 ratios relative to those estimated from models or satellite measurements. Accordingly, we applied different HCHO/NO_2 ratio thresholds to determine the O_3-NOx-VOC sensitivity based on these ratios. Blanchard (2020) suggested that for 24-average ground-based measurements, HCHO/NO_2 ratios <0.3 indicated VOC-sensitivity, ratios >1 indicated NOx-sensitivity, and intermediate values indicated transitional chemistry. We have applied these ratio thresholds in this analysis.

Table 2.2. Information about monitors in or near LADCO nonattainment areas that measured both HCHO and NO_2 concentrations, including the years this data was available.

Area	Site Name	Site ID	Years Available[5]
Chicago	Gary IITRI	180890022	2009-2016*
Chicago	Schiller Park	170313103	2013-2021
Chicago	Chicago Jardine	170310072	1997-1999; 2002-2007
Chicago	Northbrook	170314201	2001-2016; 2021
Detroit	Detroit-E 7 Mile	261630019	2001-2005; 2021
Lake MI	Grand Rapids[6]	260810020	2005-2007; 2021
Lake MI	Milw-SER	550790026	2004; 2006-2016
Lake MI	Milw-UWM	550790041	1992; 1995-1999; 2001
St. Louis	Blair Street	295100085	2013-2021

We are most interested in O_3 formation chemistry on days with high O_3 levels, ideally days with maximum daily 8-hour average (MDA8) O_3 concentrations over the level of the 2015 O_3 NAAQS (70 ppb). Unfortunately, due to the sparsity of HCHO and NO_2 sampling, as well as the fact that HCHO measurements at most locations were only made every few days, very few daily HCHO/NO_2 ratios are available for days with MDA8 values over 70 ppb, often just one or two days at a site over a 5-year period (Figure A1.2). To provide more data to help draw meaningful conclusions, this analysis focused on days with MDA8 values greater than 60 ppb (Figures 2.2 and 2.3), with data combined into 5- or 6-year bins. This analysis will include some days with MDA8 values below the level of the 2015 O_3 NAAQS. The inclusion of these days is likely to

[5] Note that HCHO/NO_2 ratios are available at Schiller Park from 2002, however, the O_3 measurements we use to filter data started at Schiller Park in 2013. All measurements were made using chemoluminescence except: Gary IITRI from 2020-21 (CAPS), Schiller Park 2020-21 (CAPS), Northbrook 2021 (CAPS), Milw-SER 2019-21 (CAPS), and Blair Street 2013-21 (photolytic chemoluminescence).

[6] While the Grand Rapids monitor here is labeled as a "Lake Michigan monitor", its location roughly 60 miles inland from the lakeshore in an urban area means that its ratios likely reflect local O_3 formation conditions rather than being heavily impacted by transport over Lake Michigan.

increase the HCHO/NO_2 ratios somewhat since the ratios generally peak at O_3 MDA8 values around 50-60 ppb and decrease at higher concentrations (Figure A1.1).

Figures 2.2 and 2.3 show that HCHO/NO_2 ratios in almost all areas of the region shifted to higher values over the 30-year time period studied. Applying the ratio thresholds from Blanchard (2020), this analysis suggests that O_3 formation at LADCO nonattainment area sites generally transitioned from VOC-sensitive in the 1990s and 2000s to transitional in the 2010s. Ozone formation became less VOC-sensitive at almost all monitors in almost all time periods. The Chicago area had the lowest HCHO/NO_2 ratios, indicating that O_3 formation in this area was the most VOC-sensitive. There was very little evidence of NOx-sensitive O_3 formation, even in the most recent time period, which is in sharp contrast to that observed from other analyses in this report. This is likely at least in part because all of the monitors were located in urban areas, where O_3 formation is anticipated to be more VOC-sensitive than in more suburban or rural areas. The maps of the data (Figure 2.3) highlight the sparsity of HCHO/NO_2 measurements in this region and thus the limitations of this approach.

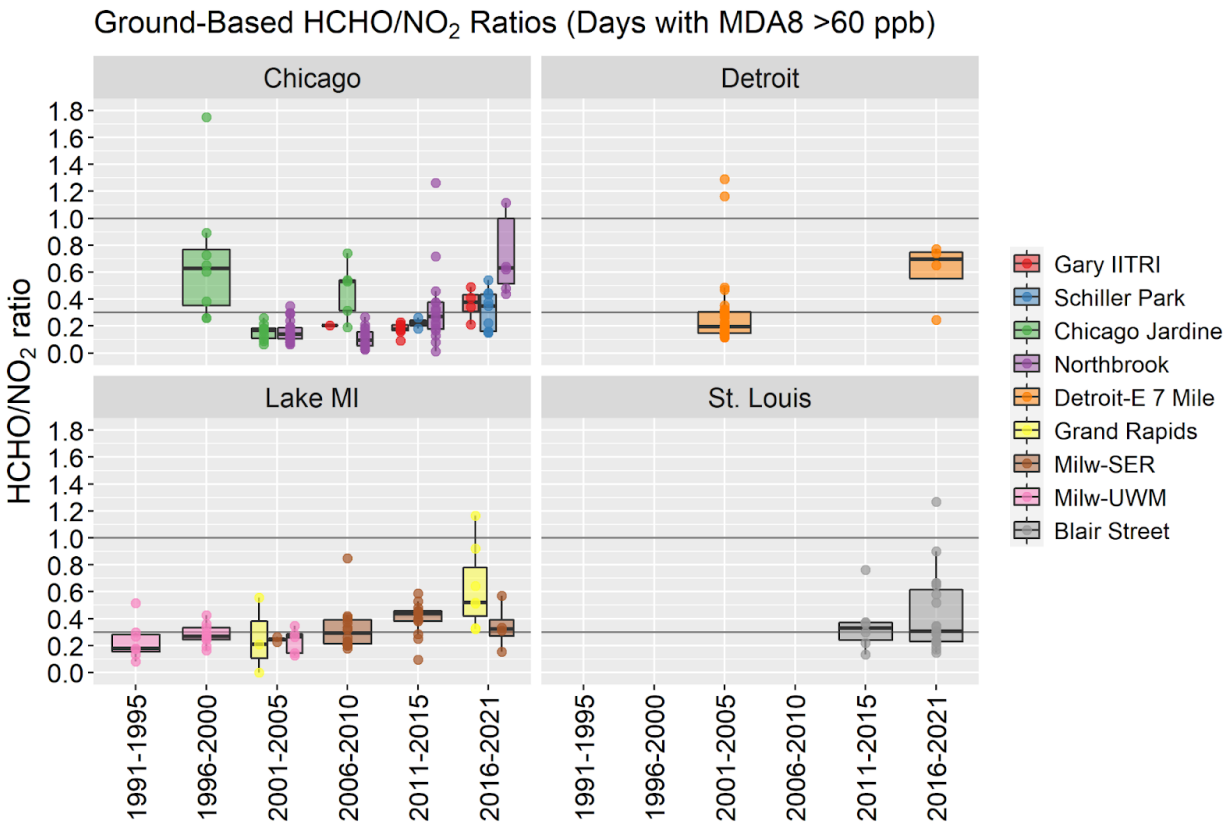

Figure 2.2. Ground-based $HCHO/NO_2$ ratios for monitors in or near LADCO nonattainment areas on days with MDA8 O_3 greater than 60 ppb.[7] Data are shown for six groupings of years. Note that the Northbrook monitor in Chicago had one day off the scale shown ($HCHO/NO_2$ ratio of 3.2) in 2016-2021. The gray lines mark the ratio thresholds between VOC-sensitive (< 0.3), transitional (0.3-1), and NOx-sensitive (> 1) chemistry based on ratio thresholds from Blanchard (2020).

[7] In the boxplots, the line goes through the median value, the box encloses the middle 50% of values, and the "whiskers" include most values. Data points representing individual days are shown as circles.

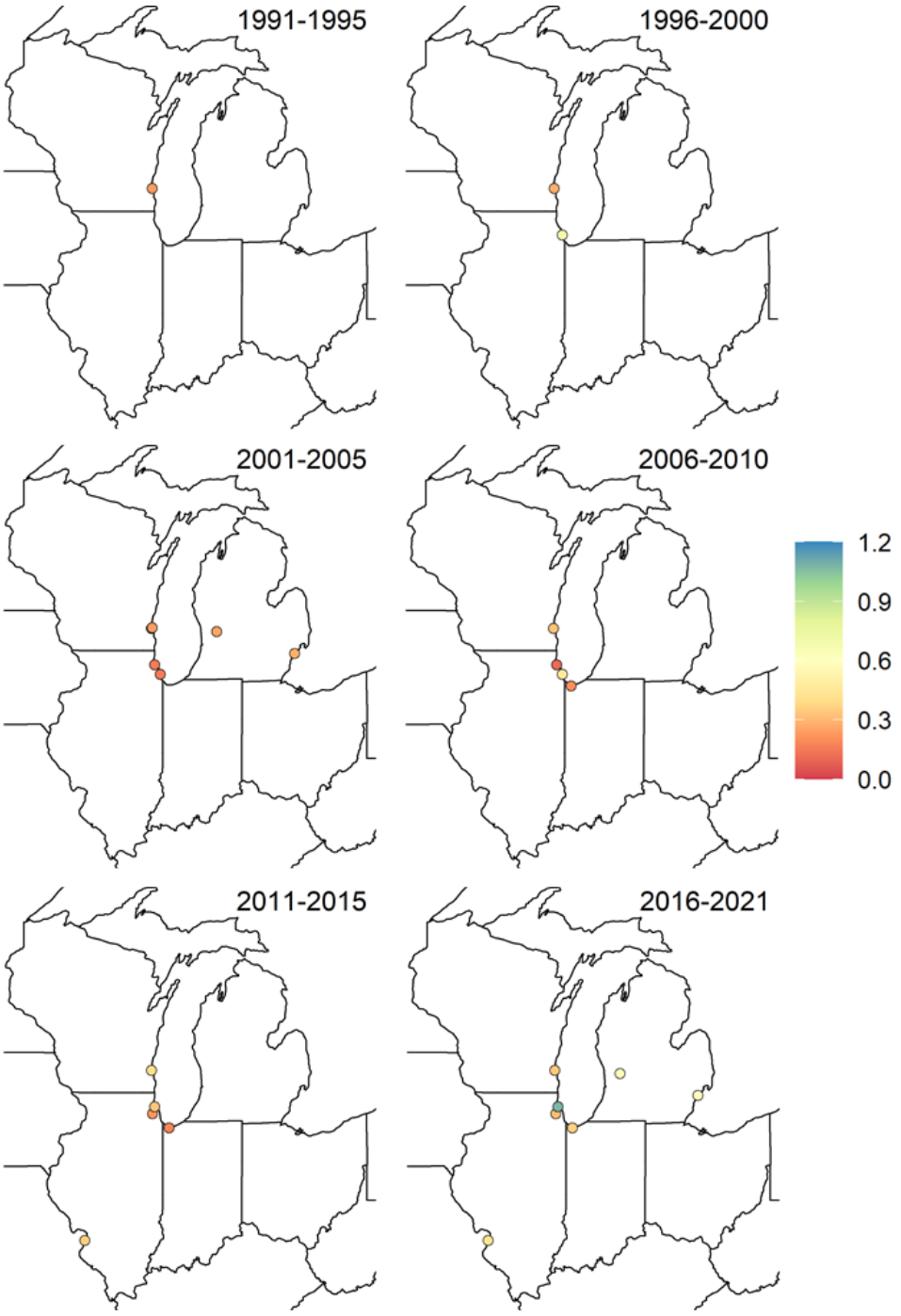

Figure 2.3. Mean ground-based $HCHO/NO_2$ ratios for monitors in or near LADCO nonattainment areas on days with MDA8 O_3 greater than 60 ppb. Data are shown for six groupings of years.

2.2.4. Conclusions

The sparsity of ground-based $HCHO/NO_2$ data both spatially and temporally limits the usefulness of this ratio for determining O_3-NOx-VOC sensitivity in most parts of the LADCO region. Nevertheless, these measurements demonstrate that O_3 formation in the urban areas of the Great Lakes states has become less VOC-sensitive over the last few decades, with O_3 formation shifting from primarily VOC-sensitive in the 1990s to primarily transitional in the 2010s. Ground-based $HCHO/NO_2$ measurements may be especially useful in combination with other estimates of O_3 formation chemistry, such as from satellites, models, and spatial and temporal patterns in O_3 concentrations. The rest of this report examines such analyses and then combines the different approaches to develop a clear understanding of O_3 formation chemistry in the region.

2.3. Satellite-Based Indicator Ratios: TROPOMI-Derived Formaldehyde-to-NO_2 ($HCHO/NO_2$) Ratio

2.3.1. Introduction

Satellite measurements of $HCHO/NO_2$ have the best spatial coverage available from a routine observational platform but limited temporal and vertical resolution. Satellite-based measurements of HCHO and NO_2 have the advantage of being able to "see" everywhere, including unmonitored areas that are far away from ground-based monitoring stations. With nearly uniform spatial coverage, it is possible to determine $HCHO/NO_2$ ratios using satellite data over the entire country. Current satellites can resolve measurements on scales of a few kilometers; the spatial resolution of the TROPOMI satellite is 3.5 x 5.5 km^2 (Acdan, 2021).
As satellites measure the tropospheric "columns" of pollutants, which integrates the concentrations of the pollutant at all heights in the troposphere, these data are not directly proportional to pollutant concentrations measured at ground level. Formaldehyde tends to be present throughout the tropospheric column, whereas NO_2 tends to be highly concentrated at the lower altitudes. These different vertical distributions generally increase satellite-observed $HCHO/NO_2$ ratios relative to ground-based observations. Polar orbiting satellites pass over areas once daily; this passover is in the afternoon (around 13:30 LST) for the TROPOMI satellite, which coincides with the hours of peak O_3 production and the time when O_3 formation sensitivity ratios are valid. In addition, to account for gaps in data from periodic cloud cover and low signal-to-noise ratios, satellite data generally must be averaged over many days to yield meaningful patterns. Finally, many assumptions and approximations are needed to convert the spectral signal recorded by the satellite into column concentrations of pollutants, including assumptions about the distribution of pollutants through the column (Judd et al., 2019).

In this section, we use $HCHO/NO_2$ ratios from the TROPOMI satellite to examine $HCHO/NO_2$ ratios around the LADCO region on both high O_3 concentration days and during the O_3 season as a whole in 2018 and 2019. We then apply ratio thresholds from Jin et al. (2020) to determine

the O_3-NOx-VOC sensitivity in these areas and examine the impacts of different emissions sources on this O_3 formation sensitivity.

2.3.2. Methods

TROPOMI satellite retrievals.

Jerrold Acdan and Brad Pierce of UW-Madison completed the initial downloading and processing of the TROPOMI satellite retrievals for LADCO. See Acdan (2021)[8] for a complete description of the methods used to prepare the TROPOMI satellite data. Retrievals of tropospheric HCHO and NO_2 from the Sentinel-5 Precursor (S5P) satellite's TROPOspheric Monitoring Instrument (TROPOMI) Version 1 orbital level 2 data for the O_3 seasons of 2018 and 2019 were downloaded from the NASA Goddard Earth Sciences Data and Information Services Center. TROPOMI uses an ultraviolet-visible-near infrared-shortwave infrared spectrometer and provides daily data at approximately 13:30 local sun time. TROPOMI retrievals have much higher spatial resolution than earlier satellites.

Acdan and Pierce completed the following steps to prepare the TROPOMI satellite retrievals for LADCO.

- Gridded the data to the LADCO modeling platform's 12 km x 12 km grid with a Lambert Conformal Conic projection.
- Created daily retrievals by combining retrievals on (1) a monthly basis, from June[9] through September 2018 and May through September 2019, and (2) days on which at least one monitor's maximum daily 8-hour MDA8 O_3 concentrations exceeded 70 ppb, the level of the 2015 O_3 NAAQS ("ozone exceedance days"). The daily composites were constructed using quality controlled level 2 retrievals based on the recommended qa_value > 0.75 (Eskes et al., 2020; De Smedt et al., 2020) and applying additional "detection limit" filters of 1.5 x 10^{15} molecules/cm^2 (mol/cm^2) for NO_2 (Duncan et al., 2010) and 1.8 x 10^{15} mol/cm^2 for HCHO (Chance [Ed.], 2002).

[8] https://www.aos.wisc.edu/aosjournal/Volume38/Acdan_MS.pdf

[9] We did not construct a May 2018 composite because TROPOMI HCHO data were not available for the entire month.

LADCO determined the combined 2018 and 2019 O_3 season composites from the monthly composites by computing the weighted mean NO_2 and HCHO columns based on the number of observations per grid per month for June through September 2018 and May through September 2019. LADCO calculated the HCHO/NO_2 ratios by dividing the composited HCHO columns by the NO_2 columns. Ozone exceedance days were determined for the different nonattainment areas in the LADCO region based on days from late May through September 2018 and May through September 2019. The Chicago area had the most exceedance days (33), and Sheboygan, WI had the fewest (12). Sheboygan exceedance days were chosen as being representative of exceedance days along the Wisconsin lakeshore, and exceedance days at the three Western Michigan nonattainment were combined into one analysis. Table A1 lists the O_3 exceedance days included in each composite.

Nonattainment area analyses.

LADCO used ArcGIS Pro (Version 2.7.1) and R (Version 4.0.3, run in RStudio Version 1.3.1093) to identify the 12km modeling grid cells that intersect nonattainment areas. We manually excluded grid cells in portions of counties that are outside of partial-county nonattainment areas in Wisconsin, Illinois, Indiana, Missouri, Kentucky and Western Michigan. We considered grid cells to be in a nonattainment area if: (1) at least 50 percent of the area of the grid cell was in that nonattainment area, or (2) the grid cell was coastal, bordering either Lake Michigan or Lake Erie and the waterways around Detroit. This second criterion ensures that we include the key coastal areas that often have the highest O_3 concentrations due to lake breezes and transport over the lakes. We manually excluded some coastal grid cells if only a tiny portion of the grid cell was in the nonattainment area. Maps showing the grid cells included in each nonattainment area are in Figure A1.

2.3.3. Results and Discussion

Daily TROPOMI satellite data was compiled in two ways: (1) O_3 season composites and (2) O_3 exceedance day composites. The O_3 season composites combine data from all days from May through September in 2018 and 2019. Since the satellite wasn't fully operational until mid-May 2018, the O_3 season composites do not include May 2018. The O_3 exceedance day composites

combine data from all days that had at least one ground-based monitor in a nonattainment area with a maximum daily 8-hour average (MDA8) O_3 concentration above 70 ppb, the level of the 2015 O_3 NAAQS. These exceedance days varied between nonattainment areas, so a different set of days is used in the exceedance day plots for each area. The list of exceedance days is included in Table A1. Satellite data were gridded to match LADCO's 12-km modeling grid. Data were composited partly to reduce the influence of noise in the HCHO retrievals (Acdan et al., 2020).

Ozone Season Composites

Figure 2.4 (left) shows maps of O_3 season composite NO_2 and HCHO columns, along with HCHO/NO_2 ratios for the LADCO region. Figure A2.2 shows these same O_3 season maps zoomed in on different parts of the region. These maps show the highest NO_2 columns in the Chicago area, with values over 6 x 10^{15} mol/cm^2 in downtown Chicago. Enhanced columns of NO_2 are also apparent in most large urban areas, with values over 4 x 10^{15} mol/cm^2 in downtown Detroit and somewhat lower values in other urban areas. The O_3 season boxplots show the distribution of NO_2 columns within all of the grid cells in each nonattainment area. This figure shows the highest median and range in NO_2 columns in Chicago, followed by Detroit and Cincinnati. The lowest NO_2 columns are over Western Michigan, the Wisconsin lakeshore, and St. Louis.

In contrast to NO_2, the distribution of HCHO appears to be primarily driven by the abundance of biogenica VOCs from warm forests, with the greatest concentrations in the Ozarks in southeastern Missouri and in the forests of Kentucky and Tennessee (Figure 2.4). TROPOMI also appears to detect small HCHO plumes in urban areas that are likely due to urban VOC emissions, however, this signal is much smaller than the biogenic emissions. The O_3 season boxplots show that of the LADCO nonattainment areas, St. Louis had the highest columns of HCHO, followed by Louisville. Western Michigan and Cincinnati had intermediate levels, and the other areas had lower columns.

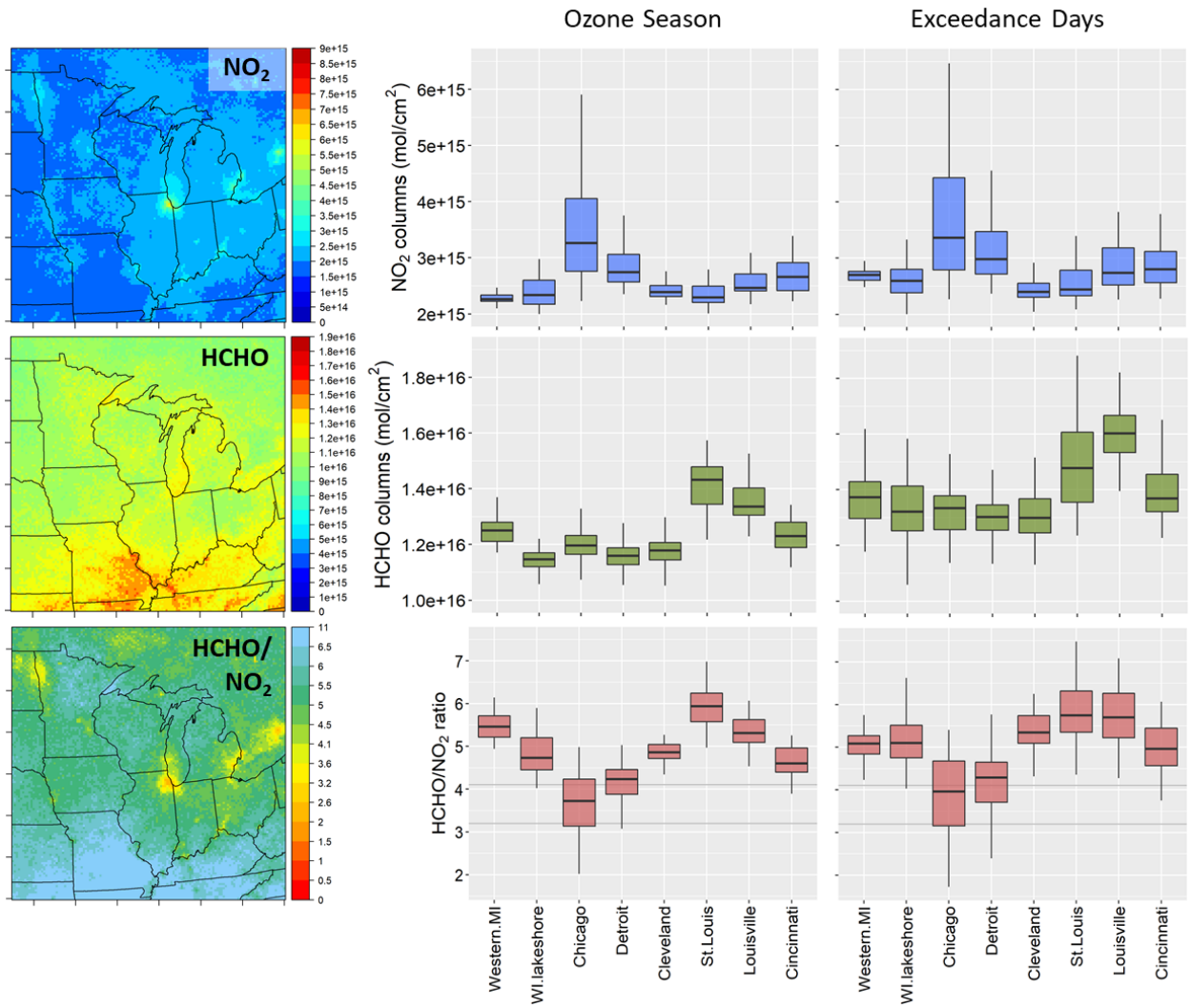

Figure 2.4. TROPOMI satellite NO_2 columns (top, mol/cm^2), HCHO columns (middle, mol/cm^2), and HCHO/NO_2 ratios (bottom) for 2018 and 2019, shown as (left) a map of O_3 season averages, (middle) boxplots of O_3 season values in the different nonattainment areas, and (right) boxplots of values on exceedance days in each nonattainment area. Boxplots[10] for Western Michigan and the Wisconsin lakeshore combine values for multiple nonattainment areas in these regions. Figure A4 shows the results for each individual nonattainment area.

[10] In boxplots, the line goes through the median value, the box encloses the middle 50% of values, and the "whiskers" include most values.

The HCHO/NO_2 ratio appears to be influenced by both urban NO_2 plumes and biogenic VOC plumes in the south. The ratios are highest in the southern areas corresponding with the highest HCHO column retrievals in the region. Ratios in the southern cities are lower than in the surrounding rural areas but quite a bit higher than in the northern cities. HCHO/NO_2 ratios are lowest in Chicago and Detroit, with O_3 season averages around 2-3 in almost all of Cook County in central Chicago and in smaller patches in Detroit (Figure 2.4). The O_3 season boxplots show a median ratio of around 3.7 for Chicago, the lowest of all the areas, and a median ratio of 6 for St. Louis, the highest of the areas.

Ozone Exceedance Day Composites

Figure 2.4 (right) shows the NO_2 columns, HCHO columns, and HCHO/NO_2 ratios on O_3 exceedance days in each of the nonattainment areas. The column retrievals and ratios on O_3 exceedance days are similar to those during the O_3 season as a whole, with the highest NO_2 columns in Chicago and Detroit and the highest HCHO columns in the southern nonattainment areas. NO_2 columns in urban nonattainment areas are very similar on exceedance days as during the O_3 season as a whole. The downwind nonattainment areas along Lake Michigan, in Western Michigan and on the Wisconsin lakeshore, have higher NO_2 columns on exceedance days, likely because these areas generally only exceed the NAAQS when O_3 is transported from upwind source regions, primarily Chicago, and this transported air would also be enriched in NO_2. HCHO columns are considerably higher on exceedance days than during the O_3 season as a whole. This is likely because exceedance days tend to have higher temperatures, which also increases emissions of VOCs from both biogenic and anthropogenic sources. As a result of the higher HCHO columns on exceedance days, these days also have higher HCHO/NO_2 ratios in most areas. The main exceptions are St. Louis, which did not see a large increase in HCHO on exceedance days, and Western Michigan, which had a large increase in NO_2 on exceedance days.

Ozone-NOx-VOC Sensitivity

As described previously, HCHO/NO_2 ratios are useful indicators of O_3-NOx-VOC sensitivity. A number of studies have determined the HCHO/NO_2 ratio thresholds that separate NOx- from VOC-sensitive chemistry. Acdan (2021) recommended the use of ratio thresholds from Jin et al.

(2020) as the most appropriate to distinguish between NOx- and VOC-sensitivity based on satellite retrievals. These thresholds interpret $HCHO/NO_2$ ratios below 3.2 as VOC-sensitive, ratios between 3.2 and 4.1 as transitional, and ratios above 4.1 as NOx-sensitive. We applied these thresholds to our $HCHO/NO_2$ ratios to determine the O_3-NOx-VOC sensitivity of O_3 formation in the LADCO region. Figure 2.5 shows the results of this application for O_3 season days as a whole and for exceedance days in each LADCO region O_3 nonattainment area. These formation sensitivity classifications are mapped out, with the Chicago exceedance days shown as an example, and also shown as composites for each nonattainment area. The differences in O_3-NOx-VOC sensitivity are relatively small between the ozone season and exceedance days. Chicago and Detroit are the only LADCO areas that show any VOC-sensitivity. Chicago has roughly similar percentages of VOC-sensitive, transitional, and NOx-sensitive grid cells, with slightly more NOx-sensitivity on exceedance days. Detroit had slightly more VOC-sensitivity on exceedance days than on all O_3 season days, but similar distributions of NOx-sensitivity. Western Michigan, Cleveland, and St. Louis are entirely NOx-sensitive on both sets of days, and the remaining areas have only small areas of transitional chemistry.

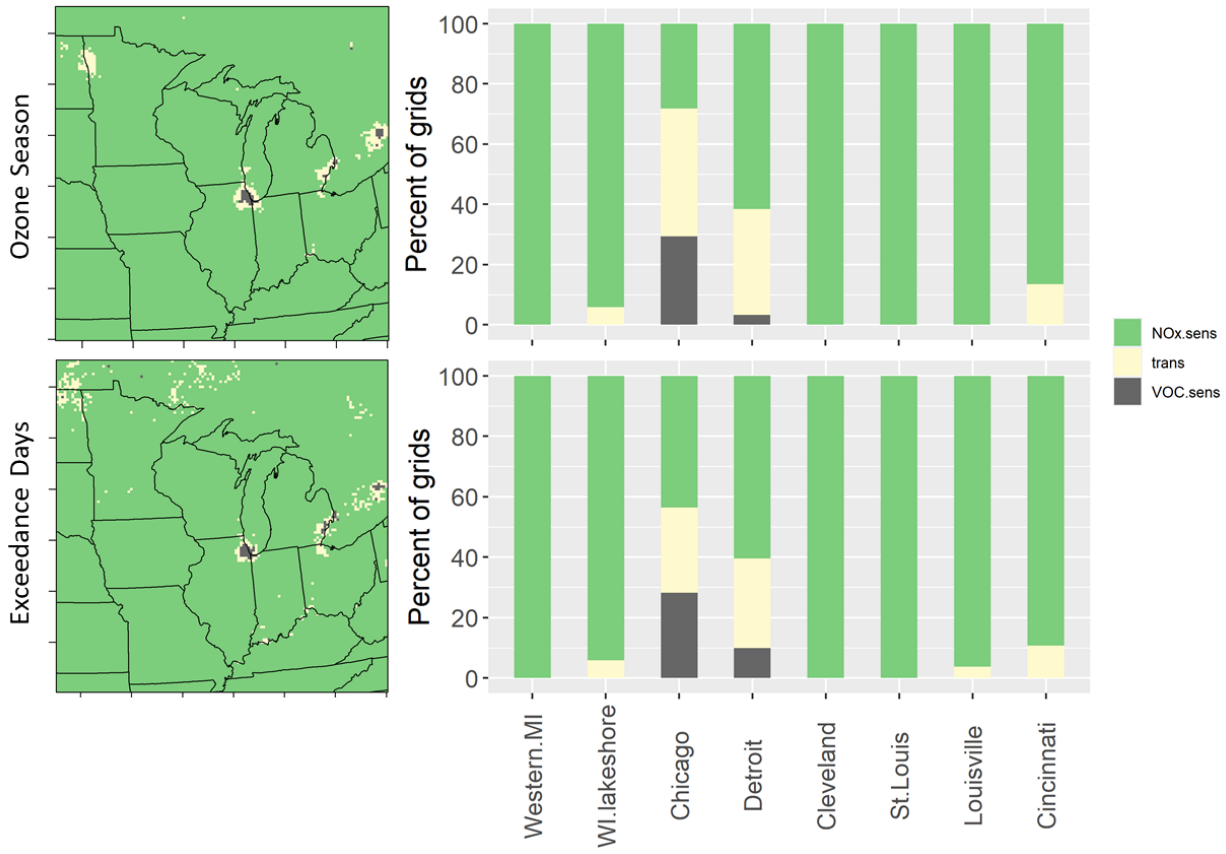

Figure 2.5. Ozone chemistry regimes. (Left) Maps of ozone formation chemistry regime on (top) the average of all O_3 season days, and (bottom) exceedance days in Chicago. (Right) The distribution of O_3 formation sensitivity within nonattainment days on (top) the average of all O_3 season days and (bottom) exceedance days within each nonattainment area. chemistry regimes are determined from $HCHO/NO_2$ ratios using ratio thresholds from Jin et al. (2020). Distributions for Western Michigan and the Wisconsin lakeshore combine values for multiple nonattainment areas in these regions.

Drivers of Ozone-NOx-VOC Sensitivity on Ozone Exceedance Days in Nonattainment Areas

Examination of patterns within NO_2 and HCHO columns and their ratios can provide insight into how O_3-NOx-VOC sensitivity varies within different areas and what factors drive these patterns. Figures 2.6, 2.8, and 2.9 show maps of NO_2 and HCHO columns, $HCHO/NO_2$ ratios and O_3-NOx-VOC sensitivity classifications on O_3 exceedance days in the different O_3 nonattainment

areas and regions. To help with interpretation of the satellite images, Figure 2.7 shows the location of some important sources of O_3 precursor emissions: urban areas, highways, coal-fired power plants, and tree canopy cover, since trees are an important source of biogenic VOCs. Table A2.2 lists the columns and ratios for the grid cells containing ground monitors.

Southern Areas: St. Louis, Louisville, and Cincinnati. St. Louis, Louisville, and Cincinnati were all designated as nonattainment for the 2015 O_3 NAAQS. All three nonattainment areas encompass two states: Missouri and Illinois for St. Louis, Indiana and Kentucky for Louisville, and Ohio and Kentucky for Cincinnati. These three areas are located in the southern part of the LADCO region and share some similar properties. All three areas show visible urban NO_2 plumes from emissions within urban boundaries on O_3 exceedance days (Figure 2.6). NO_2 plumes from large, coal-fired power plants in each of the areas are also visible (Figures 2.6 and 2.7). These plumes are particularly visible in the Ohio River Valley near Louisville and Cincinnati, where a number of particularly large power plants are located.

In contrast, the patterns of HCHO on O_3 exceedance days roughly track the distribution of tree canopy cover in these areas (Figures 2.6 and 2.7), with higher HCHO and tree canopy cover west and south of St. Louis, west and south of Louisville, and along the Ohio River Valley, which forms the east-west state boundaries in this region. Trees are significant sources of biogenic VOCs, particularly during hot weather, and these biogenic VOCs can react to form HCHO. The high columns of HCHO in the urban areas, particularly in St. Louis and Louisville, likely indicate urban HCHO plumes in addition to the biogenic sources.

The HCHO/NO_2 ratios in these areas are quite a bit higher than in the other areas (Figures 2.6, 2.8, and 2.9), primarily because of the larger columns of HCHO. The lowest ratios occur near large, coal-fired power plants (Figure 2.7) and in the Cincinnati area. Ratios remain relatively high in both the St. Louis and Louisville areas. When the ratio thresholds from Jin et al. (2020) are applied to the HCHO/NO_2 ratios, all of the St. Louis area and almost all of the Louisville area are classified as NOx-sensitive on O_3 exceedance days (Figure 2.6). Only one grid cell in the

Louisville area is classified as transitional, and this grid cell contains a coal-fired power plant (Figure 2.7). The Cincinnati area has a small number of transitional grid cells, some of which contain coal-fired EGUs and others primarily impacted by urban NOx plumes.

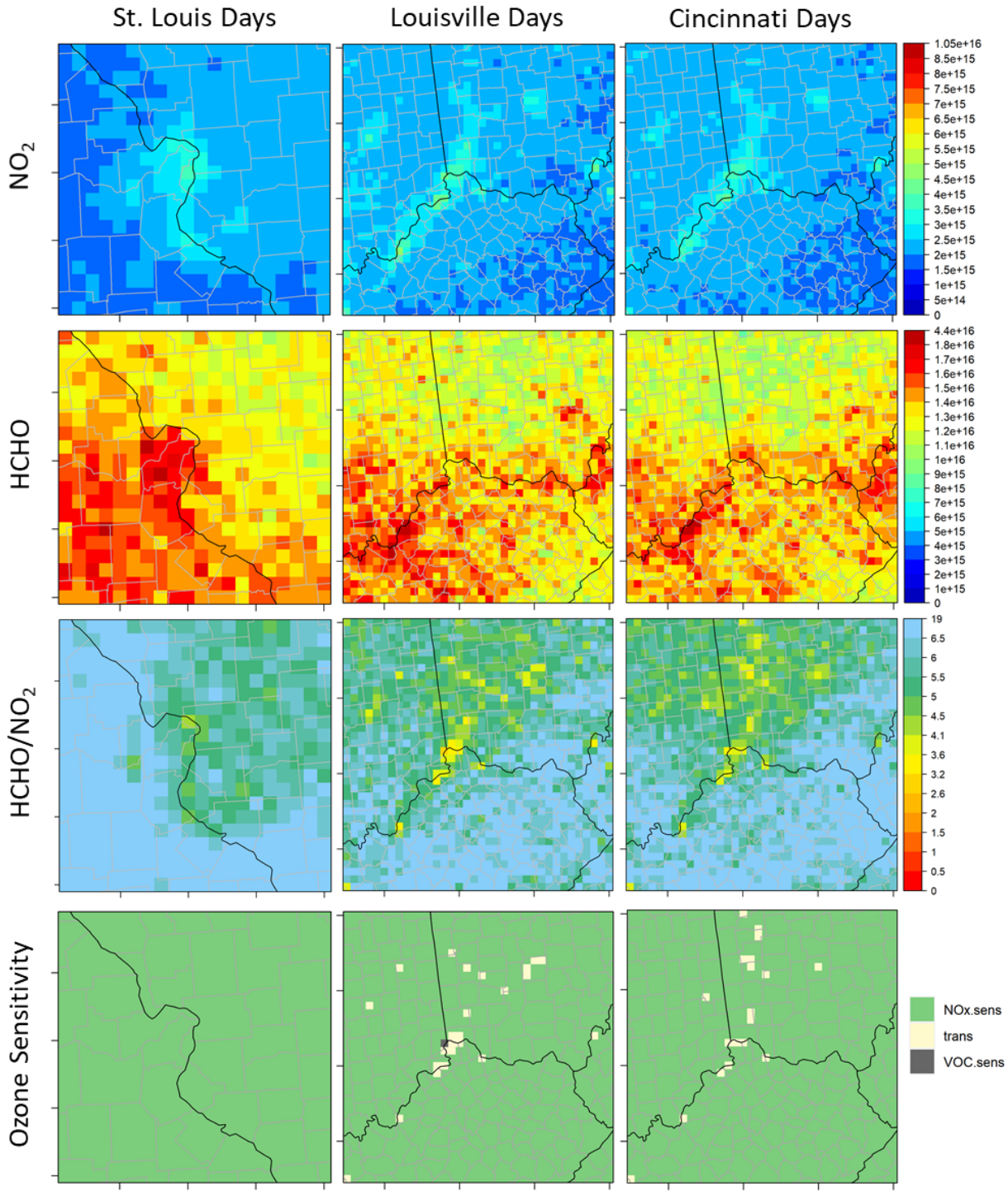

Figure 2.6. Maps of (top) NO_2 columns (mol/cm^2), (2nd row) HCHO columns (mol/cm^2), (3rd row) HCHO/NO_2 ratios, and (bottom) O_3 chemistry regimes on exceedance days in (left) St. Louis, (middle) Louisville, and (right) Cincinnati.

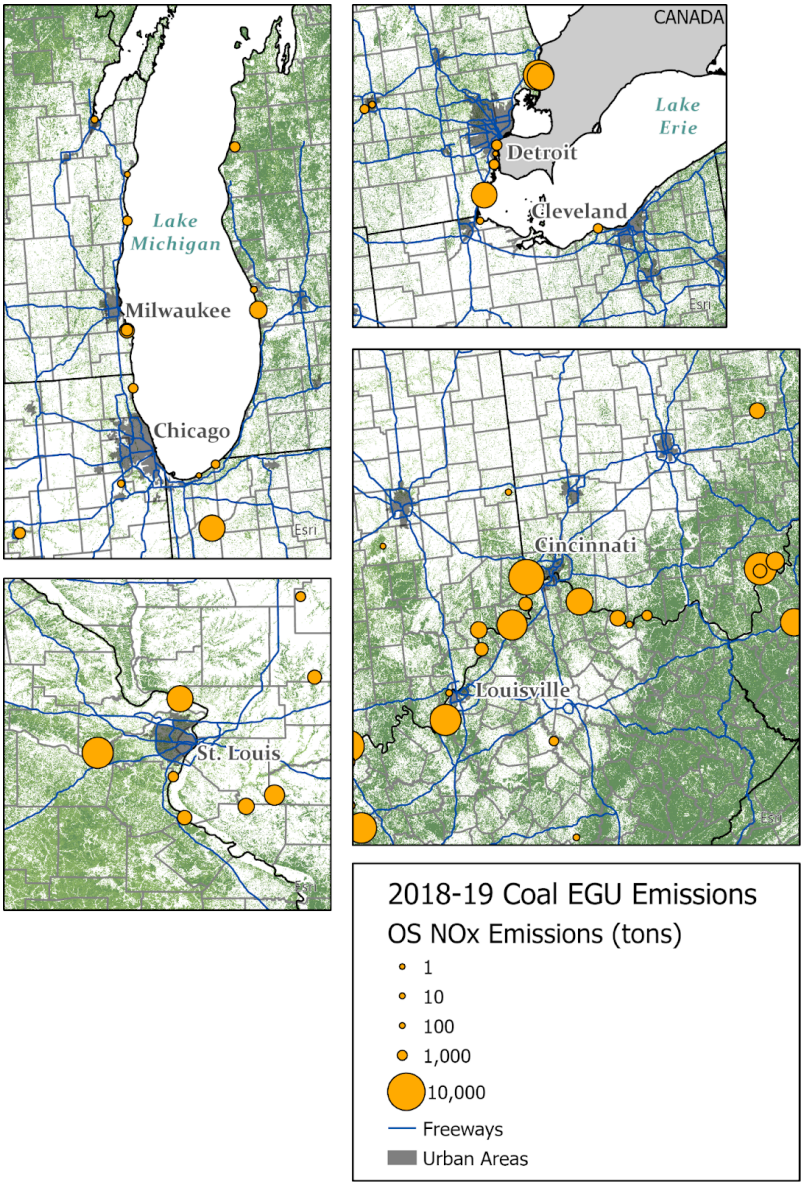

Figure 2.7. Maps of large emissions sources, including total O_3 season NOx emissions (tons) from coal-fired electricity generating units (EGUs) in 2018 and 2019, urban areas, freeways, and tree canopy cover (green) in the different parts of the LADCO regions. Maps include (top left) Chicago, Wisconsin Lakeshore and Western Michigan areas, (top right) Detroit and Cleveland, (bottom left) St. Louis, and (bottom right) Louisville and Cincinnati.[11] EGU data are from EPA's Air Markets Program Data[12] for May-September, and tree canopy cover is from the National Land Cover Database, available through ArcGIS's Living Atlas.

