Next Tier HDOH Low-NO$_x$ Regulation: The Need And Opportunity For A Paradigm Shift

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Riverside, California
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Overview

1. What's the scope and nature of the relevant air quality issue?
   - ozone attainment is core issue
   - area-specific issues dominate (albeit covering densely populated areas)
   - SoCAB is the key nonattainment area
   - non-linear air quality relationships complicate the matter
   - targeted solutions will be necessary

Overview

2. What's the actual real-world impact of HDOH NO_x emissions?
    - near-zero standards already
    - aggregate in-use performance is robust
    - need for new in-use data to assess potential for further HDOH NO_x reductions
    - significant research efforts are underway

Overview

3. What’s the best path forward?
    - FTP-oriented development efforts?
    - focus on cold-start emissions? light-load emissions?
    - need to preserve feasibility of GHG targets
    - focus on real-world real-time emissions data
    - establish actual relevant in-use baseline emissions from which to assess potential targeted in-use emissions improvements
    - consider role for NO_x sensors and telematics
    - vehicle/engines families as the new “lab” to generate aggregated in-use emissions data

Overview

4. What’s next?
    - develop data-driven real-world in-use NO_x-emissions baseline for “non-credit” HDOH engines/vehicles
    - develop data-driven real-world in-use targeted NO_x reductions
    - develop appropriate in-use metric for compliance
    - develop targeted in-use standards assessed against aggregated in-use emissions data
    - streamline outmoded regulatory requirements and procedures
    - implement a new in-use-focused regulatory paradigm

1. Scope and Nature of the Issue

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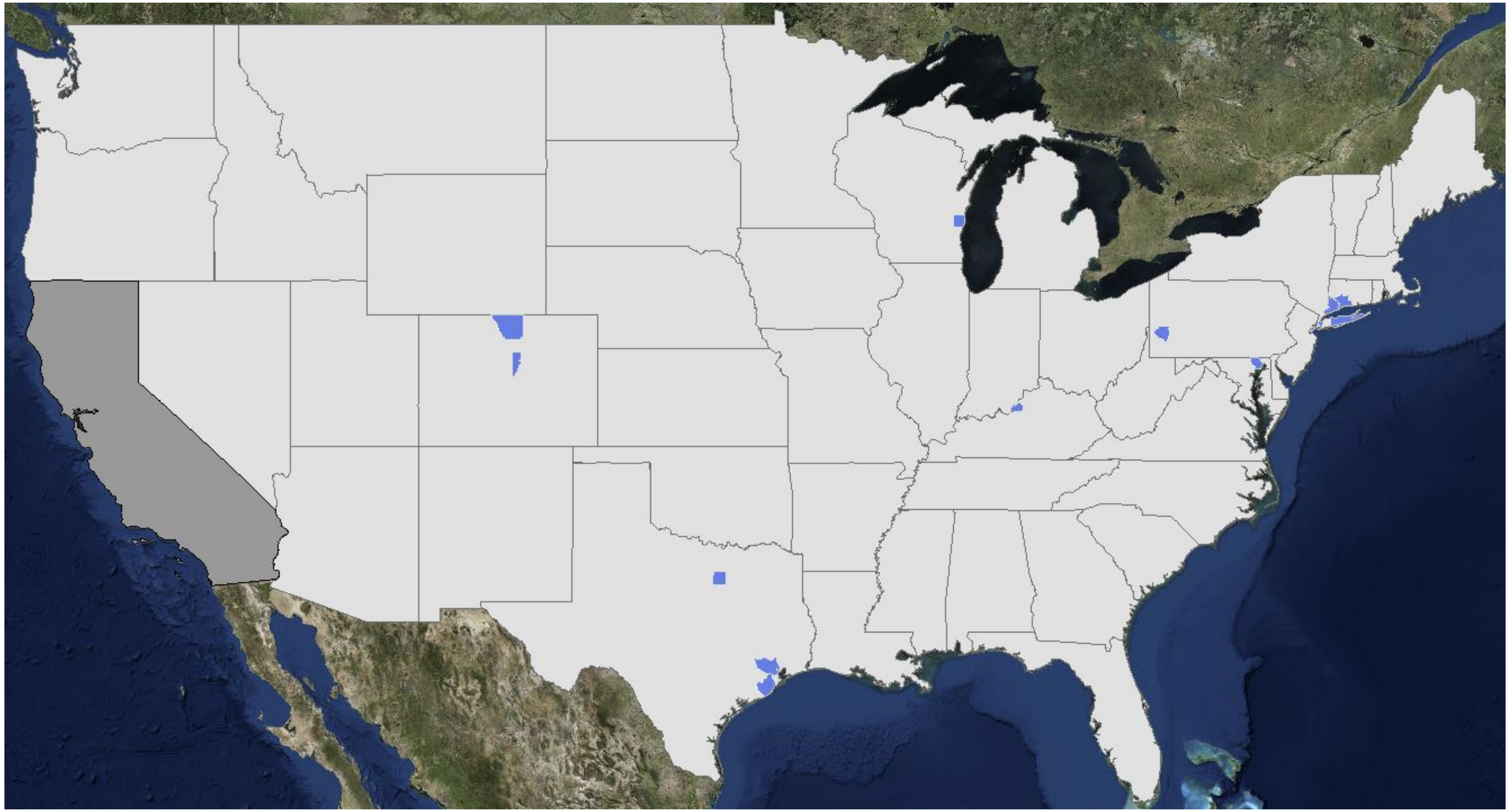
    - SoCAB is the key nonattainment area
    - non-linear air quality relationships complicate the matter
    - targeted solutions will be necessary

1. Scope and Nature of the Issue

14 Non-CA Counties Projected >70ppb in 2025* (EPA Data)

*Nonattainment Areas Could Be Smaller



- Is this truly a nationwide attainment issue?

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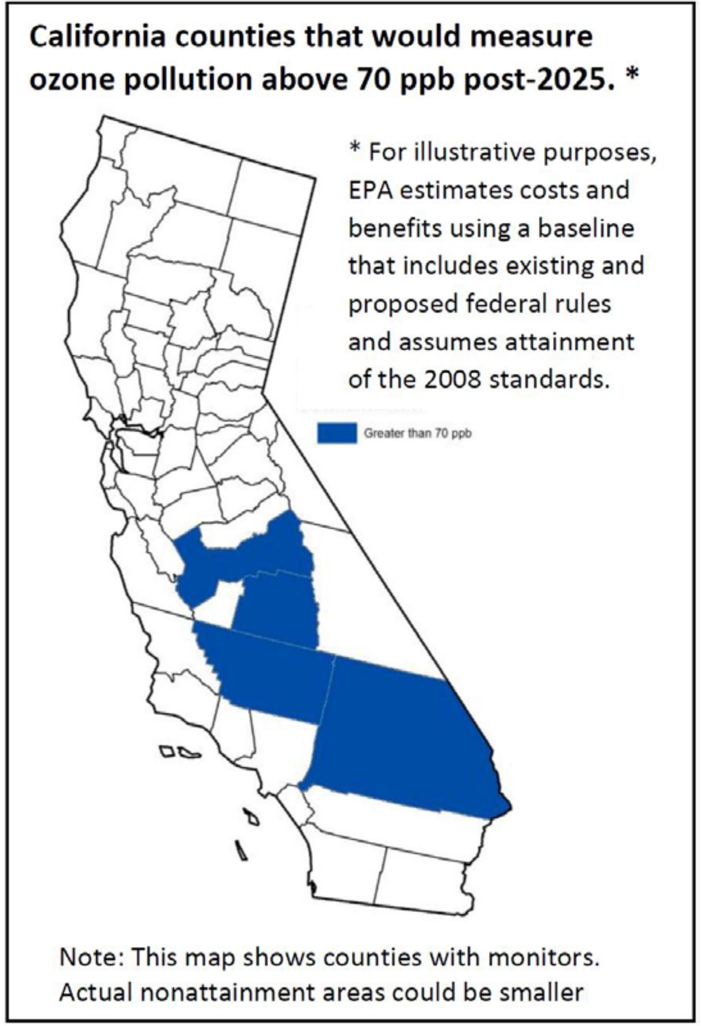
1. Scope and Nature of the Issue

CA Counties Projected >70ppb in 2025 (EPA Data)



