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Knocking Down NOx: Examining the Effects of Transportation Electrification on Urban Ozone Production in the South Coast Air Basin

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Abstract

With last year's commitment to all in-state sales of new passenger cars and trucks being zero-emission by 2035 (California Executive Order N-79-20), California is leading the charge for transportation electrification in the United States. Despite being at the forefront of climate change management and mitigation, California has some of the worst air quality in the nation. While primarily motivated by a desire to reduce carbon dioxide emissions and reliance on fossil fuels, transportation electrification will also have a significant impact on local air quality. The goal of this study is to quantify and qualify this impact in the context of urban ozone production. From robust studies of the weekend ozone effect, we know that reductions in vehicle emissions on weekend days can actually increase urban ozone concentrations. By examining data from eight ground monitoring stations in California's South Coast Air Basin (SoCAB) over a period of 40 years, we show that this region is a volatile organic compound (VOC)-limited system in which the weekend ozone effect is a clear trend. Additionally, these data reveal that despite a significant decline in average annual nitrogen oxides (NOx) emissions, mean ozone levels have changed very little. With this in mind, the question looking forward becomes: how will local atmospheric chemistry and air quality evolve as transportation electrification accelerates? To investigate this question, VOC-NOx ratios are modeled for varying rates of light and heavy-duty vehicle electrification in order to gauge how urban ozone production will be affected. While it is clear that vehicle electrification will ultimately improve air quality and help mitigate climate change, this study provides a unique perspective into the less understood transient impacts of electrification.

Keywords

air quality, ozone, weekend ozone effect, transportation electrification

Introduction

While ozone is naturally present in extreme concentrations in the stratosphere (maximum around 8 ppm), the presence of enhanced ozone concentrations in the lower troposphere is both unnatural and unhealthy for living organisms [7]. Tropospheric ozone (O_3) is a human health hazard as well as a danger to plant and animal life. Despite its close resemblance to oxygen (O2), a sustainer of nearly all living organisms, ozone is a powerful oxidant that damages respiratory tissue when inhaled [1]. Breathing in enhanced concentrations of ozone burns one's lungs and airways, causing difficulty breathing and shortness of breath [4]. Moreover, the long term effects of this exposure are "linked to aggravation of asthma" and even "deaths from respiratory causes" [4]. With the natural surface background concentration of ozone sitting around 10 ppb, the Environmental Protection Agency (EPA) defines unhealthy exposure as 8 hours, or longer, of exposure to concentrations equal to or greater than 70 ppb O_3 [6].

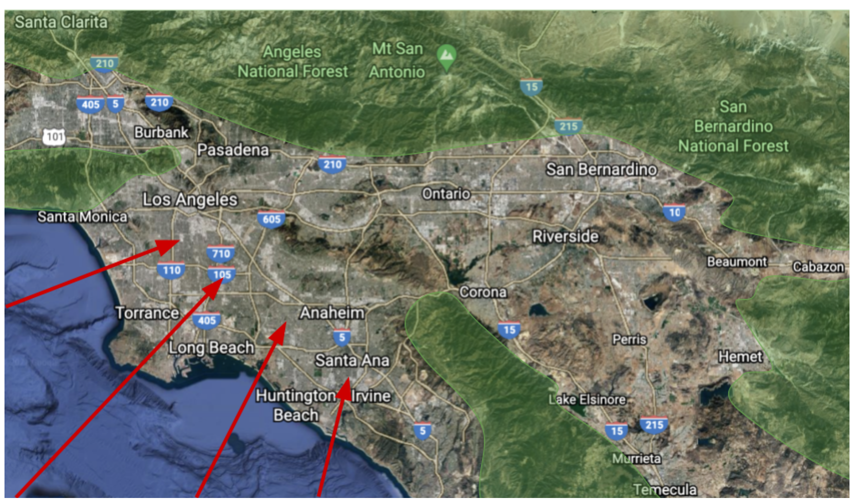


Figure 1: SoCAB Map [Google Earth, annotated] (sea breeze red arrows, mountains in green).

The sheer number of emission sources in major cities (vehicles, residences, commercial buildings, power plants, refineries, trees, plants, bodies of water, etc.) make them some of the most interesting, dynamic, and potentially hazardous photochemical environments. In cities like Los Angeles, this mixture of gases gets trapped by the meteorological and geographic features of the region. The South Coast Air Basin (SoCAB), in which Los Angeles resides, is bounded by large mountains to the north and east and affected by a strong and persistent sea breeze from the south and west. The result of this is that pollution emitted within the basin is blown inland and trapped against the mountains. When these gases are then exposed to the piercing southern California sun, photochemistry ensues. All together, these factors make the SoCAB one of the worst EPA ozone nonattainment areas in the United States [8].