[11] All maps are shown at a 1:5,000,000 scale except the St. Louis map, which is a 1:1,600,000 scale.
[12] https://gaftp.epa.gov/DMDnLoad/emissions/daily/quarterly/

Lake Erie Areas: Detroit and Cleveland. Both Detroit and Cleveland were designated nonattainment for the 2015 O_3 NAAQS. Both nonattainment areas encompass a number of counties within one state (Michigan or Ohio, respectively) and stretch along water bodies: Lakes Erie and St. Clair and the Detroit and St. Clair rivers for Detroit and Lake Erie for Cleveland. Consequently, O_3 formation and transport in these two areas can be impacted by lake breezes and other dynamical features along the land-water interface.

On O_3 exceedance days, Detroit shows a clear urban NO_2 plume, with higher columns than are apparent in the southern areas (Figure 2.8). Detroit also has a large NO_2 plume located to the northeast of downtown just across the border in Ontario, Canada. This plume is likely due to emissions from two large, coal-fired power plants in the area: DTE St. Clair and DTE Belle River (Figure 2.7). In contrast, the urban NO_2 plume from Cleveland is quite a bit more diffuse, with much lower NO_2 columns, particularly on exceedance days in Cleveland. No power plant NO_2 plumes are evident in Cleveland from the satellite images.

HCHO columns in Detroit and Cleveland on exceedance days are much lower than those in the southern areas (Figure 2.8). HCHO columns in the two nonattainment areas appear to be slightly higher than in the surrounding areas, but the differences are subtle. Neither area is heavily forested, so we would not anticipate biogenic sources of HCHO and other VOCs to be very high.

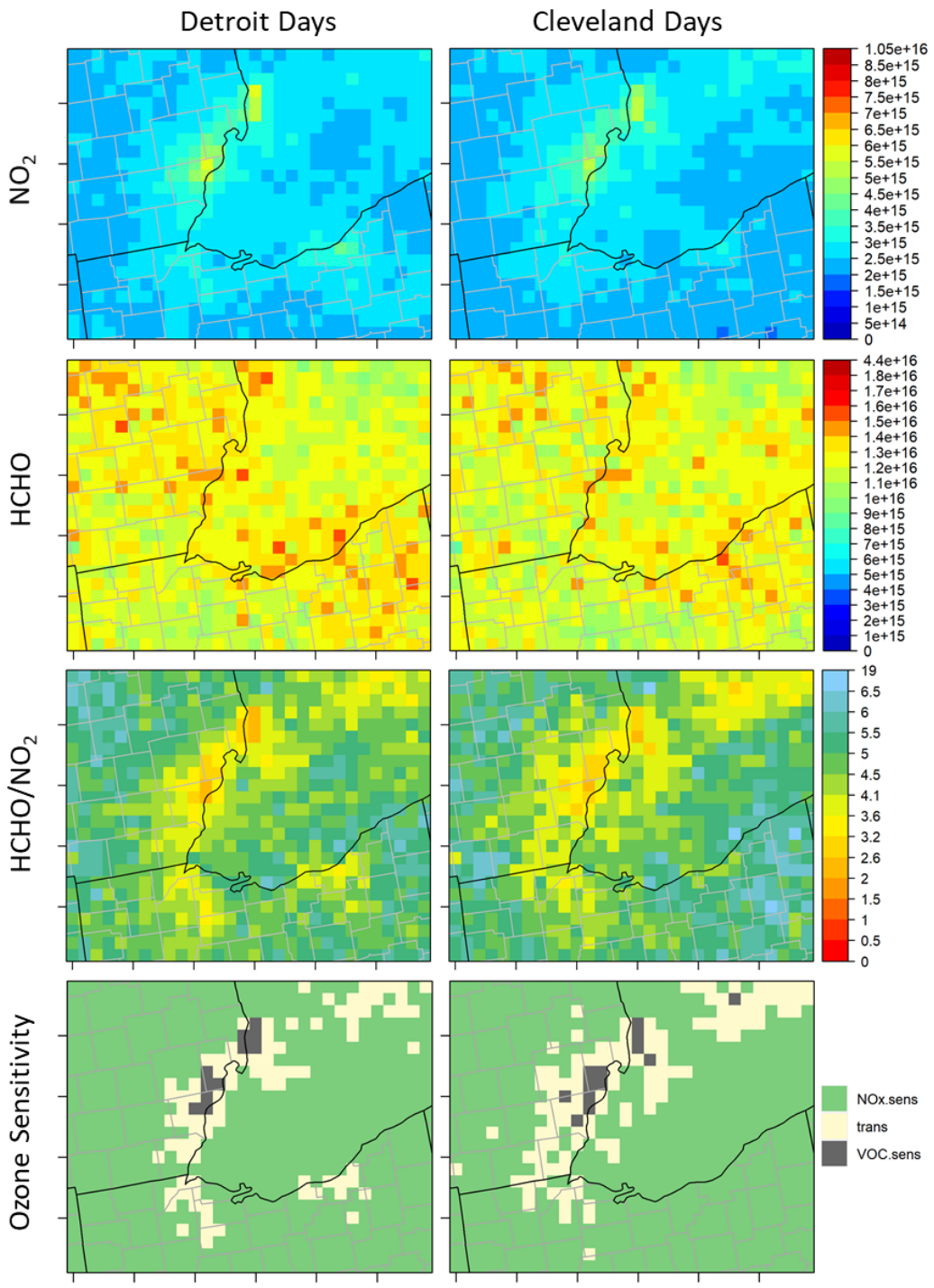

Figure 2.8. Maps of (top) NO_2 columns (mol/cm^2), (2nd row) HCHO columns (mol/cm^2), (3rd row) HCHO/NO_2 ratios, and (bottom) O_3 chemistry regimes on exceedance days in (left) Detroit and (right) Cleveland.

The $HCHO/NO_2$ ratios on exceedance days are quite a bit lower in the Detroit area compared with the southern areas (Figure 2.8). On exceedance days in Cleveland, $HCHO/NO_2$ ratios in Cleveland are much higher than those in Detroit on Detroit exceedance days. Converting these ratios to O_3 formation classifications finds two patches of VOC-sensitivity in the Detroit area on exceedance days: one in and near downtown Detroit and the other to the northeast near the NO_2 plume from the power plants. On exceedance days, O_3 formation in the Cleveland area appears to be entirely NOx-sensitive, while there is a considerable area with transitional chemistry in Cleveland on exceedance days in Detroit.

The Lake Michigan Region. Several areas of the Lake Michigan shoreline are designated nonattainment areas for the 2015 O_3 NAAQS. The Chicago nonattainment area includes parts of eleven counties in three states (Illinois, Indiana, and Wisconsin). There are four additional nonattainment areas stretching across eight counties along the Wisconsin lakeshore and three nonattainment areas in Western Michigan (Figure 1.2). This analysis examines composite values on O_3 exceedance days in three areas around Lake Michigan: (1) Chicago, (2) Sheboygan, which is used as a representative of the Wisconsin lakeshore nonattainment areas, and (3) Western Michigan, which includes days that exceeded the O_3 NAAQS at any of the Western Michigan monitors. Ozone distribution in all of these areas is heavily influenced by O_3 formation over Lake Michigan, northward (Wisconsin) or northeasterly (Michigan) transport of O_3 and O_3 precursors over the lake, and lake breezes that pull O_3-rich air onshore (e.g., Dye et al., 1995).

NO_2 columns are highest in the Chicago region on all three sets of O_3 exceedance days, with the greatest columns on Chicago exceedance days. NO_2 columns on all sets of exceedance days peaked at higher levels than during the O_3 season as a whole (Figures 6 and A2). However, NO_2 distribution patterns on Chicago exceedance days were very similar to those of the O_3 season as a whole. On Chicago exceedance days, elevated NO_2 columns were localized in a circular pattern in the Chicago area, extending over Lake Michigan. In addition, a lower-concentration plume extended northward over southeastern Wisconsin and the western two-thirds of Lake Michigan. In contrast, the NO_2 plume on Sheboygan exceedance days extended farther

northward over the lake and over both Wisconsin and Michigan lakeshores, with moderate NO_2 columns extending along the Wisconsin lakeshore up to Milwaukee. The NO_2 plume on these days does not extend as far southward as on Chicago exceedance days. On Western Michigan exceedance days, the plume is even more dispersed. NO_2 on these days has lower peak concentrations in Chicago, and the plume covers most of the map region and has higher NO_2 columns over Lake Michigan and extending over to Western Michigan.

These differences in distribution of the NO_2 plume likely reflect the differences in prevailing winds on exceedance days in the different parts of the Lake Michigan region. Chicago tends to have the highest O_3 concentrations when winds are calm and local pollutant emissions can build up in the area. In contrast, the Wisconsin lakeshore generally has O_3 exceedances when southerly winds transport O_3 and O_3 precursors northward from Chicago. Similarly, Western Michigan has the highest O_3 concentrations when southwesterly winds carry O_3 and precursors from Chicago and the southwest of Lake Michigan across the lake to the Michigan lakeshore. The satellite recorded the signal of these different wind patterns, with the calm winds on Chicago exceedance days keeping NO_2 (and O_3) pollution localized, southerly winds on Sheboygan exceedance days carrying the pollution northward, and southwesterly winds on Western Michigan exceedance days carrying this pollution farther east over the lake. There are some small NO_2 plumes apparent from coal-fired power plants, but these features are dwarfed by the impacts of Chicago on regional air pollution.

Exceedance day columns of HCHO around Lake Michigan are lower than in the southern areas of the region but higher than in Detroit or Cleveland. The highest columns are present over southern and eastern Lake Michigan. These over-lake HCHO plumes are likely due to a combination of urban VOC emissions from Chicago that are transported over the lake and biogenic VOC emissions from forests in Western Michigan (Figure 2.7).

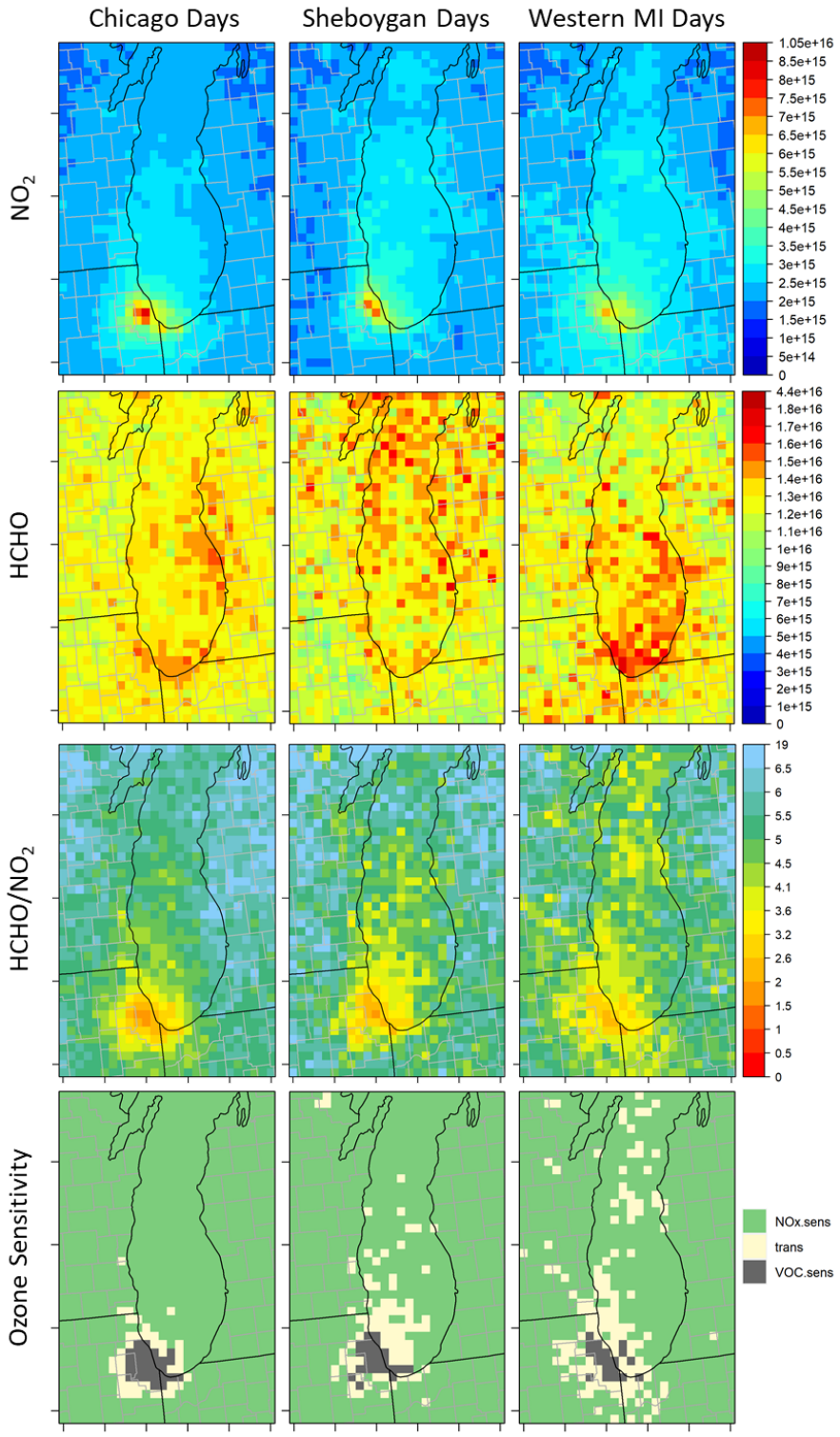

Figure 2.9. Maps of (top) NO_2 columns (mol/cm^2), (2nd row) HCHO columns (mol/cm^2), (3rd row) HCHO/NO_2 ratios, and (bottom) O_3 chemistry regimes on exceedance days in (left) Chicago, (middle) Sheboygan, WI, and (right) Western Michigan.

Ratios of $HCHO/NO_2$ in the Lake Michigan region appear to be primarily driven by NO_2 columns. $HCHO/NO_2$ ratios reach their lowest levels in the LADCO region in central Chicago on Chicago exceedance days (Figure 2.9). Ratios are also low in Chicago on days that exceeded the NAAQS in Sheboygan, WI and in Western Michigan. The ratios follow a similar distribution to NO_2 over Lake Michigan, with the lowest ratios where NO_2 columns are highest. The relatively high HCHO columns over the southern and eastern lake on Western Michigan exceedance days elevates the $HCHO/NO_2$ ratios somewhat in these areas on these days. Applying the Jin et al. (2020) ratio thresholds to the $HCHO/NO_2$ ratios shows an area of VOC-sensitivity centered in the urban core of Chicago. This area is present on all three sets of exceedance days but largest on Chicago exceedance days. On days that exceeded the NAAQS in Chicago, this large VOC-sensitive area is enclosed in a narrow ring of transitional chemistry, with almost all other areas being NOx-sensitive. However, on exceedance days in Sheboygan and Western Michigan, the transitional areas extend northward along the lakeshore and into the middle of Lake Michigan. This transitional region covers a larger area on downwind exceedance days than on Chicago exceedance days because the NO_2 plume is distributed more widely on these days. The availability of this transported NO_2 pushes the over-lake O_3 formation chemistry from NOx-sensitive into a regime in which O_3 formation is sensitive to both NOx and VOC emissions ("transitional"). The presence of elevated levels of HCHO over the southeastern lake on Western Michigan exceedance days kept this area NOx-sensitive, despite the transported NO_2 plume.

2.3.4 Conclusions

This analysis of TROPOMI satellite data finds the highest NO_2 columns in the Chicago area, followed by Detroit, with similar levels on days with O_3 exceeding the 2015 O_3 NAAQS and over the O_3 season as a whole. The highest HCHO columns were observed in the southern areas of the region, particularly St. Louis and Louisville on O_3 exceedance days in those areas. Application of ratio thresholds from Jin et al. (2020) to observed $HCHO/NO_2$ ratios estimated that O_3 formation chemistry in most nonattainment areas in the LADCO region was sensitive to NOx emissions. According to this analysis, all of the Western Michigan areas, Cleveland and St. Louis and almost all of the Wisconsin lakeshore, Louisville and Cincinnati were NOx-sensitive on O_3 exceedance days. Chicago and Detroit were the only areas with any VOC-sensitive areas, and

the VOC-sensitive area was larger in Chicago than in Detroit. However, approximately half or more of the grid cells in these areas remained NOx-sensitive on exceedance days, primarily in the outlying parts of the nonattainment areas. These patterns are driven by a combination of high NO_2 columns in Chicago and Detroit from urban plumes and high HCHO columns from biogenic emissions in the southern areas. NO_2 emissions from coal-fired power plants also impacted the O_3-NOx-VOC sensitivity, particularly near the largest plants in the Ohio River Valley.

2.4. Model-Based Indicator Ratios: Formaldehyde-to-NO_2 ($HCHO/NO_2$) and Hydrogen Peroxide-to-Nitric Acid (H_2O_2/HNO_3) Ratios

2.4.1. Introduction

Ozone formation chemistry indicator ratios derived from modeling provide more ubiquitous spatial and temporal coverage than the monitor-based ratios. As the model results produce a large number of intermediate and terminal ozone chemistry species, modeling data also provide a greater set of ratio options than the monitor data. One important limitation to model-derived O_3-NOx-VOC sensitivity determinations is that photochemical modeling inherently relies on a vast number of assumptions and approximations, the validity of which determine the accuracy of the model outcomes. Another limitation is the difficulty in verifying the accuracy of model simulations of these species due to the lack of observations. For LADCO's modeling, estimates are available for every hour of the O_3 season for the entire contiguous United States and parts of Canada and Mexico. The modeling runs analyzed here were done using 12 km x 12 km resolution grid cells.

In this section, we used 12-km modeling conducted by LADCO for the years 2016, 2020, and 2028 to determine $HCHO/NO_2$ and H_2O_2/HNO_3 ratios in the early afternoon on exceedance days. We then applied the ratio threshold from Duncan et al. (2010) to the $HCHO/NO_2$ ratios and thresholds from Sillman (2022) to the H_2O_2/HNO_3 ratios to determine the O_3-NOx-VOC chemical regimes in different areas of the Great Lakes region. We compare the results from the two ratios and discuss how O_3 chemistry regimes are projected to change over time.

2.4.2. Methods

This study analyzes pollutant concentrations output from two different modeling runs conducted by LADCO for other purposes. Both model runs used the Comprehensive Air Quality Model with Extensions (CAMx) v7.10, with a 12-km model grid and 2016 base year meteorology and emissions. The first modeling run was conducted in 2020 for state attainment

demonstrations for the 2008 O_3 NAAQS for the Chicago area. This run (referred to as the LADCO_2016aa2a run) projected emissions from the 2016 base year to 2020. LADCO projected O_3 season NOx emissions reductions of 10-17% from 2016 to 2020, primarily due to mobile source emissions reductions. VOC reductions were smaller at around 1% of total VOCs and around 5% of anthropogenic VOCs.[13] The second modeling run was conducted in 2021 to support state regional haze plans. This run (referred to as the LADCO_2016abc run) projected emissions from the 2016 base year to 2028. LADCO projected O_3 season NOx emissions reductions of 39% and VOC emissions reductions of 14% over this timeframe.[14] There are some minor differences in the emissions used for the two 2016 base year model runs. This document primarily uses the 2016 run from the LADCO_2016abc run, but we have been clear throughout which 2016 model run we have used.[15] All results are shown for the first (ground-level) layer of the model.

Table 2.3. Emissions of NOx and anthropogenic VOCs used in each model run; emissions in tons/day.

	Model run LADCO_2016aa2a						Model run LADCO_2016abc					
	NOx			VOCs			NOx			VOCs		
	2016	2020	% change	2016	2020	% change	2016	2028	% change	2016	2028	% change
IL	975	861	12%	994	955	4%	953	606	36%	1016	894	12%
IN	895	734	18%	660	628	5%	841	459	45%	673	578	14%
MI	807	693	14%	820	777	5%	792	517	35%	847	708	16%
MN	634	526	17%	712	686	4%	565	350	38%	829	740	11%
OH	957	806	16%	928	884	5%	922	570	38%	956	813	15%
WI	510	429	16%	472	448	5%	492	292	41%	502	420	16%
Total	4778	4049	15%	4586	4376	5%	4565	2793	39%	4824	4153	14%

[13] The modeling is described in greater detail in: LADCO (2020) Attainment Demonstration Modeling for the 2008 Ozone National Ambient Air Quality Standard: Technical Support Document. https://www.ladco.org/wp-content/uploads/Documents/Reports/TSDs/O3/LADCO_2008O3_SeriousNAASIP_TSD_19Nov2020.pdf

[14] The modeling is described in greater detail in: LADCO (2021) Modeling and Analysis for Demonstrating Reasonable Progress for the Regional Haze Rule 2018-2028 Planning Period: Technical Support Document. https://www.ladco.org/wp-content/uploads/Projects/Regional-Haze/Round2/LADCO_RegionalHaze_Round2_TSD_17June2021_Final.pdf

[15] LADCO also analyzed modeled projections from 2016 to 2023 using nested 1.3-4-12-km grids and refined meteorology. While these model runs produced differences compared with the 12-km modeling presented in this document, the over trends and distributions were similar, such that use of this modeling does not substantially change the interpretation of the results. We have therefore not included this refined modeling in this document.

This analysis focuses on the early afternoon hours, defined as 13:00-16:59 LDT. These are the hours of peak O_3 formation as shown in Figure 2.10 and are also hours for which the indicator ratios $HCHO/NO_2$ and H_2O_2/HNO_3 should be valid. This time period also includes the TROPOMI satellite overpass time, which facilitates comparison of these results with the satellite-based ratios presented in Section 2.3. One exception is that while the Western Michigan sites are in the Eastern Time Zone, these data were examined during the hours of 13:00-16:59 CDT to be consistent with the times used for the upwind Chicago area. Figures for the early morning hours of peak emissions, defined as 5:00-8:59 LDT, are included in Appendix 3.

In this section, we analyze the model-based ratios on modeled O_3 exceedance days in the 2015 O_3 nonattainment areas in the LADCO region. Ozone exceedance days are identified as days when any grid cell in a nonattainment area had a modeled MDA8 value that exceeded 70 ppb. This approach identifies a somewhat different set of exceedance days than identified from monitoring in the area. The O_3 exceedance days are different for each nonattainment area and are listed in Table A3.1. This analysis combines four nonattainment areas along the Wisconsin lakeshore (the Milwaukee area, Sheboygan, Manitowoc, and Door counties) into one area to streamline the discussion. Similarly, it combines three nonattainment areas in Western Michigan (Berrien, Allegan, and Muskegon counties) into one area. Appendix 6 shows the results for each of these nonattainment areas individually. Model grid cells were linked to nonattainment areas using the approach described in Section 2.3.2.. The grid cells included in each nonattainment area are shown in Figure A2.1.

2.4.3. Results and Discussion

The figures in this section show composites of all O_3 exceedance days in each 2015 O_3 nonattainment area in the Great Lakes region. There is significant variability between the individual exceedance days that this approach does not examine, but it does provide insight into the overall patterns of O_3 chemistry on days when MDA8 concentrations exceed the 2015 O_3

NAAQS. This analysis focuses on the patterns within and across the areas, but Table A2.2 lists the concentrations and ratios for individual grid cells that contain ground monitors.

Diurnal Trends

Figure 2.10 shows the diurnal patterns in mean concentrations of O_3 and O_3 precursors, along with O_3 sensitivity indicator ratios on O_3 exceedance days in the different nonattainment areas. The figure shows the growth in O_3 concentrations during the day, reaching a peak in the early afternoon hours, roughly 13:00-16:59. Future analyses will focus on these "peak-O_3" hours. Mean O_3 concentrations are below 70 ppb on these O_3 exceedance days because they represent an average of all of the grid cells in each nonattainment area. While at least one grid cell in each nonattainment area by definition must have had an MDA8 value over 70 ppb on each of these days, the average across all grid cells on all exceedance days was below 70 ppb for all nonattainment areas. The peak O_3 times were later in Western Michigan and on the Wisconsin lakeshore compared with the other, urban nonattainment areas. This occurs because the O_3 in these areas is transported significant distances from source regions in Chicago and other upwind areas, which can take many hours (Dye et al., 1995).

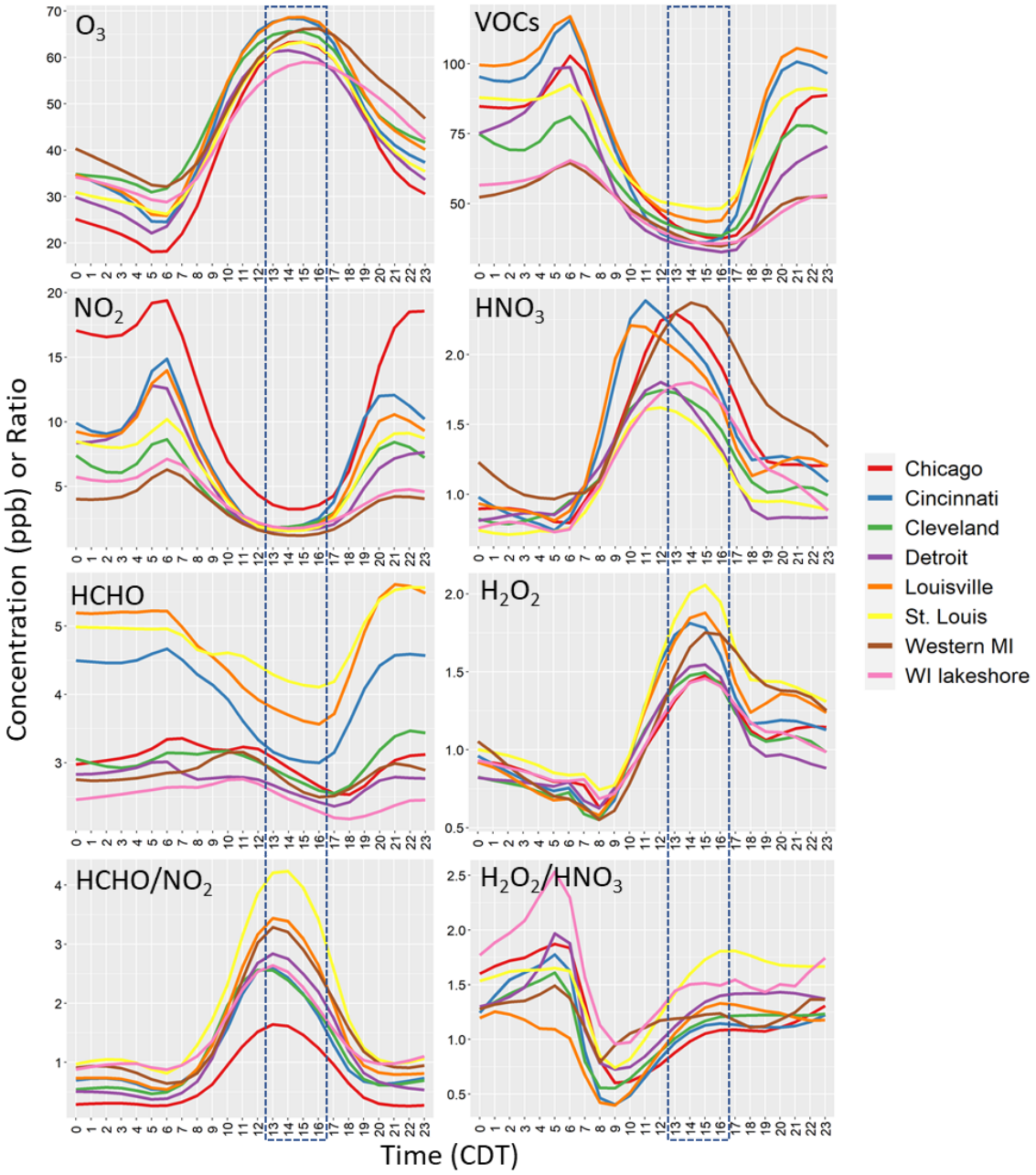

Figure 2.10. Diurnal cycles of mean pollutant concentrations and ratios on exceedance days in the nonattainment areas for the 2016 base year using the LADCO_2016aa2a modeling run. The dashed box encloses the early afternoon times used in subsequent analyses, although values are plotted here versus time in CDT, whereas afternoon values for further analysis were determined using LDT, which is EDT for many of the nonattainment areas.[16]

[16] Western Michigan is an exception; these sites are located in the Eastern time zone, but we used Central time stamps for these sites to ensure they were directly comparable to sites in the upwind Chicago area.

Model concentrations of NO_2, HCHO, and VOCs all peak in the early morning and have minima during the hours of peak O_3. This familiar pattern results from a combination of the early morning rush hour, which contributes to the morning peaks, followed by the growth of the boundary layer during the daytime, which dilutes pollution. Note however that the diurnal differences in HCHO are much smaller than those of NO_2, presumably because HCHO is also formed during the daytime from reactions of VOCs, particularly biogenic VOCs (De Smedt et al., 2015).

HNO_3 and H_2O_2 have very different diurnal patterns, with relatively low concentrations overnight and large increases during daylight hours (Figure 2.10). Both compounds reach peak concentrations near the hours of peak O_3, with more variability in the timing of the peak for HNO_3 than for H_2O_2. Both compounds are produced by the same reactions that produce O_3, with more HNO_3 forming under VOC-sensitive conditions (with excess NOx) and more H_2O_2 forming under NOx-sensitive conditions (with excess VOCs). These compounds therefore have similar diurnal patterns as O_3.

Both the HCHO/NO_2 and H_2O_2/HNO_3 indicator ratios increase from mid-morning to early-to-mid-afternoon, reaching daytime peak values during the hours of peak O_3 (Figure 2.10). The two indicator ratios have very different patterns overnight, when concentrations of HNO_3 and H_2O_2 are very low. However, Sillman (2022) stated that indicator ratios refer to values between the hours of noon and sunset only, and that ratios in the mornings and evenings will have different correlation patterns and may be impacted by surface deposition and other factors. The identified hours of peak O_3 (13:00-15:59) are therefore the most relevant for evaluating these O_3 chemistry indicator ratios. In addition, the early afternoon values of both indicator ratios are highest during the summer and lower in the spring and in September (Figure A3.2). This result suggests that O_3 formation may be more VOC-sensitive in the spring and September compared with the summer, likely because biogenic VOC emissions are lower during these months than in the summer.

Pollutant Trends and Changes over Time by Nonattainment Area

Ozone. The concentrations of most pollutants changed over the different modeling periods, with concentrations decreasing from 2016 to 2020 to 2028. Figure 2.11 shows that the model projected the highest median O_3 concentrations on O_3 exceedance days in Louisville and Cincinnati and the lowest median concentrations along the Wisconsin lakeshore and in Chicago, Detroit, and St. Louis. This variability likely reflects the size and extent of the nonattainment areas and the heterogeneity of O_3 within those nonattainment areas. The Chicago and Detroit nonattainment areas are particularly large, and the Wisconsin lakeshore stretches out over a large area. These characteristics make it likely that O_3 concentrations varied significantly within the nonattainment areas, such that some parts had much lower ozone concentrations while other parts were exceeding the NAAQS. This could lead to lower median O_3 concentrations. In contrast, the Louisville and Cincinnati nonattainment areas are relatively small and compact, which should lead to more homogenous O_3 concentrations and higher median concentrations on exceedance days.

The modeled changes in O_3 concentrations are shown in both concentration and percentage units in Figure 2.11. Ozone decreased in each progressive time period in all nonattainment areas. The reductions from 2016 to 2020 were about half of those from 2016 to 2028, with median decreases of 3 to 4 ppb (5 to 6.5 %) from 2016 to 2020 and of 7 to 9 ppb (12 to 14 %) from 2016 to 2028. The spatial distribution of O_3 and O_3 reductions were similar in all sets of years. The southern areas (St. Louis, Louisville, and Cincinnati) had the largest simulated O_3 reductions, whereas the Wisconsin lakeshore, Chicago, and Detroit had the smallest reductions.

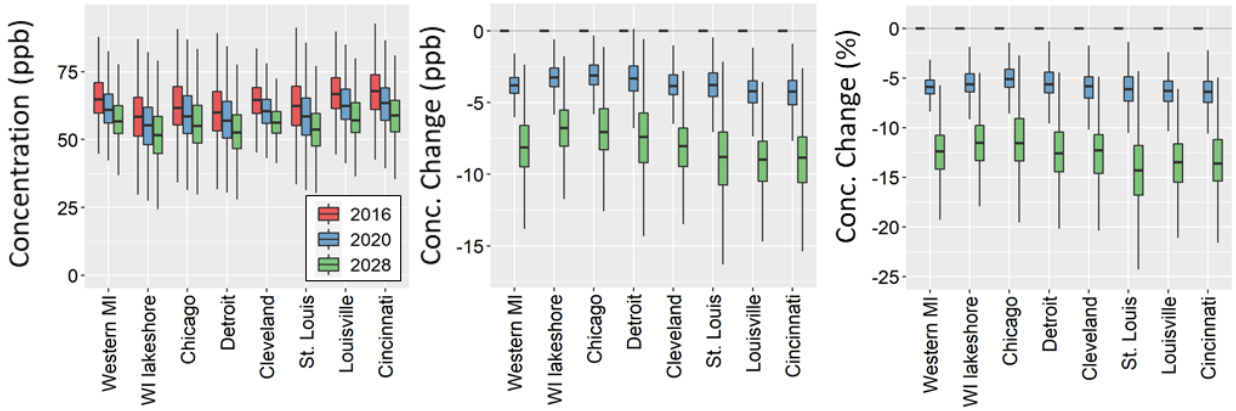

Figure 2.11. Modeled ozone concentrations (left) and concentration changes in ppb (middle) and percentage of 2016 values (right) in the early afternoon (13:00-16:59 LDT) on exceedance days in the nonattainment areas. The 2016 values are from the LADCO_2016abc model run. Boxplots[17] for Western Michigan and the Wisconsin lakeshore combine values for multiple nonattainment areas in these regions. Figure A6.3 shows the results for each individual nonattainment area.

Figure 2.12 shows the spatial distribution of O_3 concentrations on O_3 exceedance days in 2016 in each of the nonattainment areas. These maps show that the highest O_3 concentrations in the urban areas were located in the central urban core, with concentrations decreasing away from the city center. On exceedance days in nonattainment areas around Lake Michigan and Lake Erie, the highest O_3 concentrations were located over the lakes. On Wisconsin lakeshore exceedance days, the plume of peak O_3 extended farther north and westward than it did on Chicago exceedance days. On Western Michigan exceedance days, the O_3 plume was localized farther westward than on Chicago or Wisconsin lakeshore days and farther southward than on Wisconsin lakeshore exceedance days. Lake Erie had much higher O_3 concentrations on Cleveland exceedance days than on exceedance days in nearby Detroit, when the O_3 plume was centered over downtown Detroit. There was not a clear O_3 plume over Lake St. Clair by Detroit, which is a much smaller lake than either Lake Michigan or Lake Erie. In addition, a high-O_3

[17] In boxplots, the line goes through the median value, the box encloses the middle 50% of values, and the "whiskers" include most values.

plume is evident in the Ohio River Valley between Louisville and Cincinnati, likely due to NOx emissions from the many power plants located in this area.

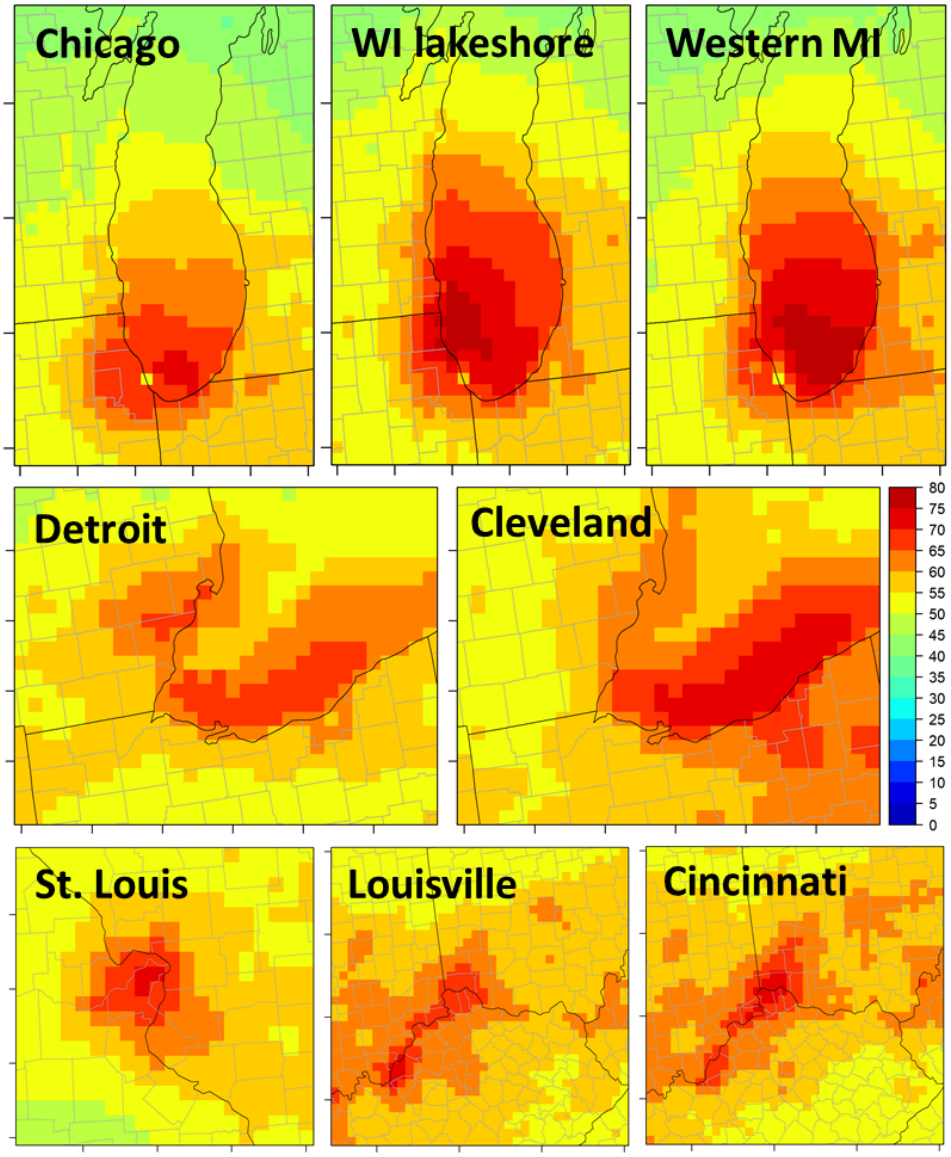

Figure 2.12. Mean ozone concentrations (ppb) in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas in 2016. Values are the mean concentration within each grid cell based on the LADCO_2016abc model run.

Figure 2.13 shows maps of the spatial distribution of projected ozone changes between 2016 and 2028 on O_3 exceedance days in the different nonattainment areas. In the southern areas, O_3

reductions are projected to be largest in the urban cores, with smaller reductions towards the city suburbs and outlying areas. In contrast, Chicago,[18] Detroit, and Cleveland all had the largest O_3 reductions in a ring outside the city in the suburbs with smaller decreases in the urban cores. This suggests NOx-suppression/VOC-sensitivity in the downtown areas and the movement of the areas of peak O_3 production from outlying areas of cities towards the downtown areas. Jin et al. (2020) observed these changes in the monitoring data for Chicago, New York City, and Los Angeles. We use monitoring data to explore how areas of peak O_3 concentrations have shifted within nonattainment areas over time in Section 4 of this report. Along the Wisconsin lakeshore, the largest O_3 reductions are projected to be just inland of the lakeshore, while the lakeshore itself is projected to have very small changes in O_3 between Chicago and Milwaukee, suggesting some NOx suppression/VOC sensitivity. In comparison, the Western Michigan lakeshore is projected to have the largest reductions in southern areas, peaking at the Indiana border, with smaller reductions to the north.

[18] For Chicago, the darkest blue grid cell (with large ozone reductions) northwest of the city center is O'Hare airport, which had large and increasing NO_2 emissions, and thus increasing ozone titration, consistent with the U.S. Energy Information Agency's estimates of large growth rates at airports (U.S. EIA, 2017; Table: Air Travel Energy Use). The red grid cell with large ozone increases is located in downtown Chicago, where seven major highways converge and building density is extremely high. These factors result in very high NO_2 emissions, which leads to ozone titration in this grid cell. Over time, the model projects ozone increases due to decreased titration from lower NO_2 concentrations through 2028.