California counties that would measure ozone pollution above 70 ppb post-2025. *

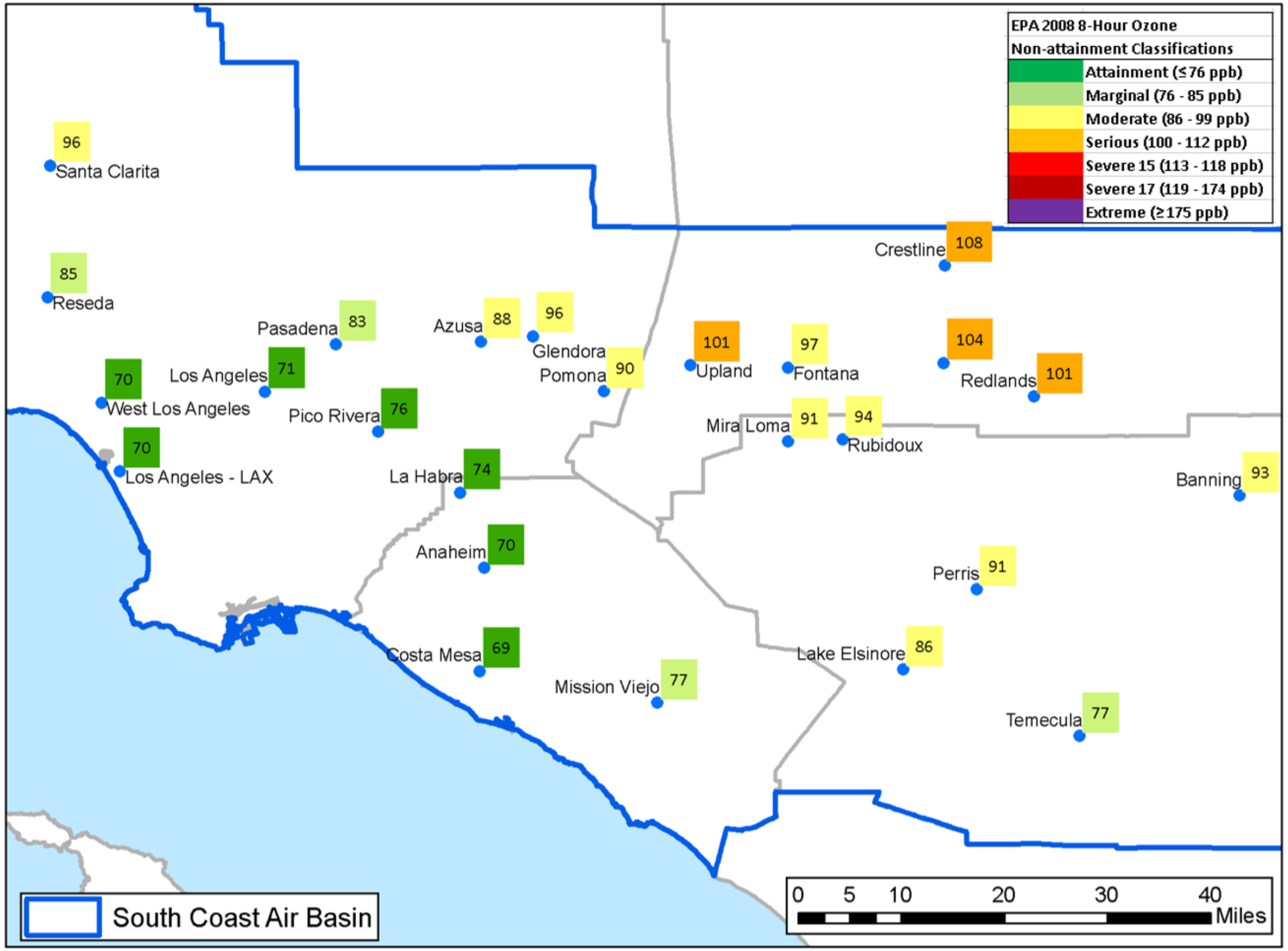
* For illustrative purposes, EPA estimates costs and benefits using a baseline that includes existing and proposed federal rules and assumes attainment of the 2008 standards.

Note: This map shows counties with monitors. Actual nonattainment areas could be smaller

- Or is this an area or county-specific attainment issue (albeit covering densely populated areas)?

1. Scope and Nature of the Issue

Measured 8-hour Ozone Design Values in 2016 (AQMP Data)



- **Much of the SoCAB appears on the path to ozone attainment**
- But highest individual Design Value (DV) out of all air monitoring stations sets DV for entire SoCAB
- The monitoring site at Crestline has set the DV for the entire air basin for over 20 years
- **Attainment is a county-specific (and even seasonal) issue**

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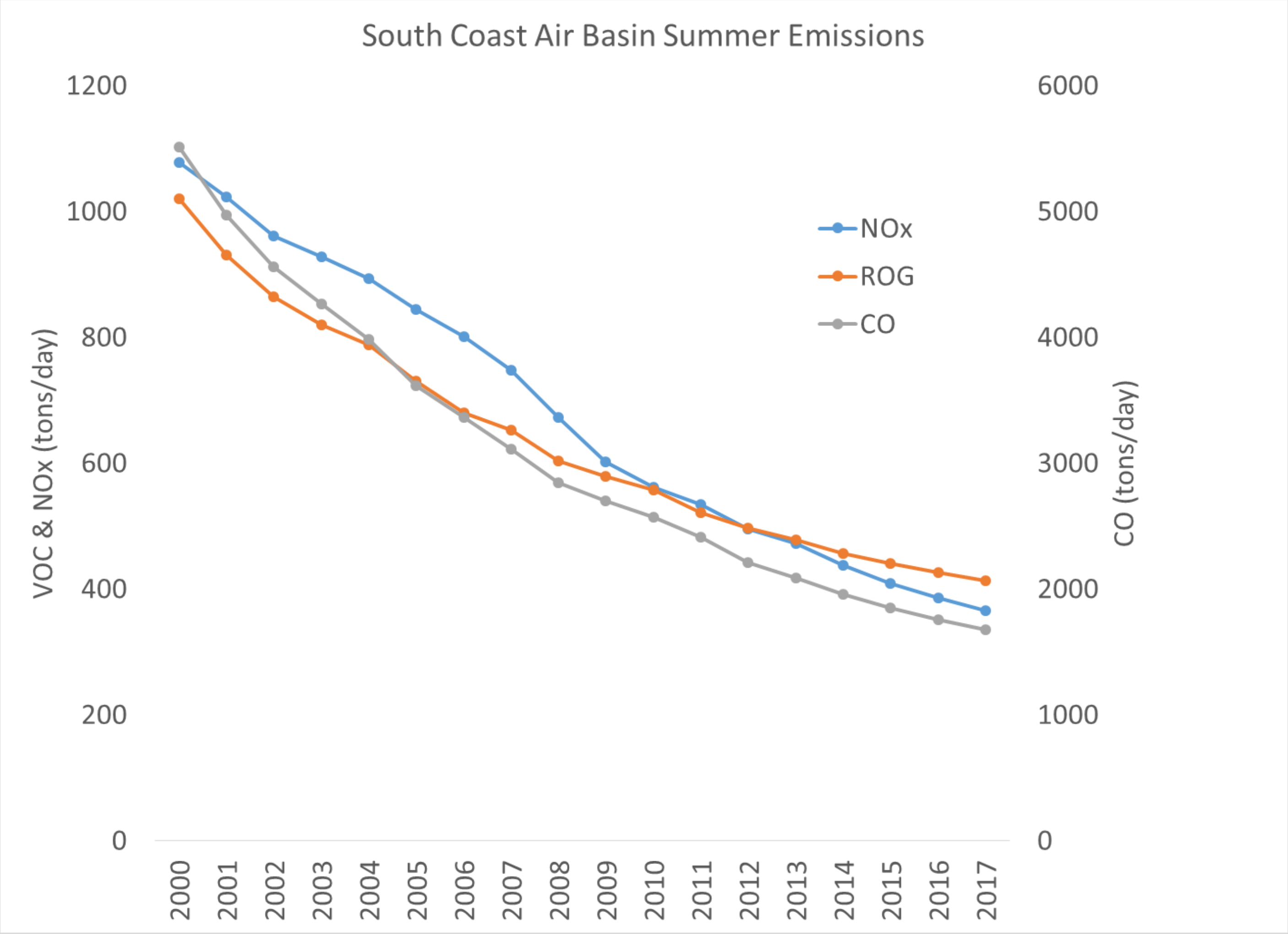
1. Scope and Nature of the Issue

CARB South Coast Air Basin Anthropogenic Emissions (2012 Base Year)



- Progress toward attainment has resulted from significant reductions in precursor emissions (excludes biogenics and wildfires)
- **Consistent significant NO_x (blue line) reductions in SoCAB** since 2000 with increasing VOC/NOx ratios