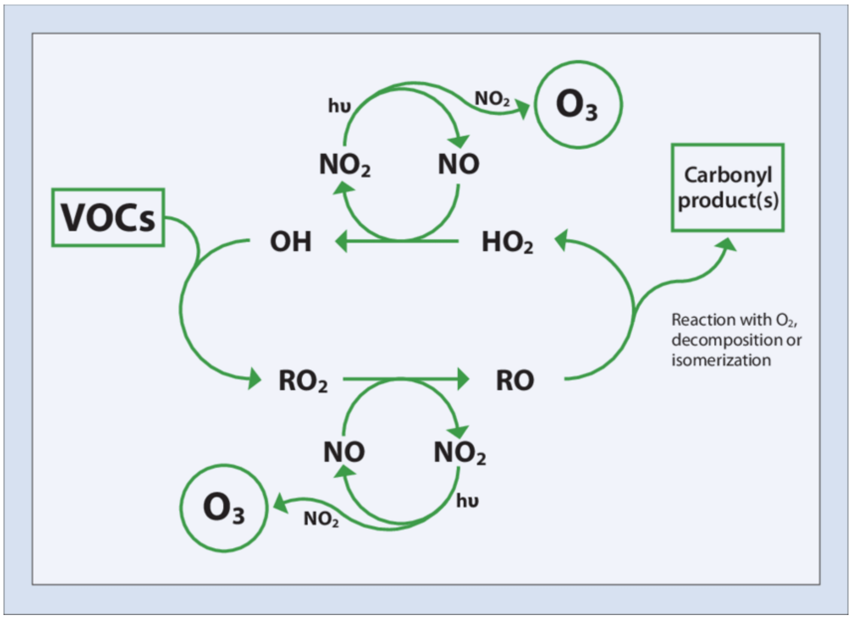


Figure 2: Ozone producing reaction schematic [5]; VOCs, NO_x, and sunlight ($h\nu$) are inputs, O_3 and carbonyl products are outputs. See Appendix for graph of O_3, NO_x, and VOC cycling.

Ozone enhancements in the troposphere, particularly those in nonattainment with EPA ozone standards, most commonly occur in urban areas as a result of photochemical reactions of nitrogen oxides (NO and NO_2, considered jointly as NO_x), primarily from vehicle emissions, and volatile organic compounds (VOCs), from a multitude of both natural and anthropogenic sources [4]. The combination of NO_x, VOCs, and sunlight leads to a cyclical reaction (Figure 2) that results in the production of ozone. Naturally, this reaction accelerates when the energy input is increased (i.e. when sunlight is more intense, especially daytime in the summer), but the efficiency of the reaction is also modulated by the ratio of VOCs to NO_x [3].

The effect of the VOC-NO_x ratio on the overall efficiency of the ozone-producing reaction is what gives rise to what is known as the weekend ozone effect. The weekend effect is a phenomenon in which, despite a general decrease in pollution on weekends (primarily a decline in vehicle emissions), ozone production increases [11]. This is the result of two main factors: "(1) decreased ozone loss by titration and (2) increased ozone production due to an increase in the ratio of VOCs to NO_x" [9]. Both of these can be attributed to the fact that the weekend decline in on-road vehicle traffic, particularly heavy-duty[1] vehicle traffic, results in lower concentrations of NO_x on weekends. This is evidenced by the fact that heavy-duty vehicles, which are responsible for significantly more NO_x emissions than light-duty vehicles on a per vehicle basis, exhibit a 40-80% decrease on weekends in the SoCAB [9].