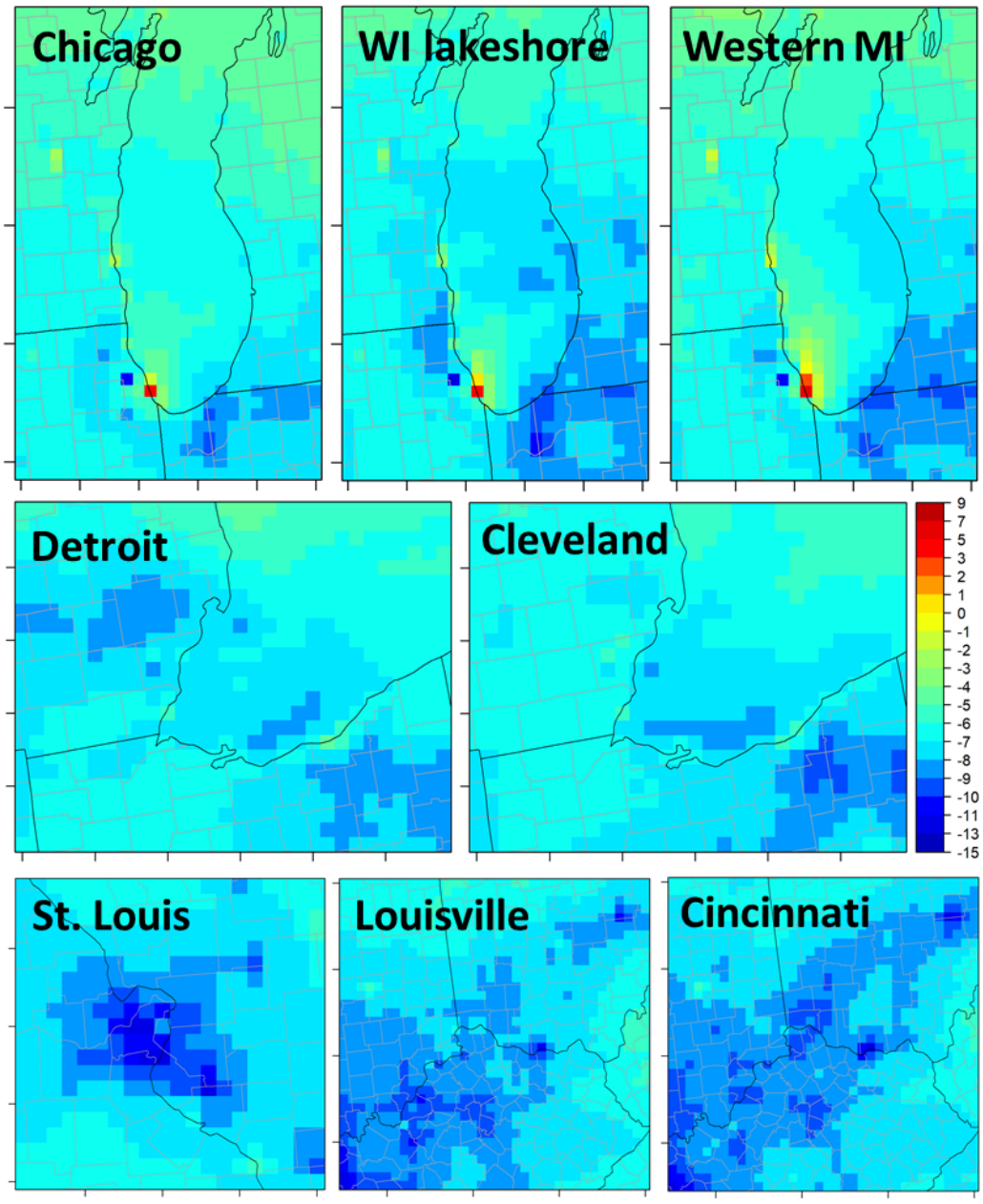

Figure 2.13. Mean change in ozone concentrations (ppb) from 2016 to 2028 in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas. Values are the mean concentration change within each grid cell based on the LADCO_2016abc model run.

NO_2, HCHO, and VOCs. Boxplots of early afternoon concentrations and concentration changes on O_3 exceedance days from 2016 to 2028 for NO_2, HCHO, and total VOCs are shown in Figure

2.14. NO_2 concentrations are by far the highest in Chicago and the lowest in Western Michigan, which is a downwind, mostly rural area. Reductions in NO_2 concentrations are projected to be quite consistent across nonattainment areas, with median reductions of 15 to 20% by 2020 and 35 to 40% by 2028. Appendix 3 includes maps of NO_2 concentrations and concentration changes. These maps show that NO_2 concentrations are highest in the urban cores, and NO_2 reductions are the greatest in the areas with the highest concentrations in 2016. Areas of high NO_2 concentrations are also visible near some large power plants, as seen in the TROPOMI satellite images (Figure 2.7).

In contrast with NO_2, modeled HCHO concentrations were highest in the southern areas and lower to the north, particularly along the Wisconsin lakeshore and in Detroit (Figure 2.14). HCHO concentrations are projected to decrease in all areas but at a much slower rate than the NO_2 concentrations. The model projects 2.5 to 4.5% reductions by 2020 and decreases of 7-8% in most areas by 2028, with smaller reductions of 5 to 6% around Lake Michigan. HCHO concentrations are highest in the rural, forested areas in the southern parts of the region, such as southwest of St. Louis, south of Cincinnati, and including the southwestern parts of Louisville itself (Appendix 3). Reductions in HCHO are projected to be more evenly distributed in the region than are NO_2 reductions.

VOC data are only available from the LADCO modeling for 2016 and 2020. Early afternoon model VOC concentrations on O_3 exceedance days were highest in the southern areas of St. Louis and Louisville and lowest along the Wisconsin lakeshore and in other northern areas. The model projected small VOC reductions of around 1 to 2% in the Lake Michigan areas by 2020, small increases in St. Louis, and few changes in the other areas. The model projected much larger reductions of 2 to 7% of VOCs in all areas in the early morning (5:00 to 8:59 am, not shown), when VOCs are at their highest levels, but these reductions have largely disappeared by the early afternoon. The model projects that the urban cores have both the highest VOC concentrations and concentration decreases (Figure A3.13 and A3.14). Forested areas in the southern parts of the region are also projected to have high VOC concentrations.

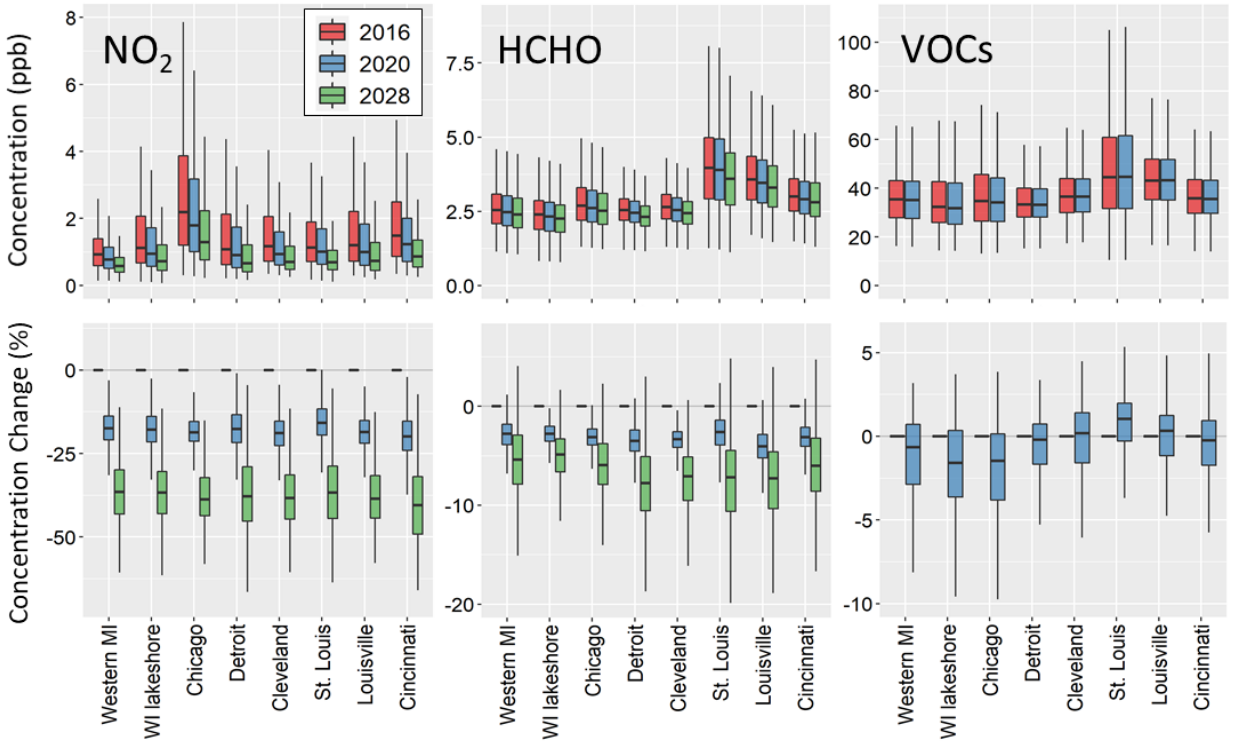

Figure 2.14. Modeled concentrations (top) and percent concentration changes (bottom) of NO_2 (left), HCHO (middle), and total VOCs (right) in the early afternoon (13:00-16:59 LDT) on exceedance days in the nonattainment areas. The 2016 values are from the LADCO_2016abc model run except for VOCs, which come from the LADCO_2016aa2a run. Note that we do not have VOC data for 2028.

HNO_3 and H_2O_2. Early afternoon concentrations and projected concentration changes for HNO_3 and H_2O_2 are shown in Figure 2.15 on O_3 exceedance days in the region. HNO_3 concentrations are highest in an assortment of areas, including Western Michigan, Chicago, Louisville, and Cincinnati. The model projects large reductions in HNO_3, similar in magnitude to those projected for NO_2: 16 to 20% by 2020 and 34 to 38% by 2028. The model predicts the highest HNO_3 concentrations over southern Lake Michigan offshore of Chicago, and over Lake Erie. The model also predicts higher HNO_3 concentrations over urban areas. The areas with the highest concentrations are also projected to have the greatest reductions. Since HNO_3 is produced when O_3 formation is VOC sensitive, the lower HNO_3 concentrations predicted by the model in 2028

suggests a decrease in VOC sensitivity (or a trend toward greater sensitivity to NOx reductions) in these areas.

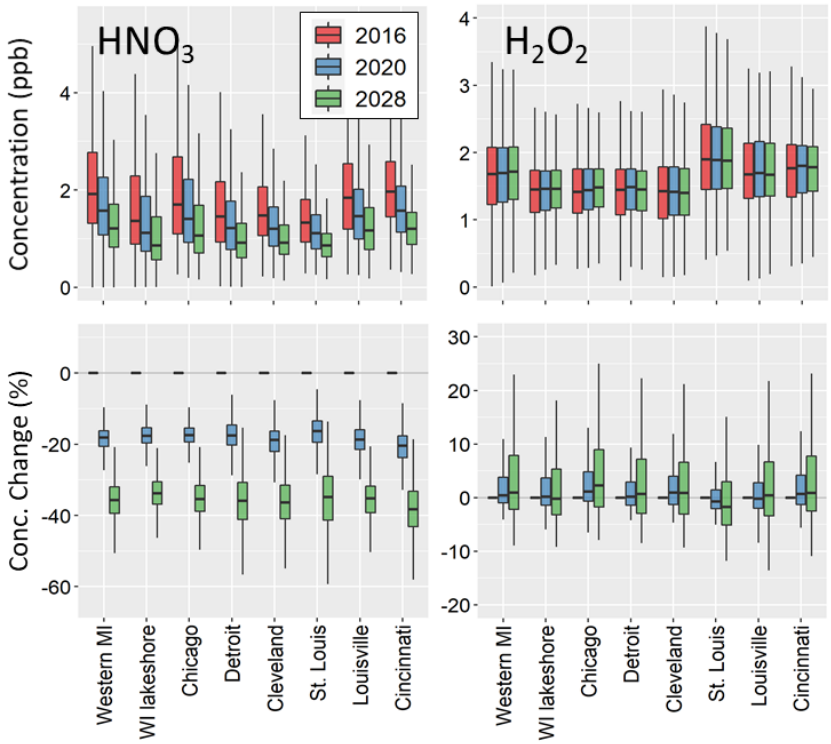

Figure 2.15. Modeled concentrations (top) and percent concentration changes (bottom) of HNO_3 (left) and H_2O_2 (right) in the early afternoon (13:00-16:59 LDT) on exceedance days in the nonattainment areas. The 2016 values are from the LADCO_2016abc model run.

Similar to HCHO patterns, H_2O_2 concentrations are highest in the southern areas, and in Western Michigan. However, H_2O_2 concentrations are projected to remain steady over the years, with very small increases of generally less than 1 to 2% by 2028, although levels in St. Louis are projected to decrease slightly. H_2O_2 concentrations are relatively low in urban areas (Appendix 3). Since H_2O_2 is formed when O_3 formation is NOx-sensitive, this suggests that these urban areas are more VOC-sensitive. H_2O_2 concentrations are higher in southern areas that have more biogenic VOCs. The model projects that H_2O_2 concentrations will increase dramatically over southern Lake Michigan, with smaller increases over Lake Erie and in the cities. These increases

likely indicate that these areas are becoming more NOx-sensitive, which leads to the production of more H_2O_2.

Ozone Formation Chemistry Indicator Ratios and Regimes

HCHO/NO_2 Ratios. Figure 2.16 shows the two O_3 chemistry indicator ratios for the different nonattainment areas on O_3 exceedance days. The modeled HCHO/NO_2 ratios are the lowest (e.g., most VOC-sensitive) in Chicago, with the median value falling in the transitional range in 2016 and 2020 and at the edge of the NOx-sensitive range in 2028. The model projected the highest ratios in St. Louis, Louisville, and Western Michigan, indicating that these areas are the most NOx-sensitive. The ratios are projected to increase over time in all areas, suggesting that O_3 chemistry is becoming more NOx-sensitive throughout the region. The HCHO/NO_2 ratios were lowest in the city centers (Figure 2.17). Along Lake Michigan and Lake Erie, relatively low ratios extend along the lakeshore away from the large urban areas and offshore over the lakes.

We applied the indicator ratio thresholds from Duncan et al. (2010) to determine the O_3-NOx-VOC chemistry regime for each grid cell in each early afternoon hour on O_3 exceedance days. The percentage of these grid cells that fell into each chemistry regime is shown in Figure 2.16. NOx-sensitivity accounted for the majority of the grid cells and hours in the LADCO region. However, all nonattainment areas had some areas of VOC sensitivity and of transitional chemistry. These areas are projected to shrink everywhere over time as the areas of NOx sensitivity expand. The model predicted that roughly 35% of the model grid cells overlying the Chicago NAA in 2016 were VOC-sensitive, 40% transitional, and 25% NOx-sensitive. The VOC-sensitive areas of Chicago are projected to decrease to 15% of the total in 2028 and NOx-sensitive areas are projected to expand to 50% of the area. The Wisconsin lakeshore, Detroit, Cleveland, and Cincinnati all have considerable areas of VOC sensitivity in 2016 (15 to 19% of grid cells), and these areas are projected to decrease to 5% or less by 2028. The other areas have smaller VOC sensitive areas in all years but follow similar trends.

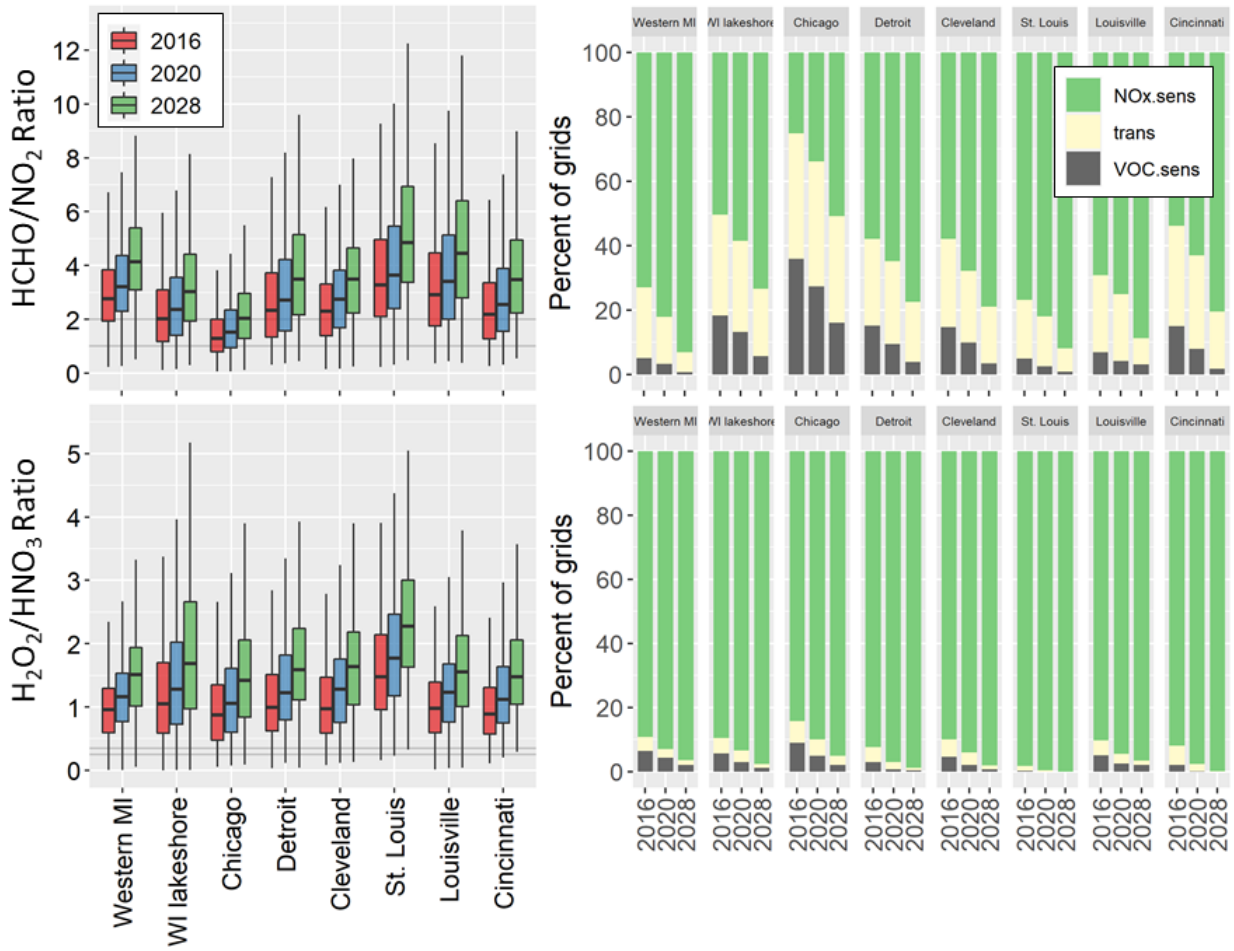

Figure 2.16. Modeled pollutant ratios (left) and ozone chemistry regimes determined from the pollutant ratios (right), for $HCHO/NO_2$ ratios (top) and H_2O_2/HNO_3 ratios (bottom). The gray lines mark the ratio thresholds between VOC-sensitive ($HCHO/NO_2 < 1$; $H_2O_2/HNO_3 < 0.25$), transitional ($HCHO/NO_2$ of 1-2; H_2O_2/HNO_3 of 0.25-0.35), and NOx-sensitive ($HCHO/NO_2 > 2$; $H_2O_2/HNO_3 > 0.35$) chemistry. Values are shown for the early afternoon (13:00-16:59 LDT) on exceedance days in the nonattainment areas. The 2016 values are from the LADCO_2016abc model run. Ozone chemistry regimes were determined by applying ratio thresholds from Duncan et al. (2010) to the $HCHO/NO_2$ ratios and from Sillman et al. (2022) to the H_2O_2/HNO_3 ratios.

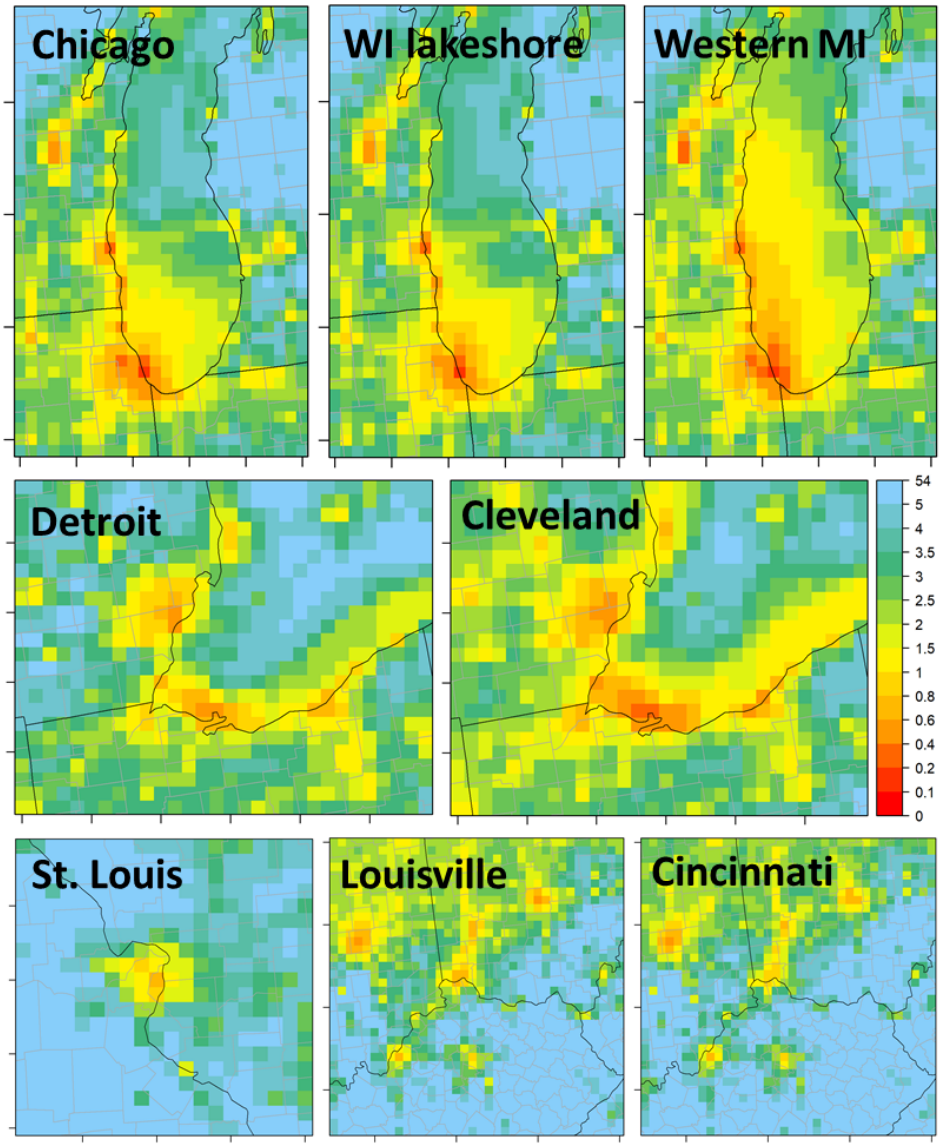

Figure 2.17. Mean HCHO/NO_2 ratios in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas in 2016. Values are the mean ratio within each grid cell based on the LADCO_2016abc model run. Note that reds and oranges show areas of VOC sensitivity, yellows show areas of transitional chemistry, and greens and blues show areas of NOx sensitivity using the Duncan et al. (2010) indicator ratio thresholds.

H_2O_2/HNO_3 Ratios. Almost all areas have H_2O_2/HNO_3 ratios greater than 0.5 (Figure 2.16), which suggests that almost all O_3 formation is NOx-sensitive according to the thresholds reported in Sillman (2022). This is a very different conclusion than that suggested by the HCHO/NO_2 ratios

discussed previously, which found significant areas of VOC-sensitivity and transitional chemistry. The H_2O_2/HNO_3 ratios are highest in St. Louis and fairly similar in all other areas although slightly lower in Chicago and Cincinnati. The H_2O_2/HNO_3 ratios are projected to increase in all areas, indicating that O_3 formation will become even more NOx-sensitive over time. Maps of the H_2O_2/HNO_3 ratios find the lowest ratios over southern Lake Michigan followed by Lake Erie, as well as somewhat depressed ratios in the cities (Figure 2.18).

Applying the H_2O_2/HNO_3 ratio thresholds from Sillman (2022) suggests that O_3 formation is much more NOx-sensitive than suggested by the $HCHO/NO_2$ ratios (Figure 2.16). For example, the maximum extent of VOC sensitivity using the H_2O_2/HNO_3 ratio was 9% in Chicago in 2016, as compared to roughly 35% VOC-sensitive based on the $HCHO/NO_2$ ratios. Application of the H_2O_2/HNO_3 ratios also suggests that the extent of VOC-sensitive areas will shrink over time, reaching negligible levels by 2028.

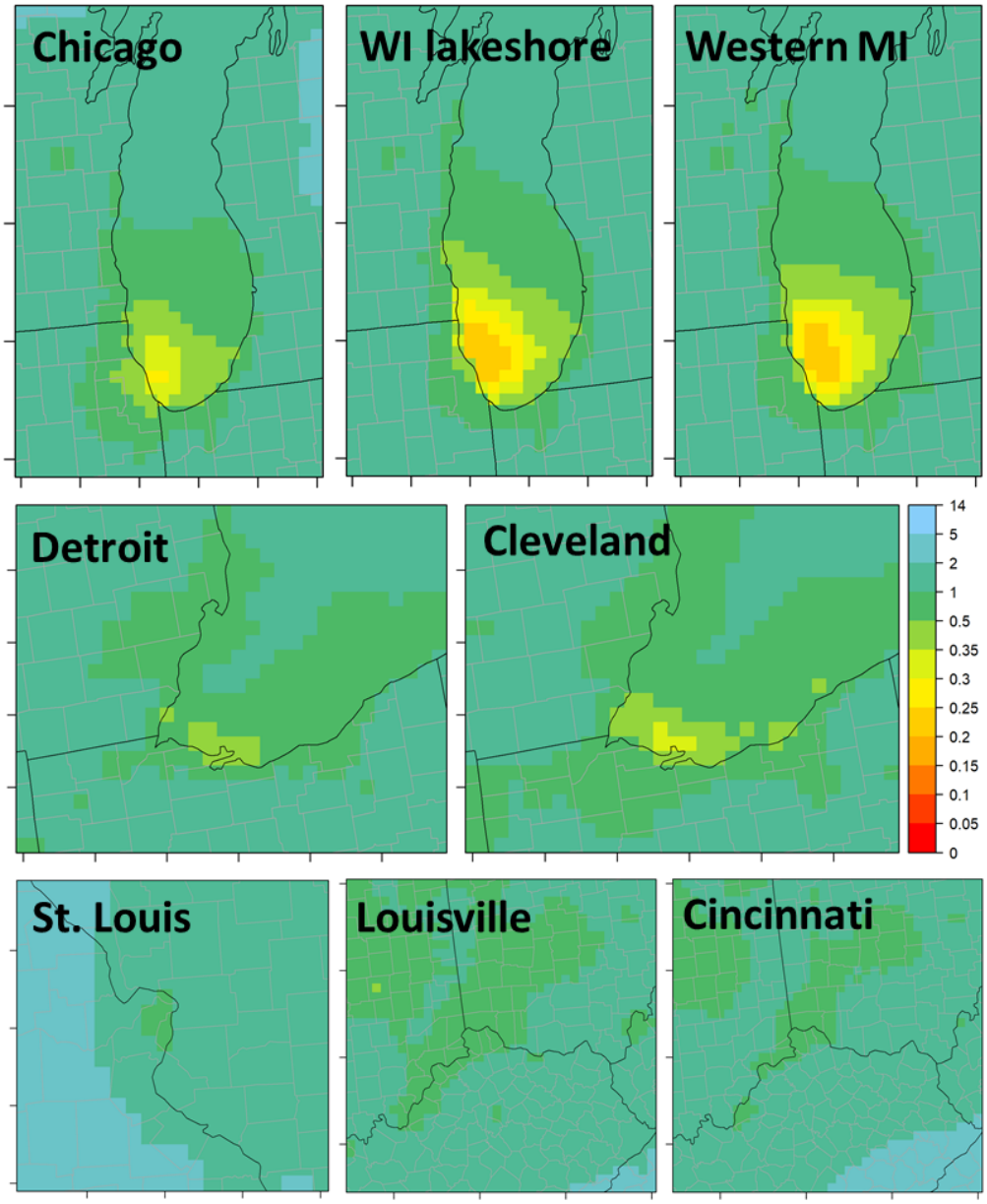

Figure 2.18. Mean H_2O_2/HNO_3 ratios in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas in 2016. Values are the mean ratio within each grid cell based on the LADCO_2016abc model run. Note that reds and oranges show areas of VOC sensitivity, yellows show areas of transitional chemistry, and greens and blues show areas of NOx sensitivity using the Sillman (2022) ratio thresholds.

Spatial Distribution of Ozone Formation Chemistry Regimes

Figures 2.19, 2.20, and 2.21 show maps of the modeled O_3 formation chemistry regimes as determined from $HCHO/NO_2$ ratios on high concentration days in each of the O_3 NAAs in the region. The chemistry regime classification for each grid cell is based on the average $HCHO/NO_2$ ratio in that cell on all O_3 exceedance days and applying the ratio thresholds from Duncan et al. (2010).[19] The 2016 maps for the Lake Michigan region show a large VOC-sensitive area over Chicago on all exceedance days in 2016 (Figure 2.19). The VOC-sensitive region extends northward along the lakeshore to Milwaukee on all exceedance days and extends farther eastward over the lake on Western Michigan exceedance days. The model also suggests there are small areas of VOC-sensitivity in smaller cities such as Rockford, IL and Grand Rapids, MI, as well as over Lake Winnebago and the Fox River Valley in Wisconsin. The VOC-sensitive region is surrounded by a transitional zone that is much wider over the lake than over land and just reaches the Western Michigan shoreline. The VOC-sensitive and transitional areas are both projected to shrink moving from 2016 to 2020 to 2028. In 2028, a smaller area of Chicago is projected to be VOC-sensitive. The Wisconsin lakeshore, especially in Milwaukee, are also projected to have smaller VOC-sensitive areas in 2028 relative to 2016.

The modeled $HCHO/NO_2$-based O_3 chemistry regimes on O_3 exceedance days indicate a large VOC-sensitive area over the city of Detroit and a narrow VOC-sensitive area that hugs the Lake Erie shoreline by Cleveland (Figure 2.20). There is also a large VOC-sensitive area over the western extent of Lake Erie near Toledo. As in the Lake Michigan region, the VOC-sensitive areas are surrounded by transitional areas, which extend farther over Lake Erie on exceedance days in Cleveland than on Detroit exceedance days. The VOC-sensitive areas are projected to shrink over time in the Detroit and Cleveland areas but persist over western Lake Erie and Toledo.

[19] Note that adding up the totals of the regime classifications based on the maps will not give exactly the same distributions shown in the bar plots in Figure 7 because the maps show the averages for all days for each grid cell whereas the bar plots do not average over time for individual grid cells.

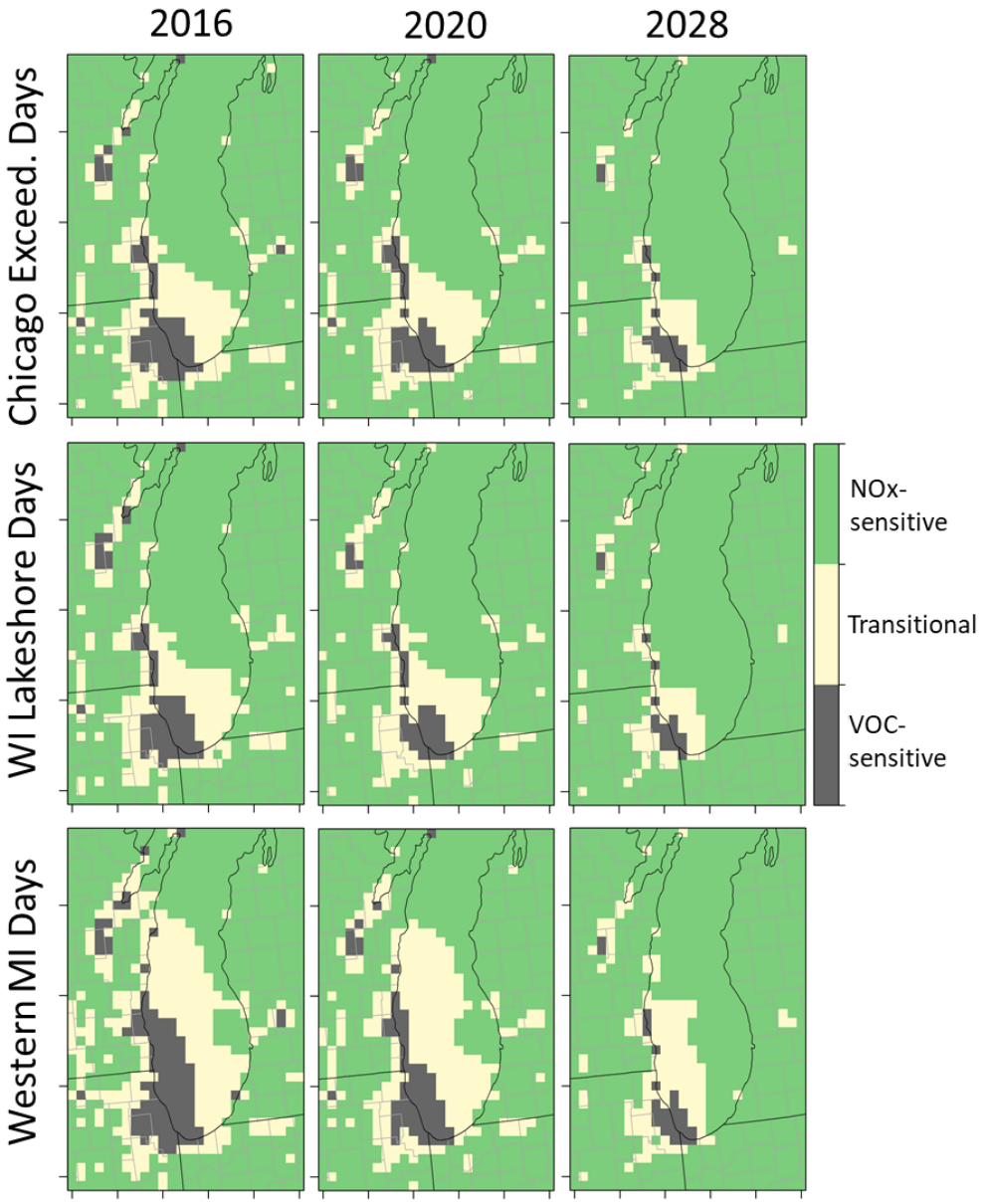

Figure 2.19. Mean ozone chemistry regimes in the three years in the Lake Michigan region based on the HCHO/NO_2 ratios in the early afternoon (13:00-16:59 LDT) on O_3 exceedance days in the nonattainment areas. Values are based on the mean ratio within each grid cell based on the LADCO_2016abc model run. Ozone chemistry regimes were determined by applying ratio thresholds from Duncan et al. (2010) to the HCHO/NO_2 ratios.

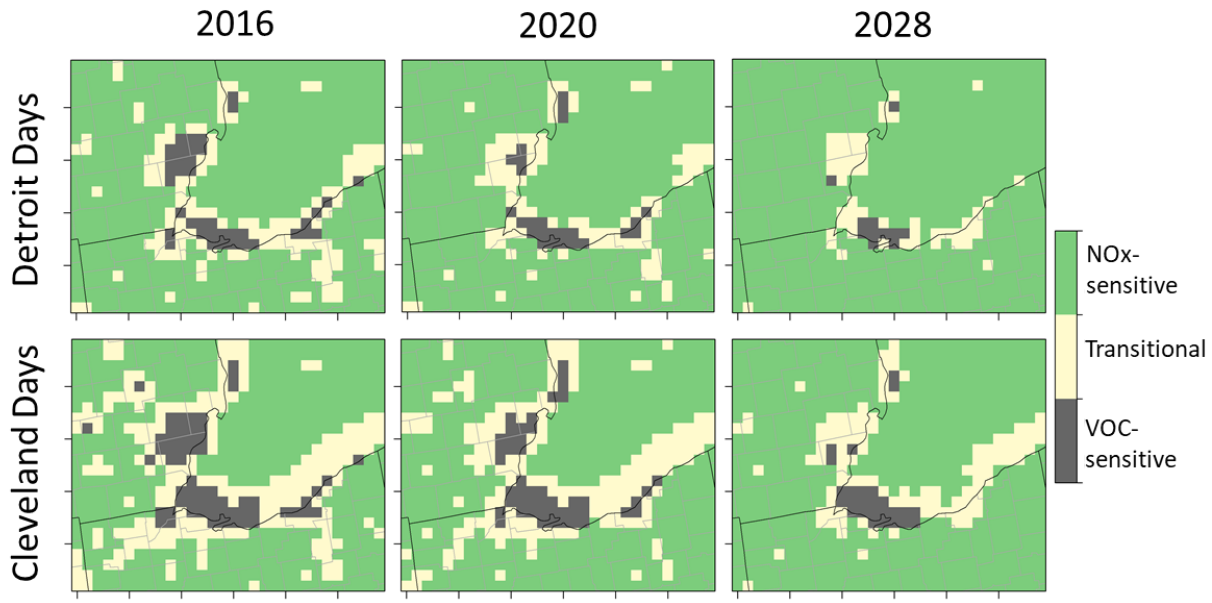

Figure 2.20. Mean O_3 chemistry regime in the three years in the Lake Erie region based on the $HCHO/NO_2$ ratios in the early afternoon (13:00-16:59 LDT) on O_3 exceedance days in the nonattainment areas. Values are based on the mean ratio within each grid cell based on the LADCO_2016abc model run. Ozone chemistry regimes were determined by applying ratio thresholds from Duncan et al. (2010) to the $HCHO/NO_2$ ratios.

Ozone chemistry regime maps based on $HCHO/NO_2$ ratios for the southern areas show much smaller VOC-sensitive areas over the cities than found over northern cities (Figure 2.21). The model also projects some areas of transitional chemistry near big power plants in these areas (compare with Figure 2.7). As found for the other areas, the VOC-sensitive areas are projected to shrink over time and be almost completely gone by 2028. The model predicts that in 2028 almost all of the southern areas will be NOx-sensitive, with just a few transitional areas and one VOC-sensitive grid cell in Louisville.

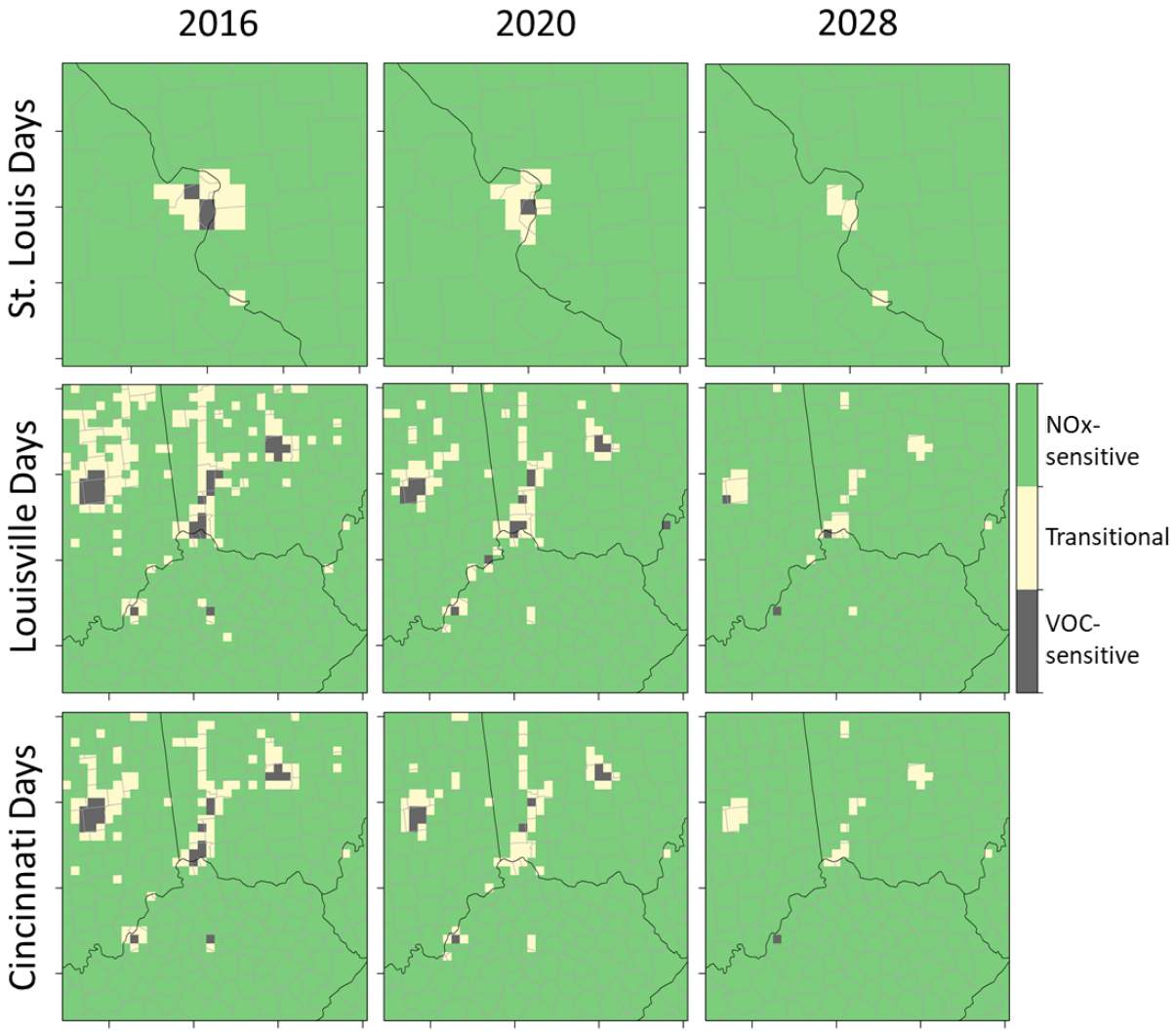

Figure 2.21. Mean ozone chemistry regime in the three years in the southern areas based on the HCHO/NO_2 ratios in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas. Values are based on the mean ratio within each grid cell based on the LADCO_2016abc model run. Ozone chemistry regimes were determined by applying ratio thresholds from Duncan et al. (2010) to the HCHO/NO_2 ratios.