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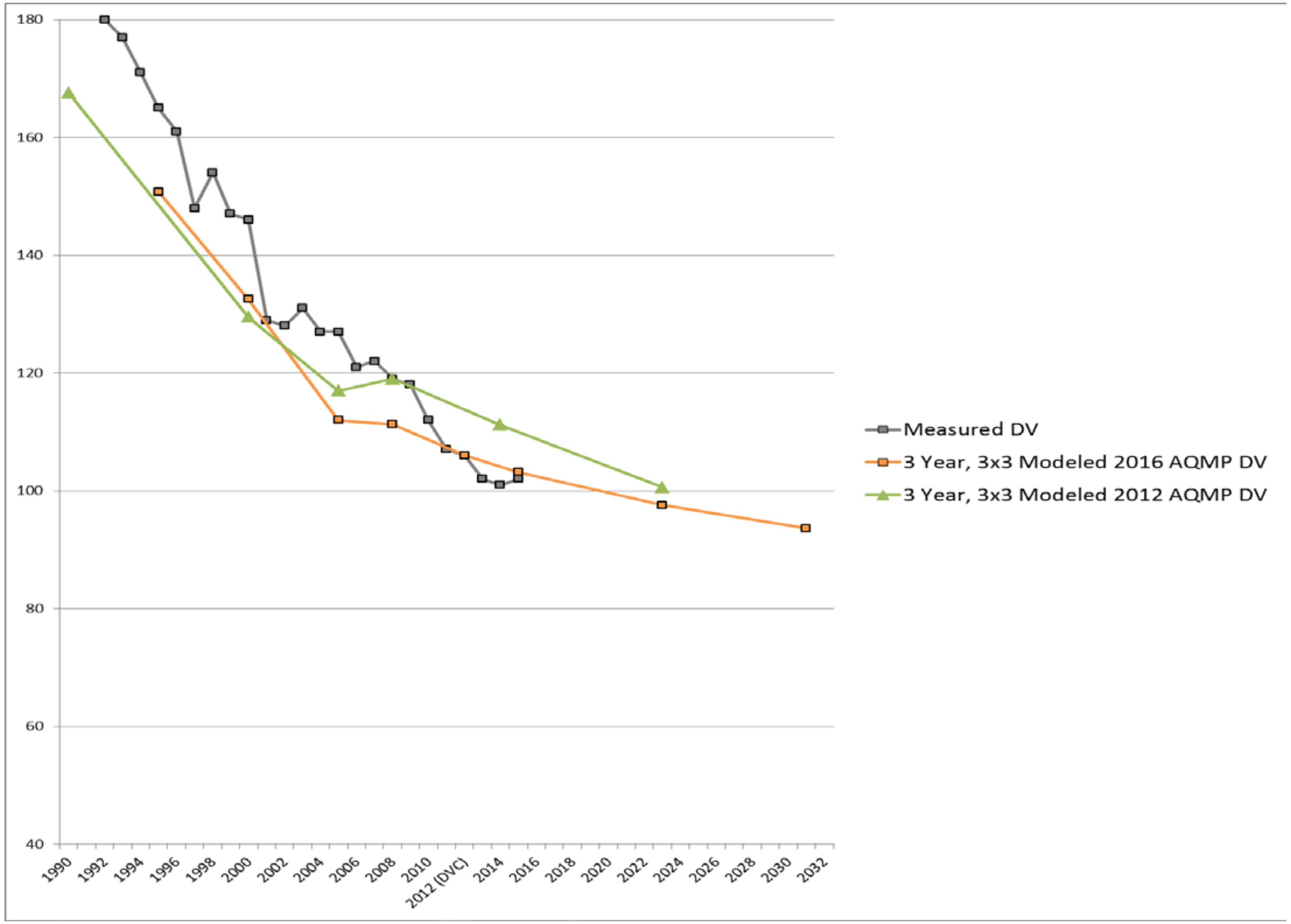
1. Scope and Nature of the Issue

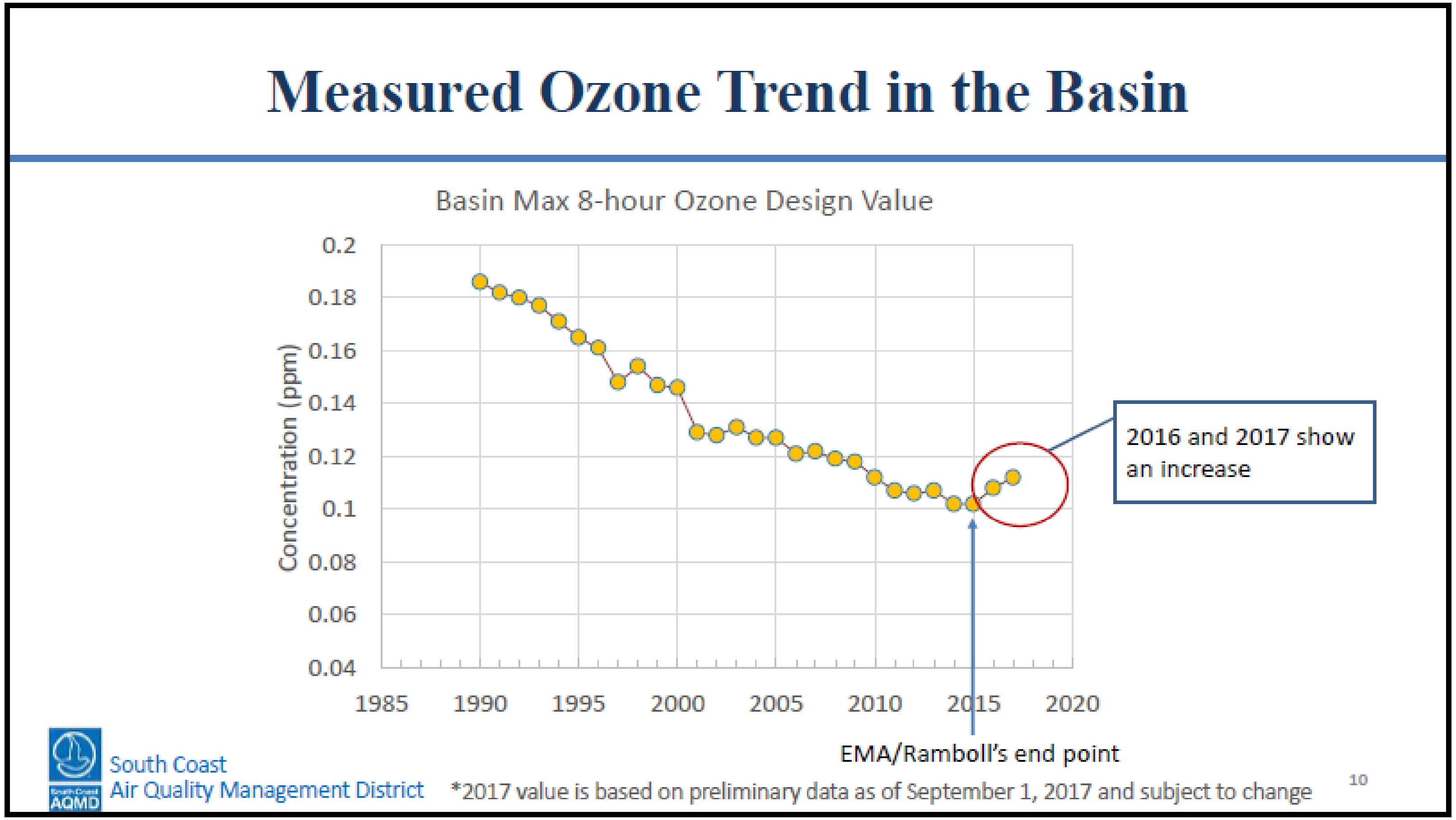
Projected Ozone Reductions Have Become Flatter (Crestline) (SCAQMD Data)



- **More recently, the rate of ozone reduction is flattening** and not matching rate of reduction of precursor emissions
- Ozone-reduction dynamics may be changing

1. Scope and Nature of the Issue

Recent Upticks in Ozone Levels (SCAQMD Data)



Measured Ozone Trend in the Basin

2016 and 2017 show an increase

EMA/Ramboll's end point

South Coast Air Quality Management District

*2017 value is based on preliminary data as of September 1, 2017 and subject to change

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- Even more recently, **ozone levels have moved in the opposite direction of precursor emissions**
- Uptick is not consistent with modeled projections
- Have we hit ozone-formation "ridgeline" where incremental NO_x reductions (and other factors) can increase ozone concentrations?

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1. Scope and Nature of the Issue

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TECHNICAL PAPER

Projected ozone trends and changes in the ozone-precursor relationship in the South Coast Air Basin in response to varying reductions of precursor emissions

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ABSTRACT

This study examined the effects of varying future reductions in emissions of oxides of nitrogen (NO_x) and volatile organic compounds (VOC) on the location and magnitude of peak ozone levels within California's South Coast Air Basin (SoCAB or Basin). As ozone formation is currently VOC-limited in the Basin, model simulations with 2030 baseline emissions (−61% for NO_x and −32% for VOC from 2008) predict 10–20% higher peak ozone levels (i.e., NO_x disbenefit) in the western and central SoCAB compared with the 2008 base simulation. With additional NO_x reductions of 50% beyond the 2030 baseline emissions (−81% from 2008), the predicted ozone levels are reduced by about 15% in the eastern SoCAB but remain comparable to 2008 levels in the western and central Basin. The Basin maximum ozone site shifts westward to more populated areas of the Basin and will result potentially in greater population-weighted exposure to ozone with even a relatively small shortfall in the required NO_x reductions unless accompanied by additional VOC reductions beyond 2030 baseline levels. Once committed to a NO_x-focused control strategy, NO_x reductions exceeding 90% from 2008 levels will be necessary to attain the ozone National Ambient Air Quality Standards (NAAQS). The findings from this study and other recent work that the current VOC emission estimates are underestimated by about 50% suggest that greater future VOC reductions will be necessary to reach the projected 2030 baseline emissions. Increasing the base year VOC emissions by a factor of 1.5 result in higher 2008 baseline ozone predictions, lower relative response factors, and about 20% lower projected design values. If correct, these findings have important implications for the total and optimum mix of VOC and NO_x emission reductions that will be required to attain the ozone NAAQS in the SoCAB.