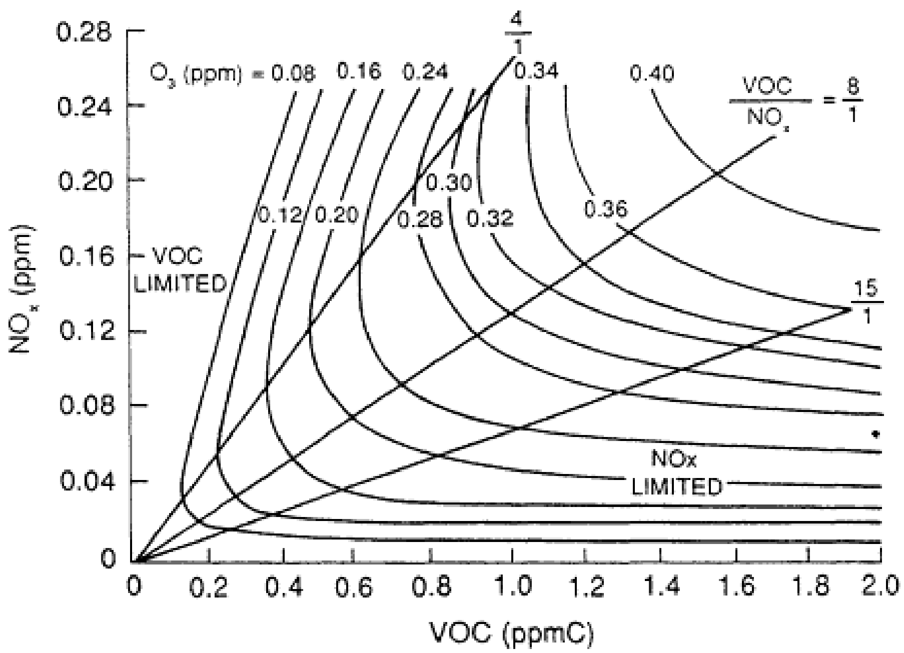


Figure 3: Ozone isopleth [3]; O_3 production is maximized with a VOC-NO_x ratio of 8:1, a system is considered VOC-limited when the ratio is less than 8:1 and considered NO_x-limited when the ratio is greater than 8:1.

The effect of this is best visualized using an ozone isopleth, which shows how ozone concentrations change with both NO_x and VOC emissions. Figure 3 reveals that ozone production is maximized at a VOC-NO_x ratio of 8:1, and

[1]In this paper, heavy-duty will be used interchangeably with diesel powered and light-duty with gasoline powered. While there are some deviations from this rule, it is a useful and valid delineation in the context of this study.

consequently, there are two distinct regimes on either side of this maximum: (1) a NO_x-limited regime (ratio $>$ 8:1) in which decreases in NO_x correlate most strongly with decreases in O_3 and (2) a VOC-limited regime (ratio $<$ 8:1) in which decreases in VOCs correlate most strongly with decreases in O_3. Using the isopleth, it is easy to see how, in the VOC-limited regime, decreases in NO_x actually cause *enhancements* in ozone because the reaction efficiency increases; the VOC-NO_x ratio moving closer to the ideal 8:1. With the Los Angeles Area's car culture (around 10 million vehicles in 2020) and VOC-limited atmosphere, the weekend ozone effect continues to be a clear and present trend in the SoCAB [2].

Approach and Methods

The initial goal of this investigation was to assess the presence, periodicity, and effects of the weekend ozone effect in the SoCAB. Using a webscraping algorithm, data was pulled from the South Coast Air Quality Management District (SCAQMD) and the EPA and subsequently analyzed to develop a stronger understanding of the historical ozone trends in the basin. By plotting the data over various timescales (daily, weekly, monthly, yearly) and in comparison to other pollutants and trace gases, primarily NOx and VOCs, the dynamics of the SoCAB's weekend ozone effect were discerned. The results (see Appendix) show that:

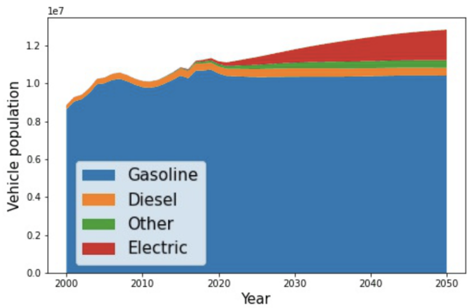
1. the SoCAB's weekend ozone effect is driven by an increase in the VOC-NO_x ratio which increases the efficiency of the ozone producing reaction;

2. this increase in the VOC-NO_x ratio, or, equivalently, this decrease in mean NO_x concentrations, is directly attributable to the weekend decline in heavy-duty vehicle usage;

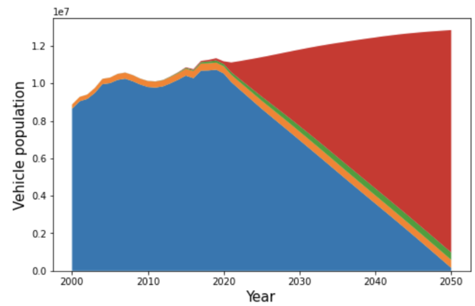
3. annual ozone averages since 1980 show the presence of a distinct and substantial weekend effect in ozone;

4. despite targeted vehicle emissions regulations, which have caused mean NO_x levels to decreases, there has been comparatively little change in mean O_3 concentrations.