Ozone chemistry regime maps based on H_2O_2/HNO_3 ratios suggest that almost all of the LADCO region was NOx-sensitive in 2016 (Figure 2.22), as also shown in the bar plots in Figure 2.16. These maps show significant VOC-sensitive areas offshore of Chicago over Lake Michigan on O_3 exceedance days on the Wisconsin lakeshore and Western Michigan. This spatial distribution is

very different from that found from $HCHO/NO_2$ ratios, which suggested the greatest VOC sensitivity over the Chicago metropolitan area. The maps also project a small area of transitional chemistry over Lake Erie near Toledo, but estimate that all of the remaining nonattainment areas were NOx-sensitive in 2016. By 2028, the model projects that all of the LADCO region will be NOx-sensitive on O_3 exceedance days based on H_2O_2/HNO_3 ratios (Appendix 3).

Differences between the Two Ozone-NOx-VOC Chemistry Indicator Ratios

As discussed above, the modeled $HCHO/NO_2$ and H_2O_2/HNO_3 indicator ratios both indicate the largest areas of VOC sensitivity in the Chicago area, although the $HCHO/NO_2$ ratio locates this area over the city itself whereas the H_2O_2/HNO_3 ratio puts this zone offshore of Chicago. These differences in location of the VOC-sensitive areas likely reflect the impacts of transport and the different origins of the nitrogen species in each ratio. NO_2 is a primary pollutant and is also formed very rapidly from the primary pollutant NO, so its concentrations are greatest near the emissions sources on land. In contrast, HNO_3 is a secondary pollutant produced from NO_2 during O_3 formation, so its concentrations will peak downwind from the primary emissions sources, in this case, over the lake. In both cases, the presence of VOC-sensitive plumes by Chicago likely indicate that O_3 formation in the central Chicago plume is primarily VOC-sensitive. The different locations of the areas of lowest ratios simply reflects whether the components of the ratio are products of O_3 formation (e.g., HNO_3), and thus heavily influenced by transport, or precursors to O_3 formation (e.g., NO_2), and thus present before O_3 formation and transport.

In general, the trends from the two O_3 chemistry indicator ratios are fairly consistent, with the lowest ratios and most VOC sensitivity in Chicago and the highest ratios in the southern nonattainment areas. Both ratios indicate that O_3 formation in all parts of the region is becoming more NOx-sensitive and less VOC-sensitive. The most significant difference between the results of the two indicator ratios was in the magnitude and extent of the estimated VOC sensitivity around the urban areas. Almost all of the observed H_2O_2/HNO_3 ratios were well above the threshold between transitional and NOx-sensitive chemistry (indicating mostly NOx-sensitive O_3 chemistry, Figure 2.16). In contrast, many of the $HCHO/NO_2$ ratios fell in the

transitional and VOC-sensitive range. This mismatch may indicate that the thresholds we applied for the H_2O_2/HNO_3 ratios were too low.

Many studies have focused on constraining the best ratio thresholds for $HCHO/NO_2$ ratios using data from ground-based monitors, models, and satellites (e.g., Duncan et al., 2010; Jin et al., 2020; Schroeder et al., 2017; Blanchard, 2020). However, many fewer studies have investigated the best ratio threshold for H_2O_2/HNO_3 ratios (e.g., Sillman, 1995; Sillman and He, 1999; Sillman, 2022), and most of these were out of one research lab. This is in part because these compounds are much more difficult to measure in the environment and may also be challenging to model accurately. Additionally, most of the work on H_2O_2/HNO_3 ratios was conducted 20 or more years ago when concentrations of O_3 and O_3 precursors were much higher and O_3 formation chemistry was much more VOC-sensitive. It is possible that lower H_2O_2/HNO_3 ratio thresholds are more appropriate, but we are not aware of any studies that have attempted to refine them for more contemporary ambient conditions. It is also possible that the CAMx model is not accurately modeling either H_2O_2 or HNO_3 concentrations, which would affect the resultant ratio. While there are still considerable uncertainties in determining the most appropriate $HCHO/NO_2$ ratio thresholds to apply in a given location, measurement platform, and time (e.g., Schroeder et al., 2017), these uncertainties are likely much smaller magnitude than those for the H_2O_2/HNO_3 ratios.

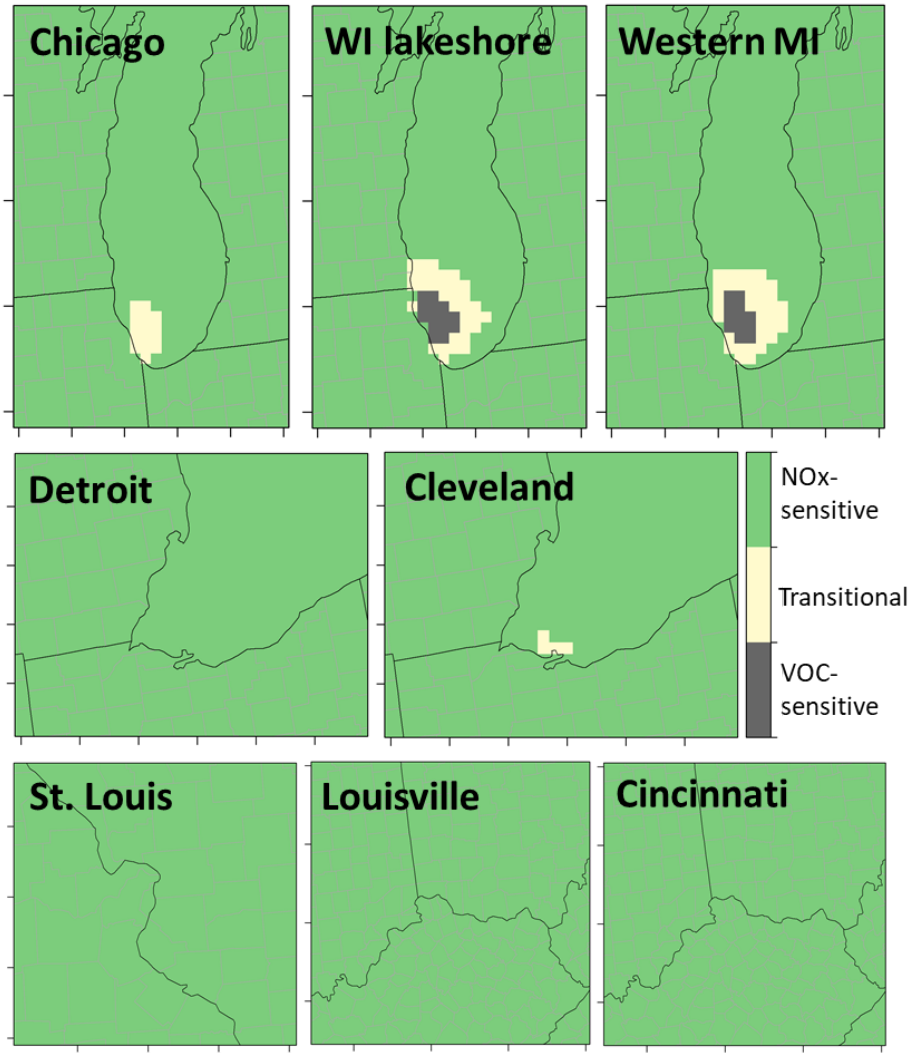

Figure 2.22. Mean ozone chemistry regime in the three years in the nonattainment areas based on the H_2O_2/HNO_3 ratios in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas in 2016. Values are based on the mean ratio within each grid cell based on the LADCO_2016abc model run. Ozone chemistry regimes were determined by applying ratio thresholds from Sillman (2022) to the H_2O_2/HNO_3 ratios.

Ozone Changes Under Different Ozone-NOx-VOC Chemistry Regimes

The degree to which O_3 concentrations are projected to decrease in future years varies depending on the O_3 chemistry regime (Figure 2.23). Areas that are NOx-sensitive experienced the greatest reductions in O_3 in both 2020 and 2028 whereas VOC-sensitive areas experienced the smallest O_3 reductions. Transitional areas had intermediate levels of O_3 reductions. These

results were observed when applying both the $HCHO/NO_2$ and H_2O_2/HNO_3 ratios, although the differences were larger when applying the H_2O_2/HNO_3 ratio. The differential O_3 reductions based on chemistry likely result because of the differences in projected reductions of NOx versus VOCs. NOx emissions and concentrations are projected to decrease much more than VOC emissions and concentrations (Table 2.3 and Figure 2.14). It follows that areas that are sensitive to NOx changes will experience larger O_3 reductions since NOx concentrations are projected to change more than are VOC concentrations.

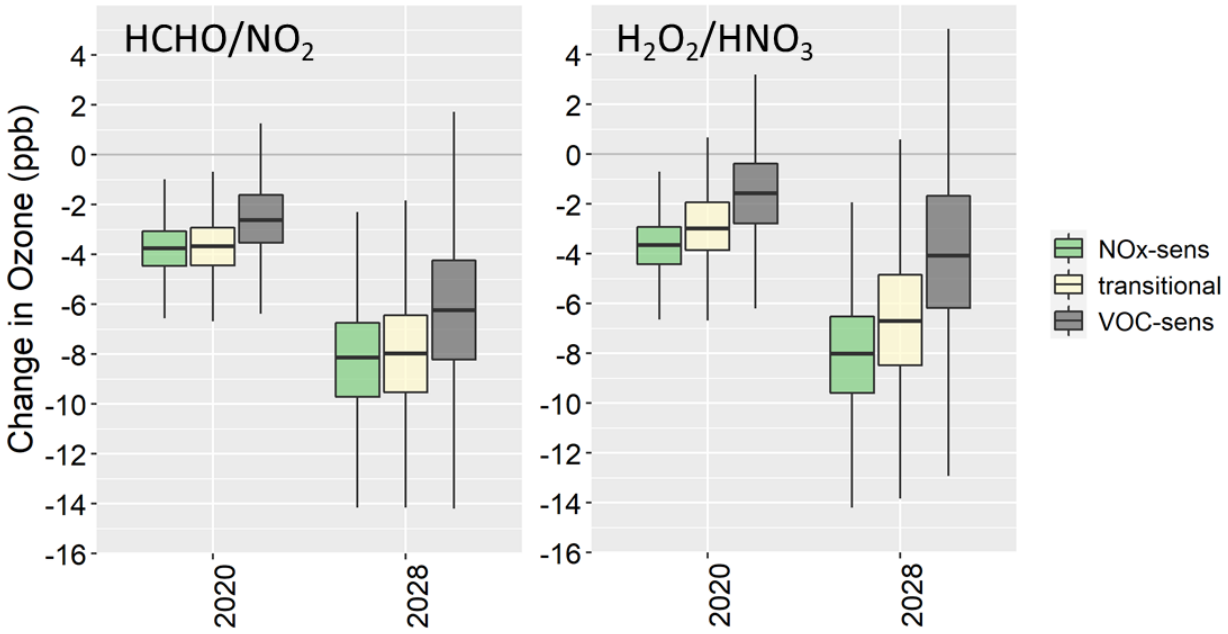

Figure 2.23. Changes in O_3 concentrations (ppb) from the 2016 base year, with the data grouped according to ozone chemistry regime in the early afternoon (13:00-16:59 LDT) on ozone exceedance days in the nonattainment areas. Chemistry regime was determined based on $HCHO/NO_2$ ratios using ratio thresholds from Duncan et al. (2010) (left) or H_2O_2/HNO_3 ratios using ratios from Sillman (2022) (right). Data for all nonattainment areas are combined in this plot.

2.4.4. Conclusions

Results from recent LADCO modeling indicate that concentrations of O_3 and precursor compounds will continue to decrease throughout the region. Analysis of model-derived O_3 chemistry indicator ratios show that O_3 formation is shifting away from VOC-sensitivity and towards more NOx-sensitivity throughout the region. The Chicago area is consistently the most VOC-sensitive area, and southern areas, particularly St. Louis, are the most NOx-sensitive. The $HCHO/NO_2$ ratio suggests the presence of some areas of VOC sensitivity in all of the nonattainment areas in 2016, although the majority of the grid cells in most of the nonattainment areas are NOx-sensitive. In contrast, the H_2O_2/HNO_3 ratio suggests that at least 80 to 90% of the grid cells in all of the nonattainment areas were NOx-sensitive in 2016, with much smaller areas of VOC-sensitivity and transitional chemistry. The differences between the chemistry regime classifications based on the two indicator ratios may indicate an issue with the ratio threshold estimates, most likely with the H_2O_2/HNO_3 ratio thresholds. The modeled trend towards increased NOx-sensitivity over time across all NAAs in the region indicates that NOx emissions reductions will be the most effective way to reduce O_3 concentrations on days with conditions that are conducive to O_3 formation.

3. Weekday-Weekend Analysis

3.1. Introduction

Differences in the observed surface O_3 concentrations between weekdays and weekends are a useful empirical indicator of the O_3 formation chemistry of an area. Analysis of weekday-weekend (W-W) effects on O_3 takes advantage of what is essentially a natural experiment in the atmosphere every week to determine O_3 formation chemistry. Emissions of NOx decrease substantially on the weekends, primarily due to decreases in heavy-duty diesel truck traffic (Marr and Harley, 2002; Harley et al., 2005; Murphy et al., 2007; Pusede and Cohen, 2012). At the same time, emissions of VOCs remain relatively steady (Marr and Harley, 2002). These differences in emissions patterns support an analysis of how O_3 concentrations in the atmosphere respond to changing NOx emissions while holding VOC emissions relatively constant, which in turn provides insight into the ozone-NOx-VOC chemistry of the atmosphere. Figure 3.1 presents the W-W effect schematically, with the top box showing that NOx emissions and concentrations decrease on the weekends relative to weekdays. Under NOx-sensitive conditions, this decrease in NOx leads to a decrease in O_3(left arrow), causing weekend O_3 concentrations to be lower than weekday O_3 concentrations. In contrast, under VOC-sensitive conditions (right arrow), the decrease in NOx causes decreased NOx-saturation, leading to increased O_3 concentrations on weekends compared with weekdays. In this analysis, we compare O_3 concentrations on weekdays and weekends to infer whether O_3 formation is sensitive to NOx or VOCs.

There are a number of advantages to this W-W approach to determining ozone-NOx-VOC sensitivity compared with the approaches using indicator species ratios discussed in Section 2. The main advantage to the W-W analysis is that it is based upon direct measurements of atmospheric conditions and does not require complex models with inherent assumptions or interpretation of satellite retrievals. Another advantage is that this analysis relies primarily on O_3

monitoring data, which are widely available and have a long historical record. This allows examination of how O_3 formation sensitivity has changed over time.

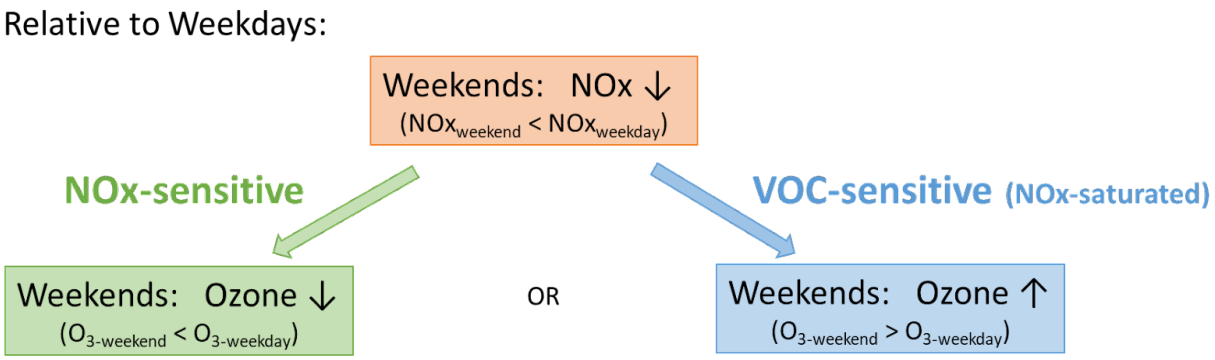

Figure 3.1. Schematic of the weekday-weekend effect of reduced weekend NOx emissions on O_3 concentrations under (left) NOx-sensitive or (right) VOC-sensitive conditions.

Previous W-W analyses have found shifts from strongly VOC-sensitive (NOx-saturated) to transitional or NOx-sensitive in urban areas (Jin et al., 2020; Pusede and Cohen, 2012; Koplitz et al., 2022; Abeleira and Farmer, 2017). These shifts have occurred in response to large reductions in NOx emissions over time. In particular, Koplitz et al. (2022) and Jin et al. (2020) found that O_3 formation in the Chicago area had shifted from VOC-sensitive to transitional or NOx-limited chemistry over the last decade or two. Koplitz et al. (2022) also found that O_3 formation in the Detroit area was NOx-limited in both 2007 and 2016. However, this analysis only examined those two years and did not account for potentially significant meteorological impacts in the W-W effects.

Plotting O_3 versus NOx concentrations provides insight into the role that both NOx and VOCs play in O_3 formation and chemistry without relying upon measurements of VOCs, which are rarely available. Figure 3.2 shows these relationships schematically using a figure from Pusede and Cohen (2012). This figure shows how O_3 varies as NOx concentrations change for three different levels of VOC reactivity, shown as three different curves. Ozone can be represented as O_3 production (PO_3), mean O_3 concentrations, or as O_3 exceedance probability: all three

parameters are related and will follow similar curves (Pusede and Cohen, 2012). This figure shows that for a given level of VOCs and starting at high NOx levels, as NOx concentrations decrease, O_3 concentrations will initially increase as NOx suppression decreases; this is demonstrated by moving from points 1 to 2 in the figure. Once ozone production reaches its maximum level (at point 2), additional reductions in NOx will lead to reductions in O_3 concentrations (from points 2 to 3). Ozone formation has transitioned from being VOC-sensitive/NOx-suppressed (points 1-2) to NOx-sensitive (points 2-3). Additionally, as reactive VOC concentrations decrease, points will trace out a different curve, with lower O_3 concentrations for a given concentration of NOx. If only VOC concentrations were to decrease, ozone would drop to a lower curve (e.g., from points 2 to 4), and ozone formation chemistry could also change regime, in this case changing from transitional to VOC-sensitive. If NOx and VOCs both decreased, as is more common over longer timeframes, O_3 formation would drop to a different curve and also move farther left along that curve (e.g., from points 2 to 5).

With the W-W analysis, for a given year or set of years, O_3 formation on weekdays versus weekends should trace a single curve with constant VOCs and differences in NOx driving the O_3 concentration changes. In this case, negative slopes indicate VOC-sensitive formation and positive slopes indicate NOx-sensitive conditions. Comparison of W-W curves over different years or sets of years shows the impacts of both NOx and VOC reductions: if VOC concentrations were constant or not impacting O_3 formation (as under extremely NOx-sensitive conditions, the curves for the different time periods will lie on top of each other. If VOC concentrations were decreasing and had an important impact on O_3, the W-W points for the different sets of years will trace different curves.

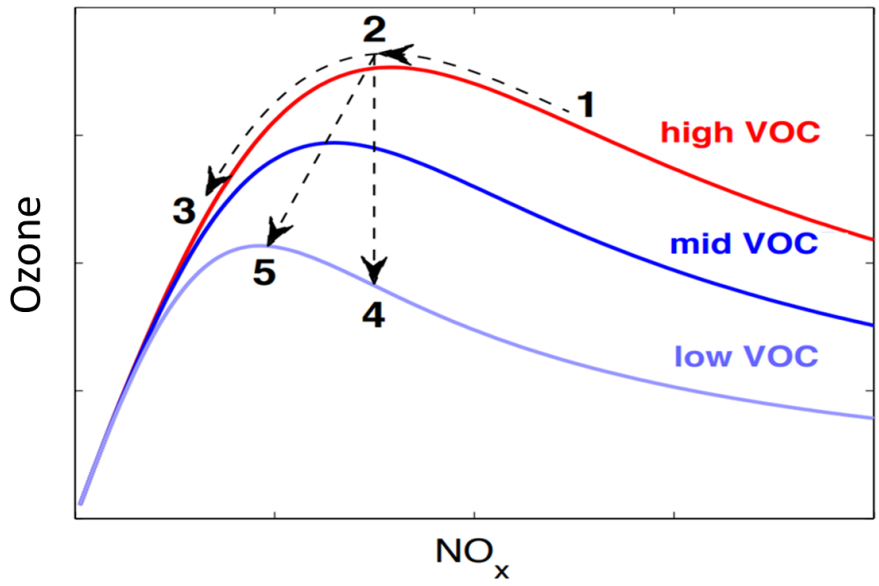

Figure 3.2. Schematic diagram showing ozone as a function of NOx concentrations for three categories of VOC reactivity. From Pusede and Cohen (2012). Ozone can be shown as ozone production, mean ozone concentrations, or as ozone exceedance probability.

Meteorology is an important driver of O_3 that has the potential to confound attempts to infer O_3 formation chemistry from W-W O_3 differences. Hot temperatures increase O_3 formation in at least three different ways: through increasing emissions of biogenic VOCs and evaporative emissions of VOCs, through increased formation of HOx and NOx via thermal decomposition, and by increasing the frequency of high insolation, stagnation, and favorable wind patterns (such as occurrence of the lake breeze over the Great Lakes) (Ableira and Farmer, 2017). Large but random differences in temperature on weekdays and weekends can occur within a given year that can drive W-W differences in O_3 (e.g., weekends may be hotter than weekdays in one year and cooler than weekdays in another year). Without correcting for temperature, W-W differences in O_3 resulting from these temperature differences could be mistaken as indicating differences in O_3 formation chemistry (Pierce et al., 2010). We found that large W-W differences in temperature occurred even when data is averaged over five years, underlining how crucial it is to consider temperature impacts in any W-W analysis. Many studies have done so by

examining only days with “hot” or “moderate” temperatures (e.g., Pusede and Cohen, 2012; Jin et al., 2020).

Many other meteorological factors besides temperature have important impacts on O_3 concentrations in the Great Lakes region, so a simple adjustment for temperature may not be adequate for this region. The occurrence of southerly winds and a lake breeze that carry O_3 and O_3 precursors from source regions to downwind locations onshore in the Lake Michigan and Lake Erie regions are crucial drivers of high O_3 in these areas (e.g., Dye et al., 1995; Lennartson and Schwartz, 2002; Brook et al., 2013). It is highly likely that there would be random but important differences in the occurrence of lake breezes and southerly winds on weekdays and weekends in different time periods and that these differences could impact W-W O_3 differences. While these impacts are the greatest around the Great Lakes themselves, transport of O_3 and O_3 precursors is important throughout the LADCO region, as demonstrated by modeling from both EPA (U.S. EPA, 2016) and LADCO (LADCO, 2018). Accordingly, it is important to account for other meteorological parameters (wind direction, wind speed, transport distance, etc.) in addition to temperature in any W-W analysis in the Great Lakes region.

This section presents an analysis of W-W differences in O_3 concentrations in nonattainment areas in the Great Lakes region to identify trends in ozone-NOx-VOC chemistry over a 20-year period, from 2001 to 2020. This analysis focused on days with ozone-conducive meteorology, identified via a Classification and Regression Tree (CART) analysis. Comparison with monitored NO_2 concentrations provided insight into the relative importance of NOx and VOC emissions reductions in driving trends in O_3 concentrations and O_3 formation chemistry.

3.2. Methods

3.2.1. Determination of ozone-conducive days: CART analysis

LADCO conducted Classification and Regression Tree (CART) analyses in order to select days with O_3-conducive meteorology. The selected O_3-conducive days were subsequently analyzed for

their W-W differences. CART is a statistical tool used to classify data. Here, it is applied to daily maximum 8-hour average (MDA8) O_3 concentrations and daily meteorological data to determine the meteorological conditions most commonly associated with high-concentration O_3 days in O_3 NAAs in the LADCO region.

The Air Quality Analysis Group within EPA's Office of Air Quality Planning & Standards processed surface meteorological data at all airports in the U.S. for the years 2001 through 2020 and provided these data to LADCO. EPA also processed HYSPLIT data for the years 2001 through 2019; LADCO processed the HYSPLIT data for 2020 because EPA is no longer processing these data. Comparisons of 2019 HYSPLIT data prepared by EPA and LADCO demonstrated that LADCO's analysis exactly reproduced EPA's analysis for the variables used here. The meteorological parameters used in the analysis are listed in Table A4.2. 2015 meteorological data were removed from the analysis for data quality issues, as described in Appendix 4.

LADCO downloaded MDA8 O_3 concentrations for regulatory monitors for the CART analysis from EPA's Air Data website (https://aqs.epa.gov/aqsweb/airdata/download_files.html). Ozone data were only included for monitors with long-term records, defined as monitors that were missing no more than two years of data from 2001 to 2020.

LADCO conducted CART analyses for each nonattainment area, with the meteorological parameters described above as input variables and MDA8 O_3 values as the response variable. We conducted one CART analysis for each NAA, except that we conducted three CART analyses for different monitor sets in the Chicago nonattainment area (Far North, Central, and Indiana Lake) because of the different factors impacting O_3 formation in different parts of this large area. We also combined multiple NAAs into one CART analysis for the Wisconsin North Lake area and for the Western Michigan area. The ozone monitors and airport meteorological stations used in each CART analysis are listed in Table A1.

LADCO conducted the CART analyses in *R* using the *ctree* function from the package *partykit*. *Ctree* is a non-parametric class of regression tree that avoids overfitting data by applying a statistical approach using a significance test (using a p-value) for each split. We pruned the

regression trees using the *ctree_control* options: *maxdepth, minsplit, minbucket, and maxsurrogate*, with *maxdepth* set to 4 or 5, *minsplit* set to two times *minbucket*, and *maxsurrogate* set to 3. These options control the maximum depth of the tree, the minimum number of days in a node to allow it to be further split, the minimum number of days in a terminal node, and the number of surrogate splits allowed in case of missing data, respectively. The values for these parameters used in each CART analysis are listed in Table A1. The aim was to produce a tree that (1) had at least one terminal node with relatively high average O_3 concentrations (65 ppb to greater than 70 ppb), such that days in this node would impact attainment of the 2015 O_3 NAAQS, and (2) was not too complicated; ideally, the trees would contain 14 or fewer terminal nodes (e.g., sets of meteorologically similar days)[20], however, some trees contained up to 17 terminal nodes.

We used O_3 and meteorological data from the years 2001-2010 to determine the meteorological conditions that lead to high O_3 concentrations via the CART analysis. We then applied the CART analysis to data from the years 2011-2020 to determine which days from these years had O_3-conducive meteorology. We limited the initial CART analysis to data from the first decade in order to minimize the impacts of lowered emissions of O_3 precursors on O_3 concentrations used in the analysis. The CART analysis uses differences in O_3 concentrations on different days to classify days based on their meteorology; however, over time, emissions reductions have also been greatly influencing O_3 concentrations. This approach minimizes the impact of this potentially confounding factor.

After running the CART analysis, we selected the meteorologically similar days ("nodes") that had average MDA8 values >60 ppb in either 2001-2010 or 2011-2020. These day types are considered to be "ozone-conducive" and are listed in Table 2. The data for all of the O_3-conducive days in each area were combined for the weekday-weekend analysis.

[20] A node is a set of days with a shared set of meteorological conditions (for example, days with afternoon temperature over 85 ℃, average relative humidity less than 50%, and at least 150 km of southerly transport over 24 hours). Terminal nodes are sets of days at the bottom of the CART tree that will not be further subdivided.

3.2.2. Ozone monitoring data

MDA8 O_3 concentrations for May through September for the years 2001 through 2020 were downloaded from EPA's Air Quality System (AQS; https://aqs.epa.gov/aqs/). Ozone was measured using Federal Reference Methods (FRM) or Federal Equivalent Methods (FEM), mostly using chemilumiscence (FRM) or ultraviolet absorption (FEM). Figure 3.3 shows the location of O_3 monitors used in the analysis along with the 2015 O_3 NAAQS nonattainment areas. In order to provide more data for the statistical analyses, we combined data from two to four monitors to form monitor groups, with one to five monitor groups in each nonattainment area. Monitors were combined based on their proximity to each other, similarities in their locations (e.g., being located on a lakeshore or in an urban core), and similarities in their weekday/weekend difference trends. Only monitors with data for at least 18 out of 20 years that were active in 2020 were used. Several monitors were not used because they could not be grouped with other similar monitors. Analyses for some of these monitors (in central St. Louis, central Louisville, central Milwaukee, and in Toledo) are included in Appendix 4. Note that the monitor groups in the Lake Michigan category combine monitors from multiple nonattainment areas, all located downwind from Chicago along the Lake Michigan shoreline (Figure 1.2).

We also combined the data into five-year bins, as shown in the figures below. This averaging should improve the statistics of the analysis by increasing the number of days in each point and also help average out any random differences in meteorology on weekdays and weekends that are not accounted for in our analysis. "Weekday" values are the combination of data from all Tuesdays, Wednesdays, and Thursdays in a time period, whereas "weekend" values include all data from Sundays. Pusede and Cohen (2012) considered Mondays and Saturdays to be transition days that are impacted by carryover from the previous day, so we did not include these days in the analysis.

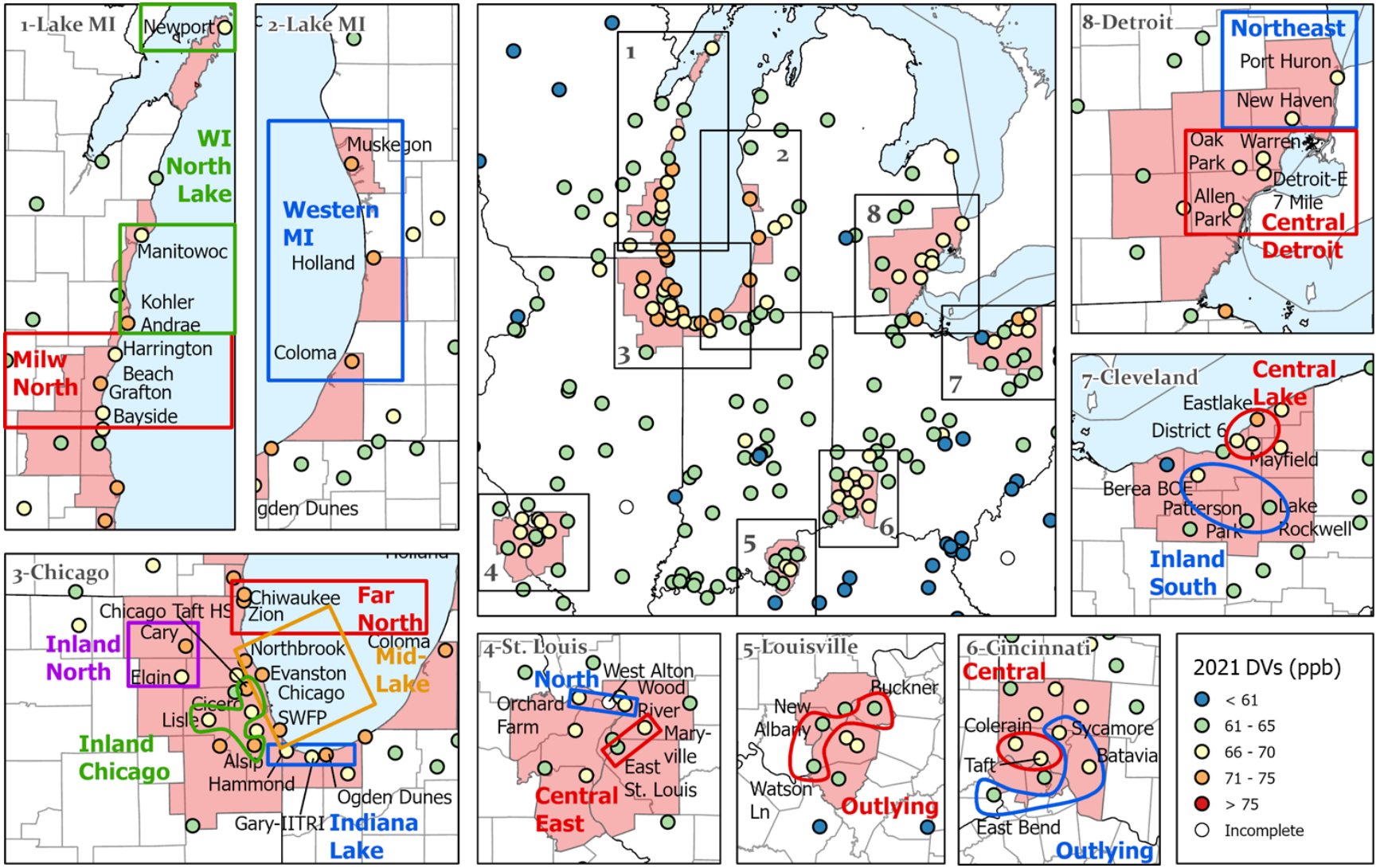

Figure 3.3. Maps of 2019-2021 O_3 design values and nonattainment and maintenance areas (in pink) for the 2015 O_3 NAAQS. The central map shows most of the LADCO region, and numbered maps show each nonattainment area with the groups of monitors (with colored labels) used for the weekday-weekend analysis. Only monitors used in the W-W analysis are labeled.

3.2.3. Nitrogen dioxide (NO_2) monitoring data

Hourly NO_2 data for the years 2001 through 2020 were downloaded from EPA's AQS as described above for ozone. Our analysis uses "midday" NO_2, which averages NO_2 concentrations from 9:00 to 14:59 LST from May through September on O_3-conducive days, identified as described above. Data were averaged for O_3-conducive weekday (Tuesday-Thursday) and O_3-conducive weekend day (Sundays) groups within each group of years.

Monitored NO_2 concentrations were available from a limited number of monitors in each nonattainment area. Because of this, we averaged NO_2 concentrations at all monitors in a nonattainment area that met the following criteria: (1) the monitor was located in the core county(ies) within a nonattainment area, (2) the monitor was not classified as a "near-road" monitor, and (3) the monitor operated for at least five years. In a few cases, we eliminated monitors that met these criteria because they operated for limited periods of time and monitored very different concentrations than the long-term monitor operating in the area. We also eliminated a few monitors located at the extreme (rural) edges of core counties. The monitors used in the analysis are listed in Table 1, along with the years that they operated. For the Lake Michigan O_3 analysis areas, there was very little NO_2 monitoring data available. Because these monitors are heavily influenced by NO_2 pollution transported from the Chicago area, we compared these monitors' O_3 concentrations to the NO_2 concentrations in the upwind Chicago area.

NO_2 was primarily measured using chemiluminescence, which is the FRM for NO_2. Chemilumiscence is non-specific for NO_2, meaning that it also detects some amount of higher oxides of nitrogen as NO_2, such that measurements made using this method overestimate the actual concentrations of NO_2. Beginning in 2010, some monitoring agencies began using photolytic chemiluminescence to detect NO_2. This FEM is more specific to NO_2 than the FRM but is still an indirect measurement. Since 2015, agencies have been deploying "direct NO_2" instruments that use cavity attenuated phase shift spectroscopy (CAPS, another FEM) to

measure "true NO_2" in the atmosphere. NO_2 concentrations measured by CAPS will be lower than those measured by the other methods and are believed to be more representative of actual NO_2 concentrations. In 2020, approximately a third of the NO_2 monitors in the LADCO region measured NO_2 by CAPS. Because of the limited NO_2 measurements available, indirect and "true" NO_2 measurements are combined in this analysis, which introduces some additional uncertainty to the trends shown.

Table 3.1. NO_2 monitors used in the analysis along with the years they operated.[21]

Nonattainment Area	Site ID	Years
Chicago	170310063	2001-2017
Chicago	170310072	2001-2011
Chicago	170310076	2002-2020
Chicago	170313103	2001-2020
Chicago	170314002	2001-2020
Chicago	170314201	2001-2015
Detroit	261630016	2001-2006
Detroit	261630019	2001-2018
Cleveland	390350060	2001-2020
St. Louis	171630010	2001-2020
St. Louis	291890004	2001-2010
St. Louis	291890006	2001-2005
St. Louis	291890014	2005-2010
St. Louis	291893001	2001-2010
St. Louis	295100085	2013-2020
St. Louis	295100086	2001-2018
Louisville	211110067	2010-2020
Louisville	211111021	2001-2009
Cincinnati	390610040	2001-2020
Cincinnati	390614002	2001-2005

[21] All monitors used chemiluminescence except the following used CAPS: 170313103 in 2020, 211110067 in 2017-2020, and 390610040 in 2019-2020. 295100085 used photolytic chemiluminescence in 2013-2020, and 170314201 used an open path NO analyzer from 2001-2009.

The NO_2 concentrations are much less representative of the nonattainment area than are the ozone concentrations. This is partly because of the limited number of NO_2 monitors operating, as well as the shorter atmospheric lifetime of NO_2 and greater spatial heterogeneity of NO_2 in the atmosphere. NO_2 is known to be particularly high near roadways and large stationary sources, so nearby monitors may record very different concentrations of NO_2 depending on their location relative to these sources. Because we generally only have data from a small number of NO_2 monitors in a nonattainment area, the records may not be representative of the area as a whole.

3.2.4. Weekday-weekend analysis

We averaged the daily MDA8 values for all O_3-conducive weekdays (Tuesday-Thursday) and weekend days (Sunday) in each set of years for each group in a NAA. We then subtracted the mean weekend MDA8 values from the mean weekday MDA8 values to determine the W-W mean MDA8 differences. This value will be used as a metric of O_3 formation sensitivity.

To determine the statistical significance of these W-W mean MDA8 differences, we performed a Welch's t-test on each W-W pair for each group of monitors in each group of years. For example, one Welch's t-test determined whether the MDA8 concentrations were statistically different on weekdays and weekends on O_3-conducive days for the Western Michigan monitors for the years 2001-2005. W-W mean MDA8 differences were considered to be significant at the 95 percent confidence level if the t-test *p*-values were less than 0.05. The Welch's t-test performs well with unequal sample sizes and is valid even for very small sample sizes.

For the plots of weekday and weekend MDA8 versus NAA mean NO_2 (Figure 3.8), we determined the shapes of the curves using an analytical model based on code provided by Dr. Sally Pusede and applied in Pusede and Cohen (2012). This model is described in Appendix A of Pusede et al. (2014). The model is derived from equations describing the kinetics of O_3 formation and reaction, with O_3 as the dependent variable and NO_2 concentrations as the independent variable. We used the *nlsLM* function from the *minpack.lm* package in *R* to fit this nonlinear model to the weekday-weekend trends for each set of years. We also assumed the

presence of 30 ppb of background O_3 that would not be responsive to changes in NO_2 or VOC emissions. This model determines the appropriate amount of reactive VOCs (VOCR) needed and applies a scaling factor to fit the data. These fits should not be considered quantitative but are included to aid with interpretation of the data.

3.3. Results and discussion

The goal of this analysis is to determine the sensitivity of O_3 formation to NOx and VOC emissions based on the response of O_3 concentrations to reductions in NOx emissions on weekends versus weekdays. Meteorology is another important driver of O_3 formation that can vary significantly (though presumably randomly) between weekdays and weekends, even when averaged over many years. For example, a LADCO analysis found that the five-year average of mean daily maximum temperature during the O_3 season could be much as 1.5 °F different on weekdays or weekends (Figure A4.15). These temperature differences are large enough to impact the resultant weekday and weekend O_3 concentrations. Because of this, any weekday-weekend analysis must account for the impacts of meteorology. Most previous analyses have done so by analyzing high-temperature and medium-temperature days separately (e.g., Pusede and Cohen, 2012). However, meteorological parameters besides temperature, primarily related to wind directions and transport, can be equally important in driving O_3 formation and transport in the LADCO region. These other factors are important primarily because of the large role played by transport of O_3 and O_3 precursors, especially over Lake Michigan (Dye et al., 2015; Stanier et al., 2021). Accordingly, LADCO used CART to determine the meteorological conditions that are conducive to O_3 formation and then applied the weekday-weekend analysis to days with O_3-conducive conditions.

3.3.1. Selection of ozone-conducive days

LADCO determined the meteorological conditions that lead to high O_3 concentrations using a CART analysis as described in the Methods section. The meteorological conditions on O_3-conducive days are listed in Table 2. Each set of meteorological conditions is called a “node”. This approach identified two to five nodes with mean MDA8 concentrations of 60 ppb or higher

in either 2001-2010 or 2011-2020 within each analysis. These O_3-conducive days accounted for roughly 20% of all O_3 season (counted here as May to September) days and roughly 80% of the days when O_3 exceeded the level of the 2015 O_3 NAAQS (70 ppb). This indicates that these O_3-conducive days included the vast majority of days with O_3 NAAQS exceedances.

Temperature was the most important factor in all of the O_3-conducive nodes except those in the northern lakeshore region of Wisconsin and in Louisville, where southerly transport and relative humidity were the most important, respectively (Table 2). In general, high temperatures were important for O_3 formation everywhere. Southerly transport and/or southerly winds were important in downwind sites around Lake Michigan. Low relative humidity was a contributing factor, particularly in the southernmost cities. High atmospheric pressure, particularly on the previous day, also contributed to O_3 formation in many locations, and relatively stagnant winds or short transport distances led to high levels of O_3 in many of the cities. Along Lake Michigan, the strength of westerly winds was also a factor, with weak westerly winds helping O_3 formation on the Wisconsin lakeshore (since westerly winds would oppose a lake breeze) and strong westerly winds contributing to O_3 transport on the Western Michigan shoreline since they help transport plumes from Chicago over the lake.

Table 3.2. Description of the meteorological conditions on ozone-conducive days in each area, along with information about each set of ozone-conducive days. The exceedance probability is the probability of a day in that group having a MDA8 value above 70 ppb.