Implications: Results of this study indicate that ozone levels in the western and central SoCAB would remain the same or increase with even a relatively small shortfall in the projected NO_x reductions under planned NO_x-focused controls. This possibility, therefore, warrants a rigorous analysis of the costs and effects of varying reductions of VOC and NO_x on the formation and combined health impacts of ozone and secondary particles. Given the nonlinearity of ozone formation, such analyses should include the implications of gradually increasing global background ozone concentrations and the Basin's topography and meteorology on the practical limits of alternative emission control strategies.

PAPER HISTORY
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Introduction

California's South Coast Air Basin (SoCAB or Basin) has historically experienced the most severe ground-level ozone (O_3) pollution in the United States. The Basin encompasses 10,743 square miles and is home to over 17.8 million people (2010 U.S. Census). Prior to the implementation of emission reduction measures in the early 1950s, hourly averaged ozone mixing ratios in the SoCAB approached 700 ppb and Stage III episodes (ozone exceeding 500 ppb) were relatively frequent events in the 1960s. Four decades of progressively more stringent controls of volatile organic compound (VOC) and oxide of nitrogen (NO_x) emissions have reduced the number of exceedances of the 2008 8 hr ozone National Ambient Air Quality Standard (NAAQS) of 75 ppb from 211 days in 1975 to 88 days in 2013 and the Basin design value (DV) from 275 to 107 ppb. Although substantial progress has been made, the ozone NAAQS is still exceeded in the Basin on most summer days and attainment of the standard remains a long-term challenge that has become more difficult with the recent revisions of the ozone NAAQS from 75 to 70 ppb (U.S. Environmental Protection Agency [EPA], 2015).

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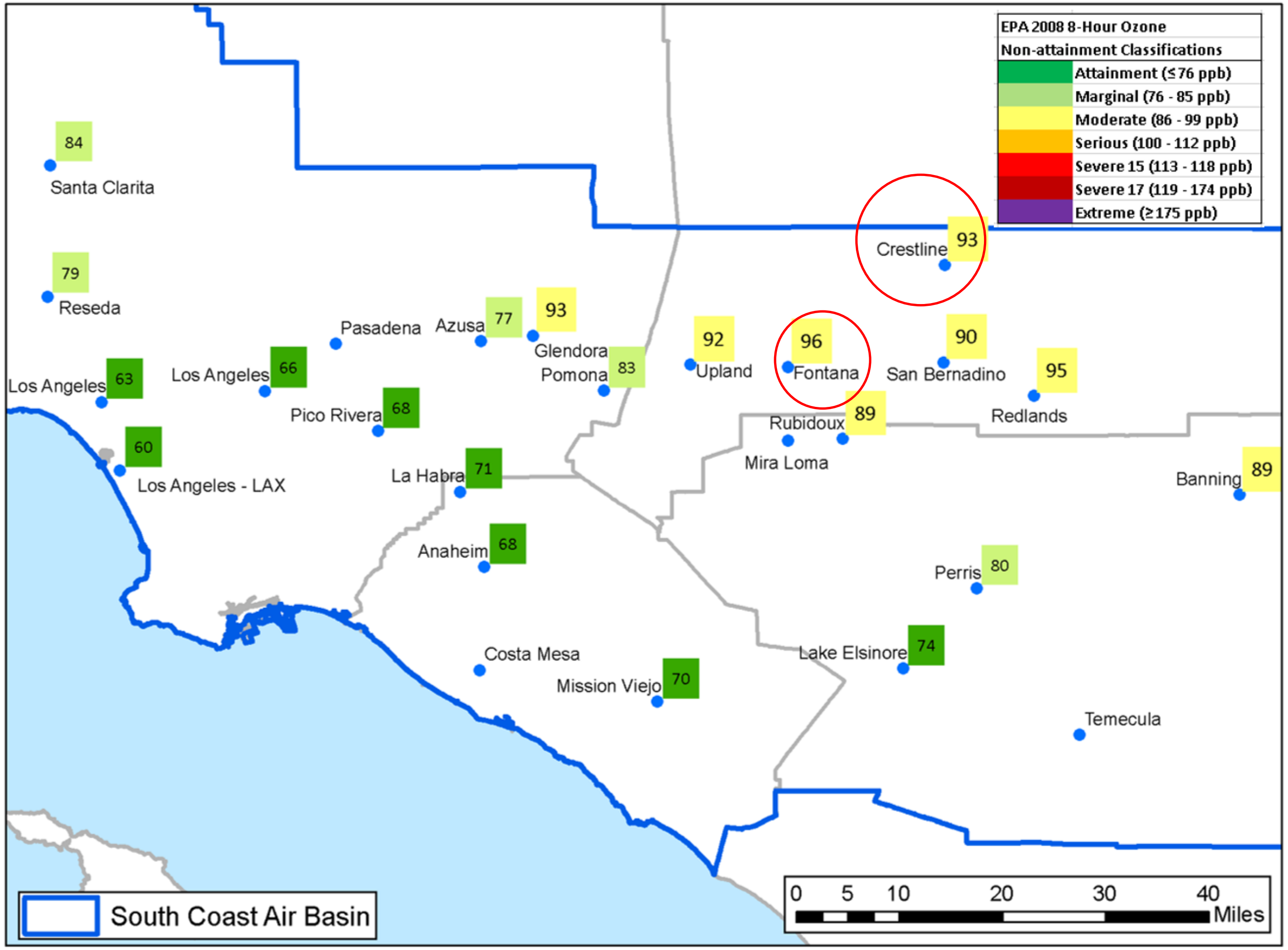
Supplemental data for this article can be accessed on the publisher's website.

- Fujita, et al. (2016), JAWMA Article
- Ridgeline "VOC-limited" conditions pertain in the SoCAB
- **Planned NO_x reductions may cause ozone levels to increase (10-20%) and move Westward in the SoCAB**
- "NO_x disbenefit" issues warrant careful consideration when assessing next-tier NO_x standards
- **Trends of future "baseline" ozone levels (next slides) need to be considered when assessing regulatory strategies**

1. Scope and Nature of the Issue

Projected Future “Baseline” Ozone Design Values in **2023** (AQMP Data)



- Projected ozone levels under current “base” scenario (without additional NO_x controls)
- Fontana (not Crestline) is projected to set the SoCAB DV in 2023
- **Growing area across the SoCAB will achieve attainment under “baseline” scenario**

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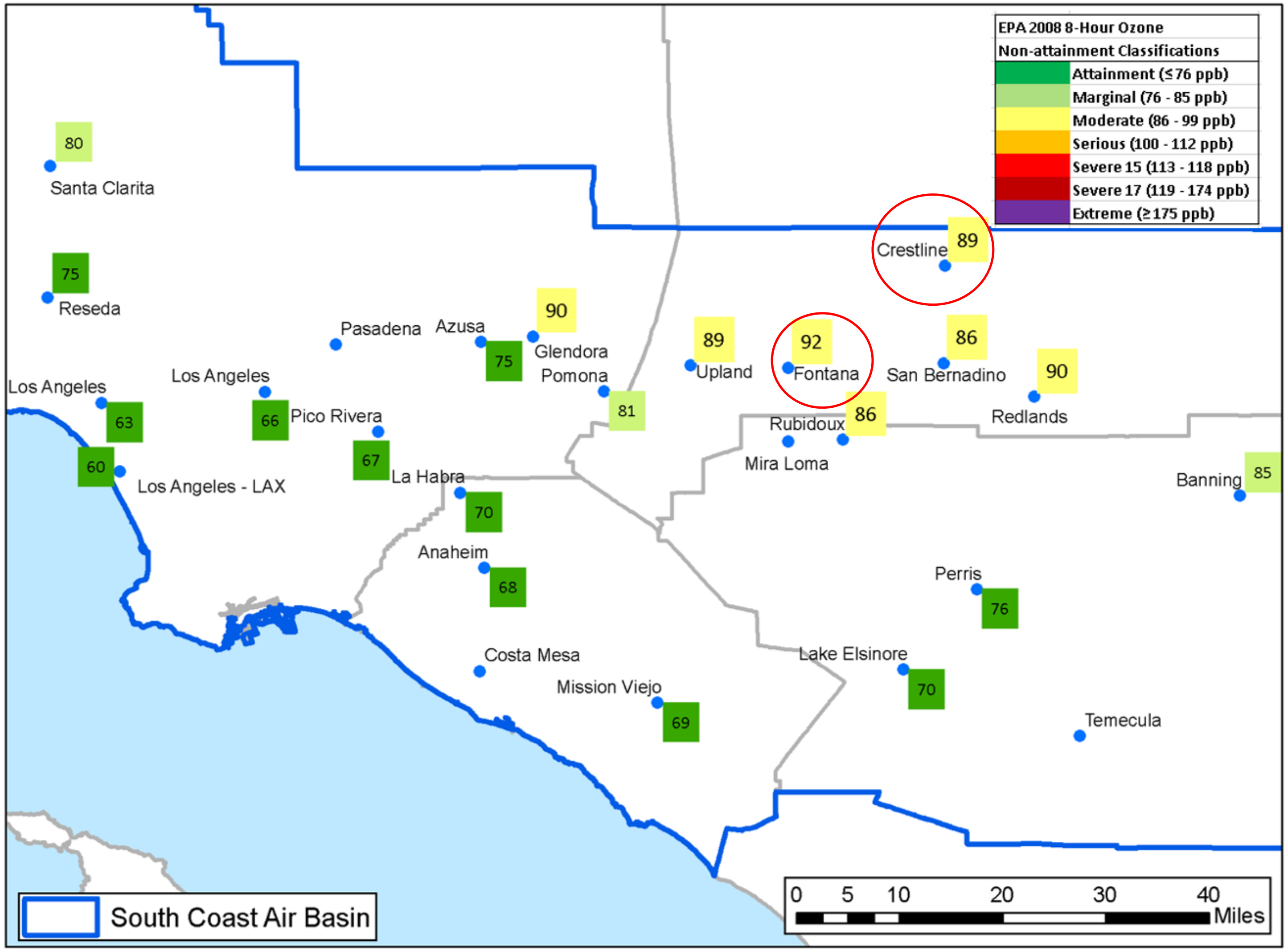
1. Scope and Nature of the Issue