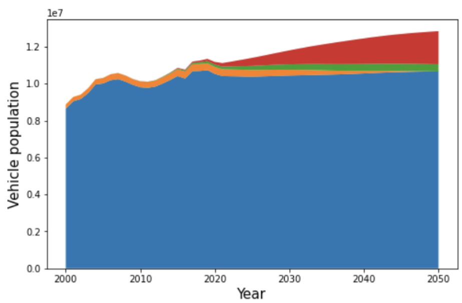
With a clear understanding of historical air quality trends in the SoCAB, the question moving forward becomes: how will air quality in the SoCAB change as vehicle emissions change? Specifically, how will transportation electrification impact urban ozone production?



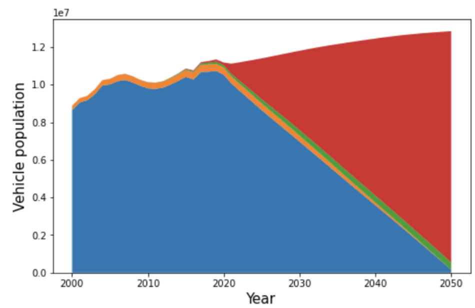
(a) Current projected electrification



(b) Full gasoline electrification



(c) Full diesel electrification



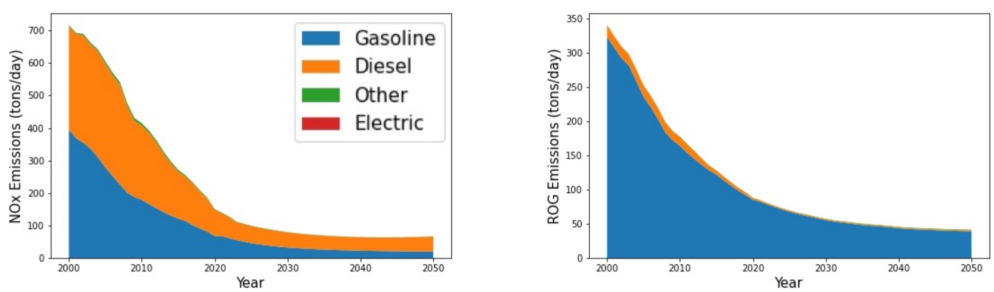
(d) Full fleet electrification

Figure 4: SoCAB vehicle populations over time for potential electrification pathways (gasoline vehicles in blue, diesel vehicles in orange, hybrid vehicles in green, electric vehicles in red).

To answer this question, the aforementioned historical air quality data are combined with vehicle emissions projections from the California Air Resources Board (CARB) in order to construct a model for how average ozone concentrations will evolve over the next 30 years. Furthermore, the model is extended to allow for additional (hypothetical) vehicle electrification pathways to be considered, each with intentionally different emissions profiles. The first path considered is one in which the goals set forth by California Executive Order N-79-20 are met by 2035, but not exceeded: the current projected electrification trajectory. The others are variations of this, with intentional modulations of the emissions profiles. One alternate is full gasoline electrification, in which all gasoline vehicles are electrified by 2050. Another is full diesel electrification, in which all diesel vehicles are electrified by 2050. The last is full fleet electrification, in which all vehicles are electrified by 2050. Each of these vary in their feasibility (each increasingly more technically prohibitive than the last), but all of them are important case studies of the effect transportation electrification has on urban ozone production in cities like Los Angeles. Thus, the expectation is that the different emissions profiles of each of these potential electrification pathways will produce distinguishable and uniquely interesting ozone projections when modeled.

Results and Discussion

The preliminary results of this investigation show that electrification, across the board, will improve air quality in the SoCAB. This is most obvious in the reductions exhibited in primary pollutants like NO_x and VOCs. Because on-road vehicle transportation is responsible for 25% of total organic gases and 55% of all NO_x emitted in the SoCAB, this result is unsurprising, yet also reassuring for the validity of the model [9]. The more interesting and pertinent data are the ozone projections and the ratio of VOCs to NO_x. Because O_3 is a secondary pollutant, its prevalence in the atmosphere over time is more difficult to predict. And because the VOC-NO_x ratio is modulated in distinct ways by each electrification pathway, these data give insight into how ozone pollution in the SOCAB will change over time.