Node	Meteorological conditions*	Mean MDA8 Ozone (ppb)	Exceedance Probability (%)	% of Days	% of Exceedances
Chicago - Far North					
23	T_{avgpm} 80.4 - 84.9 °F, $lagStP_{avg}$ > 992.4 mb & RH_{avg} ≤ 66.8	60.8	23%	5%	14%
27	T_{avgpm} > 80.4 - 84.9 °F, $tran_{west}$ ≤ 219.6 km, avg_W_am ≤ 0.3693 m/s	63.7	28%	4%	14%
28	T_{avgpm} > 84.9 °F, $tran_{west}$ ≤ 219.6 km, avg_W_am > 0.3693 m/s	71.7	51%	6%	39%
30	T_{avgpm} > 84.9 °F, $tran_{west}$ > 219.6 km, $ws_{2\text{-}day}$ ≤ 3.5 m/s	64.9	30%	3%	12%
Combined High-Ozone Nodes		*65.8*	*35%*	*18%*	*79%*
Chicago - Inland North, Chicago Central, Mid-Lake					
31	T_{avgpm} > 85.6 °F, trandis ≤ 618.2 km, $lagStP_{avg}$ ≤ 992.2 mb	59.0	17%	6%	21%
32	T_{avgpm} > 85.6 °F, trandis ≤ 618.2 km, $lagStP_{avg}$ > 992.2 mb	66.2	34%	6%	43%
Combined High-Ozone Nodes		*62.6*	*25%*	11%	64%
Chicago - Indiana Lake					
24	T_{max} 79.1 - 85.0 °F, $lagStP_{avg}$ > 994.4 mb, lag_S_wn > -0.1 m/s	54.9	5%	4%	4%
27	T_{max} > 85.0 °F, RH_{avgmid} ≤ 59.8 %, $lagStP_{avg}$ ≤ 991.6 mb	55.6	10%	9%	19%
28	T_{max} > 85.0 °F, RH_{avgmid} ≤ 59.8 %, $lagStP_{avg}$ > 991.6 mb	62.8	29%	10%	59%
Combined High-Ozone Nodes		*58.6*	*17%*	*23%*	*82%*
Lake Michigan - WI North Lake					
20	$tran_{south}$ > -147.3 km, T_{max} > 73.5 °F, avg_S_pm ≤ 4.7 m/s, T_{avgam} > 74.4 °F	60.8	25%	9%	24%
21	$tran_{south}$ > -147.3 km, T_{max} > 73.5 °F, avg_S_pm > 4.7 m/s	69.2	47%	10%	50%
Combined High-Ozone Nodes		*65.2*	*36%*	19%	74%
Lake Michigan - Milwaukee North					
22	T_{max} > 78.9 °F, avg_S_pm > 2.4 m/s, avg_W_pm ≤ -1.9 m/s	67.3	40%	8%	52%
25	T_{max} > 84.2 °F, avg_S_pm > 2.4 m/s avg_W_pm > -1.9 m/s	61.0	22%	7%	26%
Combined High-Ozone Nodes		*64.3*	*31%*	15%	78%
Lake Michigan - Western MI					
13	T_{max} ≤ 80.1 °F, avg_S_win > 0.74 m/s, RH_{avg} ≤ 68.1 %, $tran_{south}$ > 86.2 km	59.6	14%	5%	8%
23	T_{max} > 80.1 °F, avg_S_pm > -0.25 m/s & T_{avgpm} ≤ 83.3 °F, lagStPavg ≤ 992.6 mb	57.6	12%	5%	7%
24	T_{max} > 80.1 °F, avg_S_pm > -0.25 m/s, T_{avgpm} ≤ 83.3 °F, $lagStP_{avg}$ > 992.6 mb	63.5	28%	7%	24%
26	T_{max} > 80.1 °F, avg_S_pm > -0.25 m/s, T_{avgpm} > 83.32 °F, avg_W_am ≤ 1.0 m/s	65.7	34%	4%	18%
27	T_{max} > 80.1 °F, avg_S_pm > -0.25 m/s, T_{avgpm} > 83.3 °F, avg_W_am > 1.0 m/s	73.9	58%	4%	29%
Combined High-Ozone Nodes		*63.8*	*28%*	*25%*	*85%*
Detroit					
20	T_{avgpm} 80.1 - 86.1 °F, $lagStP_{avg}$ ≤ 996.2 mb & trandis ≤ 243.0 km	56.5	13%	4%	10%
22	T_{avgpm} 80.1 - 86.1 °F, $lagStP_{avg}$ > 996.2 mb	61.3	23%	5%	18%
24	T_{avgpm} > 86.1 °F, wndrun ≤ 443.1 km	66.3	39%	7%	42%
25	T_{avgpm} > 86.1 °F, wndrun > 443.1 mb	59.7	17%	6%	16%
Combined High-Ozone Nodes		*61.4*	*25%*	*21%*	*85%*

* avg_S_pm = average afternoon wind south (v) vector, avg_S_win = average wind south (v) vector, avg_W_am = average morning wind west (u) vector, avg_W_pm = average afternoon wind west (u) vector, lag_S_wn = previous day wind south (v) vector, $lagStP_{avg}$ = previous day station pressure, RH_{avg} = average daily relative humidity, RH_{avgmid} = average midday relative humidity, StPavg = average station pressure, T_{avgam} = average morning temperature, T_{avgpm} = average afternoon temperature, T_{max} = maximum daily temperature, trandis = 24-hour transport distance, tranw = vertical (z) component of 24-hr transport vector, $tran_{west}$ = westerly (u) component of 24-hr transport vector, $tran_{south}$ = southerly (v) component of 24-hr transport vector, wndrun = 24-hr scalar wind run, $ws_{2\text{-}day}$ = average 2-day wind speed.

Table 3.2 (continued).

Node	Meteorological conditions*	Mean MDA8 Ozone (ppb)	Exceedance Probability (%)	% of Days	% of Exceedances
Cleveland					
21	T_{avgpm} 77.1 - 83.8 °F, trandis ≤ 213.8 km, $tran_{south}$ > 2.1 km	58.4	14%	3%	8%
27	T_{avgpm} > 83.8 - 86.6 °F, wndrun ≤ 406.8 km	62.9	26%	4%	17%
28	T_{avgpm} > 86.6 °F, wndrun ≤ 406.8 km	70.7	49%	4%	32%
30	T_{avgpm} > 83.8 °F, wndrun > 406.8 km & RH_{avgmid} ≤ 53.0 %	61.8	22%	6%	22%
Combined High-Ozone Nodes		*63.4*	*28%*	*18%*	*79%*
St. Louis					
14	T_{avgpm} 79.8 - 86.6 °F, RH_{avgmid} ≤ 50.4 %, tranw ≤ -0.0075 km	60.7	17%	5%	10%
20	T_{avgpm} > 86.6 °F, RH_{avgmid} ≤ 50.4 %, $ws_{2\text{-}day}$ ≤ 3.8 m/s, $lagStP_{avg}$ ≤ 991.3 mb	62.2	22%	9%	23%
21	T_{avgpm} > 86.6 °F, RH_{avgmid} ≤ 50.4 %, $ws_{2\text{-}day}$ ≤ 3.8 m/s, $lagStP_{avg}$ > 991.3 mb	65.5	37%	8%	37%
27	T_{avgpm} > 79.8 °F, RH_{avgmid} 50.4 - 62.8 %, wndrun ≤ 517 km, $lagStP_{avg}$ > 993.3 mb	61.2	22%	3%	9%
Combined High-Ozone Nodes		*62.8*	*26%*	*25%*	*79%*
Louisville					
9	RH_{avgmid} ≤ 46.5 %, T_{avgpm} 79.8 - 85.0 °F, wndrun ≤ 544.2 km	57.7	8%	6%	8%
12	RH_{avgmid} ≤ 47.3 %, T_{avgpm} > 85.0 °F, wndrun ≤ 544.2 km	63.4	26%	15%	63%
13	RH_{avgmid} 47.3 - 60.2 %, T_{avgpm} > 85.0 °F, wndrun ≤ 544.2 km	55.6	9%	13%	18%
Combined High-Ozone Nodes		*59.4*	*16%*	33%	89%
Cincinnati					
18	T_{avgpm} 82.3 - 87.6 °F, trandis ≤ 399.4 km, RH_{avgmid} ≤ 56.8 %	63.5	23%	10%	24%
21	T_{avgpm} > 87.6 °F, trandis ≤ 399.4 km, StP_{avg} ≤ 1000.4 mb	68.6	40%	6%	25%
22	T_{avgpm} > 87.6 °F, trandis ≤ 399.4 km, StP_{avg} > 1000.4 mb	71.9	52%	4%	20%
24	T_{avgpm} > 82.3 °F, trandis > 399.4 km, RH_{avgmid} ≤ 53.8 %	60.0	16%	8%	14%
Combined High-Ozone Nodes		*64.7*	*29%*	*28%*	*83%*

* avg_S_pm = average afternoon wind south (v) vector, avg_S_win = average wind south (v) vector, avg_W_am = average morning wind west (u) vector, avg_W_pm = average afternoon wind west (u) vector, lag_S_wn = previous day wind south (v) vector, $lagStP_{avg}$ = previous day station pressure, RH_{avg} = average daily relative humidity, RH_{avgmid} = average midday relative humidity, StPavg = average station pressure, T_{avgam} = average morning temperature, T_{avgpm} = average afternoon temperature, T_{max} = maximum daily temperature, trandis = 24-hour transport distance, tranw = vertical (z) component of 24-hr transport vector, $tran_{west}$ = westerly (u) component of 24-hr transport vector, $tran_{south}$ = southerly (v) component of 24-hr transport vector, wndrun = 24-hr scalar wind run, $ws_{2\text{-}day}$ = average 2-day wind speed.

3.3.2. Trends in NO_2 and MDA8 ozone on ozone-conducive weekdays and weekend days

Figure 3.4 shows the trends in mean NO_2 on weekdays and weekends in the different urban nonattainment areas over the last twenty years, with the data grouped into five-year bins. These trends average monitored concentrations across all included NO_2 monitors in the areas, as described in the Methods section. In some areas (e.g., Cleveland), the record is entirely from a single monitor, whereas in other areas (e.g., Chicago and St. Louis), the record is the average of up to 6 or 7 monitors (Table 1). NO_2 concentrations can vary dramatically within urban areas,

with peak concentrations near roadways and other local sources. These nonattainment area averages therefore do not indicate the NO_2 concentrations throughout the nonattainment area, particularly when derived from only one or two monitors. However, the trends in NO_2 shown should provide insight into how NO_2 concentrations in these areas have changed over time, as well as how concentrations vary on weekdays and weekends.

Mean NO_2 concentrations decreased in each time period in each urban nonattainment area on both weekdays and weekends (Figure 3.4). The largest NO_2 reductions (in ppb) generally occurred early in the study period, from 2001-05 to 2006-10, which corresponds with the implementation of a number of emissions control programs (including the NOx SIP Call and Tier 2 vehicle emissions standards). NO_2 concentrations continued to decrease through 2016-20, although the later reductions were smaller than in earlier time periods. In all areas, NO_2 concentrations were higher on weekdays than on weekends, with weekend concentrations decreasing by a third to a half compared with weekdays. NO_2 concentrations were highest in Chicago and Cleveland and lowest in St. Louis and Detroit. However, as discussed above, because of the limited monitors available, these concentrations may not be representative of area-wide concentrations. In particular, concentrations at the one Cleveland monitor are likely much higher than those in the city as a whole due to the monitor's location.[22]

[22] This monitor, GT Craig, is located near two interstate highways and is essentially an informal near-road monitor. From 1995 through 2008, there was a series of additional NO_2 monitors operating in Cleveland, all of which measured weekday concentrations that were roughly half of those observed at the GT Craig monitor. However, besides a formal near-road monitor, only the GT Craig monitor has operated in Cuyahoga County since 2009, so we are showing this monitor.

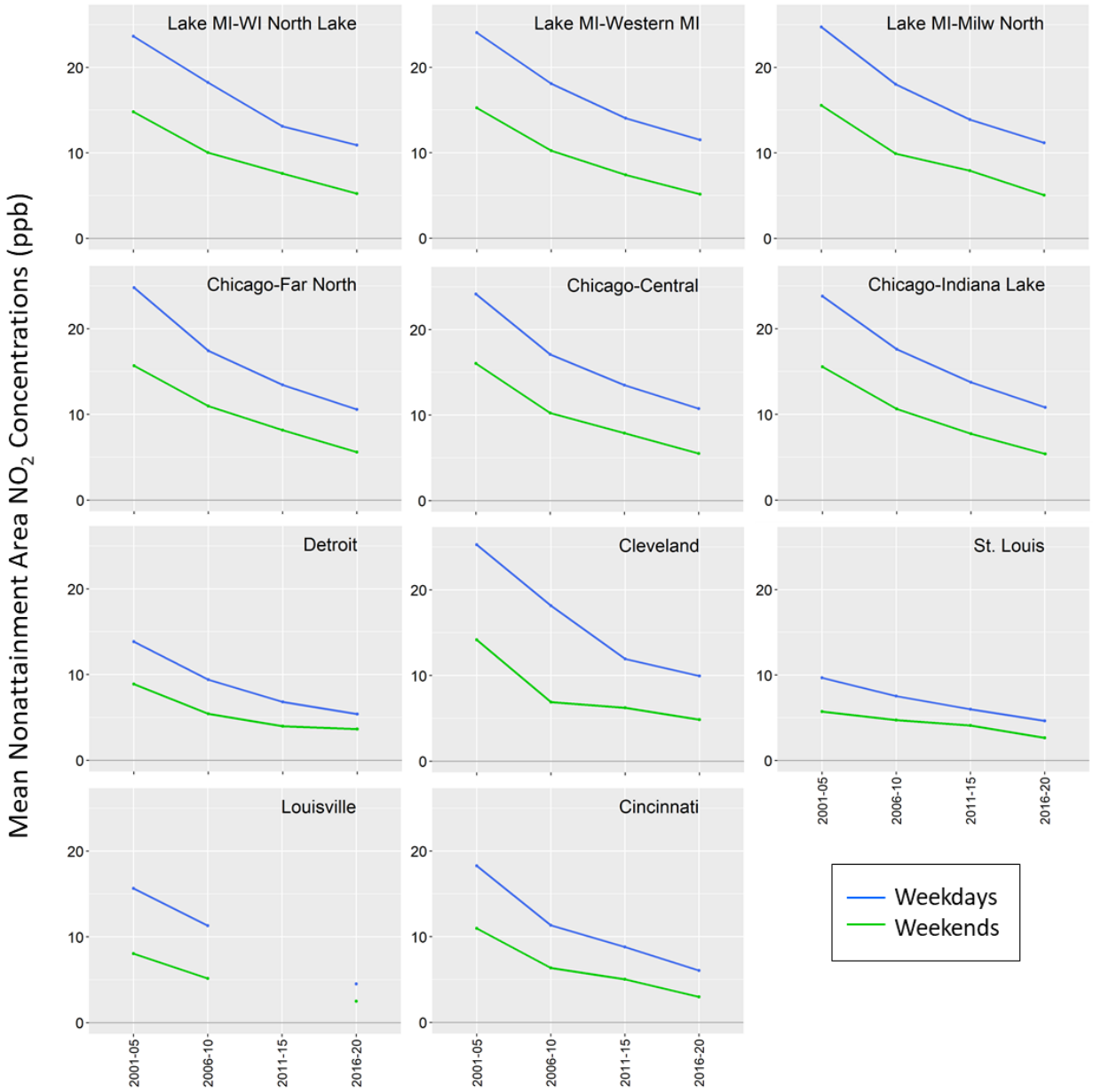

Figure 3.4. Mean nonattainment area concentrations of NO_2 on ozone-conducive weekdays (Tue-Thu) and weekend days (Sun). NO_2 concentrations were measured during midday hours (9:00-14:59 LST) from May through September. NO_2 concentrations shown for the Lake MI monitor groups were measured upwind of these areas in Chicago on ozone-conducive days in the Lake MI region. NO_2 concentrations in the three Chicago areas were measured at the same set of monitors in Chicago on different sets of ozone-conducive days. Louisville had no NO_2 data for ozone-conducive days during the 2011-15 period.

Mean MDA8 O_3 values on O_3-conducive days have decreased in all areas over the last 20 years, as shown in Figure 3.5. Reductions on weekends were generally larger than reductions on weekdays, with mean MDA8 reductions of 17.5 ppb on weekends and 13.6 ppb on weekdays over this time period. The largest reductions were located on the fringes of urban areas in the north, with weekend reductions of 28 ppb in the Milwaukee North area outside Milwaukee, 25 ppb in the Indiana Lake area outside Chicago, and 22 ppb in the Inland South area outside of Cleveland. The smallest reductions occurred in central Chicago on weekdays, with the Inland Chicago, Chicago Mid-Lake, and Chicago Inland North monitors only decreasing by 2, 6, and 7 ppb, respectively, during this time. Ozone concentrations at these central Chicago monitors seem to be either flat or slightly increasing over the last two time periods (Figure 3.5).

Jin et al. (2020) also observed that peak mean O_3 in urban areas, including Chicago, has been moving away from outlying areas and towards the city centers. In part, this is a response to decreased titration in the urban cores due to decreased concentrations of NO in these areas. Mean MDA8 values on O_3-conducive days in the southern NAAs (St. Louis, Louisville, and Cincinnati) decreased by 10-20 ppb over the 20-year time period to current mean MDA8 concentrations of 49-57 ppb. Mean MDA8 reductions on O_3-conducive days were around 15 ppb in both Detroit and Cleveland, although mean MDA8 values in Central Lake Cleveland were about 5 ppb higher in 2016-20 than in the other areas. The Lake Michigan areas had reductions of 13 to 20 ppb over this time period, with the exception of the Milwaukee North area weekends discussed above, and these areas had mean MDA8 values on O_3-conducive days of around 55 ppb, despite the occurrence of some days with much higher concentrations.

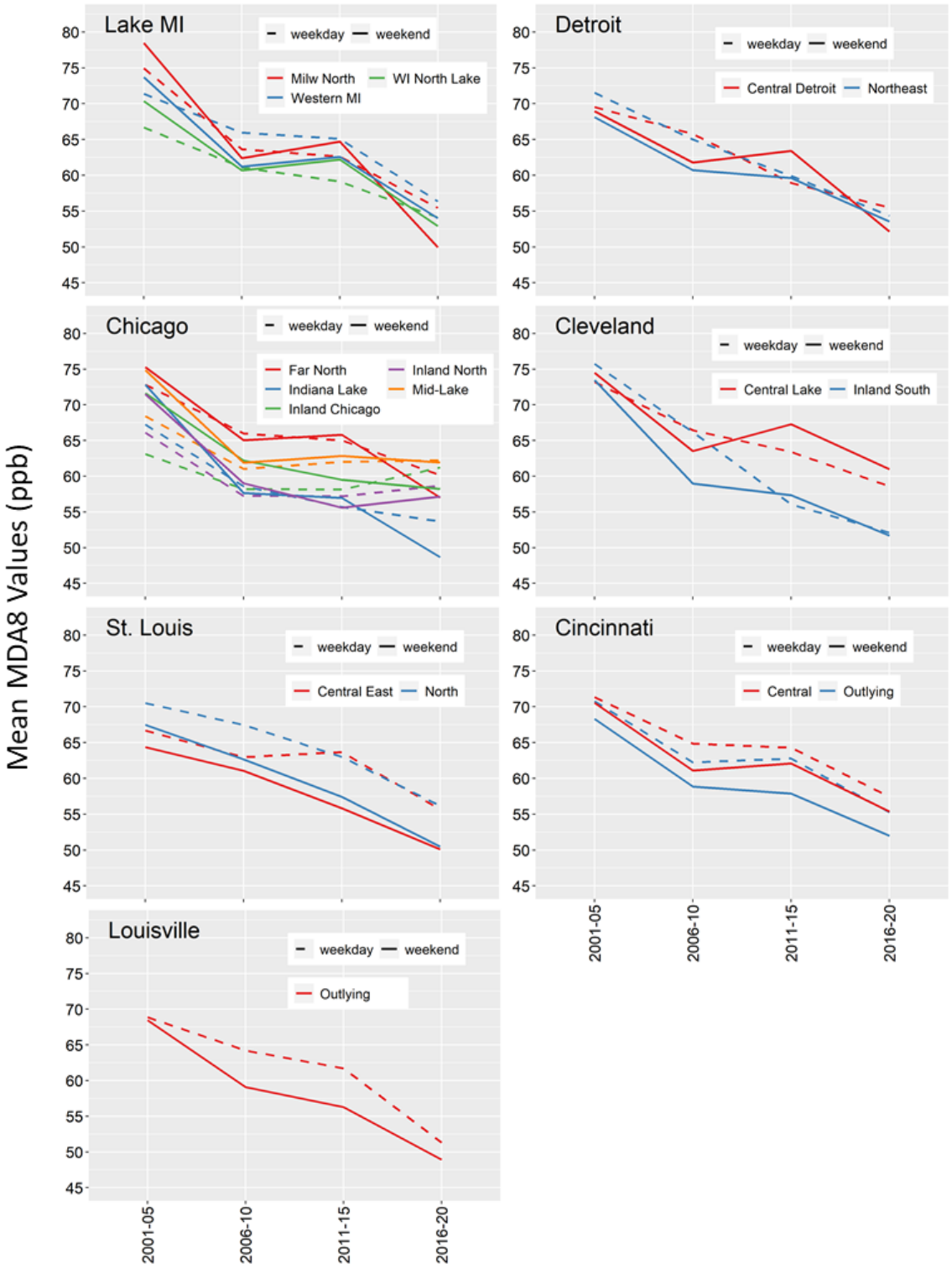

Figure 3.5. Trends in mean maximum daily 8-hour ozone (MDA8) concentrations on weekdays (Tue-Thu) and weekends (Sun) in the different monitor groups within the nonattainment areas.

3.3.3. Weekday-weekend differences in MDA8 ozone

We used the difference between mean weekday and weekend MDA8 concentrations as our key metric of O_3 formation sensitivity. The W-W mean MDA8 difference is determined by subtracting the mean weekend MDA8 value from the mean weekday MDA8 value for a given set of monitors and years. For example, the Milwaukee north monitors had mean MDA8 values of 74.9 ppb on weekdays and 78.4 ppb on weekends in 2001-05, so the W-W mean MDA8 difference for these years was 74.9 ppb - 78.4 ppb = -3.5 ppb. Negative values of this metric indicate higher O_3 concentrations on weekends (when NOx is lower) than on weekdays (when NOx is higher), which is associated with VOC-sensitivity. Positive values indicate greater ozone concentrations on weekdays, which is associated with NOx-sensitivity. Values near zero indicate transitional chemistry. We performed a Welch's t-test to determine whether these W-W mean MDA8 differences were significant, with significant points indicated by closed circles in Figure 3.6.

Figure 3.6 shows the W-W mean MDA8 differences on O_3 conducive days for the different parts of the LADCO region. Ozone formation at the beginning of the study period (2001-05) was VOC-sensitive in the Lake Michigan and Chicago region, with statistically significant differences in most of the Chicago area. In contrast, in the central parts of most of the NAAs, W-W MDA8 differences began with values close to zero, indicating transitional chemistry, in which O_3 formation is sensitive to both NOx and VOC emissions. Ozone chemistry in the outlying parts of these NAAs was NOx-sensitive in 2001-05, with the exception of Louisville, which was transitional. These patterns confirm that urban cores were the most VOC-sensitive/least NOx-sensitive parts of the nonattainment areas, with O_3 formation becoming more NOx-sensitive with increasing distance from the urban core. This same pattern is apparent in Chicago, where the Inland Chicago area was the most VOC-sensitive part of the NAA until the most recent period.

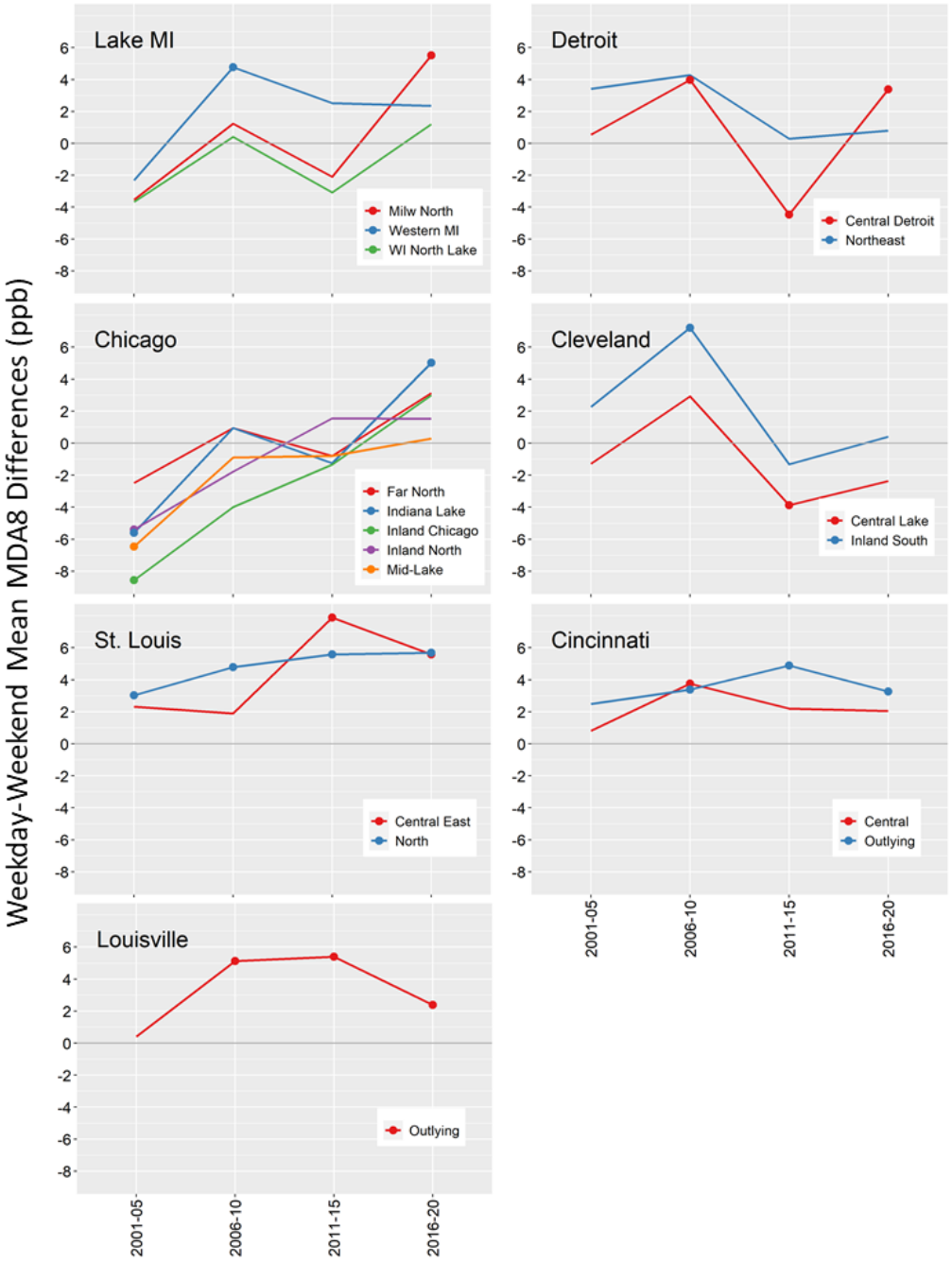

Figure 3.6. The weekday-weekend (W-W) difference in the mean MDA8 value for the LADCO nonattainment areas on ozone-conducive days. The filled circles indicate statistically significant W-W differences. Positive values indicate NOx sensitivity and negative values indicate VOC sensitivity. Multiple nonattainment areas are grouped together into the Lake Michigan area groups.

The W-W MDA8 differences increased over the 20-year study period in most of the NAAs, indicating a shift to more NOx-sensitivity on O_3-conducive days. This shift is clearest in Chicago, in which most monitor groups began as significantly VOC-sensitive, with W-W MDA8 differences of -8.6 to -5.4 ppb, and ended with positive W-W MDA8 differences, indicating transitional to NOx-sensitive O_3 formation. Similarly, all of the monitor groups in the Lake Michigan region began as VOC-sensitive and ended as NOx-sensitive. Ozone formation in most monitor groups in northern regions shifted to more VOC-sensitive (or less NOx-sensitive) during 2011-15 before shifting towards increased NOx-sensitivity in 2016-20. Unusually, the two Cleveland monitor groups were less NOx-sensitive and more VOC-sensitive in the last two time periods than in the first two, with ozone formation being significantly VOC-sensitive in the Central Lake area in 2011-15.

In contrast, W-W MDA8 differences in the southern areas (St. Louis, Louisville and Cincinnati) were always positive, indicating transitional to NOx-sensitive O_3 formation on O_3-conducive days over the 20-year period. However, W-W MDA8 differences became more positive during the study period, reflecting a shift to more strongly NOx-sensitive O_3 formation.

We cannot definitively define the range of mean MDA8 values that corresponds to transitional chemistry. Koplitz et al. (2022) defined any W-W difference that was not significant as transitional. However, this approach seems likely to overestimate the transitional range as many locations may be primarily responsive to either NOx or VOCs, but these differences may not be statistically significant. In order to approximate the transitional range, we used a hybrid of the approach used by Koplitz et al. (2022) and that used by Jin et al. (2020). Our approach used the relationships between the significance of the W-W MDA8 differences, determined through the p value from the Welch's t-test, and the W-W MDA8 differences themselves, shown in Figure A4.22. This relationship shows that p values peak at W-W MDA8 differences close to zero. Jin et al. (2020) defined the transitional range based on satellite-derived $HCHO/NO_2$ ratios for the days with the highest 10% exceedance probability. If we apply this top-10% criterion to our analysis, we would say that the top-10% of analyses with the highest p values could be defined as

transitional. The top-10% of values had W-W mean MDA8 differences of -0.8 to +0.4. To be more conservative, we extend this "transitional" range to mean MDA8 differences of -1 to +1, which encompasses the top 20% of p values. This is a much smaller range than would be determined using the Koplitz et al. (2022) approach, which would define a range of roughly -4 to +3.5 as transitional, which includes the majority of the observations. Our thresholds are not definitive, and they may label areas that are actually NOx- or VOC-sensitive as transitional or vice versa, but this seems like a reasonable and conservative approach.

Figure 3.7 shows these same W-W MDA8 differences displayed on a map, with all monitors in a monitor group color-coded to show the monitor group's values. These maps demonstrate how widespread VOC-sensitivity was around Lake Michigan in 2001-05, with the greatest VOC-sensitivity in central Chicago. The maps also clearly show how these monitors shifted to transitional and NOx-sensitive chemistry over the next 15 years. These maps also show the more subtle shifts toward increasing NOx-sensitivity in the southern areas. In the most recent time period, 2016-2020, O_3 formation in most of the LADCO region was NOx-limited, including in central Chicago. The only VOC-limited area was the Central Lake area of Cleveland. Chicago, Detroit, and Cleveland all had areas with transitional chemistry.

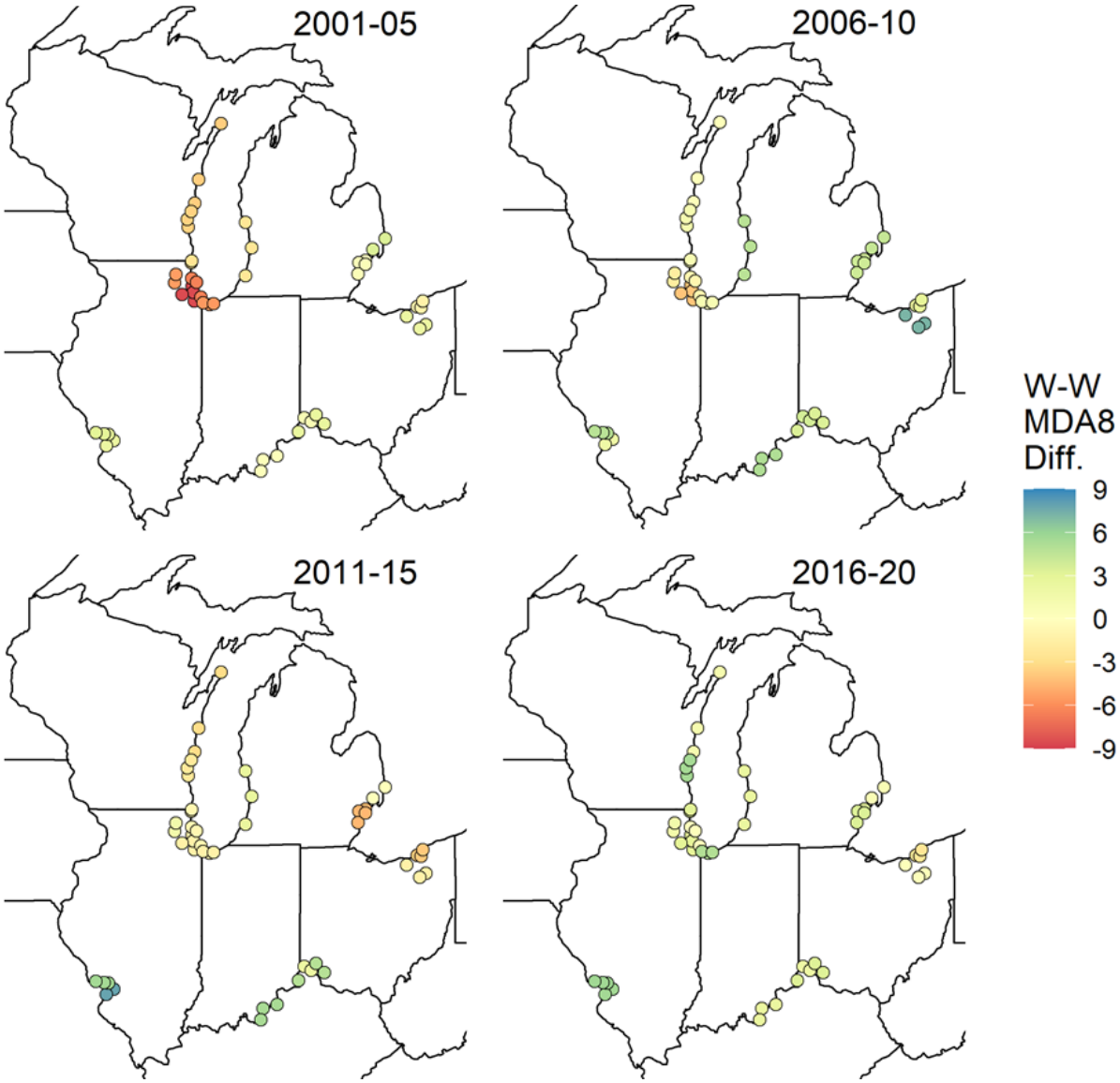

Figure 3.7. Maps of Weekday-Weekend (W-W) MDA8 ozone difference (ppb) for different monitor groups for each year group. All monitors in each monitor group are colored according to that monitor group's value. Positive values (greens and blues) indicate NOx sensitivity, yellow indicates transitional chemistry, and negative values (reds and oranges) indicate VOC sensitivity.

Our approach to account for meteorological impacts on O_3 formation appears to have done a good job adjusting for the impacts of temperature on W-W MDA8 differences. The W-W difference trends in temperature-related parameters (Figures A4.13-A4.18) are quite different

from both the trends in W-W MDA8 differences and the maximum daily temperature trends for all ozone season days (unadjusted for meteorology). However, some of the variability in the apparent trends over time may be due to variability in other meteorological parameters that were not fully accounted for in our methodology. For example, in some of Lake Michigan areas, several parameters related to southerly transport ($trans_{south}$, avg_S_pm, etc.) have minima on weekdays compared with weekends in 2011-2015 (Figures A4.13-A4.16), the same time when the W-W MDA8 difference decreases. It is possible that relatively lower southerly transport on weekdays in this time period contributed to lower MDA8 O_3 on weekdays. Similarly, Cleveland and Detroit both had relative increases in transport-related parameters (wndrun and trandis) on weekdays in 2011-2015 (Figures A4.16-A4.17); increased transport could have decreased weekday O_3 levels in these areas, leading to the dips on W-W MDA8 differences in these years. However, it is beyond the scope of this analysis to fully investigate the origins of these relatively minor differences.

3.3.4. Drivers of trends in ozone concentrations

Plots of weekday and weekend O_3 versus NO_2 concentrations can help distinguish the relative importance of concurrent NOx and VOC reductions on O_3 concentration trends. Pusede and Cohen (2012) looked at the slopes and changes in O_3 versus NO_2 plots for weekdays and weekends over different time periods. These plots connect the W-W O_3 differences discussed above with the NO_2 concentration changes underlying these effects and are similar to the schematic shown in Figure 3.2. Fitting the observed data to curves provides insight into the role of concurrent VOC emissions reductions on O_3 concentrations.

Figure 3.8 shows this kind of plot for the different LADCO region monitor groups, where the solid lines connect the weekday and weekend points for each time period. The NO_2 concentrations are the nonattainment area midday means on ozone-conducive days, as discussed above. When the lines connecting the weekday and weekend points have negative slopes, that corresponds to periods with negative W-W MDA8 differences in Figure 3.6. This indicates that decreasing NO_2 led to increasing ozone exceedance probability due to

VOC-sensitive chemistry. Periods with positive slopes had positive W-W MDA8 differences and demonstrated lower weekend ozone with lower NO_2 due to NOx-sensitivity. The dashed curves were determined using an analytical model in which VOCR was tuned and the curve was scaled to fit the ozone MDA8 values. These lines are not quantitative but aid in interpretation of the trends. Vertical offsets between these curves, particularly at higher NO_2 levels, can indicate different concentrations of reactive VOCs. In interpreting these plots, keep in mind that the NO_2 concentrations shown may not be representative of the concentrations in the area as a whole, as discussed above, but the trends should be consistent.

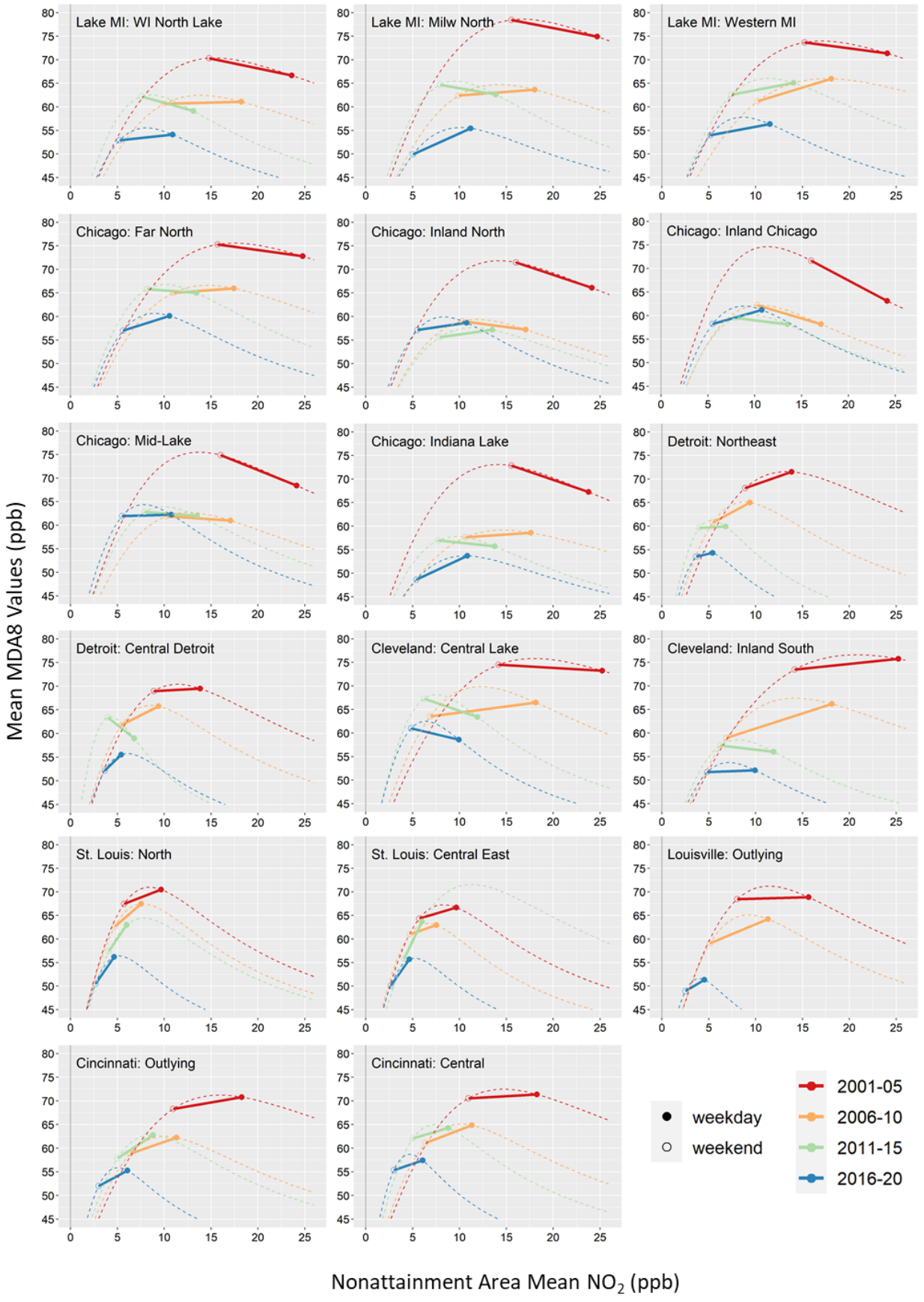
Lake MI: WI North Lake
Lake MI: Milw North
Lake MI: Western MI
Chicago: Far North
Chicago: Inland North
Chicago: Inland Chicago
Chicago: Mid-Lake
Chicago: Indiana Lake
Detroit: Northeast
Detroit: Central Detroit
Cleveland: Central Lake
Cleveland: Inland South
St. Louis: North
St. Louis: Central East
Louisville: Outlying
Cincinnati: Outlying
Cincinnati: Central
Mean MDA8 Values (ppb)
Nonattainment Area Mean NO_2 (ppb)
weekday
weekend
2001-05
2006-10
2011-15
2016-20

Figure 3.8. Plots of mean maximum daily 8-hour average (MDA8) ozone concentrations versus midday nonattainment area mean NO_2 concentrations on ozone-conducive weekdays (solid symbols) and weekend days (open symbols) during four sets of years. Curves (dashed lines) are included as visual aids and are not meant to be quantitative; these curves were developed as described in the text using an analytical model in which VOCR was tuned and the curve was scaled to fit the ozone MDA8 values. MDA8 values for monitor groups around Lake Michigan are plotted versus Chicago area mean NO_2 concentrations. Louisville had no NO_2 data for ozone-conducive days during the 2011-15 period.