Projected Future “Baseline” Ozone Design Values in **2031** (AQMP Data)



- **By 2031, there will be continuing progress across the majority of the SoCAB** toward attainment under “baseline” scenario
- A relatively small number of remaining county-specific concerns (albeit covering significant populations)
- County-specific concerns could support the potential consideration of “geofencing” and other targeted strategies

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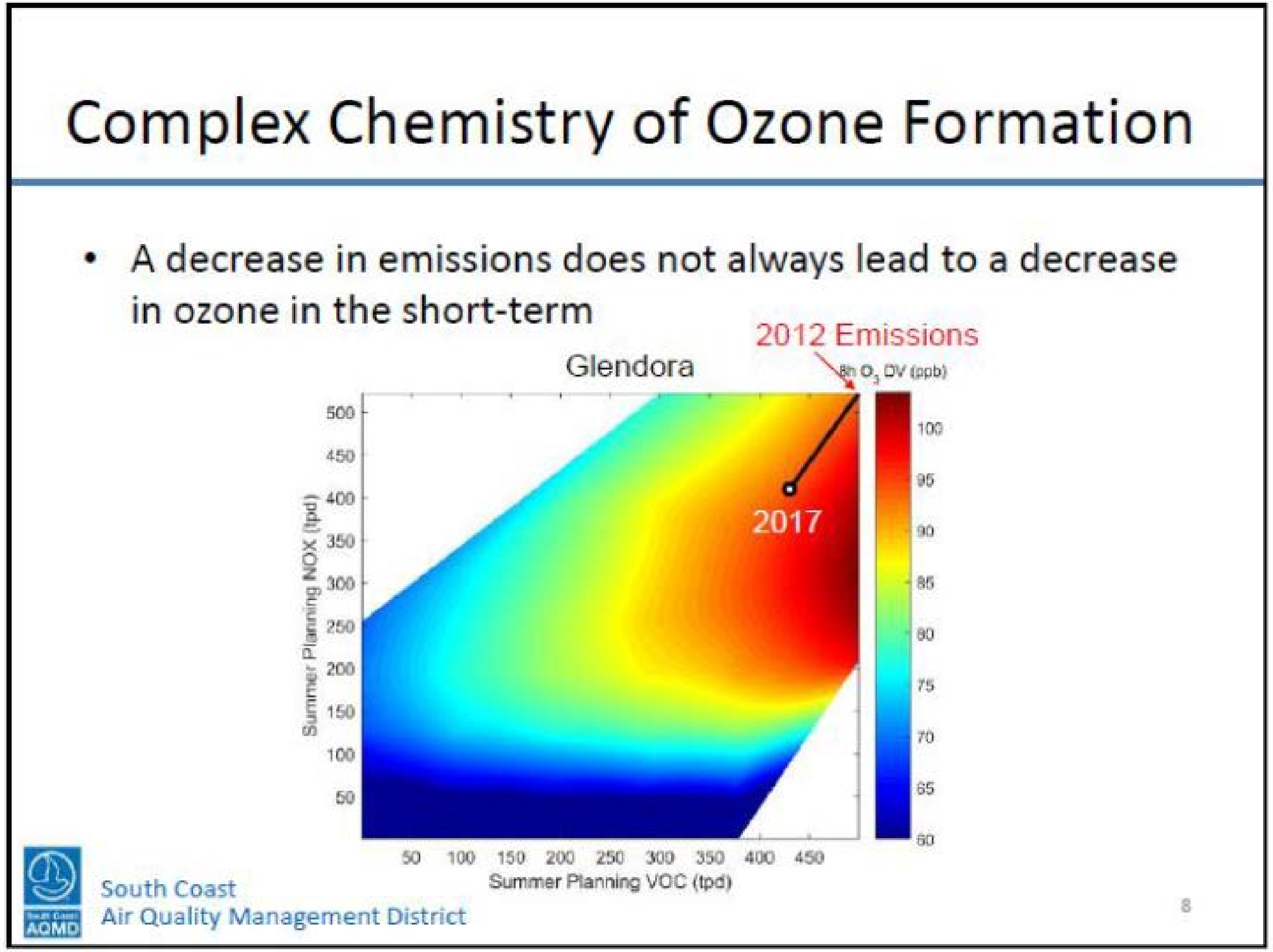
1. Scope and Nature of the Issue



Complex Chemistry of Ozone Formation

- A decrease in emissions does not always lead to a decrease in ozone in the short-term

South Coast
Air Quality Management District

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- “Ridgeline” ozone isopleth conditions illustrate the potential NO_x disbenefit phenomenon at the key nonattainment sites across the SoCAB
- Incremental NO_x-focused reductions can increase ozone levels
- **“NO_x-only approach leads to increased ozone and its exposure in the more densely populated western Basin during interim years** [such that] millions of residents would experience worse ozone air quality…” (VOC Controls, 2016 AQMP White Paper, p.10.)

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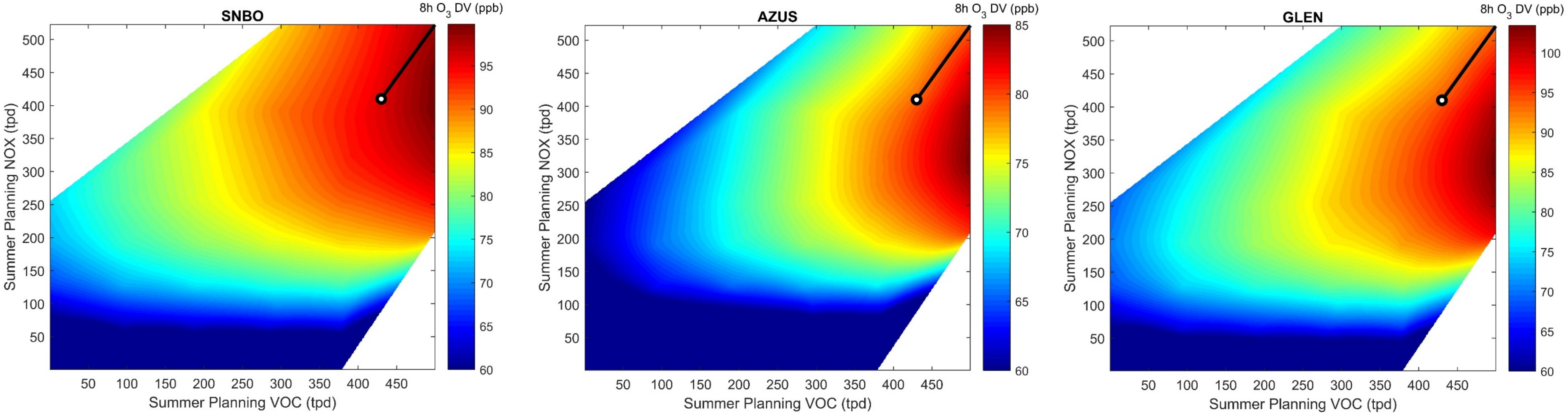
1. Scope and Nature of the Issue