(a) NO_x Emissions (b) VOC Emissions

Figure 5: Change in NO_x and VOC emissions from 2000-2050 under current projected electrification pathway (gasoline vehicle emissions in blue, diesel vehicle emissions in orange).

Using a model developed at the University of Georgia, these results can be more effectively and accurately interpreted. The model uses an empirically derived formula to relate NO_x and VOC emissions to projected ozone design values[2] (ODV) concentrations [10].

[2] A design value is a statistic that describes the air quality status of a given location relative to the level of the National Ambient Air Quality Standards (NAAQS) [8]

By passing the results of this investigation through this equation, it becomes clear that while the general trend of each electrification pathway is towards reduced ozone concentrations, the end behavior of each is consequentially divergent (see Figure 6).

$$\begin{aligned} ODV\left(E_{NO_x}, E_{VOC}\right) &= 1.03 + 0.13E_{NO_x} + 0.11E_{VOC} + 3.5 \times 10^{-5} E_{NO_x} E_{VOC} \\ &\quad -1 \times 10^{-4} E_{NO_x}^2 - 1 \times 10^{-5} E_{VOC}^2 \end{aligned} \tag{1}$$

First, it is unsurprising that full fleet electrification results in the greatest ozone reductions (roughly 12% from 2020-2050) because this pathway removes all vehicle pollution from the SOCAB's atmospheric chemistry. When comparing the other pathways, gasoline vehicle electrification and diesel vehicle electrification are the most interesting and informative. While the model suggests that the two pathways lead to relatively similar ozone concentrations (90.9 ppb and 91.3 ppb respectively), it also shows us that, despite this, their VOC-NO_x ratios are noticeably different. This difference is attributable to the types of gases that each of these pathways minimize. Gasoline vehicle electrification targets VOCs whereas diesel vehicle electrification targets NO_x (see Figure 5). In the long-term of this electrification model, this difference manifests as a more VOC-limited system under gasoline vehicle electrification and a more NO_x-limited system under diesel vehicle electrification. This implies that, while nominal compared to pre-2020 conditions, the weekend ozone effect will be stronger in the long-term under gasoline vehicle electrification than under diesel vehicle electrification.

Lastly, it is obvious that the current projected electrification pathway is likely to produce the least substantial air quality improvements. That said, it remains the most economically viable option of the four pathways considered and the only likely option given the current political climate around electrification and renewable energy in the United States.

Electrification Pathway	**Percent Change**	**Final ODV (ppb)**
Current Projected Electrification	-6.7%	94.0
Gasoline Vehicle Electrification	-9.8%	90.9
Diesel Vehicle Electrification	-9.4%	91.3
Full Fleet Electrification	-12.5%	88.2

Table 1: Percent change (2020-2050) and final ODV (2050) for each pathway.