Figure 3.8 shows that the large NO_2 reductions between weekdays and weekends in the 2001-05 period led to increases in mean MDA8 concentrations on weekends in Chicago and around Lake Michigan on O_3-conducive days. As NO_2 concentrations continued to decrease in subsequent periods, the slopes of the lines switched from negative to positive as MDA8 O_3 values began to decrease in response to decreasing NO_2 on the weekends in these northern areas. In most of these areas around Lake Michigan and Chicago, consistent reductions in the height of the fit curves suggest that fairly consistent decreases in reactive VOCs contributed to the observed reductions in MDA8 O_3 values along with reductions in NO_2.

In contrast, mean MDA8 values remained relatively steady from 2006-10 to 2016-20 in the central Chicago areas of Inland North, Inland Chicago and Mid-Lake, with few changes either from weekdays to weekends or between year periods. The curve fits for these monitor groups show that O_3 formation remained near peak levels for these periods, and reactive VOC levels did not decrease as much as in the outlying Chicago and downwind Lake Michigan areas. This suggestion that reactive VOCs did not decrease much in central Chicago in these years is consistent with the available measurements of VOCs in the area (Figure A4.23). Concentrations of hydrocarbons, one class of VOCs, increased over this time period at the one central Chicago VOC monitor while they decreased at the three Indiana lake monitors. Concentrations of another class of VOCs, carbonyls, increased during this time period at two central Chicago and one Indiana lake monitor. While VOC monitoring data is sparse, complex, and challenging to

interpret, the available data supports the conclusion from the curve fit (Figure 3.8) that reactive VOCs have not decreased that much in central Chicago over the last 15 years.

In Detroit and Cleveland, both NO_2 and VOC reductions appeared to contribute to the reductions in mean MDA8 concentrations over time on O_3-conducive days. Decreases in reactive VOCs inferred from the curve fits were particularly large between 2001-05 and 2011-15 and much smaller between 2011-15 and 2016-20. The apparent and unusual shift from NOx-sensitive to VOC-sensitive O_3 formation in 2011-15 in the two Cleveland groups and in Central Detroit appears to result from these large reductions in reactive VOCs, which shift O_3 formation to the VOC-sensitive portions (with negative slopes) of MDA8-NO_2 curves with lower reactive VOC levels. Monitored hydrocarbons in Cleveland show exactly this pattern, with concentrations dropping steeply through the early 2010s and then leveling off through the late 2010s (Figure A4.23). Monitoring of VOC compounds in Detroit shows large drops in both hydrocarbons and carbonyls in the mid-2000s (Figure A4.23). However, concentrations either stabilized or increased again in the early 2010s. These results generally support the estimates of reactive VOCs from the curve fits.

In St. Louis, Louisville, and Cincinnati, O_3 formation in almost all monitor groups and years fell in the NOx-sensitive area (positive slope) of the curve on O_3-conducive days and were accompanied by large reductions in O_3 concentrations over time. However, even when O_3 formation was primarily NOx-sensitive, reductions in reactive VOCs appeared to contribute to reductions in mean MDA8 values, as apparent by the decreases in the height of the curve fits. Reactive VOC reductions appeared to be the least important in the St. Louis North area, which also had some of the most NOx-sensitive O_3 formation (Figure 3.6) in the region. However, even in this very NOx-sensitive area, VOC reductions still contributed to reductions in ozone MDA8 concentrations.

Alternatively, it is possible that the vertical offsets in the O_3 versus NO_2 curves could result in part from changes in regional levels of baseline O_3 instead of from decreasing reactive VOC

concentrations. Simon et al. (2015) found that summertime 5th percentile O_3 concentrations at rural sites in the eastern U.S. decreased by 0.1-1 ppb/year from 1998 to 2013. The authors found larger reductions of 1-2 ppb/year in 95th percentile O_3. Such decreases in baseline O_3 could lead to similar offsets to those seen in Figure 3.8, complicating efforts to determine the role of VOCs in O_3 formation.

Overall, Figure 3.8 suggests that reductions in both NOx and reactive VOC emissions contributed to reductions in O_3 concentrations around the LADCO region. Notably, VOC reductions were important even in areas with NOx sensitive O_3 formation chemistry, such as St. Louis. This finding suggests that future reductions in O_3 will be achieved through strategies that employ a combination of NOx and VOC emissions reductions.

3.4. Conclusions

Weekday-weekend analysis of O_3-conducive days in the LADCO region shows that O_3concentrations have decreased in almost all areas over the past 20 years. As NO_2 has decreased, almost all areas have shifted towards more NOx-sensitive ozone formation. Ozone formation in southern areas (St. Louis, Louisville, and Cincinnati) was NOx-sensitive for most of this time period and became more so during this time. Ozone formation in Chicago and around Lake Michigan shifted from significantly VOC-sensitive to NOx-sensitive in most areas, and central Cleveland was the only VOC-sensitive part of the region in 2016-20. The reductions in MDA8 O_3 concentrations appeared to have been driven by reductions in both NOx and VOC emissions. Importantly, reductions in reactive VOCs contributed to decreasing O_3 concentrations on O_3-conducive days even when O_3 formation was highly NOx-sensitive. This finding indicates that future planning strategies should use a combination of NOx and VOC emissions reductions to achieve the greatest reductions in O_3 concentrations.

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4. Ozone Trends over Space and Time

4.1. Introduction

The emissions of O_3 precursors, NOx and VOCs, have decreased dramatically over the past 30 years (e.g., EPA, 2021; Simon et al., 2015). Due to the complex, nonlinear chemistry of O_3 formation, these reductions in emissions may lead to increases, decreases, or no change in O_3 concentrations in different areas. Simon et al. (2015) found that O_3 concentrations generally increased in more urbanized areas from 1998 to 2013. These increases occurred because of reduced titration of O_3 by high NOx concentrations ("NOx suppression"). The authors also found that O_3 generally decreased in more rural areas, where O_3 concentrations were responsive to changes in NOx concentrations. As a result of this complex chemistry combined with reductions in both NOx and VOC emissions, the locations of peak O_3 concentrations have changed, as have the directions of trends in O_3 Concentrations (increasing versus decreasing) over time. For example, Jin et al. (2020) found that in Chicago, New York, and Los Angeles, the areas of peak O_3 have moved from the outer edges of the cities inwards toward the city centers.

Figure 4.1 demonstrates how O_3 concentrations may change in response to changing NOx concentrations under different chemical regimes and VOC concentrations. Note that the x-axis in this figure is flipped from the usual convention, showing high NOx concentrations on the left and low NOx on the right. This is done so that the changes in NOx concentrations are oriented in the same way as the changes moving from the city center (high NOx) to rural areas (low NOx) or from early years (high NOx) to recent years (lower NOx). This figure shows that when O_3 formation chemistry is VOC-sensitive (at high NOx concentrations), O_3 concentrations would be lowest in the city centers and in early years and would increase moving outward from the city center and in time towards later years. When O_3 formation is in a transitional regime, surface O_3 concentrations would be at their peak levels. Since O_3 concentrations in transitional conditions are relatively flat with changing NOx concentrations, O_3 concentrations in a transitional regime

may hold steady for some time and space. Under NOx-sensitive conditions (at low NOx concentrations), O_3 concentrations will decrease away from the city center and over time.

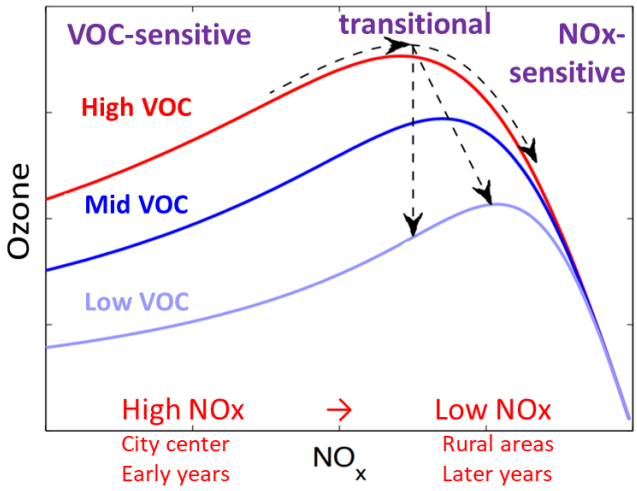

Figure 4.1. Schematic diagram showing ozone as a function of NOx concentrations for three categories of VOC reactivity. Note that the x-axis is shown with the highest levels of NOx on the left and the lowest levels of NOx on the right. Modified from Pusede and Cohen (2012).

An approach that uses O_3 trends over space and time to infer O_3-NOx-VOC chemistry assumes that NOx reductions are much greater than VOC reductions over space and over time, such that NOx reductions are the main drivers of changes in O_3 chemistry. This assumption likely holds true in most times and locations, but VOC reductions will definitely also occur over both space and time. The concurrent VOC reductions will somewhat confound interpretation of O_3 formation chemistry from this trends analysis. However, the impacts of the VOC reductions are predictable and can be considered in the interpretation. In general, VOC reductions will make O_3 formation chemistry less VOC-sensitive and more NOx-sensitive. In particular, under VOC-sensitive conditions, VOC reductions will counter the increase in O_3 due to decreasing NOx, leading to flatter O_3 concentration response curves. Under transitional conditions, concurrent VOC reductions will decrease O_3, making it harder to identify peak O_3 concentrations; O_3 concentrations may actually be at peak levels even though they are decreasing over space and/or time because of the combination of NOx and VOC reductions. If O_3 formation is in a

NOx-sensitive regime, VOC reductions will either have no effect or exaggerate the O_3 reductions, enhancing the signal of NOx-sensitive O_3 formation.

This analysis examines how O_3 concentrations have changed over space relative to areas of peak NOx emissions in city centers and over time in the last 30 years in the LADCO region. In this study, the distance from the city center and advancing years are both used as proxies for decreasing NOx concentrations. This work attempts to answer two questions: (1) how have O_3 concentrations changed over time in the different parts of the region, and how are these concentrations currently changing, and (2) what can we infer about the O_3-NOx-VOC sensitivity in different areas and times based on these changes. Both of these questions are useful to build our understanding of the types of emissions controls that will be effective at reducing O_3 concentrations under current atmospheric conditions in this region.

4.2. Methods

We downloaded hourly NO_2 data from AQS and selected long-term monitors (excluding designated near-road monitors) in the central parts of the nonattainment areas using the approach described in greater detail in Section 3.2.3. We calculated the mean NO_2 concentrations for May through September in each 5- or 6-year bin, combining data from all of the selected NO_2 monitors into one mean value for the nonattainment area. We used early morning data, from 5:00 to 8:59 LDT, to capture the hours of peak NO_2.

To determine NO_2 trends with distance from the city center, we relied upon ground-level NO_2 concentrations from 12-km modeling conducted by LADCO for 2016 (model run abc; LADCO 2021). We determined the distance of the centerpoint of each grid cell from the closest city center using the “Near” tool in ArcGIS Pro and then determined the mean NO_2 concentration within each distance bin.

We defined the city centers as the location of the city hall. In all cities in the LADCO region, the city halls are located in the central part of the downtown. All city halls are also located in or

near the 12-km grid cell that had the highest ground-level NO_2 concentrations based on LADCO's 2016 abc modeling. We imported both the city hall locations and the locations of ozone monitors into ArcGIS Pro and used the "Near" tool to determine the distance of each ozone monitor from the nearest city hall.

We downloaded MDA8 O_3 values from EPA's AQS and selected the fourth highest value for each year with at least 115 valid days. This number corresponds to 75% of the days for a five-month O_3 monitoring season, the length of the shortest monitoring season in the LADCO region. We only included data from O_3 monitors with at least five years of data. We determined the mean fourth high concentration by 5-year (with one 6-year) time bins and by 10-km distance bins, and we only included a monitor in an average if it contained at least two years of data in that year bin. For the analysis of urban areas, we included all monitors located within 100 km of a city center regardless of whether they were in the nonattainment area or not. For the Lake Michigan analysis, we excluded monitors in most of Milwaukee County because they're heavily influenced by local emissions. We include an analysis of these monitors in Appendix 6. We included the Bayside monitor in Milwaukee County because it is located at the northern county border near the lakeshore and is primarily influenced by transport from the south over Lake Michigan. We excluded monitors located more than 10 miles from the lakeshore since these will be less influenced by lakeshore transport. We also excluded the Sheboygan Haven monitor because it has been demonstrated to have significantly lower O_3 than the nearby lakeshore monitor due to inland mixing and other factors (e.g., Cleary et al., 2022). We used larger distance bins for the Lake Michigan analysis than for the urban areas because it encompasses a larger area.

4.3. Results and Discussion

4.3.1. Trends in ozone precursors over distance and time

We examined NO_2 and VOC trends in urban areas over space (distance from the city center) and over time, with mean concentrations binned into 10-km bins and into 5- or 6-year groups of year. The over-distance analysis was based on modeling for 2016, and the over-space analysis

was based on monitoring data. This analysis shows that in all NAAs, the highest NO_2 concentrations were located within 10 km of the city center (Figure 4.2). NO_2 concentrations decreased with distance from the city center, with the steepest decreases closest to the city centers and a gradual flattening of the NO_2 trends farther away from the city center. The largest city in the region, Chicago, had the highest concentrations and also the longest tail, with NO_2 concentrations still decreasing at 100 km from the city center. Detroit, Cincinnati, and St. Louis all had smaller NO_2 peaks away from the city center. Maps of model NO_2 concentrations (Figure A5.1) show that in Detroit, this smaller peak is from emissions in Toledo, OH and Sarnia, Ontario. Cincinnati has urban areas to its northeast, including Dayton, OH with elevated NO_2 emissions. St. Louis has a cluster of one cement and two lime plants with large NOx emissions located to its southeast. These factors suggest that NO_2 and O_3 trends at these greater distances from the city are more reflective of the impacts of local NO_2 sources on O_3 formation chemistry than they are of the urban plumes.

NO_2 concentrations in all nonattainment areas have decreased over each subsequent time period (Figure 4.2).[23] There was an especially large reduction in NO_2 concentrations in the mid-2000s in the northern areas (Chicago, Cleveland, and Detroit) but not in southern areas. This reduction likely resulted because of large reductions in NOx emissions due to implementation of a number of control programs including the NOx SIP Call, Tier 2 vehicle standards, and other programs. Some of these programs would have also decreased VOC emissions. The patterns of NO_2 reductions were somewhat steadier in the southern areas. In particular, Cincinnati had larger decreases before the mid-2000s. The rate of decrease in NO_2 levels has been smaller over the last decade in many but not all areas; reductions in Chicago, Cleveland, and Cincinnati continued to be large through the 2010s.

Total mean VOCs followed similar spatial patterns in the nonattainment areas, with the greatest concentrations at the city centers (Figure 4.2). However, the magnitude of change was much

[23] Note that the magnitude of the NO_2 concentrations may not be representative of NO_2 concentrations around the city because of the small number of monitors available, as discussed in the weekday-weekend analysis section, but the relative changes over time should be representative.

smaller than that of NO_2. Generally, NO_2 concentrations decreased twice as much as VOC concentrations over the 100 km from the city center, with even greater relative reductions in southern areas like St. Louis, which is influenced by biogenic VOC emissions. In the largest northern areas of Chicago and Detroit, NO_2 concentrations decreased 1.6 to 1.7 times faster than did VOCs.

It is harder to determine how VOCs have changed over time in the nonattainment area because of the impossibility of measuring all of the thousands of types of VOCs present and reacting in the atmosphere. Very few monitors in the LADCO region measured all of the 54 hydrocarbon VOCs required by the Photochemical Assessment Monitoring Stations (PAMS) network or any carbonyl VOCs. Figure A5.2 shows the trends in available hydrocarbon monitoring data, and Figure A5.3 shows trends in HCHO, a carbonyl VOC. Monitored VOC trends are much more irregular than trends in monitored NO_2, with some monitors showing steady reductions and others showing increasing concentrations over the last 20 years. Because of the paucity of VOC monitoring data, trends in VOC emissions data may be more informative of overall trends in VOC concentrations in the different areas. Figure 4.2 shows that annual total VOC emissions for the different states decreased on average 40 percent from 1990 to 2016-21, whereas monitored NO_2 concentrations decreased by an average of 54 percent from 1991-95 to 2016-21. VOC emissions reductions would be even smaller starting from 1991-95, although this data is unavailable. If we approximate 1991-95 emissions by interpolating between 1990 and 1996-00 emissions, we estimate that NO_2 concentrations decreased 1.5 times faster than did VOC emissions over the last 30 years. Taken together, the emissions trends combined with the variable trends in monitored VOC concentrations suggest that the variability in NO_2 concentrations is greater over time than that of VOC concentrations.

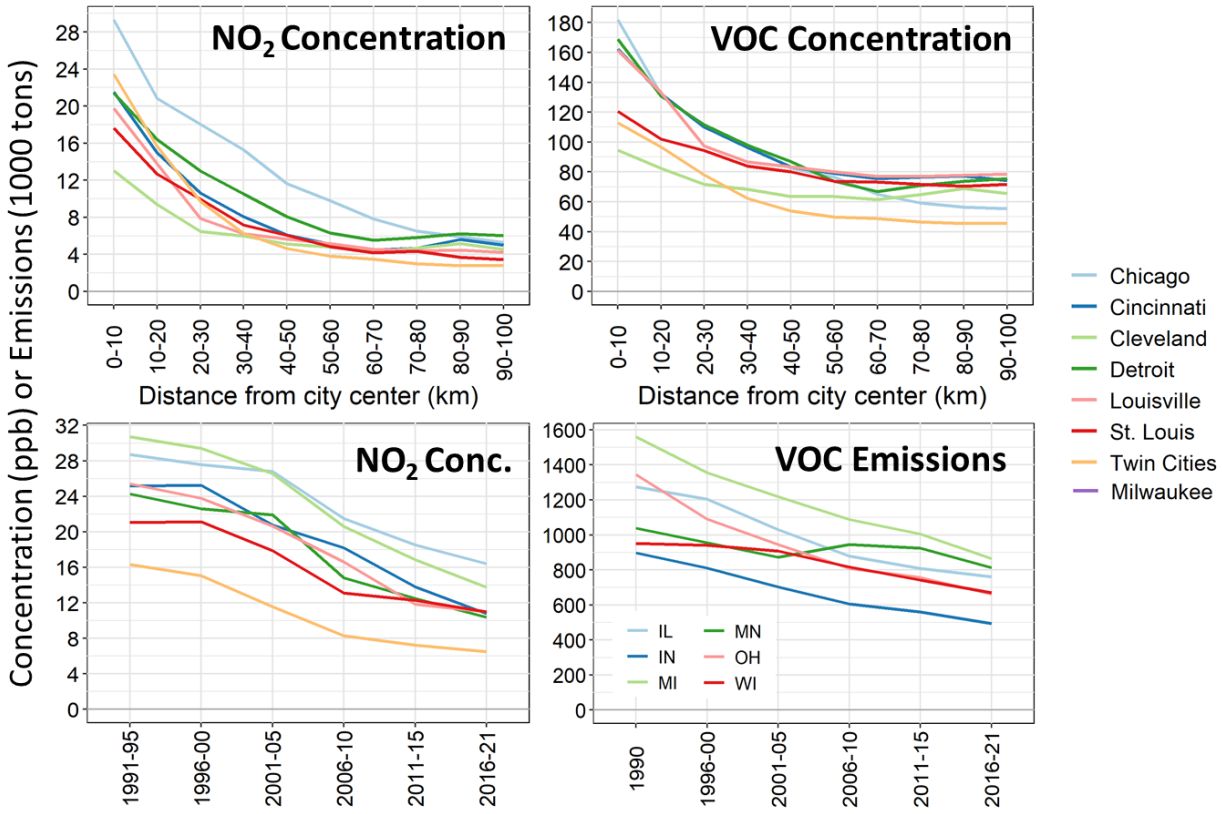

Figure 4.2. Trends in mean early morning (5:00-8:59) NO_2 (top left) and total VOC (top right) concentrations for May through September in the LADCO nonattainment areas plotted versus distance from the city center, and trends versus groups of years for (bottom left) early morning NO_2 concentrations for May through September and (bottom right) annual statewide VOC emissions. Concentrations shown versus distance are based on LADCO modeling for 2016 (model run abc for NO_2 and model run aa2a for VOCs), and concentrations versus time are based on monitoring data. Emissions versus time are the sum of anthropogenic VOC emissions from EPA's air pollutant emissions trends data[24] and biogenic VOC emissions (held constant) from LADCO's 2016b emissions modeling platform[25]. Note that the legend on the right only applies to the concentration plots; the emissions plot has its own legend.

[24] https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data
[25] LADCO, Technical Support Document: Attainment Demonstration Modeling for the 2015 Ozone National Ambient Air Quality Standard, 2022, https://www.ladco.org/wp-content/uploads/Projects/Ozone/ModerateTSD/LADCO_2015O3_ModerateNAASIP_TSD_27July2022.pdf.

The greater variability in NO_2 compared with VOCs suggests that while changes in VOCs over space and time will influence O_3 concentrations, the impact of NOx changes is likely to be the dominant factor. As a result of the variability of NOx concentrations over these dimensions, we would expect to have different O_3 formation chemical regimes at different distances from the city center and over time. Accordingly, studying how O_3 concentrations have changed with distance from the city centers and over time should provide insight into the O_3-NOx-VOC chemistry and how it has changed. However, it will be important to remember that changes in VOC concentrations may complicate interpretation of patterns.

4.3.2. Spatial and temporal trends in ozone in urban areas

This analysis studies the changes in O_3 concentrations over space and over time in and around nonattainment areas in the LADCO region from 1991 through 2021. In examining trends in O_3 concentrations over three decades, it is important to keep in mind that monitoring networks have changed over this time period, with some monitors being discontinued and others starting up. As a result, the monitors included in each time and distance bin also change over time, which adds some additional variability to this analysis. For example, an apparent increase in O_3 concentrations over time might actually result from the shutdown of a relatively low-O_3 monitor, which makes the average concentration in that bin appear higher. In this analysis, we focus on the overall trends over space and time rather than on every small fluctuation, which may be due to changing networks, meteorological variability, or other factors.

This analysis focuses on six urban nonattainment areas: the southern areas of St. Louis, Louisville, and Cincinnati, and the northern areas of Chicago, Detroit, and Cleveland. A second analysis focuses on the Lake Michigan region. The Milwaukee area is not included in the main report because its O_3 is heavily impacted by two different factors, which will confound each other: urban NOx and VOC emissions from Milwaukee itself and lakeshore transport of O_3 from Chicago and other areas to the south. The first factor primarily impacts the central Milwaukee monitors, whereas the second factor impacts most of the outlying monitors, such as those in neighboring Ozaukee and Racine counties and the Bayside monitor in northern Milwaukee

County near the lake. The lake-influenced monitors are included in the analysis of the Lake Michigan region, whereas the central Milwaukee monitors are included in Appendix 6.

Analysis of ozone trends in southern cities

St. Louis. The map of mean fourth high MDA8 O_3 values in the St. Louis area at the beginning of the study period (1991-95) shows the lowest concentrations in the city center, with values as low as 64 ppb close to the city center (Figure 4.3). Concentrations were much higher away from the city center, peaking at 98 ppb at a site 27 km north of the city center. This distribution follows the classic pattern seen in areas with NOx-suppression and VOC-sensitive O_3 formation. Under these conditions, high concentrations of NOx react with ("titrate") ambient O_3, leading to lower O_3 concentrations where NOx is highest and higher O_3 concentrations away from the city center. In the early 1990s, the mean concentration of the monitors within 0-10 km of the city center was 70 ppb, and O_3 levels increased steeply then more gradually to peak at 88 ppb at 20-30 km from the city center (Figure 4.3). Ozone concentrations stayed high out to 50-60 km away, then decreased. However, it is important to note that there were very few monitors located beyond 30 km from the city center in this time period, so any conclusions about these areas will be uncertain. Ozone followed a similar pattern in the late 1990s, although O_3 downtown had increased to a mean of 78 ppb, indicating a reduction in the amount of titration as NOx concentrations decreased (Figures 4.2 and 4.3). There is little evidence of titration/VOC-sensitivity in the city center in subsequent years, when O_3 concentrations in the city center were similar to those in the surrounding areas.

Examination of the O_3 trends over time (Figure 4.3) demonstrates that O_3 concentrations in the central 10 km increased from the early 1990s to peak values in the early 2000s, then decreased steadily afterwards. Concentrations at 10-20 km from the center followed a similar pattern but peaked in the late 1990s. Together, the trends over space and time suggest that O_3 formation in St. Louis was VOC-sensitive in the central 20 km in the early 1990s and transitional in the areas surrounding the center. In the late 1990s, the central 10 km were still VOC-sensitive, but the 10-20 km ring was transitional. By the early 2000s, O_3 decreased with distance away from the city center after peaking at distances around 30-40 km from the center. These trends indicate

that O_3 formation in the St. Louis area was primarily NOx-sensitive in these later years, although the consistency of O_3 concentrations in the central 40 km may indicate some transitional chemistry. The O_3 maps demonstrate that concentrations were much lower and fairly uniform throughout the St. Louis area in the most recent time period (2016-2021; Figure 4.3). In this time period, mean fourth high MDA8 concentrations only varied by 8 ppb (from 62 to 70 ppb), as opposed to 34 ppb (from 64 to 98 ppb) in the early 1990s. Appendix 5 includes figures showing O_3 concentrations plotted against both distance and time on the same plot.

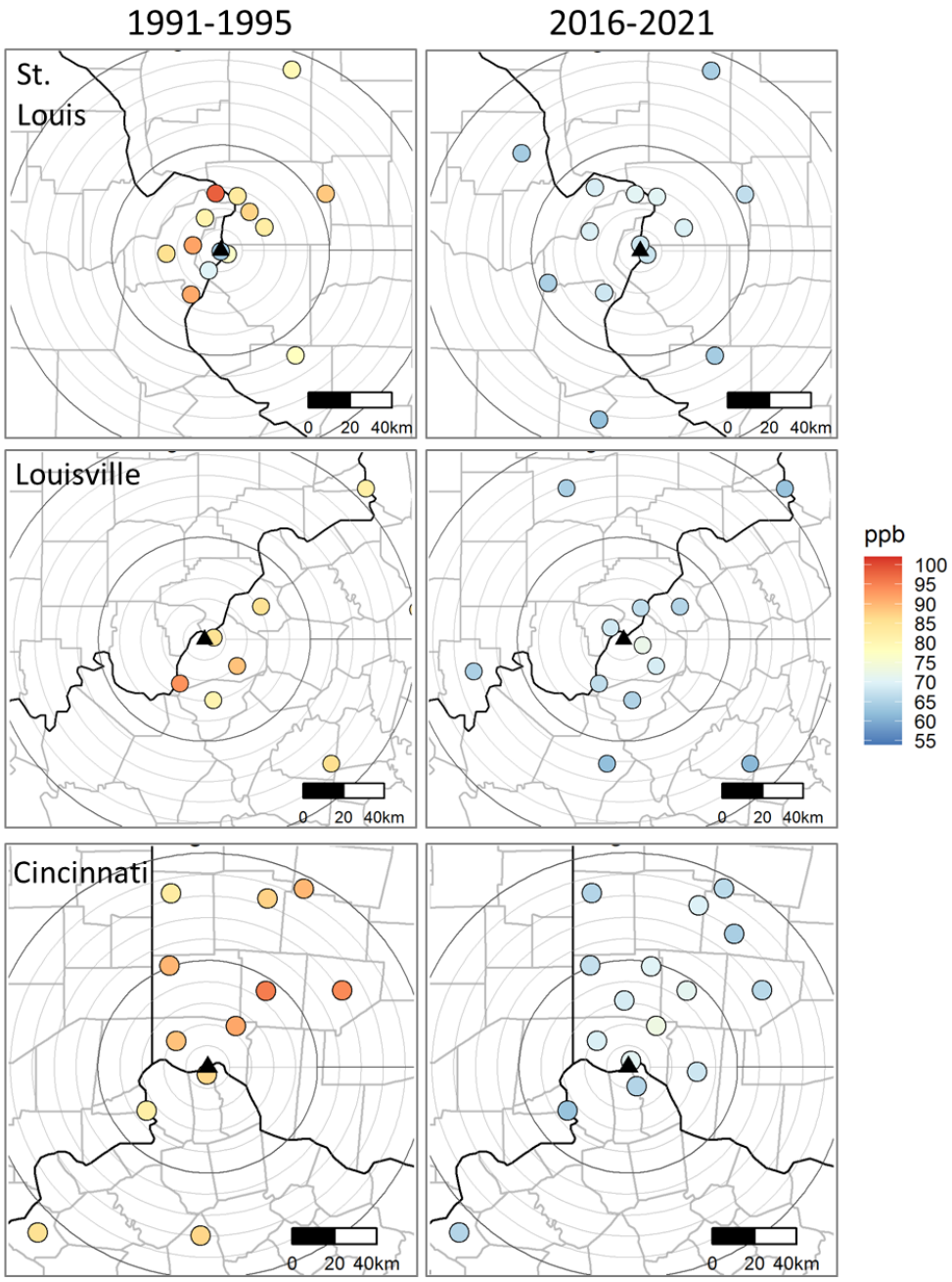

Figure 4.3. Maps of mean annual fourth high maximum daily 8-hour average (MDA8) ozone concentrations in ppb in the three southern nonattainment areas in (left) 1991-1995 and (right) 2016-2021. The black triangles show the location of the city center. The concentric circles show the distance from the city center, with the light lines being 10 km apart and the darker lines being 50 km apart. Maps for additional years are included in Appendix 5.

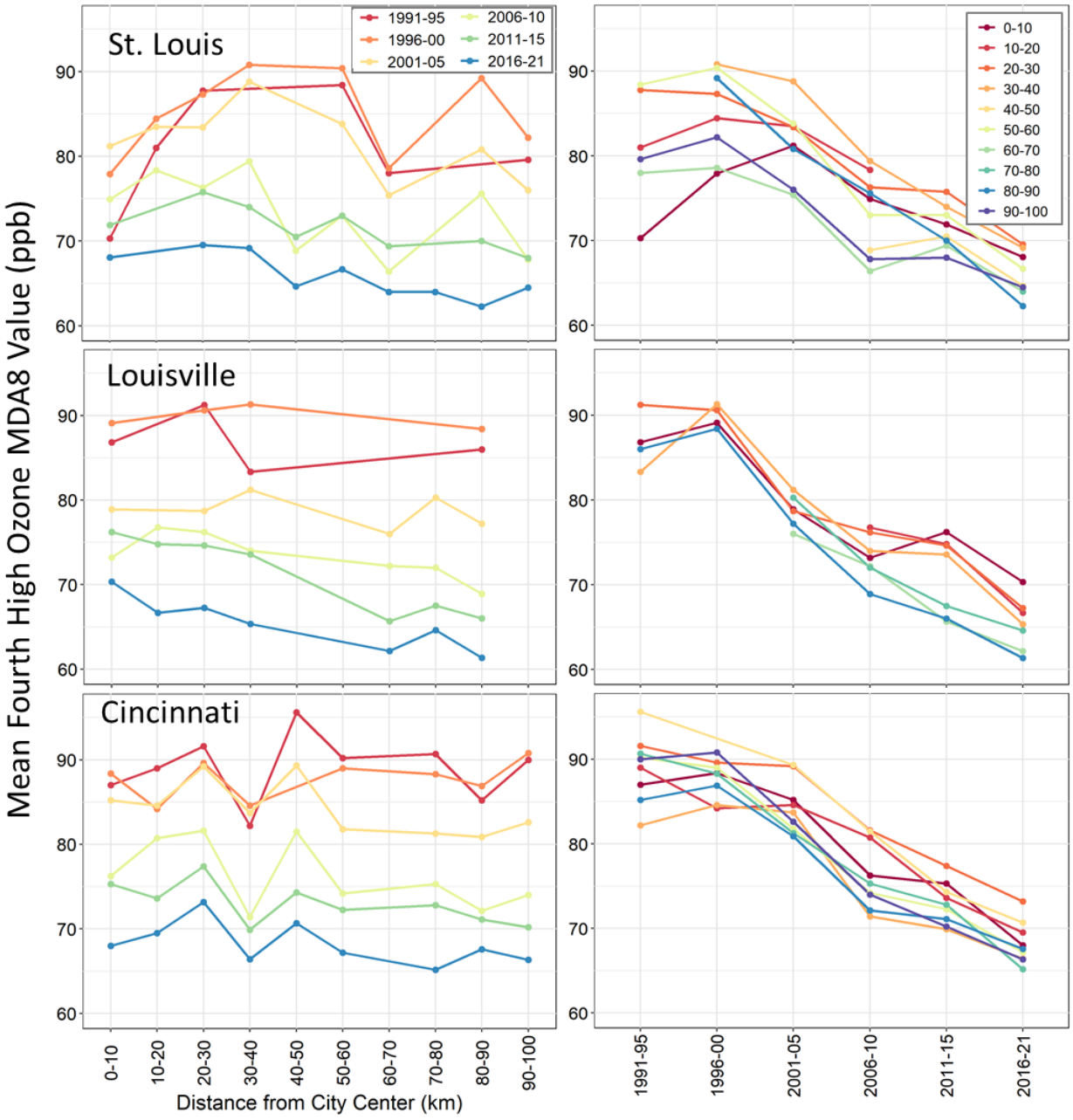

Figure 4.4. Mean fourth high MDA8 ozone concentrations for the three southern nonattainment areas plotted versus (left) distance from the city center, with different lines for the different year groups, and (right) different year groups, with different lines for the different distance bins.

Louisville and Cincinnati. There is no evidence of strong NOx titration/VOC sensitivity in Louisville and Cincinnati as there was in St. Louis. Maps of mean fourth high MDA8

concentrations show the absence of very low O_3 concentrations in the city centers in the early 1990s (Figure 4.3). Cincinnati shows the highest O_3 concentrations to the northeast of the city center in all time periods, likely reflecting influence from local NOx emissions from Dayton and other cities in this area (Figure A5.1). Note also that Louisville had very sparse monitoring in the early years. In addition, the East Bend monitor 30-40 km southwest of Cincinnati is very close to a large coal-fired power plant, so the low concentrations in this distance bin likely reflect titration from the NOx emissions from this facility.

Both cities had O_3 concentrations that were fairly flat over distance and time in the 1990s, likely indicating transitional chemistry in these areas (Figure 4.4). Starting in the early 2000s, O_3 began to decrease away from the city centers with strong and consistent decreases, which suggests that O_3 formation had shifted to a NOx-sensitive regime. In the 2010s, the highest O_3 concentrations in Louisville were in the city center, and concentrations decreased steadily away from the city center, following the classic NOx-sensitive pattern. In the 2010s, Cincinnati had moderate O_3 at the city center and higher levels at 20-30 km out, surrounded by decreases. However, this pattern likely demonstrates the asymmetry of NOx emissions in this city rather than VOC-sensitive chemistry in the city center, particularly since O_3 concentrations decreased steadily in the city center in the 2010s.

Analysis of ozone trends in northern cities

Chicago. Ozone patterns in the Chicago area were very different from those in the southern cities. The map of mean fourth high O_3 concentrations in the early 1990s shows a large area with relatively low concentrations, with a minimum of 65 ppb in the city center (Figure 4.6). More than a third of the monitors had mean values of less than 80 ppb, which was low for an urban area at the time. Outside of this area, there were clear and large peaks in O_3 at 60 to 80 km from the city center in both Wisconsin and Indiana, with mean concentrations up to 101 ppb, a 36 ppb difference from the city center.

It is important to note that lakeshore effects are extremely important in parts of the Chicago area. Formation and transport of O_3 in stable boundary layers over the lake, followed by

onshore transport of this O_3-rich air, contribute to peaks in O_3 near the lakeshore. The highest monitor (Wisconsin's Chiwaukee Prairie, located 70.5 km from the city center) is located very close to the lakeshore and is heavily impacted by lake breeze transport. This factor complicates the interpretation of O_3 formation sensitivity based on O_3 trends in the Chicago area.

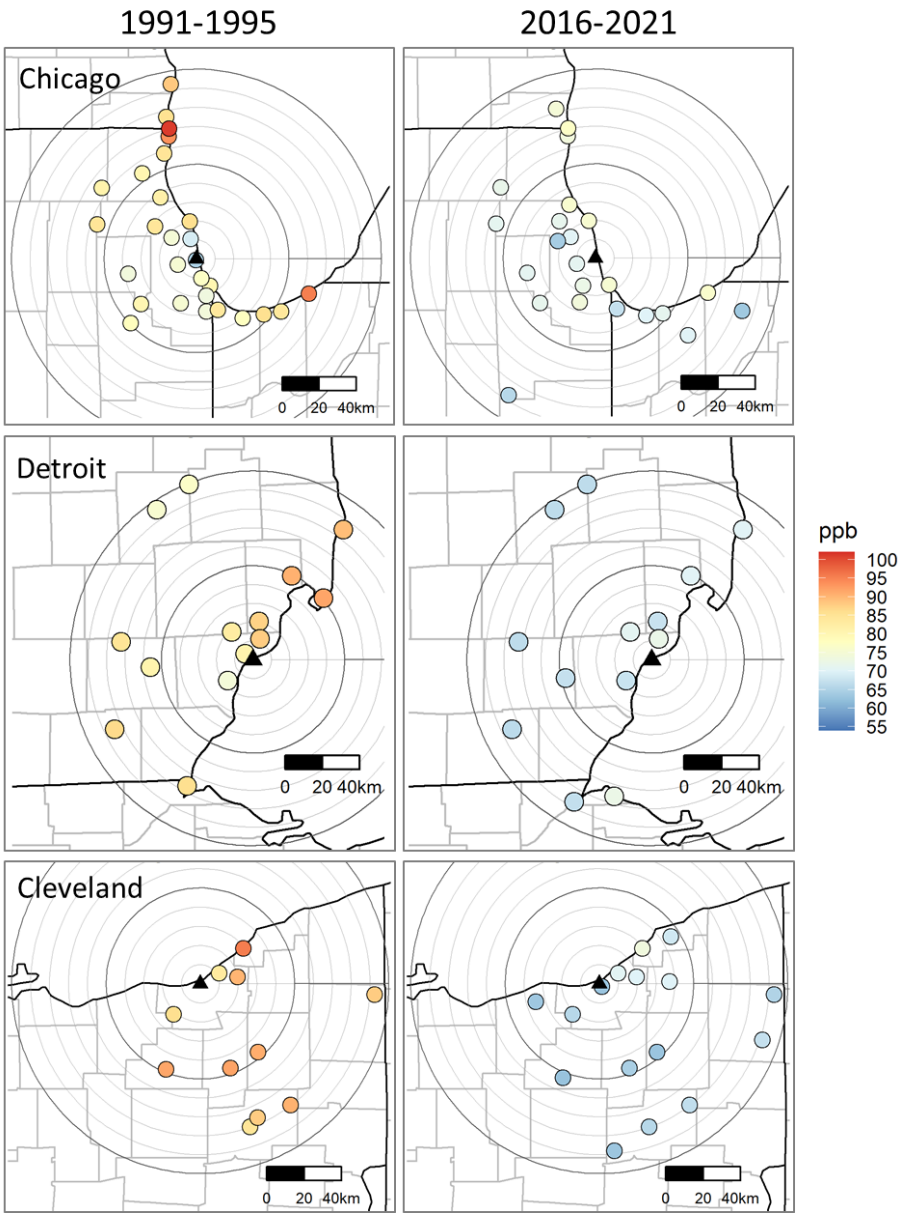

Figure 4.5. Maps of mean annual fourth high maximum daily 8-hour average (MDA8) ozone concentrations in ppb in the northern urban nonattainment areas in (left) 1991-1995 and (right) 2016-2021. The black triangles show the location of the city center. The concentric circles show the distance from the city center, with the light lines being 10 km apart and the darker lines being 50 km apart. Maps for additional years are included in Appendix 5.

Throughout the 3-decade study period, there were relatively low onshore O_3 concentrations within 60 km of the Chicago city center, with concentrations increasing to peak values at 70-80 km from the city center (at the lakeshore Chiwaukee Prairie monitor; Figure 4.7). Ozone concentrations dropped dramatically in the mid-2000s, likely as a result of the large reductions in NOx emissions discussed above. This shift appears to have resulted in a large shift in O_3 formation chemistry. Prior to the mid-2000s drop, O_3 concentrations were 10 to 16 ppb higher at 70-80 km distance than at the city center, whereas after this shift, this difference shrank to 5 to 10 ppb. In general, the O_3 decrease in the mid-2000s was much larger at outlying monitors than at those in the central city, so that concentrations across the area were more homogenous after the mid-2000s.