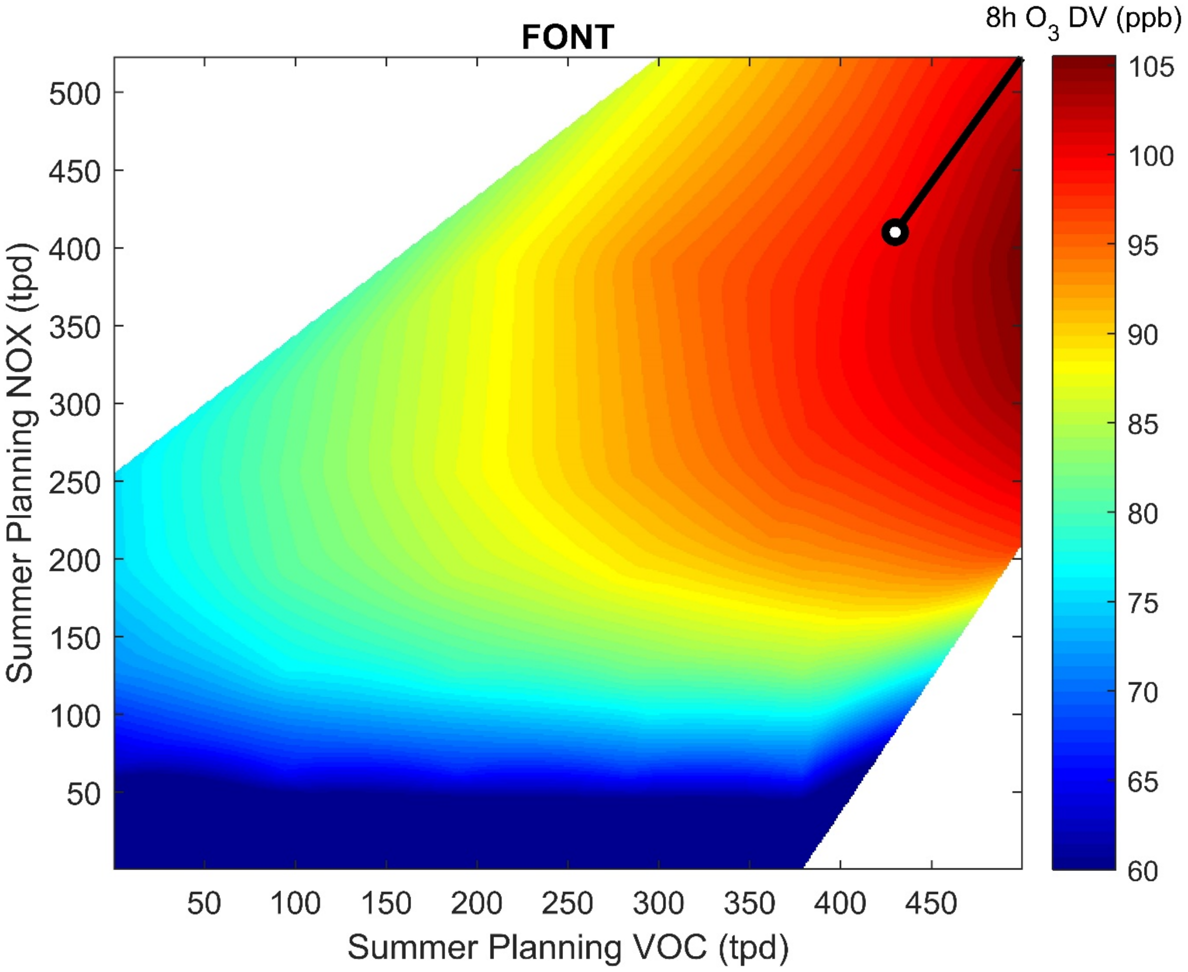
The NO_x Disbenefit Issue (SCAQMD Isopleth)



- The ridgeline/disbenefit issue is applicable at the San Bernadino, Azusa and Glendora sites

1. Scope and Nature of the Issue

The NO_x Disbenefit Issue (SCAQMD Isopleth)



- And also at the Fontana site, which is likely to set the DV for the SoCAB in the future
- Note that if the VOC emission inventories are higher than assumed, actual ozone levels will be higher than modeled
- Other issues also may be impacting the efficacy of current ozone-reduction strategies (next slides)

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1. Scope and Nature of the Issue

AGU PUBLICATIONS

JGR

Journal of Geophysical Research: Atmospheres

RESEARCH ARTICLE

10.1002/2016JD026329

Key Points:

- The temporal evolution of maximum ozone concentrations in Southern California is accurately described by a simple mathematical function
- The U.S. background ozone contribution of 62.0 ± 1.9 ppb is the lower limit achievable for the concentrations upon which the NAAQS is based
- Projections indicate that ~35 years of additional emission control efforts will be required to reach the NAAQS in the Los Angeles area

Supporting Information:

- Supporting Information S1

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Citation:

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Ozone Design Values in Southern California's Air Basins: Temporal Evolution and U.S. Background Contribution

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Abstract California's ambient ozone concentrations have two principal contributions: U.S. background ozone and enhancements produced from anthropogenic precursor emissions; only the latter effectively respond to California emission controls. From 1980 to 2015 ozone has been monitored in eight air basins in Southern California. The temporal evolution of the largest measured concentrations, i.e., those that define the ozone design value (ODV) upon which the National Ambient Air Quality Standard (NAAQS) is based, is described very well by an exponential decrease on top of a positive offset. We identify this offset as the ODV due to the U.S. background ozone (i.e., the concentration that would be present if U.S. anthropogenic precursor emissions were reduced to zero) and is estimated to be 62.0 ± 1.9 ppb in six of the basins. California's emission control efforts have reduced the anthropogenic ozone enhancements by a factor of ~5 since 1980. However, assuming that the current rate of exponential decrease is maintained and that U.S. background ODV remains constant, projections of the past decrease suggest that ~35 years of additional emission control efforts will be required to reach the new NAAQS of 70 ppb in the Los Angeles area. The growing predominance of U.S. background ozone contributions has shifted the maximum ozone concentrations in all air basins from later to earlier in the summer. Comparisons indicate that currently accepted model estimates of U.S. background ozone concentrations in Southern California are somewhat underestimated; thus, reducing ozone in this region to the 2015 NAAQS may be more difficult than currently expected.

Plain Language Summary Over the past decades, ozone air quality in Southern California has been greatly improved, but the National Ambient Air Quality Standard (NAAQS) has not yet been achieved in much of the region. The ozone standard is based on the rare, highest recorded concentrations (~98th percentile). A simple mathematical function is shown to provide an excellent description of the decrease in these ozone concentrations, which allows some implications to be inferred. Since 1980 the anthropogenic contribution to these concentrations has been reduced by a factor of ~5. However, the contribution of background ozone is estimated as ~89% of the NAAQS. Since this background contribution is so large, projection of the past rate of decrease of the anthropogenic contribution into the future suggests that ~35 years of additional emission control efforts will be required to reach the new NAAQS of 70 ppb in the Los Angeles region. The model calculations of the background ozone contribution that were considered in the formulation of the new NAAQS underestimate the background contribution. Thus, reducing Southern California ozone concentrations to the NAAQS may be more difficult than currently expected.

1. Introduction

In 1970 the U.S. passed the Clean Air Act, which required states to develop plans to improve air quality. Since its introduction, comprehensive efforts have been made to reduce emissions of the ozone precursors, oxides of nitrogen ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs), in order to meet the ozone National Ambient Air Quality Standard (NAAQS). The resulting emission reductions have produced substantial decreases in ambient ozone concentrations throughout the nation, including Southern California, which is the focus of this work. Quantification of these decreases and comparison of the decreases between different regions can potentially provide useful information for (1) partitioning ambient ozone concentrations between that produced locally and regionally from that transported from elsewhere, (2) forecasting likely

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PARRISH ET AL. SOUTHERN CALIFORNIA OZONE DESIGN VALUES 11,166

- Parrish, et al. (2017), JGR Article
- The implications of background ozone (boundary conditions) levels may not be fully understood
- **Background ozone may be higher than expected (62 ppb) and may (along with other factors) impede rate of attainment**
- Attainment of the 70 ppb NAAQS could be 35 years away

1. Scope and Nature of the Issue

SCIENCE ADVANCES | RESEARCH ARTICLE

APPLIED ECOLOGY

Agriculture is a major source of NO_x pollution in California

Maya Almaraz,[1*†] Edith Bai,[2,3†] Chao Wang,[2] Justin Trousdell,[1] Stephen Conley,[1] Ian Faloona,[1] Benjamin Z. Houlton[1,4]

Nitrogen oxides ($NO_x = NO + NO_2$) are a primary component of air pollution—a leading cause of premature death in humans and biodiversity declines worldwide. Although regulatory policies in California have successfully limited transportation sources of NO_x pollution, several of the United States' worst–air quality districts remain in rural regions of the state. Site-based findings suggest that NO_x emissions from California's agricultural soils could contribute to air quality issues; however, a statewide estimate is hitherto lacking. We show that agricultural soils are a dominant source of NO_x pollution in California, with especially high soil NO_x emissions from the state's Central Valley region. We base our conclusion on two independent approaches: (i) a bottom-up spatial model of soil NO_x emissions and (ii) top-down airborne observations of atmospheric NO_x concentrations over the San Joaquin Valley. These approaches point to a large, overlooked NO_x source from cropland soil, which is estimated to increase the NO_x budget by 20 to 51%. These estimates are consistent with previous studies of point-scale measurements of NO_x emissions from the soil. Our results highlight opportunities to limit NO_x emissions from agriculture by investing in management practices that will bring co-benefits to the economy, ecosystems, and human health in rural areas of California.

INTRODUCTION

Nitrogen oxide ($NO_x = NO + NO_2$) gases are among the most important components of air pollution, which, according to the World Health Organization, is responsible for one in eight premature deaths worldwide (*1*). These nitrogen (N) gases have been linked to upper respiratory disease, asthma, cancer, birth defects, cardiovascular disease, and sudden infant death syndrome (*2*, *3*). Global studies have pointed to similarities in the magnitude of NO_x emissions from fossil fuel combustion and soil, with the largest soil emissions from regions with heavy N fertilizer applications (*4*–*7*). Despite the significance of soil microbial NO_x emissions at the global scale, policies have focused largely on limiting NO_x from mobile and stationary fossil fuel sources (*8*, *9*). Where agriculture is an important source of NO_x, strategies to reduce nonpoint emissions will need to incorporate soil management approaches and policies that are fundamentally different from fossil fuel sources.