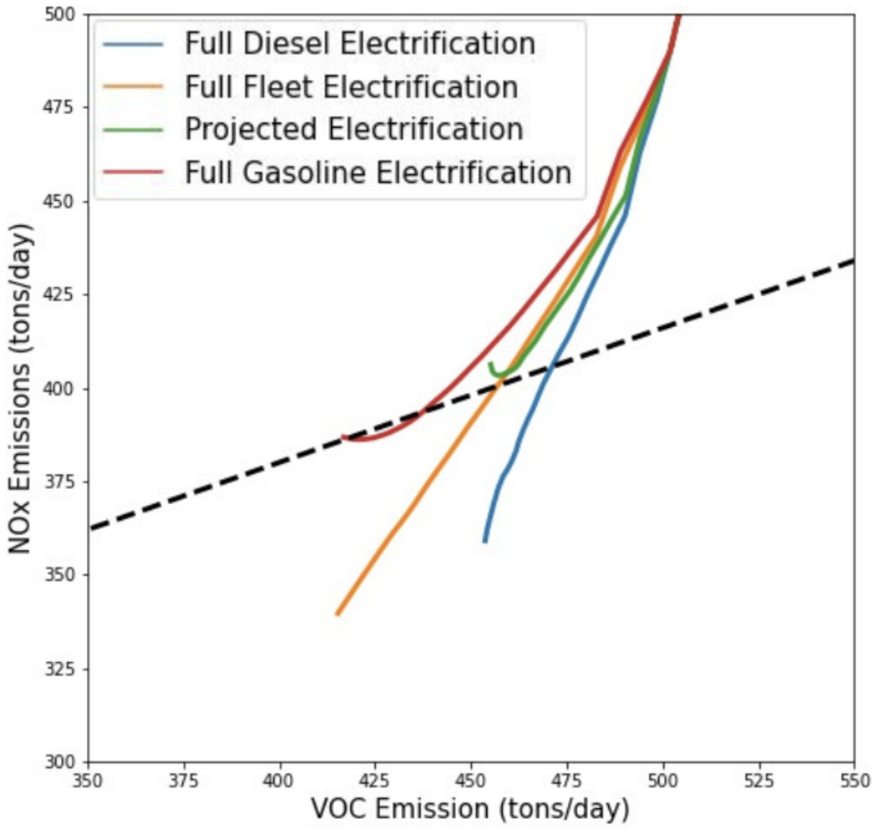


Figure 6: Ozone deign value trends from 2020-2050 for each electrification pathway (current projected electrification in green, gasoline electrification in red, diesel electrification in blue, full fleet electrification in orange).

Summary

In summary, the main takeaway is that strategic electrification decisions have tangible local air quality impacts. In the SOCAB, the geospatial context of this study, transportation electrification has the potential to be an important tool for improving local air quality as well as reducing climate impact.[3] By dissecting the air quality impacts of multiple potential electrification pathways,

[3]It would be a mistake not to note the fact that transportation electrification today simply shifts the air quality burden elsewhere and does not completely resolve the issue. While electrification would improve air quality in cities, it would, in turn, increase the burden on those living near power plants that would have to supply this increased electrical demand.

the advantages and disadvantages of each became clear.

While these data are specific to the SOCAB, the results are more generally applicable. The Los Angeles area is a model for many major cities (particularly cities with VOC-limited atmospheres) throughout the world. It serves as a case study for how transportation electrification affects local air quality and how, especially in cities with more extreme ozone pollution today, the choice of electrification pathway can have a substantial impact on ozone concentrations over time. Thus, a fertile and important expansion of this work would be to gather in situ air quality data in cities with more extreme ozone pollution, project vehicle emissions profiles under various potential electrification pathways, and then use this model to make predictions about the evolution of ozone concentrations (and primary pollutant concentrations) in these cities. Armed with this information, governments would be more able to make strategic decisions at this crucial intersection of air quality and climate change.

Acknowledgements

The vast majority of the data used in this investigation was sourced from the Environmental Protection Agency, the California Air Resources Board, and the South Coast Air Quality Management District. The accessibility and usability of this data as well as the helpfulness of the individuals working at these organizations with whom I interacted was vital to the success of the project.

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References

[1] Air Quality: Effects of Air Pollution, University Corporation for Atmospheric Research: Center for Science Education. https://scied.ucar.edu/learning-zone/air-quality/effects-air-pollution

[2] Air Quality: Historical Data, South Coast Air Quality Management District. https://xappp.aqmd.gov/aqdetail/AirQuality/HistoricalData

[3] Dodge, M. C. (1977). Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationships. *Proceedings of the International Conference on Photochemical Oxidant Pollution and its Control*, 2, 881-889. [print only]

[4] Ground-Level Ozone Pollution (updated 2021). Environmental Protection Agency. https://www.epa.gov/ground-level-ozone-pollution

[5] Jenkin, M. E. & Hayman G. D. (1999). Photochemical ozone creation potentials for oxygenated volatile organic compounds: sensitivity to variations in kinetic and mechanistic parameters. *Atmospheric Environment*, 33 (8), 1275-1293. https://doi.org/10.1016/S1352-2310(98)00261-1

[6] National Ambient Air Quality Standards (2015). Environmental Protection Agency. https://www.federalregister.gov/documents/2015/10/26/2015-26594/national-ambient-air-quality-standards-for-ozone

[7] Newman, P. A. & Nash, E. R. (2018). Ozone Watch: What is Ozone?, National Aeronautics and Space Administration. https://ozonewatch.gsfc.nasa.gov/facts/SH.html#EPA_2015

[8] Nonattainment Areas for Criteria Pollutants (Green Book) (updated 2021). Environmental Protection Agency. https://www.epa.gov/green-book