Ozone trends over time show that concentrations nearer to the Chicago city center remained the same from the early 1990s until the large drop in the mid-2000s (Figure 4.6). Since the mid-2000s, concentrations in this central area have increased slowly but steadily. Taken together, these trends indicate NOx-suppression/ VOC-sensitivity within 60 km of the Chicago city center in the first 15 years of this trends analysis. It is likely that VOC emissions reductions during this period attenuated the increases in O_3 concentrations that resulted from the NOx reductions (i.e., less titration of O_3 from NO), particularly in the first half of the record. As NOx reductions have continued, the O_3 chemistry appears to be shifting towards transitional chemistry. This shift is indicated by the increases in O_3 concentrations as the area shifts towards a chemistry regime of peak O_3 concentrations before concentrations decrease as the chemistry becomes NOx-sensitive. It isn't clear whether O_3 has peaked in the central Chicago area yet or when it will. The area of peak O_3 (70-80 km) seems to have had steady to decreasing O_3 concentrations since the late 2000s; O_3 formation in this area may be shifting to NOx-sensitive chemistry.

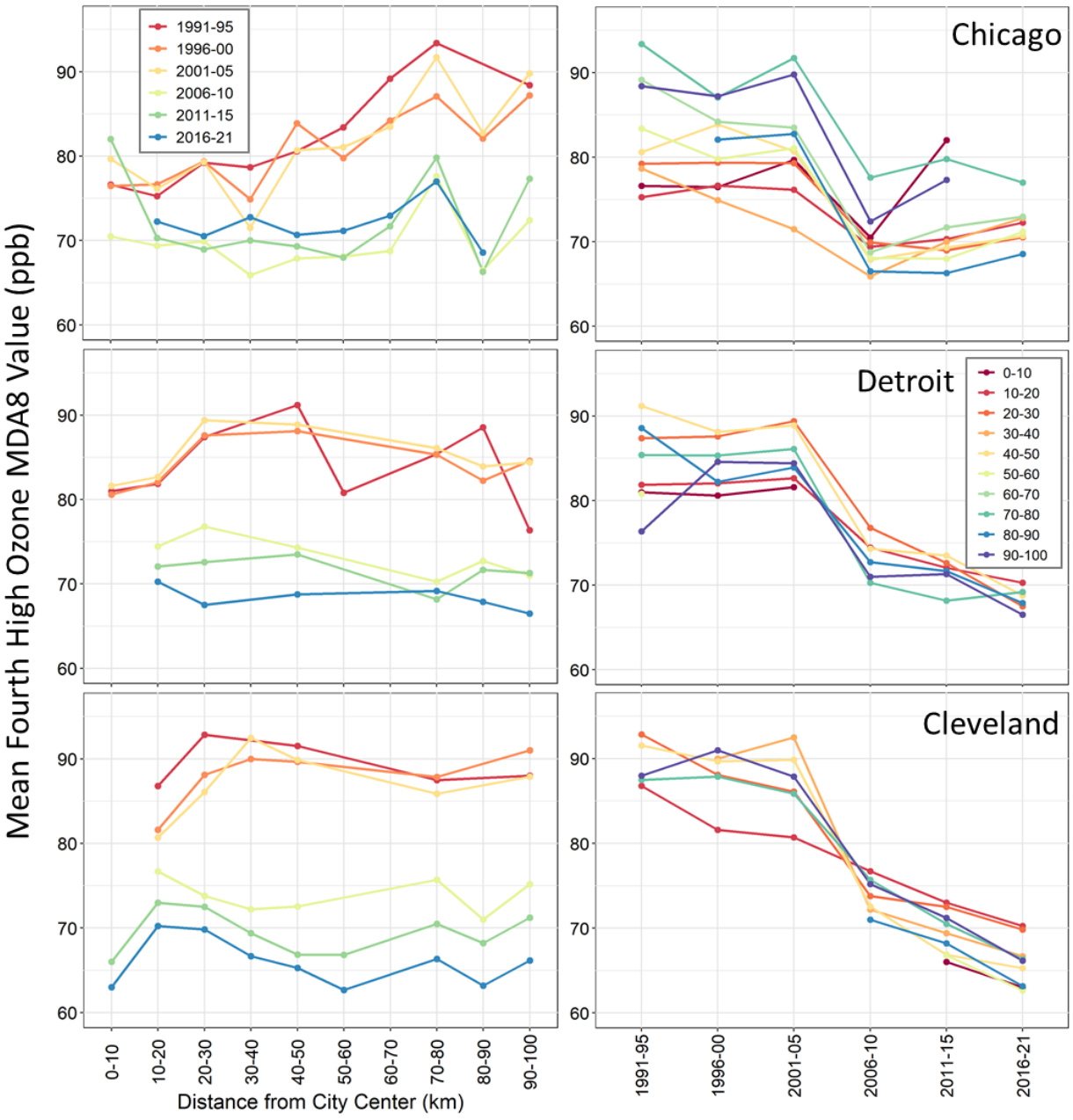

Figure 4.6. Mean fourth high MDA8 ozone concentrations for the northern urban nonattainment areas plotted versus (left) distance from the city center, with different lines for the different year groups, and (right) different year groups, with different lines for the different distance bins.

The map of mean fourth high O_3 concentrations in 2016-21 shows that ozone concentrations are much more uniform in the area than at the beginning of the study (Figure 4.6). The highest

O_3 concentrations are now located along the lakeshore, and concentrations at the central Cook County lakeshore monitors are not that different from those at outlying lakeshore monitors. Overall, in the early 1990s, high O_3 concentrations in Chicago were primarily a problem in outlying areas. Ozone concentrations are now much more uniform and are highest along the lakeshore and increasing in areas closer to the city center.

Detroit and Cleveland. As with Chicago, both Detroit and Cleveland are impacted by lakeshore and transport effects. In particular, the highest concentration monitor in Cleveland, at Eastlake, is the closest to the lakeshore (located 1.5 km inland, 29 km from the city center) and is heavily influenced by lake breezes. These lake effects will complicate attempts to infer the O_3 formation sensitivity in these areas.

Both cities show evidence of NOx-suppression/VOC sensitivity in the central 20 km in the early years of the study (Figures 4.5 and 4.6). For the first 15 years, the city centers had the lowest concentrations in the areas. City center concentrations held steady in Detroit through the early 2000s and decreased in Cleveland from the early to late 1990s then held steady through the early 2000s. During these years, the peak O_3 concentrations were found 20-50 km from the city center, generally to the northeast. These peak-O_3 areas likely had transitional chemistry, although they were also influenced by lake breezes and other lake effects. Concentrations slowly decreased away from these transitional areas, where NOx-sensitive chemistry likely dominated. The bump in O_3 concentrations at 70-90 km from Detroit is from monitors in nearby Toledo, OH and Sarnia, Ontario. Ozone in Canton, OH, at 79.7 km from Cleveland, also caused a bump in O_3 in the 70-80 km bin.

Both cities had a large drop in O_3 in the mid-2000s, as seen for Chicago. Over the last 15 years, O_3 generally peaked just outside the city centers and decreased away from them, with steady decreases at all distances. These areas of steady decreases likely have NOx-sensitive chemistry. The exception to this case is the Toledo area; see Appendix 6 for an analysis of this area. Both areas started the study period with the lowest O_3 in the city center and ended it with the

highest O_3 at or near the city center. Mean fourth high MDA8 O_3 concentrations in 2016-21 were fairly uniform around each area, with small enhancements to the northeast of each downtown, likely due to lake-related effects (Figure 4.6). The minima at the very center of Cleveland (0-10 km) in the 2010s most likely does not indicate VOC sensitivity. It is more likely that these values are low because this site is not impacted by lake effects whereas the sites to its northeast are, which elevates the means for outlying areas relative to the city center. The city centers in Detroit and Cleveland may currently be transitional or NOx-sensitive; it is difficult to distinguish between these in this analysis, particularly given the complicating influence of lake effects.

Recent trends in ozone concentrations

In addition to understanding historical trends in O_3 formation sensitivity, it is important to understand the recent trends in O_3 concentrations and the recent O_3 chemistry regimes. Because meteorology is the dominant factor impacting O_3 concentrations over short timeframes, it is important to look at O_3 over multiple years to determine trends. Toward this end, Figure 4.7 shows the difference in ozone concentrations between 2011-15 and 2016-21, the two most recent time periods studied. This figure shows that mean fourth high O_3 concentrations decreased almost everywhere in the region, indicating that O_3 concentrations are falling around the region in response to decreasing NOx (and VOC) emissions. The southern areas had the largest reductions, with the peak decrease of 13 ppb to the northeast of Louisville. The exception to this trend is the Chicago area, where O_3 increased at most monitors, with the increases ranging from 0.5 to 6.2 ppb. The smallest increases in Chicago were along the lakeshore. Most of the near-lake monitors at the far edges of the urban area had small decreases of 1-3 ppb, including the far northern monitors on the lakeshore (Chiwaukee Prairie and Zion) and the Indiana monitors in Laporte County (lakeshore and inland). The only other monitor whose mean fourth high O_3 concentrations increased over this time period was the lakeshore Toledo monitor, which increased by 2 ppb. This monitor changed locations in 2016, and it's possible the new location may be more subject to enhanced O_3 concentrations, although its location very near the old monitor makes this unlikely. Appendix 5 shows this data plotted as rolling 5-year mean concentrations, which allows examination of trends over somewhat shorter time periods; however, the same conclusions hold.

These patterns suggest that most of the LADCO region is currently NOx-sensitive and on a path to continuing reductions in O_3 concentrations in the future in response to ongoing reductions in NOx emissions. The one exception is the Chicago area, and possibly parts of Toledo, where O_3 will continue to increase in most areas until the chemistry shifts from transitional/VOC-sensitive to NOx-sensitive. At this point, O_3 concentrations will start decreasing. There is no indication that the central Chicago area has reached this threshold yet.

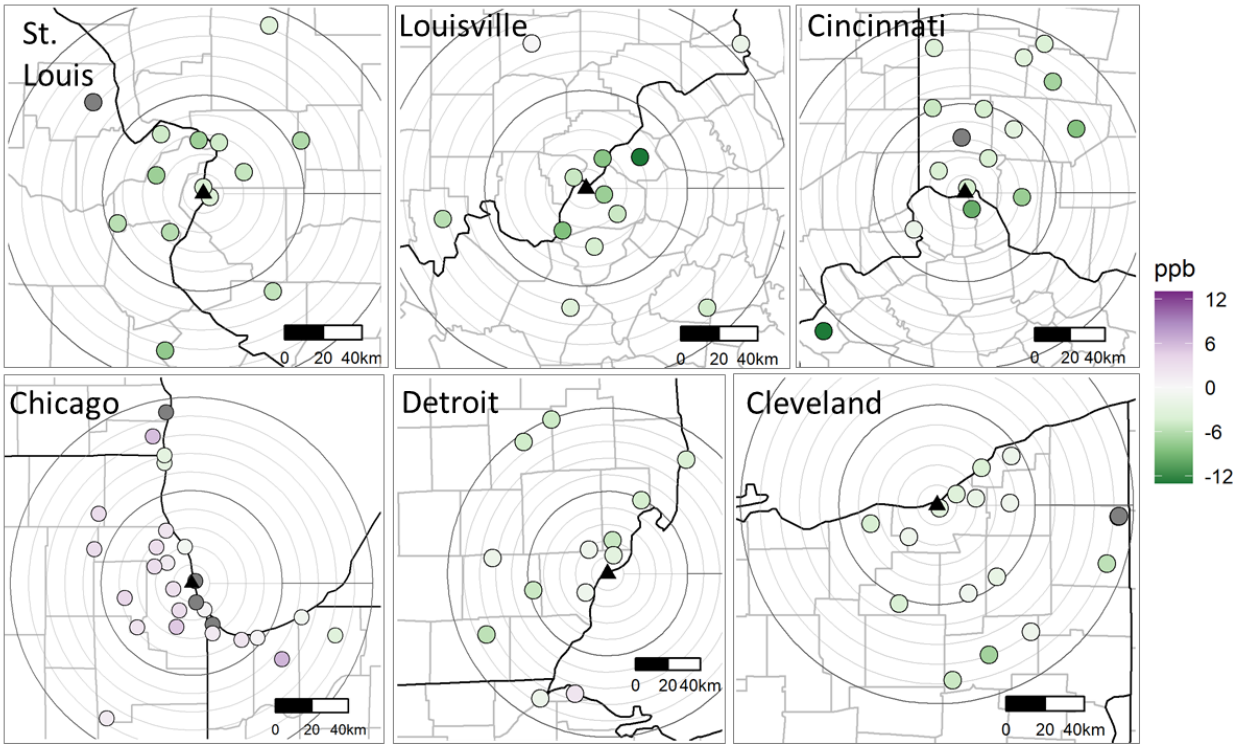

Figure 4.7. Maps of the change in mean annual fourth high maximum MDA8 ozone concentrations in ppb from 2011-15 to 2016-21, with positive values indicating increasing concentrations. The black triangles show the location of the city center. The concentric circles show the distance from the city center, with the light lines being 10 km apart and the darker lines being 50 km apart. Gray circles indicate that the monitor was missing data in one of the sets of years.

4.3.3. Spatial and temporal trends in ozone in the Lake Michigan region

In addition to the large urban nonattainment areas discussed above, there are a number of nonattainment areas located around Lake Michigan in smaller urban, suburban, and rural areas (Figure 1.2). Some of these areas regularly have the highest O_3 concentrations monitored in the entire LADCO region, and most of the areas are located tens or hundreds of kilometers downwind from major emissions sources in cities. The air quality in these areas is primarily impacted by lake-related processes. The largest source of emissions to the Lake Michigan region is Chicago, with smaller amounts from Gary, Milwaukee, and other urban areas around the lake and farther upwind. Urban and industrial emissions on the southern end of Lake Michigan are transported north and northeastward over the lake where they react in the shallow marine boundary layer to form a reservoir of high concentrations of O_3 and aged O_3 precursors. The plume of pollutants over the lake transports onshore via lake breezes or synoptic transport (e.g., Dye et al. 1995; Stanier et al., 2021).

As the pollutant plumes travel over the lake, they evolve chemically in a semi-closed system, with the O_3 precursors reacting to form O_3. That O_3 may react and reform within the plume before eventually decomposing via chain-terminating reactions that permanently remove O_3 and O_3 precursors from the system. The balance of O_3 formation and destruction in these over-lake plumes will affect the amount of O_3 that is transported to the lakeshore monitors along the shoreline. This balance will be strongly impacted by the amount of NOx and VOCs present in the plume initially. When the emissions of NOx and VOCs are relatively high, as in the earlier parts of the study period, it would take a long time for the chain-terminating reactions to overwhelm the O_3-formation reactions, meaning that high levels of O_3 could travel long distances up the lake. As the initial amounts of NOx in the plumes decreased substantially, we would expect the loss reactions to more quickly overwhelm the formation reactions, resulting in less concentrated plumes that are depleted before they can travel as far up the lake. Reductions in VOCs in the plume would also contribute to this change, although VOC changes likely played a smaller role than NOx reductions given their smaller magnitude (e.g., Figure 4.2).

To investigate how the distribution of O_3 around Lake Michigan has evolved over time, we conducted a separate analysis of the Lake Michigan monitors. We combined the Cook County, IL (e.g., central Chicago) monitors with the lakeshore monitors in Wisconsin, Indiana, and Michigan, focusing on monitors located within 10 km of the lakeshore for the downwind areas. We examined the western (IL and WI) and eastern (IN and MI) sides of the lake separately since they are generally impacted by different types of transport events, with southerly winds bringing O_3 to the western lakeshore and southwesterly winds impacting the eastern lakeshore. In addition, the lake breeze is more important along the western shoreline since synoptic southwesterly winds will carry pollution onto the eastern coastline even without the presence of a lake breeze. We excluded the central Milwaukee monitors from this analysis because they are primarily impacted by local emission; these monitors are shown in Appendix 6. This analysis examines monitors relative to their distance from the Chicago city center. This approach will ignore the contributions from Milwaukee emissions, which will impact the northern Wisconsin lakeshore and possibly the northern Michigan lakeshore. However, emissions from Chicago are much larger than those from Milwaukee, so this simplification seems warranted. We included all Cook County monitors in both analyses regardless of whether those monitors lie between the city center and the downwind monitors.

As discussed previously, there is clear evidence of NOx titration in central Chicago in the early 1990s, with peak O_3 concentrations of 101 ppb located about 75 km from the city center (Figure 4.8). Mean O_3 concentrations in this time period were above 85 ppb along the entire Wisconsin and Michigan lakeshores outside of the Chicago area.

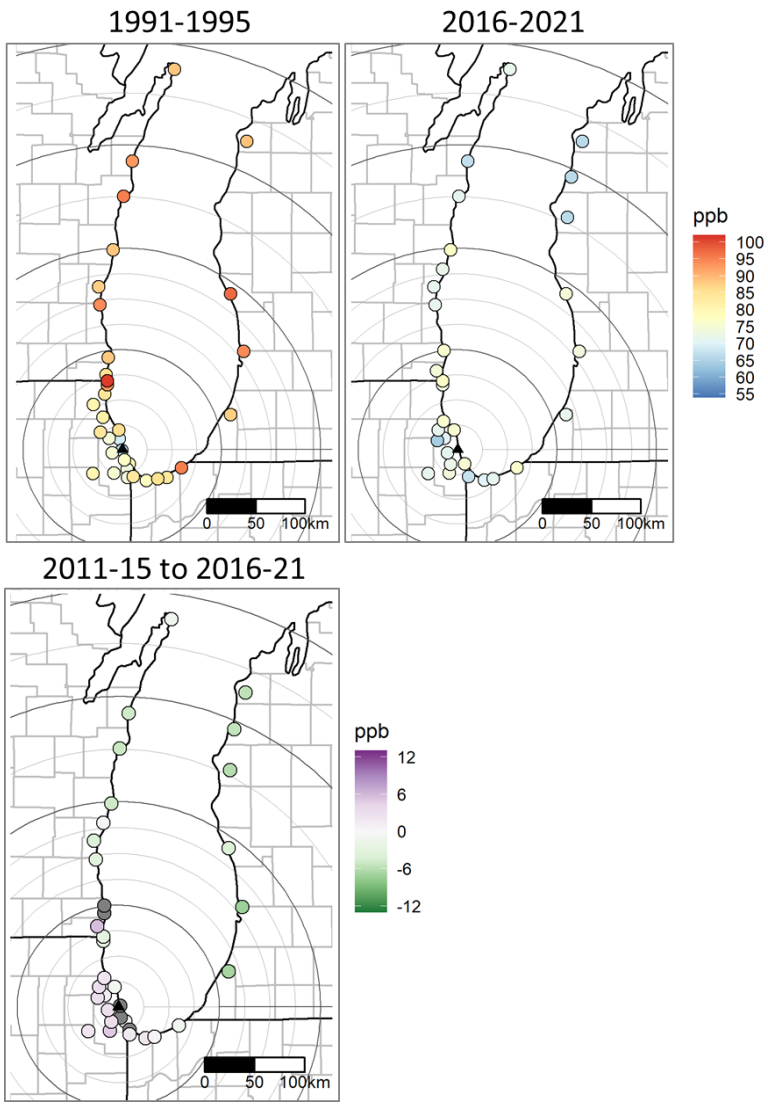

Figure 4.8. Maps of (top) mean annual fourth high maximum daily 8-hour average (MDA8) ozone concentrations in ppb in (left) 1991-1995 and (right) 2016-2021 and (bottom) the change in mean annual fourth high maximum MDA8 ozone concentrations from 2011-15 to 2016-21 in the Lake Michigan region. The black triangles show the location of the Chicago city center. The concentric circles show the distance from the Chicago city center, with the darker lines being 100 km apart and the light lines being 25 km apart for the inner 200 km and 50 km apart for the outer 200 km. Maps for additional years are included in Appendix 5.

Along the western lakeshore, O_3 concentrations peak at two areas in most years: at 50-75 km from Chicago (at the Chiwaukee Prairie, WI monitor) and at 175-200 km (at the Sheboygan

Kohler Andrae, WI monitor, Figure 4.9). Note that The Kohler Andrae monitor didn't begin operating until 1997, so it is missing from the 1991-95 data point. Both of these monitors are very close to the lakeshore so receive undiluted O_3 from lakeshore plumes (Cleary et al., 2022). Over time, O_3 concentrations at the 175-200 km peak have come down dramatically. Ozone at the 50-75 km peak has also decreased but at a much slower rate. In other words, O_3 at both peak locations has decreased over the last 30 years, but it has decreased more slowly at the sites closer to Chicago than at the sites farther downwind/north. This pattern holds true for most of the lakeshore: O_3 at the farther downwind sites has decreased more steeply and more steadily than has O_3 at sites closer to Chicago.

Ozone along the eastern lakeshore followed a similar pattern, with two peaks in most years: one at 50-75 km (which includes Michigan City along the Indiana coast) and another at 150-175 km (Allegan County) or 175-200 km (Muskegon County) (Figure 4.8). As with the western lakeshore, O_3 concentrations have decreased steeply at the farther downwind monitors and more slowly at the monitors closer to Chicago. As a result, in the late 2010s, the peak O_3 concentrations were located 50-75 km downwind of the Chicago city center. The monitors at the farthest northern extent of the Michigan lakeshore had lower O_3 than those along the southern portion of the Michigan coast. These monitors are likely less impacted by plumes from Chicago because they are located behind the bulge of the Michigan coastline.

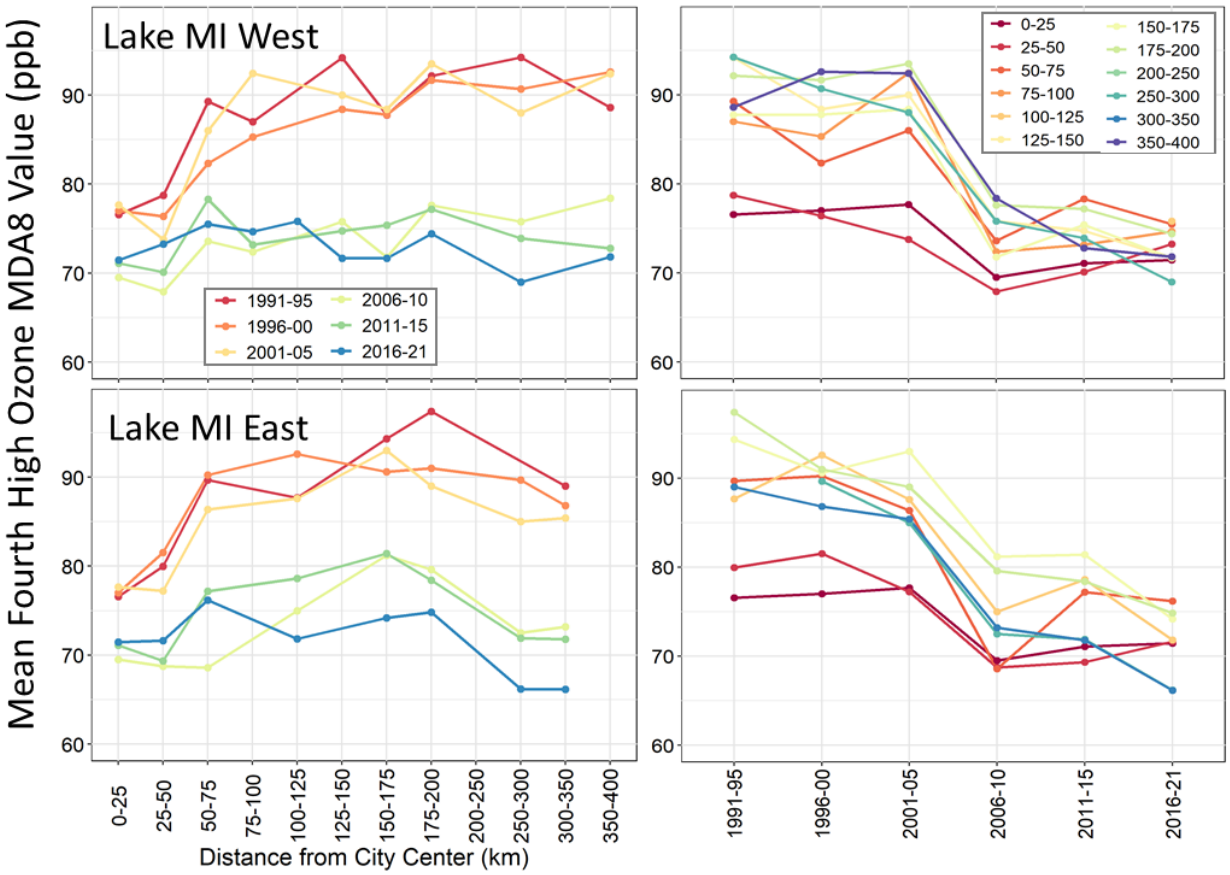

Figure 4.9. Mean fourth high MDA8 ozone concentrations for the Lake Michigan region plotted versus (left) distance from the city center, with different lines for the different year groups, and (right) different year groups, with different lines for the different distance bins. The top graphs show the western side of the lake, including all of Cook County, and the bottom graphs show the eastern side of the lake, also including all of Cook County. Note the variable intervals in the distance bins, as also shown in Figure 4.8.

Ozone concentrations over the last decade have decreased everywhere in the Lake Michigan region except in the Chicago area, as discussed above (Figure 4.8). The decreases were somewhat larger along the Western Michigan lakeshore (mean of 5.8 ppb) than along the Wisconsin shoreline (mean of 3.3 ppb).

These results are consistent with the suggestion that the trends along the lakeshore result from changes in the amount of O_3 precursors and O_3 in the plumes as they're transported over the

lake. This lakeshore O_3 trend is in contrast to the trends discussed for the urban areas, which seem to be indicative of changing O_3 formation chemistry. The farthest north monitor in this study is located 365 km away from the Chicago city center. Transport along this distance provides a long time for the plume to react and transform. These results suggest that as NOx emissions have decreased over time, the O_3 plumes transported over the lake have fewer precursors available to form O_3. As a result, for receptors that are farther downwind from the urban areas, the chain-terminating reactions that inhibit O_3 formation become more important than the O_3 formation reactions. Lower O_3 and O_3 precursor concentrations over the lake in recent years explain the steeper downward trend in O_3 concentrations at farther downwind locations. In contrast, at locations closer to the NOx sources at the southern end of Lake Michigan enough ozone precursors exist to drive O_3 formation and lead to relatively high concentrations.

4.4. Conclusions

This analysis of O_3 trends demonstrates that O_3 concentrations have decreased over the last 30 years throughout the LADCO region. The locations of O_3 reductions relative to the city centers and over time reveals how O_3 formation chemistry has changed in different parts of the region. In the southern areas of St. Louis, Louisville, and Cincinnati, areas of VOC-sensitivity or transitional chemistry in the city centers shifted to NOx-sensitivity by the mid-2000s, and O_3 has decreased steadily since then as NOx emissions have decreased. The northern areas of Chicago, Detroit, and Cleveland had a dramatic drop in O_3 concentrations accompanied by an apparent shift in O_3 chemistry in the mid-2000s. All of these city centers appear to have had VOC-sensitive chemistry early in the study period. Detroit and Cleveland appear to have mostly shifted to NOx-sensitive chemistry, with decreasing O_3 concentrations, although some areas of transitional chemistry may remain in the city centers. In contrast, most of the Chicago area appears to have chemistry that is shifting from VOC-sensitive to transitional, resulting in O_3 concentrations that are increasing over time. These three northern urban areas also had larger reductions in O_3 concentrations in outlying areas relative to the city centers.

Ozone concentrations along the Lake Michigan shoreline have decreased the most at areas far downwind (north) of Chicago, while locations closer in to the city have decreased at a slower rate. These trends likely result from the lower amounts of NOx in the relatively isolated over-lake plumes transported from the Chicago area northward. As O_3 precursor emissions have decreased over time, the precursors in the plumes appear to be “used up” faster, resulting in decreasing concentrations in downwind portions of the plumes.

5. Synthesis: Ozone-NOx-VOC Sensitivity in the LADCO Region

5.1. Introduction

This report has presented five analyses of the O_3-NOx-VOC chemistry of nonattainment areas in the LADCO region, including the use of HCHO/NO_2 ratios from ground-based monitoring, TROPOMI satellite retrievals, and CAMx modeling, as sensitivity indicators. This report has also discussed insights from other studies, including High-order Decoupled Direct Method (HDDM) modeling from two sources to the whole LADCO region (Koplitz et al., 2022 and Odman and Hu, 2022). We also discussed studies of the Lake Michigan region that applied a generalized additive model (Blanchard 2020), a paired trajectory and box model approach (Acdan et al., 2020), and a photochemical model run using different emissions scenarios (Abdi-Oskouei et al., in revision). In this section, we discuss the findings of each of these new and previous analyses and come up with our best estimates of the O_3 formation chemistry in each area. We base our best estimates of the O_3-NOx-VOC chemistry on a consideration of all of these lines of evidence. We gave somewhat heavier weight to those analyses that rely on direct observation of the atmosphere and how it responds to changes: i.e., the W-W analysis, the trends analysis and monitor-based HCHO/NO_2 ratios, where available. We also discuss any apparent biases in the different approaches and evaluate the effectiveness of each type of analysis for the LADCO region.

This analysis does not consider the analysis of the CAMx model-based H_2O_2/HNO_3 ratios, which suggested that almost the entire LADCO region was NOx-sensitive. This conclusion does not match the results from any of the other analyses. We thus consider this approach to be an outlier, likely indicating either that the model concentrations of H_2O_2 and/or HNO_3 are systematically incorrect or that the ratio thresholds applied are not appropriate for this region at this time.

We also examine trends in O_3 formation sensitivity over time based on the W-W analysis (from 2001 to 2020) and the trends analysis (from 1991 to 2021). Analysis of CAMx model projections through 2028 based on the HCHO/NO_2 ratios provides insight into anticipated future trends in O_3-NOx-VOC chemistry.

5.2. Ozone-NOx-VOC sensitivity for LADCO nonattainment areas

5.2.1. St. Louis

All lines of evidence for the St. Louis area indicate extensive NOx sensitivity in the area on high O_3 days in recent years. The TROPOMI satellite and the W-W analysis both suggest that the area is fully NOx-sensitive (Figure 5.1). The CAMx model analysis using HCHO/NO_2 ratios suggests that a small portion of downtown is VOC-sensitive, surrounded by a larger area of transitional chemistry, with the remainder of the area being NOx-sensitive. Monitored HCHO/NO_2 ratios at one downtown St. Louis monitor indicate chemistry at the border between transitional and VOC-sensitive. The trends analysis suggests that most of the area is NOx-sensitive, with an area in the central part of the city that may be transitional. The HDDM modeling from Odman and Hu (2022) suggests that the area is primarily NOx-sensitive, with one downtown monitor on the edge between NOx-sensitive and transitional (Figure 5.2). The HDDM modeling from Koplitz et al. (2022) indicated that the whole area is NOx-sensitive (not shown). Taken together, these analyses clearly indicate that most of the St. Louis area is NOx-sensitive. In addition, it is likely that a small area in central St. Louis has transitional chemistry.

Historical trends in the O_3-NOx-VOC chemistry from the W-W and trends analysis suggest that O_3 formation has primarily been NOx-sensitive throughout most of the area since the early 2000s. The trends analysis indicates that central St. Louis was VOC-sensitive in the 1990s. CAMx modeling by LADCO suggests that the area will continue to become increasingly NOx-sensitive through at least 2028. Ozone has been decreasing throughout the area and should continue to decrease with further reductions in urban NOx and VOC emissions.

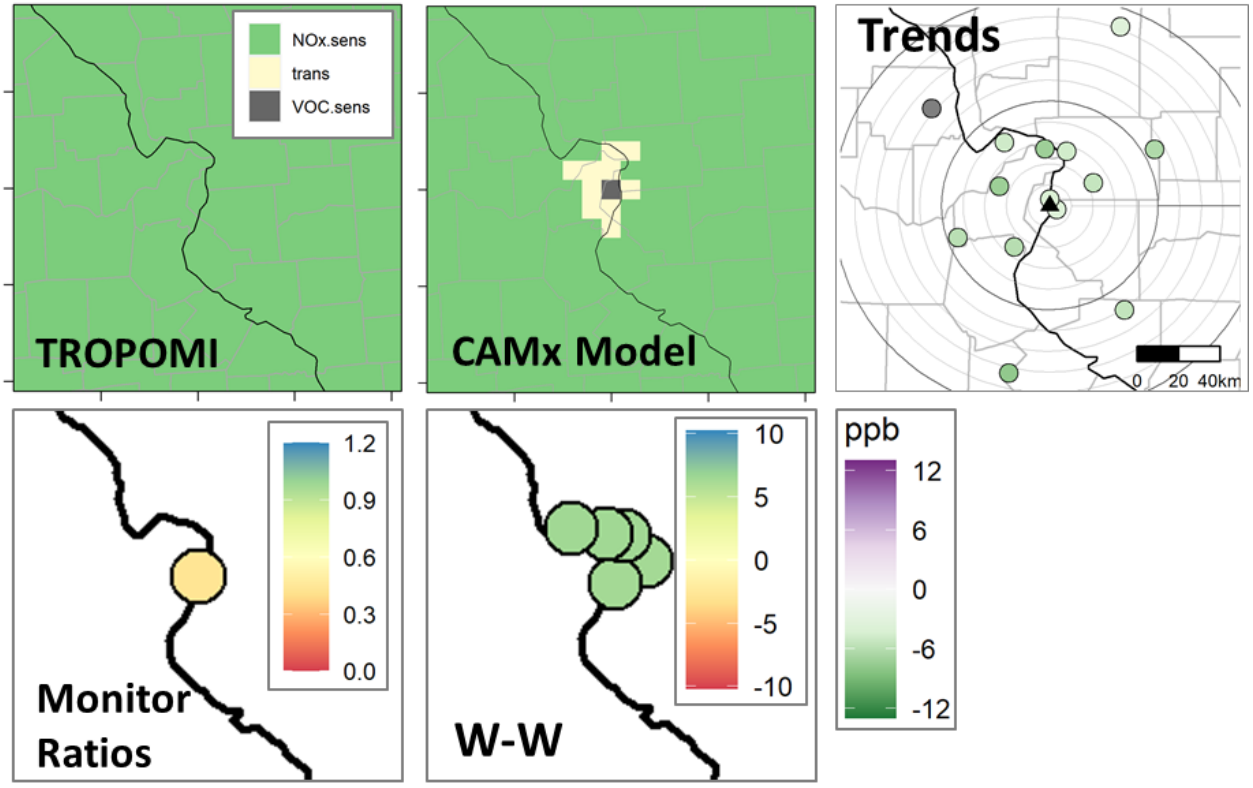

Figure 5.1. Summaries of the recent ozone-NOx-VOC sensitivity[26] for the St. Louis area based on (top left) TROPOMI satellite HCHO/NO_2 ratios, (top middle) CAMx model HCHO/NO_2 ratios, (top right) the trends analysis, (bottom left) monitored HCHO/NO_2 ratios, and (bottom middle) weekday-weekend analysis. All analyses focused on high-ozone days.

[26] TROPOMI results are for 2018-19, CAMx model results are for 2020, trends results are the difference between 2011-15 and 2016-21, and monitor ratios and W-W results are for 2016-21. Positive trends differences indicate increases in ozone, whereas negative values indicate decreases. Monitor ratios greater than 1 are considered NOx-sensitive, and ratios less than 0.3 are VOC-sensitive. W-W differences greater than 1 are NOx-sensitive and less than -1 are VOC-sensitive. High-ozone days were defined as days with a MDA8 value greater than 70 ppb for the TROPOMI and CAMx model analyses and as days with a MDA8 value greater than 60 ppb for the monitor ratios. The W-W analysis examined days with ozone-conducive meteorology, and the trends analysis focused on the annual fourth highest MDA8 value.

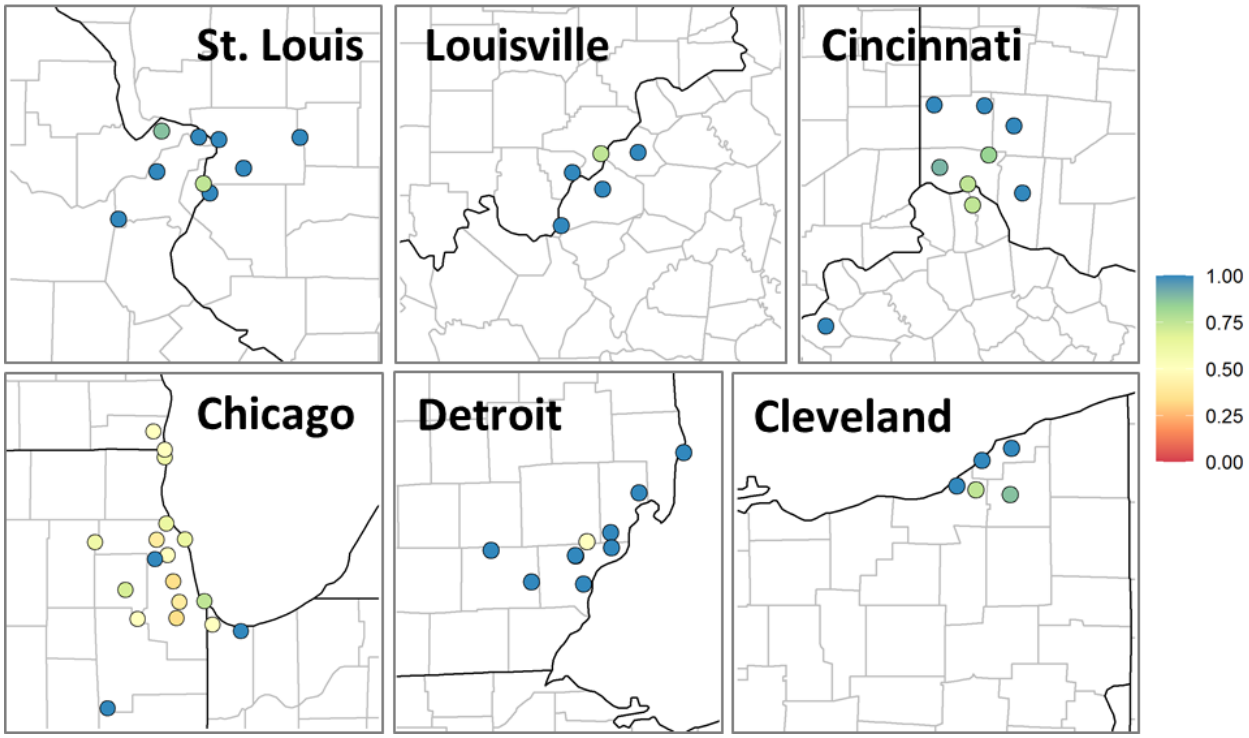

Figure 5.2. Summary of the results of the High-order Decoupled Direct Method (HDDM) modeling[27] conducted by Odman and Hu (2022), calculated based on data in their Section 4.3. Points are color-coded based on the weighted average of the chemistry on the high-ozone days studied, with a value of 0 indicating VOC sensitivity, a value of 0.5 indicating transitional chemistry, and a value of 1 indicating NOx sensitivity. Note that these values are based on a small number of exceedance days (1-9 days per site), so the value for any individual site is uncertain, but broader patterns should be more robust.

5.2.2. Louisville

All lines of evidence for the Louisville area indicate primarily NOx sensitivity in the area on high O_3 days in recent years. TROPOMI, the W-W analysis, and the trends analysis all suggest that the area is fully NOx-sensitive, except for one transitional grid cell in the TROPOMI analysis (Figure 5.3). The model-based HCHO/NO_2 ratios suggest a small area of VOC sensitivity in downtown Louisville surrounded by a thin ring of transitional chemistry and a much larger area of NOx sensitivity. Both HDDM analyses suggest that the area is mostly or entirely NOx-sensitive (Figure

[27] Modeling was conducted based on the 4-km LADCO CAMx model with High-order Decoupled Direct Method (HDDM) for the year 2016.

5.2 and Koplitz et al., 2022). There was no ground-based monitored $HCHO/NO_2$ ratio data for this area. Collectively, these analyses clearly indicate that the Louisville area is NOx-sensitive and that there may be a small area with transitional chemistry in central Louisville.

Examination of O_3 sensitivity analyses over time suggests that central Louisville had transitional chemistry through the 1990s and possibly into the early 2000s. The area has been primarily NOx-sensitive since at least the late 2000s based on the W-W and trends analyses. The model suggests that the area will become even more strongly NOx-sensitive through at least 2028. Ozone has been decreasing throughout the area and should continue to decrease with further reductions in urban NOx and VOC emissions.