California is considered the world's sixth largest economy in terms of gross national product and supports 12.2% of the U.S. food economy (*10*). The state has instituted policies to reduce NO_x pollution from fossil fuel sources, resulting in NO_x declining by 9% per year in Los Angeles, San Francisco, and Sacramento over the period of 2005 to 2008 (*11*). Recent findings have suggested that agriculture is one of the dominant sources of NO_x in the United States, particularly in the midwest region, where fertilizer inputs are substantial (*6*, *12*). In California, local field measurements have similarly ascribed high NO_x emissions to agricultural soil (*13*). Matson *et al.* (*14*) provided some of the first evidence of substantial NO_x production from agricultural soils in California's Central Valley; however, a statewide assessment, which is needed to drive new policies for NO_x pollution, is hitherto lacking. The California Air Resources Board (CARB) estimates that ~3.8% of the state's NO_x budget can be attributed to cropland soils, but these estimates are based on data limited to farms located within 200 km of Sacramento and miss many of the most heavily fertilized areas in the state (*15*). Moreover, CARB does not include these estimated emissions in their official statewide database for air quality modeling (*16*).

Here, we provide the first large-scale quantification of soil NO_x emissions for California through two different approaches: integrative "bottom-up" spatial modeling and "top-down" airborne NO_x measurements. This two-pronged approach allows us to independently examine the contribution of biogenic NO_x emissions in California while comparing these estimates to local empirical data. Our overarching hypothesis is that biogenic emissions of NO_x from agricultural areas are much higher than we used to believe and could be a major source of atmospheric NO_x statewide. Alternatively, if agricultural sources are of minor significance, then we would expect to find uniformly low emissions throughout natural and agricultural ecosystems.

RESULTS AND DISCUSSION

Our combined bottom-up and top-down estimates uniformly point to high NO_x emissions from California's agricultural soil, revealing a significant unrecognized source of N pollution statewide. Our bottom-up model reveals that 161,100 metric tons of NO_x-N year^{-1} is emitted from California soil with croplands accounting for 79% of total emissions. When combined with data on existing mobile and stationary fossil fuel sources (*16*), our results indicate that fertilized croplands account for 20 to 32% of total NO_x-N emissions from all sectors of the state, whereas natural soils account for 5 to 9% (Fig. 1). A meta-analysis of soil NO_x emissions from the existing literature demonstrates quantitative coherence between our model-based estimates and empirical measurements from different areas of the state (Table 1). Mean NO_x emissions from California cropland soils were 19.8 (±27.3 SD) kg of N ha^{-1} year^{-1} and ranged from 0 to 276 kg of N ha^{-1} year^{-1} (Fig. 2), with $^1/_4$ quartile and $^3/_4$ quartile values of 4.3 and 24.9 kg of N ha^{-1} year^{-1}, respectively. NO_x emissions were largest from agricultural soils where N fertilizer applications can reach >600 kg of N ha^{-1} year^{-1} (average N fertilizer

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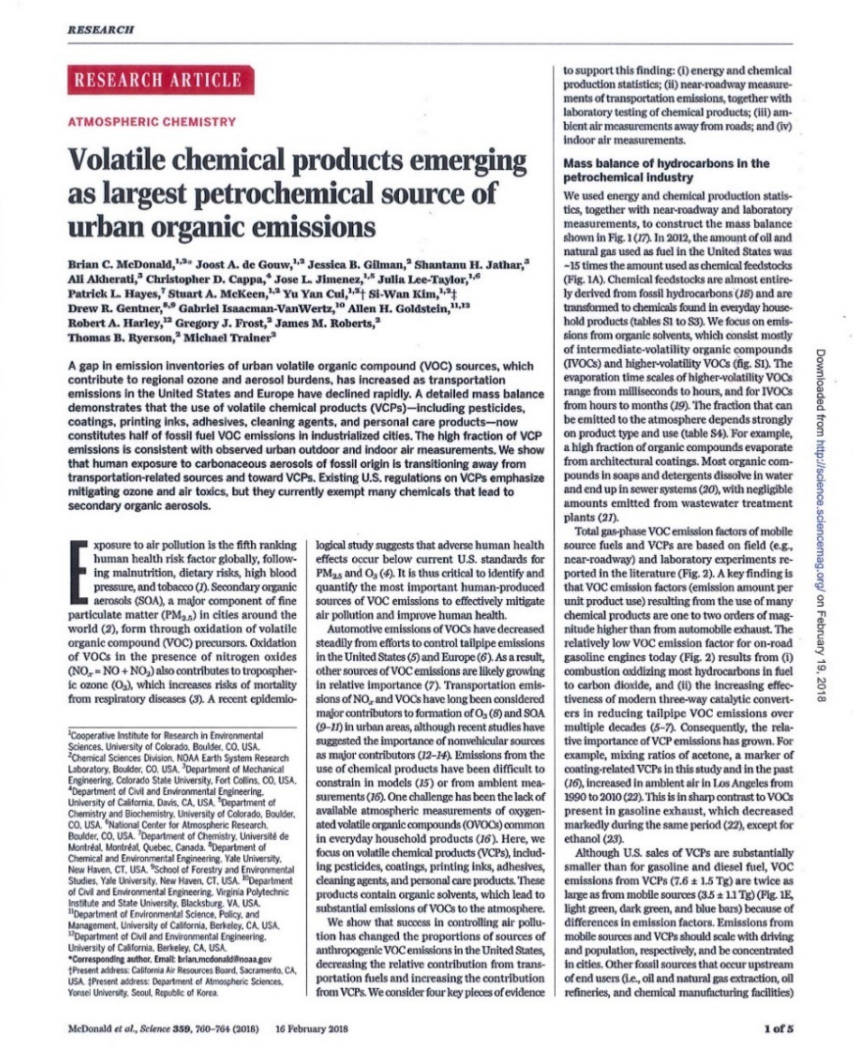
Almaraz *et al.*, *Sci. Adv.* 2018;**4**:eaao3477 31 January 2018

- Almanaz, et al (2018), Science Advances Article
- **Agricultural soils may be dominant sources of NO_x**
- Agricultural NO_x emissions may be different in the SoCAB, but lawn, garden and other horticultural-related NO_x emissions (fertilizer) may be a factor
- Again, these region/county-specific issues support the potential consideration of "geofencing" and other targeted strategies
- Differing needs for and utility of HDOH NO_x controls in different regions

1. Scope and Nature of the Issue



RESEARCH

RESEARCH ARTICLE

ATMOSPHERIC CHEMISTRY

Volatile chemical products emerging as largest petrochemical source of urban organic emissions

Brian C. McDonald,[1,2]* Joost A. de Gouw,[1,2] Jessica B. Gilman,[2] Shantanu H. Jathar,[3] Ali Akherati,[3] Christopher D. Cappa,[4] Jose L. Jimenez,[1,5] Julia Lee-Taylor,[1,6] Patrick L. Hayes,[7] Stuart A. McKeen,[1,2] Yu Yan Cui,[1,2]† Si-Wan Kim,[1,2]‡ Drew R. Gentner,[8,9] Gabriel Isaacman-VanWertz,[10] Allen H. Goldstein,[11,12] Robert A. Harley,[12] Gregory J. Frost,[2] James M. Roberts,[2] Thomas B. Ryerson,[2] Michael Trainer[2]

A gap in emission inventories of urban volatile organic compound (VOC) sources, which contribute to regional ozone and aerosol burdens, has increased as transportation emissions in the United States and Europe have declined rapidly. A detailed mass balance demonstrates that the use of volatile chemical products (VCPs)—including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products—now constitutes half of fossil fuel VOC emissions in industrialized cities. The high fraction of VCP emissions is consistent with observed urban outdoor and indoor air measurements. We show that human exposure to carbonaceous aerosols of fossil origin is transitioning away from transportation-related sources and toward VCPs. Existing U.S. regulations on VCPs emphasize mitigating ozone and air toxics, but they currently exempt many chemicals that lead to secondary organic aerosols.

Exposure to air pollution is the fifth ranking human health risk factor globally, following malnutrition, dietary risks, high blood pressure, and tobacco (*1*). Secondary organic aerosols (SOA), a major component of fine particulate matter ($PM_{2.5}$) in cities around the world (*2*), form through oxidation of volatile organic compound (VOC) precursors. Oxidation of VOCs in the presence of nitrogen oxides ($NO_x = NO + NO_2$) also contributes to tropospheric ozone (O_3), which increases risks of mortality from respiratory diseases (*3*). A recent epidemiological study suggests that adverse human health effects occur below current U.S. standards for $PM_{2.5}$ and O_3 (*4*). It is thus critical to identify and quantify the most important human-produced sources of VOC emissions to effectively mitigate air pollution and improve human health.