[9] Pollack, I. B. et al. (2012). Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin. *Journal of Geophysical Research*, 117 (D21), D00V05. https://doi.org/10.1029/2011JD016772

[10] Qian, Y. et al. (2019). Empirical Development of Ozone Isopleths: Applications to Los Angeles. *Environmental Science & Technology Letters*, 6 (5), 294-9. https://doi.org/10.1021/acs.estlett.9b00160

[11] Wolff, G. T. et al. (2013). The vanishing ozone weekday/weekend effect. *Journal of the Air & Waste Management Association*, 63 (3), 292-9. `https://doi.org/10.1080/10962247.2012.749312`

Appendix

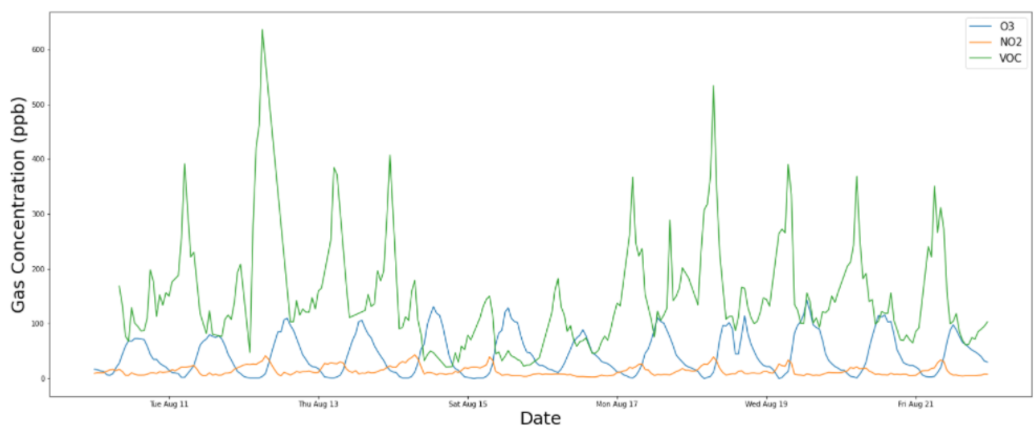

Figure 7: Diurnal oscillations in O_3, NO_x, and VOC concentrations over the course of two weeks in August 2020, relative ozone maxima on weekend days.

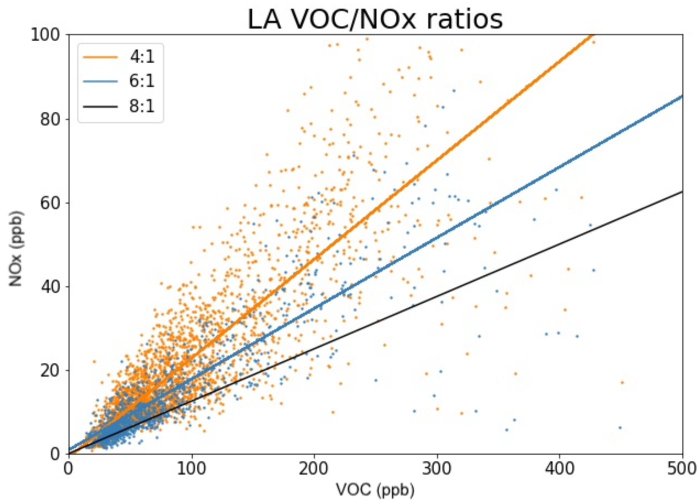

Figure 8: On weekends the VOC-NO_x ratio shifts from around 4:1 (weekdays, orange) to roughly 6:1 (weekends, blue). The most efficient ratio for producing ozone is 8:1 so it is clear that the enhanced ozone on weekends has a causal relationship with this increased ratio [3].