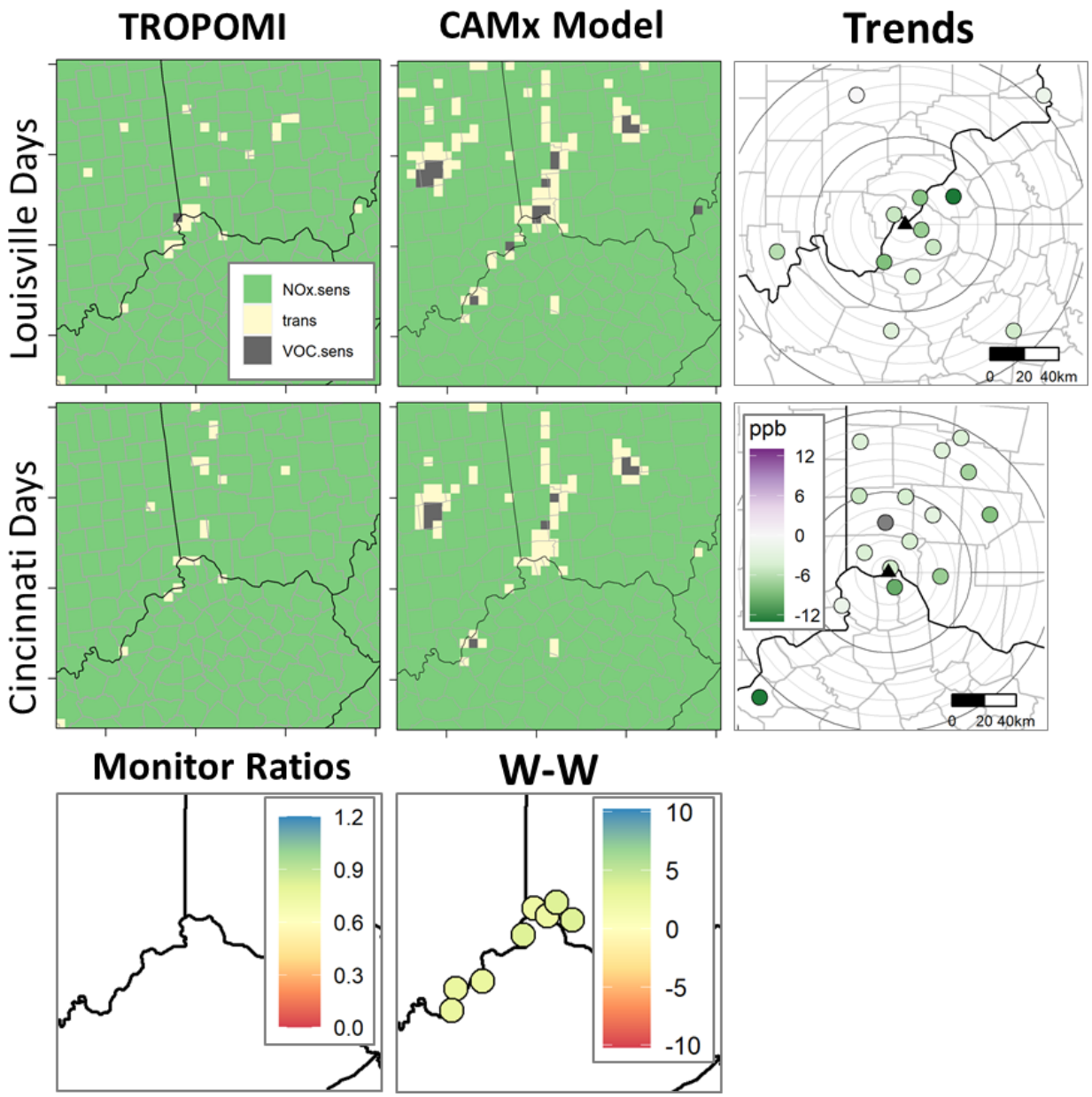

Figure 5.3. Summaries of the recent ozone-NOx-VOC sensitivity for the Louisville and Cincinnati areas based on (top left) TROPOMI satellite HCHO/NO_2 ratios, (top middle) CAMx model HCHO/NO_2 ratios, (top right) the trends analysis, (bottom left) monitored HCHO/NO_2 ratios, and (bottom middle) weekday-weekend analysis. All analyses focused on high-ozone days. See footnote 26 for more information.

5.2.3. Cincinnati

All lines of evidence for the Cincinnati area indicate primarily NOx sensitivity in the area on high O_3 days in recent years. TROPOMI and CAMx modeled $HCHO/NO_2$ ratios suggest a mixture of transitional and NOx-sensitive chemistry in the area, with the model having more transitional chemistry than the satellite and two VOC-sensitive grid cells (Figure 5.3). W-W and trends analyses both suggest the chemistry is primarily NOx-sensitive, and the trends analysis indicates some possible transitional chemistry in the urban core. HDDM modeling from both Odman and Hu (2022) and Koplitz et al. (2022) found primarily NOx-sensitive chemistry in Cincinnati. Odman and Hu (2022) also observed some days with transitional chemistry at sites in or near downtown Cincinnati (Figure 5.2). Taken together, this evidence suggests that O_3 formation in most of the Cincinnati area is NOx-sensitive, with some transitional chemistry in the city center.

Ozone formation in central Cincinnati appeared to be transitional in the 1990s based on the trends analysis, with the size of this transitional area shrinking over time but not completely going away. Outlying parts of the Cincinnati area appear to have been NOx-sensitive for at least the last 30 years. Model projections through 2028 indicate that the expansion of NOx-sensitive areas will continue in the future. Ozone has been decreasing throughout the area and should continue to decrease with further reductions in urban NOx and VOC emissions.

5.2.4. Detroit

The evidence for the O_3-NOx-VOC chemistry regime in the Detroit area iss mixed, with the different analyses suggesting different chemical regimes over the previous five years. The TROPOMI satellite and the CAMx model $HCHO/NO_2$ ratios both indicated there were some pockets of VOC sensitivity and extensive transitional areas, with NOx-sensitivity outside of these areas (Figure 5.4). The $HCHO/NO_2$ ratios at the one ground monitor in central Detroit indicated transitional chemistry, and the W-W analysis suggested that central Detroit is NOx-sensitive and some monitors to the northeast (downwind) of downtown were transitional. The trends analysis suggests that the central city area may be either transitional or NOx-sensitive, with the rest of the area being NOx-sensitive. Both HDDM analyses suggest that most of the Detroit area

is NOx-sensitive with a few small pockets of transitional chemistry (Figure 5.2 and Koplitz et al., 2022). Since none of the ground observation-based analyses, nor the HDDM modeling, finds any VOC sensitivity in the Detroit area, it is likely that the model and satellite HCHO/NO2 ratios overestimate the VOC sensitivity. Overall, it seems likely that most of the Detroit area is NOx-sensitive with areas with transitional chemistry in central Detroit and downwind of the city center to the northeast.

The trends analysis indicates an area of VOC sensitivity in central Detroit in the 1990s and early 2000s. This area shifted to transitional/NOx-sensitive chemistry in the mid-2000s with the very large drop in NOx concentrations. Unfortunately, the trends in O_3 formation sensitivity from the W-W analysis are difficult to interpret; this analysis suggests that O_3 formation chemistry alternated between being VOC-sensitive and NOx-sensitive. There is no evidence of such swings from the trends analysis, so this may indicate an issue with the W-W analysis for this area.

Model projections through 2028 indicate that the Detroit area will become increasingly NOx-sensitive in the future. Ozone has been decreasing throughout the area and should continue to decrease with further reductions in urban NOx and VOC emissions.

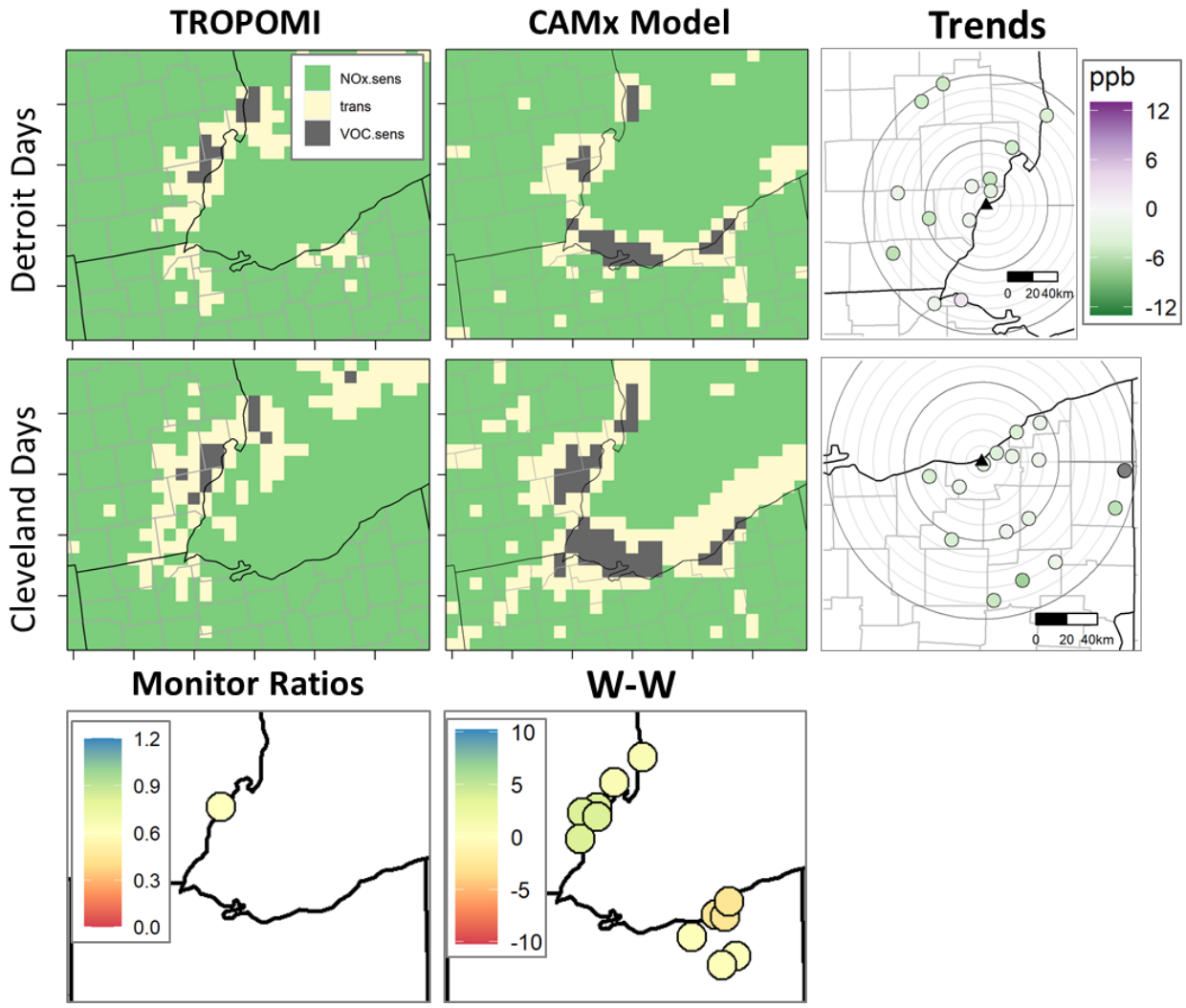

Figure 5.4. Summaries of the recent ozone-NOx-VOC sensitivity for the Detroit and Cleveland areas based on (top left) TROPOMI satellite HCHO/NO_2 ratios, (top middle) CAMx model HCHO/NO_2 ratios, (top right) the trends analysis, (bottom left) monitored HCHO/NO_2 ratios, and (bottom middle) weekday-weekend analysis. All analyses focused on high-ozone days. See footnote 26 for more information.

5.2.5. Cleveland

Patterns of O_3 formation sensitivity in Cleveland appear to be somewhat similar to those in Detroit, although some of the measurement approaches find very different results. As found for Detroit, the different analysis approaches do not always agree with each other, so some careful interpretation is required to develop a best estimate of O_3 formation sensitivity in this area. In

contrast with Detroit, the TROPOMI satellite indicates that O_3 formation throughout the Cleveland region is NOx-sensitive on high O_3 days (Figure 5.4). Both the CAMx model $HCHO/NO_2$ ratios and the W-W analysis suggest that lakeshore areas in central Cleveland are VOC-sensitive, with surrounding transitional and NOx-sensitive areas. The HDDM analysis from Koplitz et al. (2022) found a similar pattern but with less VOC sensitivity: they found transitional chemistry in a thin band along the lakeshore with NOx sensitivity elsewhere. In contrast, the HDDM analysis from Odman and Hu (2022) found that lakeshore monitors were NOx-sensitive whereas some inland monitors had some transitional chemistry (Figure 5.2). To make sense of these sometimes contradictory results, we examine the patterns in these analyses. Most of the analyses found that the central lakeshore area of Cleveland was more VOC-sensitive than were other parts of the region, and most of the analyses suggested that this area was transitional rather than VOC-sensitive. Therefore, it appears most likely that there is a small area of transitional chemistry along the lakeshore near downtown Cleveland, with the remainder of the area being NOx-sensitive.

The trends analysis suggests that O_3 formation in central Cleveland was VOC-sensitive in the 1990s, shifted to transitional chemistry in the 2000s, and appears to still be transitional. The W-W analysis suggests that O_3 formation shifted from being NOx-sensitive in the 2000s to transitional or VOC-sensitive in the 2010s. However, this shift is not evident from the trends analysis and is also counterintuitive. Therefore, we assume that this indicates a limitation of the W-W analysis, as also found for the Detroit area.

Model projections through 2028 indicate that the Cleveland area will become increasingly NOx-sensitive in the future. Ozone has been decreasing throughout the area and should continue to decrease with further reductions in urban NOx and VOC emissions.

5.2.6. Chicago

The different analyses of the Chicago area suggest more VOC sensitivity in central Chicago than found for any other part of the LADCO region. The TROPOMI satellite and the CAMx model

$HCHO/NO_2$ ratios both indicate a large area of VOC-sensitive chemistry centered over Cook County, surrounded by a ring of transitional chemistry, with NOx-sensitive formation beyond (Figure 5.5). The trends analysis also found VOC-sensitive chemistry in the central 60 or so km of the city, surrounded by transitional chemistry. This analysis also suggested that the chemistry in this area is shifting towards transitional. The ground-based $HCHO/NO_2$ ratios for two of the three monitors also indicated chemistry at the border between VOC-sensitive and transitional.[28] In contrast, the W-W analysis found transitional chemistry along the lakeshore and NOx-sensitive chemistry elsewhere in the region; the results of this analysis are outliers. Both HDDM analyses found a mixture of transitional and VOC-sensitive O_3 formation in Cook County (Figure 5.2 and Koplitz et al., 2022). These studies found transitional chemistry at the far northern lakeshore edge of the Chicago area. Koplitz et al. (2022) found a mix of transitional and VOC-sensitive chemistry in northwestern Indiana, whereas Odman and Hu (2022) found this area to be a mix of transitional and NOx-sensitive at two monitoring locations (Figure 5.2). Both HDDM analyses found transitional to NOx-sensitive chemistry farther inland. It is also apparent from the trends analysis and from a separate analysis using a Classification and Regression Tree (CART)[29] that O_3 concentrations in much of the Chicago region have been increasing over the last decade or so as NOx-suppression decreases in response to decreasing NOx emissions.

In addition to these lines of evidence, we have other studies to consider for the Lake Michigan area. Blanchard (2020) applied a generalized additive model (GAM) and determined that the Cook County lakeshore was transitional to VOC-sensitive (determined as CO-sensitivity; Figure 5.6), whereas the far northern lakeshore monitors were transitional. This study also found that two inland monitors (one in Kenosha County, WI and the other near O'Hare Airport in Cook County) were VOC-sensitive, which does not agree with other analyses. An analysis that combined trajectory and chemical box models for five O_3 episode days found average chemistry in the Cook County source regions to be a mix of VOC-sensitive and transitional (Acdan et al.,

[28] Mean ratios at the third monitor, Northbrook, were skewed by one day with a very high $HCHO/NO_2$ ratio, so the mean ratio for this site is much higher than the median ratio, which falls in the transitional range (Figure 2.1).

[29] https://www.ladco.org/wp-content/uploads/Projects/Ozone/LADCO_O3_CART-Analysis_27Oct2021-FINAL-with-Appendices.pdf

2020). This study found chemistry at the Zion monitor receptor location to the north of Chicago to be NOx-sensitive on 4 out of 5 days. Abdi-Oskouei et al. (in revision) concluded that central Chicago generally has a mixture of VOC-sensitive and transitional areas in the early afternoons.

Almost all of these analyses indicate that O_3 formation chemistry within 50-60 km of theChicago city center is currently VOC-sensitive, and a number of the studies suggest that the region is shifting towards transitional chemistry. This region of VOC-sensitive to transitional chemistry is surrounded by an area of transitional chemistry that is shifting towards NOx sensitivity at the outer edges. We view this as the most likely description of O_3-NOx-VOC chemistry in the Chicago area. Nearest the city center, O_3 is likely approaching peak production levels and will start dropping as the O_3 chemistry regime shifts away from VOC sensitivity and towards NOx sensitivity.

Both the W-W and trends analysis show a shift in O_3 formation chemistry in the mid-2000s when NOx concentrations dropped significantly. Ozone-NOx-VOC sensitivity in central Chicago at this time appears to have shifted from strongly VOC-sensitive towards chemistry that was a mix of VOC-sensitive and transitional. The chemistry at the far northern Chicago sites near the Wisconsin-Illinois border appears to have shifted from transitional to more NOx-sensitive; chemistry in this region seems to be a mixture of NOx-sensitive and transitional now.

Model projections through 2028 indicate that the Chicago area will become increasingly NOx-sensitive in the future. Ozone has been decreasing outside of the city center (>60 km) and should continue to decrease with further reductions in urban NOx and VOC emissions. Ozone concentrations in the city center have increased in recent years and will only begin to decrease through aggressive NOx and VOC emissions reductions strategies.

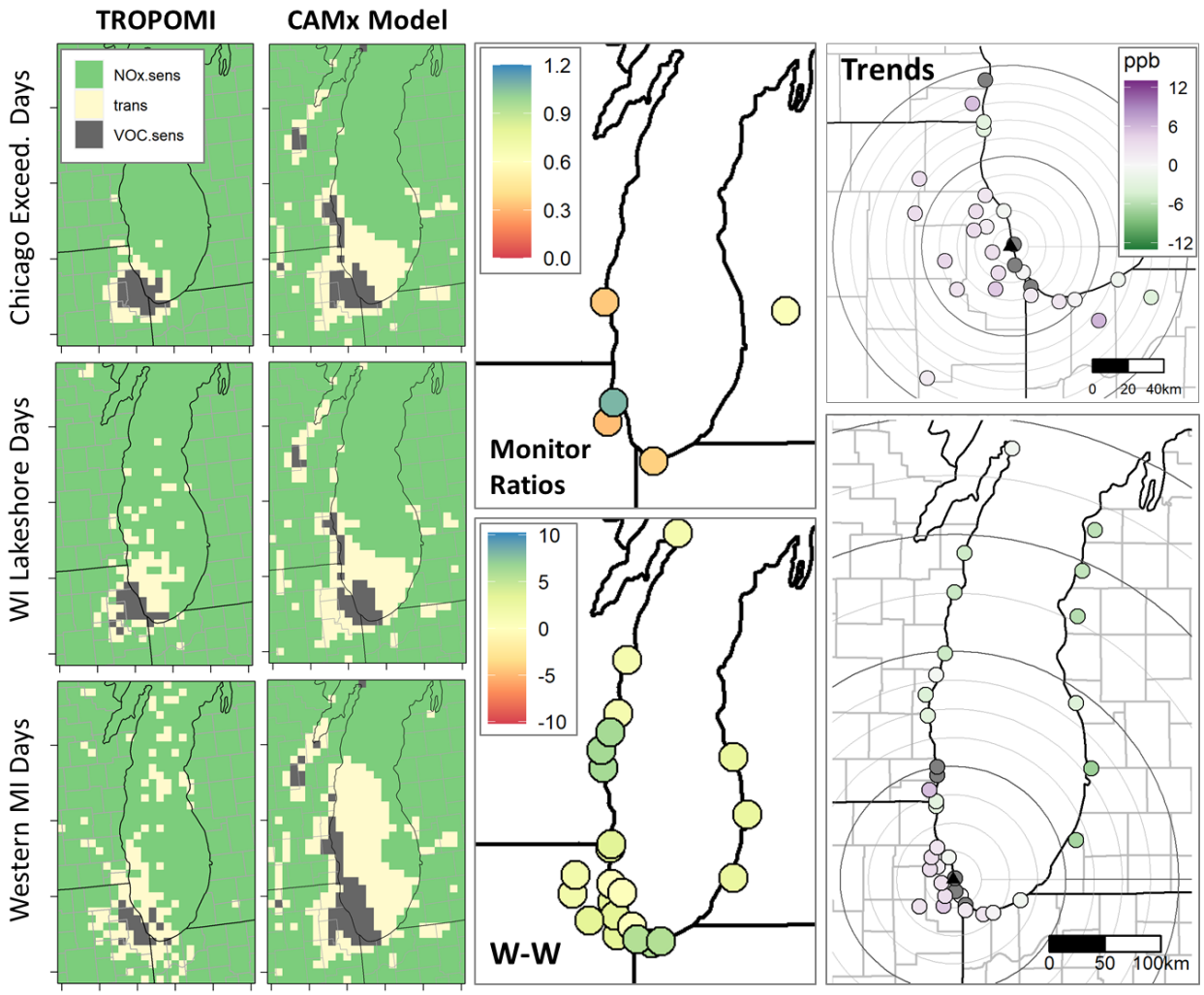

Figure 5.5. Summaries of the recent ozone-NOx-VOC sensitivity for the Lake Michigan areas based on (far left) TROPOMI satellite HCHO/NO_2 ratios, (second from left) CAMx model HCHO/NO_2 ratios, (top middle) monitored HCHO/NO_2 ratios, and (bottom middle) weekday-weekend analysis, and (right) the trends analysis. All analyses focused on high-ozone days. See footnote 26 for more information.

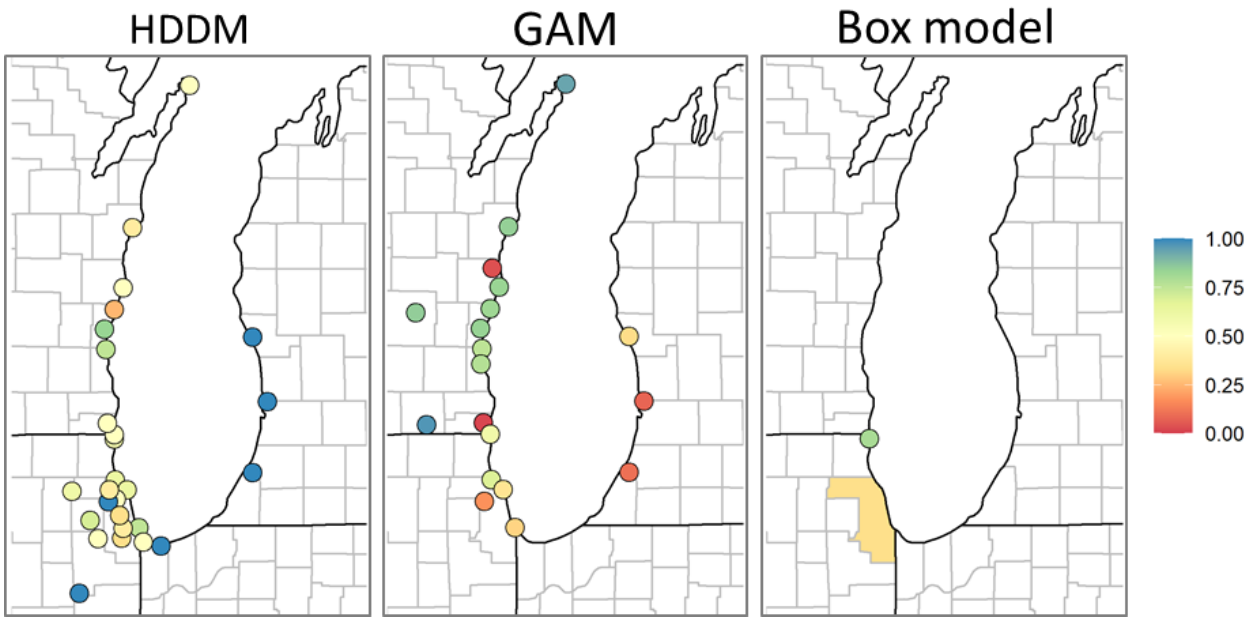

Figure 5.6. Summaries of ozone-NOx-VOC sensitivities from other studies for high ozone days in the Lake Michigan region.[30] (Left) HDDM modeling results as described in Figure 5.2, (middle) weighted average sensitivities based on a generalized additive model looking at a preference for CO (as a proxy for VOCs) or NOx, and (right) a coupled trajectory model and box model analysis tracking air parcels that passed over Chicago and reached the monitor at Zion, IL. This last plot shows the weighted average values for the Zion monitor (circle) and for Cook County. In all plots, a value of 0 = VOC-sensitive, 0.5 = transitional, and 1 = NOx-sensitive. All weighted averages were calculated by LADCO based on HDDM results from Odman and Hu (2022), GAM results from Blanchard (2020), and box model results from Acdan et al. (2020).

5.2.7. Wisconsin lakeshore nonattainment areas

Most of the data and analyses that we examined suggest that the bulk of the Wisconsin lakeshore is currently NOx-sensitive on O_3 exceedance days, with pockets of transitional chemistry in the more urbanized areas. The TROPOMI satellite analysis found areas of

[30] The GAM analysis examined the response of ozone to 10% reductions in either carbon monoxide (CO, used as a proxy for VOCs) or NOx. Note that CO is more closely linked to vehicle traffic than are VOCs in general, which likely impacts its use as a proxy. The trajectory-box model analysis examined five back trajectories that started in various locations in Cook County, IL and ended at the Zion, IL monitor. The value shown for Cook County (0.4) is the mean of the classifications for the source region on these five days.

transitional chemistry in Milwaukee and in southern lakeshore areas, with NOx-sensitive chemistry elsewhere (Figure 5.5)[31], as did the HDDM analysis in Koplitz et al. (2022) and the model analysis in Abdi-Oskouei et al. (in revision). Both the TROPOMI satellite and the model indicator ratio analysis found that O_3 formation became increasingly NOx-sensitive moving northward along the lakeshore (Figures A6.2 and A6.5). The trends analysis indicated NOx-sensitive or transitional chemistry along the lakeshore, with the lakeshore being impacted both by changes in the magnitude of the plumes as well as by the O_3 formation chemistry. The W-W analysis found NOx-sensitive chemistry, with the northern part of the lakeshore being close to transitional chemistry. The GAM analysis also found that most of the lakeshore was NOx-sensitive (Figure 5.6).

A few analyses suggested that O_3 formation along the Wisconsin lakeshore was more VOC-sensitive than indicated by the rest. The CAMx model-derived $HCHO/NO_2$ ratios indicated significant VOC sensitivity along the southern lakeshore up to Milwaukee, and the one ground-based monitor on the lakeshore had $HCHO/NO_2$ values at the threshold between transitional and VOC-sensitive in central Milwaukee (Figure 5.5). Furthermore, the HDDM analysis from Odman and Hu suggested overall transitional chemistry along the lakeshore, with individual monitors ranging from VOC-sensitive to NOx-sensitive in this area (Figure 5.6).

Considering all of the evidence, it is likely that O_3 formation along Wisconsin's Lake Michigan lakeshore is primarily NOx-sensitive on O_3 exceedance days in recent years. The exceptions are in Milwaukee and other urban areas in southeastern Wisconsin, where transitional chemistry dominates.

The W-W analysis suggests that O_3 formation along much of the lakeshore was VOC-sensitive or transitional in the early 2000s before shifting toward NOx sensitivity in the mid-2000s when NOx emissions dropped considerably. This change occurred in steps, with the chemistry

[31] Appendix 6 includes additional breakdowns of the ozone-NOx-VOC sensitivity for different parts of the Wisconsin lakeshore and western Michigan based on $HCHO/NO_2$ ratios from the TROPOMI satellite, the CAMx model, and the ozone trends analysis.

apparently shifting to transitional, then back to VOC-sensitive, and then to NOx-sensitive in the late 2010s.

Model projections through 2028 indicate that the Wisconsin lakeshore, including Milwaukee, will become increasingly NOx-sensitive in the future. Ozone has been decreasing in this area and should continue to decrease with further reductions in NOx and VOC emissions both in Milwaukee and in the upwind source regions on the southern end of Lake Michigan.

5.2.8. Western Michigan nonattainment areas

Almost all analyses indicate that O_3 formation along the western Michigan lakeshore has been NOx-sensitive in recent years. HCHO/NO_2 ratios from both the TROPOMI satellite and the CAMx model support this conclusion, with small pockets of transitional chemistry surrounded by predominantly NOx-sensitive chemistry along the entire Michigan lakeshore (Figure 5.5)[31]. The W-W analysis indicated NOx-sensitive chemistry, as did both HDDM analyses. The trends analysis suggested either NOx-sensitive or transitional chemistry in this area. The ground monitoring HCHO/NO_2 ratios at Grand Rapids fell in the transitional range, but this likely represents local conditions in this city inland from the lake. Abdi-Oskouei et al (in revision) found small pockets of VOC-sensitive O_3 formation in the urban areas of Holland and Muskegon, with the rest of the coastline being NOx-sensitive. The one outlying analysis is the GAM analysis by Charlie Blanchard, which found a strong CO preference at the three monitors along the Michigan lakeshore. Overall, it appears very likely that O_3 formation along the western Michigan lakeshore is NOx-sensitive, although there may be small pockets of transitional chemistry.

Ozone formation along western Michigan appears to have shifted from VOC-sensitive to NOx-sensitive in the mid-2000s and to have continued as NOx-sensitive since then. This shift occurred at the same time as shifts in other areas, likely as a result of large reductions in NOx emissions and concentrations.

Model projections through 2028 indicate that the Michigan lakeshore will become increasingly NOx-sensitive in the future. Ozone has been decreasing in this area and should continue to decrease with further reductions in NOx and VOC emissions in the upwind source regions on the western shore and southern end of Lake Michigan.

5.3. Overview of ozone formation sensitivity in the LADCO region

The analyses presented here clearly indicate that current O_3 formation conditions in most of the LADCO region are predominantly NOx-sensitive. LADCO's best estimates of current O_3 formation conditions for the different nonattainment areas are given in Table 5.1. Most of the urban areas have transitional chemistry in the city centers, but the only city that is clearly VOC-sensitive is Chicago. Chicago has a large area of VOC-sensitive chemistry, extending outward to roughly 60 km from the city center to the onshore areas around the city. Ozone formation in the Chicago urban area appears to be shifting to transitional chemistry, meaning that both NOx and VOC emissions reductions are needed to reduce O_3 concentrations. The areas beyond the central part of Chicago appear to be on the NOx-sensitive side of transitional chemistry.

Ozone formation in all parts of the LADCO region has become less VOC-sensitive and more NOx-sensitive over the last 30 years. The central parts of most urban areas were VOC-sensitive in the early 1990s and shifted to transitional chemistry over the intervening 30 years. Ozone formation in the southern cities of Louisville and Cincinnati began as transitional, not VOC-sensitive. The urban cores of these cities still appear to be transitional, although the extents of the transitional areas have shrunk as the surrounding NOx-sensitive areas have expanded. While Chicago has continued as VOC-sensitive, O_3 formation in this city has also shifted towards transitional and NOx-sensitive.

5.4. Evaluation of approaches to evaluate ozone-NOx-VOC sensitivity

We found that some analytical approaches to determining O_3 formation conditions more accurately captured the chemistry regimes of the region. Table 5.1 summarizes LADCO's evaluation of how accurately each analysis represented the O_3-NOx-VOC chemistry of each area. Methods using HCHO/NO_2 ratios appeared to work well when based on ground-based monitoring using ratio thresholds from Blanchard (2020), although the supporting data are sparse. Determinations using HCHO/NO_2 ratios from the TROPOMI satellite and ratio thresholds from Jin et al. (2020) matched the best estimates in many cases. However, this approach missed apparent transitional areas in St. Louis and Cleveland (which the satellite classified as NOx-sensitive) and assigned too much VOC-sensitivity to Chicago and Detroit. It appears that higher HCHO/NO_2 ratio thresholds may be appropriate for St. Louis and Cleveland, whereas lower ratios may be needed for Chicago and Detroit. The use of model-derived HCHO/NO_2 ratios and ratio thresholds from Duncan et al. (2010) appeared to overestimate the extent of VOC sensitivity in almost all parts of the region, although the patterns of O_3-NOx-VOC sensitivity match those from other analyses. This analysis suggests that the ratio thresholds (<1 = VOC-sensitive and >2 = NOx-sensitive) from Duncan et al. (2010) are too high for this region and/or for the CAMx model.

Table 5.1. Summary of LADCO's best estimates of ozone-NOx-VOC sensitivity for the most recent time period and an estimate of the accuracy of each approach in determining this sensitivity. NS = NOx-sensitive, and VS = VOC-sensitive.

		Accuracy of Estimates from Analysis							
Area	**Ozone-NOx-VOC chemistry (best estimate)**	**Monitor HCHO/ NO_2**	**Satellite HCHO/ NO_2**	**Model HCHO/ NO_2**	**W-W**	**Trends**	**HDDM (Odman and Hu)**	**HDDM (Koplitz et al.)**	**GAM (Blanchard)**
Time period		*2016-21*	*2018-19*	*2020*	*2016-20*	*2016-21*	*2016*	*2016*	*2015-19*
St. Louis	NOx-sens. w/ transitional near the city center	Good	Too NS	Too VS	Too NS	Good	Good	Mostly Good	NA
Louisville	NOx-sens. (possible transitional near the city center)	NA	Good	Too VS	Mostly Good	Good	Good	Good	NA
Cincinnati	NOx-sens. w/ transitional near the city center	NA	Good	Good	Mostly Good	Good	Good	Mostly Good	NA
Detroit	NOx-sens. w/ transitional near the city center and to Northeast	Good	Too VS	Too VS	Too NS	Mostly Good	Too NS	Mostly Good	NA
Cleveland	NOx-sens. w/ transitional near the city center and along lakeshore	NA	Too NS	Too VS	Too VS	Mostly Good	Too NS/ Too VS	Good	NA
Chicago	VOC-sens./transitional in the central 60 km or so; transitional/NOx-sens. beyond.	Mostly Good	Too VS	Too VS	Too NS	Mostly Good	Good	Good	Mostly Good
WI Lakeshore	NOx-sens. w/ transitional downtown Milwaukee & southern lakeshore	Good	Good	Too VS	Too NS	Mostly Good	Too VS	Good	Mostly Good
Western MI	NOx-sensitive	NA	Good	Good	Good	Good	Good	Good	Too VS

The model-based analysis using the H_2O_2/HNO_3 ratios suggested that O_3 formation was almost entirely NOx-sensitive throughout the LADCO region. This conclusion is not supported by any other analysis; we therefore conclude that either modeled concentrations of H_2O_2 are biased high, concentrations of HNO_3 are biased low, or the ratio thresholds used (from Sillman, 2022) are too low for this region. For these reasons, we do not include this analysis in Table 5.1.

Ozone sensitivity estimates based on the W-W analysis for the most recent time period appear to be overly NOx-sensitive compared with LADCO's best estimates. This analysis misses the transitional areas in many of the urban cores and underestimates the degree of VOC sensitivity in Chicago. This bias towards NOx sensitivity appears to be particularly large in the northern areas, especially in Chicago. On the other hand, the W-W analysis appears to overestimate the VOC sensitivity along the Cleveland lakeshore. It is unclear why the results of this analysis are biased towards NOx sensitivity in 2016-2020. This approach detected clear VOC sensitivity in earlier years and recorded strong shifts toward NOx sensitivity in the mid-2010s, which were more muted based on other analyses. The most likely explanation is that another underlying factor, such as meteorological factors that were not accounted for in this analysis, drove the observed W-W differences in ozone concentrations.[32]

The analysis of trends in O_3 concentrations over space and time suggested O_3 formation chemistry that generally agreed pretty well with LADCO's best estimates. However, this approach requires a lot of subjective analysis of trend lines and yields results that can be challenging to interpret. We recommend that this analysis be done in combination with other analyses rather than as a freestanding approach. When combined with other analyses, it appears that the trends analysis can provide useful information about the O_3 formation sensitivity in an area.

[32] The most important meteorological factors that were included in the W-W analysis had W-W differences (such as having higher temperatures on weekends, see figure A4.13-A4.18) that would push W-W ozone differences in the opposite direction than observed. These factors would tend to make ozone formation appear more VOC-sensitive.

The two HDDM modeling analyses agreed very well with most other analyses for most areas. The analysis by Koplitz et al. (2022) missed the transitional areas observed in St. Louis, Cincinnati, and Detroit. The analysis by Odman and Hu (2022) missed transitional areas in Detroit and along the Cleveland lakeshore, which their analysis classified as overly NOx-sensitive. Odman and Hu (2022) also suggested O_3 formation chemistry that wasn't NOx-sensitive enough in inland Cleveland and along the Wisconsin lakeshore. However, in most areas, the O_3-NOx-VOC chemistry determined from these approaches matched well with LADCO's best estimate.

The GAM analysis from Blanchard (2020) agreed fairly well with other approaches for Chicago and most of the Wisconsin lakeshore. However, this analysis was the only one to project VOC sensitivity for the Western Michigan monitors. It also estimated that several inland monitors around Lake Michigan (Schiller Park, IL; Kenosha Water Tower, WI; and Sheboygan Haven, WI) were VOC-sensitive, which also appears unlikely according to the other analysis methods that we considered. The issue in this case may be that the GAM was estimating the sensitivity to monitored CO rather than VOCs (because of the sparsity of VOC measurements). CO primarily derives from mobile sources, whereas VOCs have a variety of sources. These differences may account for the bias in the results from this approach.

Two additional analyses are not listed in Table 5.1: the back trajectory/chemical box model approach from Acdan et al. (2020) and the WRF-Chem modeling from Abdi-Oskouei et al. (in revision). Acdan et al. (2020) found O_3-NOx-VOC chemistry in the Chicago area that closely matched LADCO's best estimates. However, given the specialized tools required for this approach, it is unlikely to be used for routine analyses. The modeling-based analysis in Abdi-Oskouei et al. (in revision) of afternoon O_3 chemistry agreed closely with LADCO's best estimate classifications.

Our analysis highlights the need for a new study to evaluate the most appropriate ratio thresholds for model-based HCHO/NO_2 ratios. The spatial patterns in O_3 formation sensitivity

look very similar to those found from other analyses, however, all of the sensitivity classifications appear to be shifted towards VOC sensitivity, suggesting that the ratio thresholds from Duncan et al. (2010) are too high.

Considering all of the evidence together, the best approaches to determine the O_3 formation sensitivity appear to be: ground-based HCHO/NO_2 ratios using ratio thresholds from Blanchard (2020), TROPOMI satellite HCHO/NO_2 ratios using thresholds from Jin et al. (2020), HDDM modeling, and the analysis of O_3 trends over space and time. While each of these approaches lends important insights into the current O_3 formation conditions in the Great Lakes region, they all have their limitations. The TROPOMI analysis overpredicts VOC sensitivity in some areas and underpredicts it in others. Ground-based HCHO/NO_2 ratios are only available at a small number of monitoring locations, located almost exclusively in city centers, limiting the usefulness of this approach. HDDM modeling is not widely accessible since it requires a high performance computing system as well as extensive expertise and knowledge to implement and interpret. In contrast, the O_3 trends analysis only requires examination of trends in O_3 concentrations; however, this analysis requires subjective judgements and interpretations of complex trends over space and time. Overall, we suggest the use of at least two different approaches in tandem to better understand O_3 formation sensitivities.

6. Conclusions

This suite of analyses presented in this report clearly indicate that O_3 formation in most of the LADCO region is currently NOx-sensitive. Ozone concentrations in these NOx-sensitive areas will decrease most in response to reductions in NOx emissions. However, VOC emissions reductions will also have an impact throughout the region, particularly when combined with reductions in NOx emissions.

Most of the urban centers have transitional chemistry, and the only city that is clearly VOC-sensitive is Chicago. Chicago has a large area of VOC-sensitive O_3 chemistry, extending outward onshore to roughly 60 km from the city center. Ozone formation in this area appears to be shifting to transitional chemistry. Ozone concentrations in central Chicago will therefore respond to reductions in both NOx and VOC emissions. NOx emissions reductions in central Chicago will likely increase urbanO_3 concentrations in the short term. In the long term, NOx emissions reductions will shift the O_3 formation chemistry towards NOx-sensitive, which will allow the steady reductions in O_3 with additional NOx emissions reductions as seen in other parts of the LADCO region. In addition, such NOx emissions reductions will contribute to immediate reductions in O_3 concentrations in outlying parts of the Chicago region, which have traditionally had the highest O_3 concentrations in that area. These areas surrounding the central part of Chicago are likely on the NOx-sensitive side of transitional chemistry. If the Chicago area were to decrease VOC emissions at the same time as decreasing NOx emissions, it should be possible to avoid any future increases in local O_3 concentrations. Overall, the fastest route for states in the LADCO region to reduce their O_3 concentrations would be to reduce both NOx and VOC emissions in tandem, with NOx emissions reductions having the greatest impact in most of the region, particularly in the long term.

Ozone formation in all parts of the LADCO region has become less VOC-sensitive and more NOx-sensitive over the last 30 years. The central parts of most urban areas were VOC-sensitive in the early 1990s and shifted to transitional chemistry over the intervening 30 years. Ozone

formation in the southern cities of Louisville and Cincinnati began as transitional, not VOC-sensitive. The urban cores of these cities still appear to be transitional, although the extents of the transitional areas have shrunk as the surrounding NOx-sensitive areas have expanded. While Chicago has continued as VOC-sensitive, O_3 formation in this city has also shifted towards transitional and NOx-sensitive.

Ozone concentrations around the region have been decreasing and are expected to continue to decrease, with the exception of the Chicago area. Ozone concentrations in the central Chicago area, extending out to around 60 km from the city center, have been increasing over the last decade as O_3 formation chemistry shifted from strongly VOC-sensitive towards transitional chemistry. LADCO anticipates that O_3 concentrations in this area will peak and then decline as the O_3 formation chemistry becomes transitional and then NOx-sensitive in response to ongoing reductions in NOx emissions.

Considering all of the analyses, the best approaches to determine the O_3 formation chemistry appear to be: ground-based HCHO/NO_2 ratios using ratio thresholds from Blanchard (2020), TROPOMI satellite HCHO/NO_2 ratios using thresholds from Jin et al. (2020), HDDM modeling, and the analysis of O_3 trends over space and time. While each of these approaches were generally consistent in characterizing O_3 chemistry, they all have their limitations. The TROPOMI analysis overpredicts VOC sensitivity in some areas and underpredicts it in others. Ground-based HCHO/NO_2 ratios are only available at a small number of monitoring locations, located almost exclusively in city centers, limiting the usefulness of this approach. HDDM modeling is not widely accessible since it requires a high performance computing system as well as extensive expertise and knowledge. In contrast, the O_3 trends analysis only requires examination of trends in O_3 concentrations; however, this analysis requires subjective judgements and interpretations of complex trends over space and time. Overall, we suggest the use of at least two different approaches in tandem to better understand ozone formation sensitivities.

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