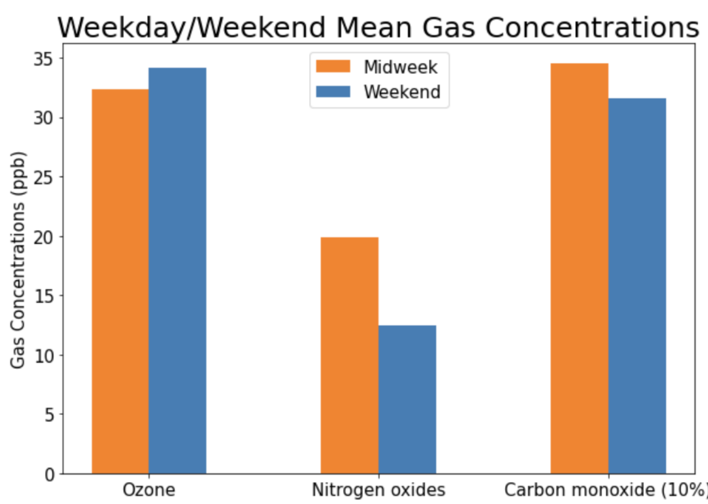

Figure 9: NO_x, an indicator of diesel vehicle usage, decreases by about 40% on weekends whereas CO, an indicator of gasoline vehicle usage, only decreases by about 5%. This suggests that the weekend effect in O_3 is driven primarily by changes in diesel vehicle traffic.

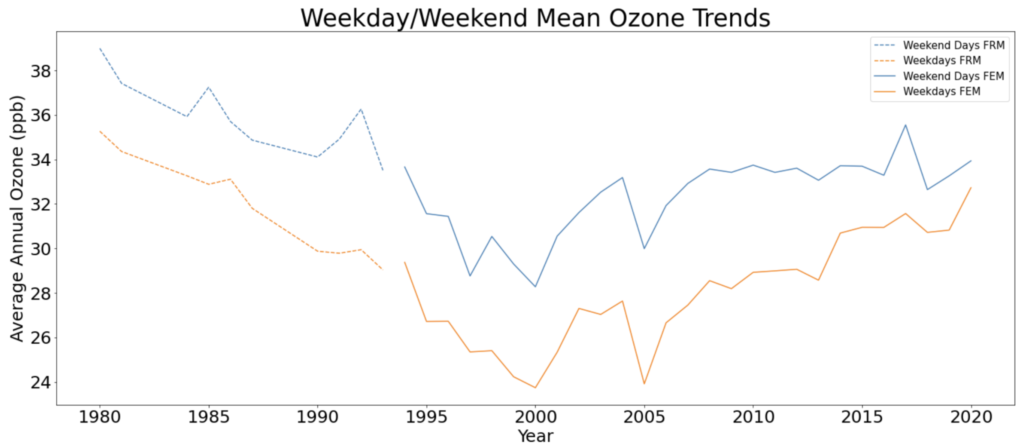

Figure 10: Long-term O_3 trends in SoCAB; mean O_3 concentrations have only varied by about ± 7 ppb over the past 40 years, with the past 20 years showing a general increase. It is also clear from this figure that throughout the past 40 years, mean O_3 concentrations have been enhanced on weekend days in comparison to weekdays.

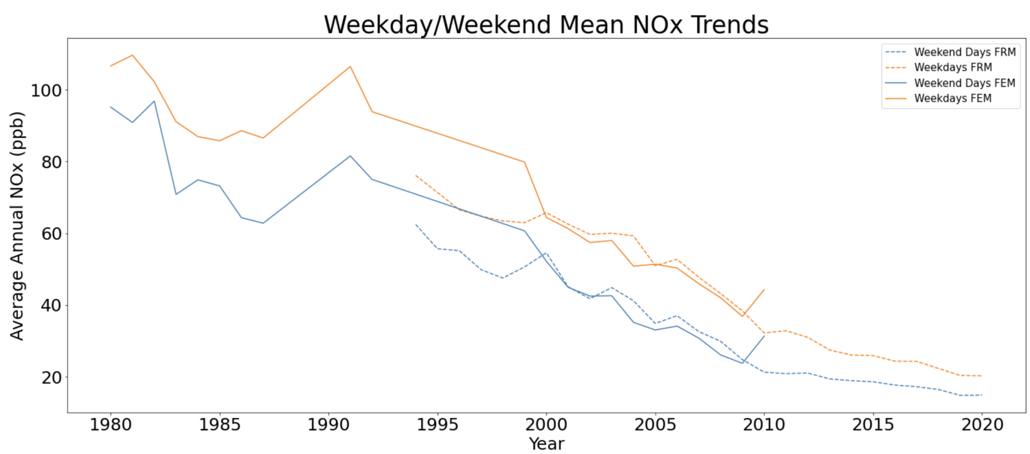

Figure 11: Long-term NO_x trends in SoCAB; mean NO_x concentrations, in contrast to O_3 levels, have dropped dramatically over the past 40 years by about 80 ppb. It is also clear from this figure that throughout the past 40 years, mean NO_x concentrations have been reduced on weekend days in comparison to weekdays.