Automotive emissions of VOCs have decreased steadily from efforts to control tailpipe emissions in the United States (*5*) and Europe (*6*). As a result, other sources of VOC emissions are likely growing in relative importance (*7*). Transportation emissions of NO_x and VOCs have long been considered major contributors to formation of O_3 (*8*) and SOA (*9–11*) in urban areas, although recent studies have suggested the importance of nonvehicular sources as major contributors (*12–14*). Emissions from the use of chemical products have been difficult to constrain in models (*15*) or from ambient measurements (*16*). One challenge has been the lack of available atmospheric measurements of oxygenated volatile organic compounds (OVOCs) common in everyday household products (*16*). Here, we focus on volatile chemical products (VCPs), including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products. These products contain organic solvents, which lead to substantial emissions of VOCs to the atmosphere.

We show that success in controlling air pollution has changed the proportions of sources of anthropogenic VOC emissions in the United States, decreasing the relative contribution from transportation fuels and increasing the contribution from VCPs. We consider four key pieces of evidence to support this finding: (i) energy and chemical production statistics; (ii) near-roadway measurements of transportation emissions, together with laboratory testing of chemical products; (iii) ambient air measurements away from roads; and (iv) indoor air measurements.

Mass balance of hydrocarbons in the petrochemical industry

We used energy and chemical production statistics, together with near-roadway and laboratory measurements, to construct the mass balance shown in Fig. 1 (*17*). In 2012, the amount of oil and natural gas used as fuel in the United States was ~15 times the amount used as chemical feedstocks (Fig. 1A). Chemical feedstocks are almost entirely derived from fossil hydrocarbons (*18*) and are transformed to chemicals found in everyday household products (tables S1 to S3). We focus on emissions from organic solvents, which consist mostly of intermediate-volatility organic compounds (IVOCs) and higher-volatility VOCs (fig. S1). The evaporation time scales of higher-volatility VOCs range from milliseconds to hours, and for IVOCs from hours to months (*19*). The fraction that can be emitted to the atmosphere depends strongly on product type and use (table S4). For example, a high fraction of organic compounds evaporate from architectural coatings. Most organic compounds in soaps and detergents dissolve in water and end up in sewer systems (*20*), with negligible amounts emitted from wastewater treatment plants (*21*).

Total gas-phase VOC emission factors of mobile source fuels and VCPs are based on field (e.g., near-roadway) and laboratory experiments reported in the literature (Fig. 2). A key finding is that VOC emission factors (emission amount per unit product use) resulting from the use of many chemical products are one to two orders of magnitude higher than from automobile exhaust. The relatively low VOC emission factor for on-road gasoline engines today (Fig. 2) results from (i) combustion oxidizing most hydrocarbons in fuel to carbon dioxide, and (ii) the increasing effectiveness of modern three-way catalytic converters in reducing tailpipe VOC emissions over multiple decades (*5–7*). Consequently, the relative importance of VCP emissions has grown. For example, mixing ratios of acetone, a marker of coating-related VCPs in this study and in the past (*16*), increased in ambient air in Los Angeles from 1990 to 2010 (*22*). This is in sharp contrast to VOCs present in gasoline exhaust, which decreased markedly during the same period (*22*), except for ethanol (*23*).

Although U.S. sales of VCPs are substantially smaller than for gasoline and diesel fuel, VOC emissions from VCPs (7.6 ± 1.5 Tg) are twice as large as from mobile sources (3.5 ± 1.1 Tg) (Fig. 1E, light green, dark green, and blue bars) because of differences in emission factors. Emissions from mobile sources and VCPs should scale with driving and population, respectively, and be concentrated in cities. Other fossil sources that occur upstream of end users (i.e., oil and natural gas extraction, oil refineries, and chemical manufacturing facilities)

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McDonald *et al.*, *Science* **359**, 760–764 (2018) 16 February 2018 **1 of 5**

- McDonald, et al. (2018), Science Article
- **Consumer-product sources of VOCs may be equivalent to (or greater than) vehicular sources**
- **VOC inventories may be understated and not fully understood**
- Potential ozone modeling impacts?
- Potential impacts on the efficacy of NO_x-only regulatory strategies?
- Do we have the right air quality projections for assessing the optimal targeted attainment strategies and control measures?

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1. Scope and Nature of the Issue

Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions

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Edited by Guy Brasseur, Max Planck Institute of Meteorology, Hamburg, Germany, and accepted by Editorial Board Member A. R. Ravishankara December 12, 2017 (received for review August 21, 2017)

Atmospheric chemistry is fueled by a large annual influx of nonmethane volatile organic compounds (NMVOC). These compounds influence ozone formation, lead to secondary organic aerosol production, and play a significant role for the oxidizing capacity of the atmosphere. The anthropogenic NMVOC budget is considerably uncertain due to the diversity of urban emission sources. Here, we present comprehensive observations of urban NMVOC eddy covariance fluxes using a newly designed proton-transfer-reaction quadrupole interface time-of-flight mass spectrometer. We found emission fluxes of a surprisingly large pool of oxygenated NMVOCs (OVOCs) with an appreciable fraction of higher oxidized OVOCs that cannot be explained by known fast photochemical turnaround or current primary emission estimates. Measured OVOC/NMVOC bulk flux ratios are two to four times higher than inferred from aggregated anthropogenic emission inventories. Extrapolating these results would double the global anthropogenic NMVOC flux. In view of globally accelerating urbanization, our study highlights the need to reevaluate the influence of anthropogenic NMVOC on atmospheric chemistry, human health, and the climate system.

NMVOC | eddy covariance | urban emissions | air pollution | mass spectrometry

There is compelling evidence that oxygenated nonmethane volatile organic compounds (OVOC) released into the atmosphere profoundly influence oxidative processes (1–3), including the formation of secondary organic aerosols (SOA) (4–6). Urban photochemical smog has been identified as particularly diverse in ozone- and SOA-forming nonmethane volatile organic compounds (NMVOC) (7–9), but predictions of associated emissions are highly uncertain. Urban areas are generally considered NMVOC-sensitive with respect to ozone production (7, 10–12), and air quality control legislation devises measures to limit the emitted OH reactivity of the anthropogenic precursor pool (13). Comparisons between modeled and measured OH reactivity suggest significant discrepancies across different photochemical regimes, including urban areas (3, 9, 14). It is assumed that urban environments in Western economies have seen a significant transformation in the composition of NMVOC emissions fueling atmospheric chemistry during recent years. Decreasing trends in concentrations of aliphatic and aromatic compounds (11, 15, 16) have largely been attributed to decreasing emissions from automobiles since the introduction of catalytic converter technology. In addition, new pollution directives (17) have mandated a gradual manufacturing shift toward oxygenated solvents. Despite reasonably good knowledge on relative concentration trends of aliphatic and aromatic compounds, the verification of absolute emissions of anthropogenic NMVOC databases remains difficult (18, 19) because the anthropogenic budget of OVOC has been identified as particularly uncertain (7, 20). Consequently, the global emission flux of anthropogenic NMVOC is quite uncertain. While oxygenated compounds are often considered less toxic and rank lower on the ozone reactivity scale (13), their influence on SOA formation is considered important due to their high solubilities and low vapor pressures (21). This has consequences for a quantitative understanding of climate feedbacks as SOA can efficiently alter cloud formation processes. An increased presence of oxygenated compounds can also potentially present an emerging challenge for air pollution management as SOA is an acute public health concern in many regions. Here we show that a surprisingly large proportion of multifunctional oxygenated NMVOC is injected into the lower atmosphere which cannot be explained by known photochemical production or inferred from bottom-up emission inventories.

Results

Measurements were performed with a newly designed proton-transfer-reaction time-of-flight mass spectrometer with quadrupole interface (PTR-QiTOF) (*Methods*) using the eddy covariance (EC) method. The instrument's performance allowed a 10-fold decrease in flux detection limits compared with previous studies. It was therefore possible to quantify a significantly larger number of individual NMVOC fluxes by this technique than in the past. Soft chemical ionization based on proton-transfer reactions (PTR) has proven a valuable method for EC measurements of NMVOC (22, 23) requiring the detection of ultrafast concentration fluctuations (e.g., 10 Hz and higher) in combination with minimal sampling losses. The EC method is fundamentally derived from the scalar budget equation after Reynolds decomposition, and in its simplest form for horizontally homogeneous flows normal to the surface, where the mean vertical motion of wind ($\bar{w}$) can be considered zero, relates the measured

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

Significance

The exchange of nonmethane volatile organic compounds (NMVOC) at the surface-atmosphere interface is a fundamental constraint and important boundary condition for atmospheric chemistry and its effects on climate. Anthropogenic emissions are thought to account for about half of the NMVOC flux into the atmosphere of the Northern Hemisphere, yet their budget is considerably uncertain due to the scarcity of appropriate top-down constraints. Here we present direct flux measurements of NMVOCs based on the eddy covariance technique, showing that the contribution of typical urban emission sources is comprised of a surprisingly large portion of oxygenated NMVOC. These results suggest that typical urban NMVOC emission sources could be significantly higher than currently projected in air chemistry and climate models.

Author contributions: T.K. designed research; T.K., M.S., M.G., A.H., and G.W. performed research; T.K., M.S., M.G., A.H., and G.W. analyzed data; and T.K., M.G., A.H., and G.W. wrote the paper.

The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1714715115/-/DCSupplemental.

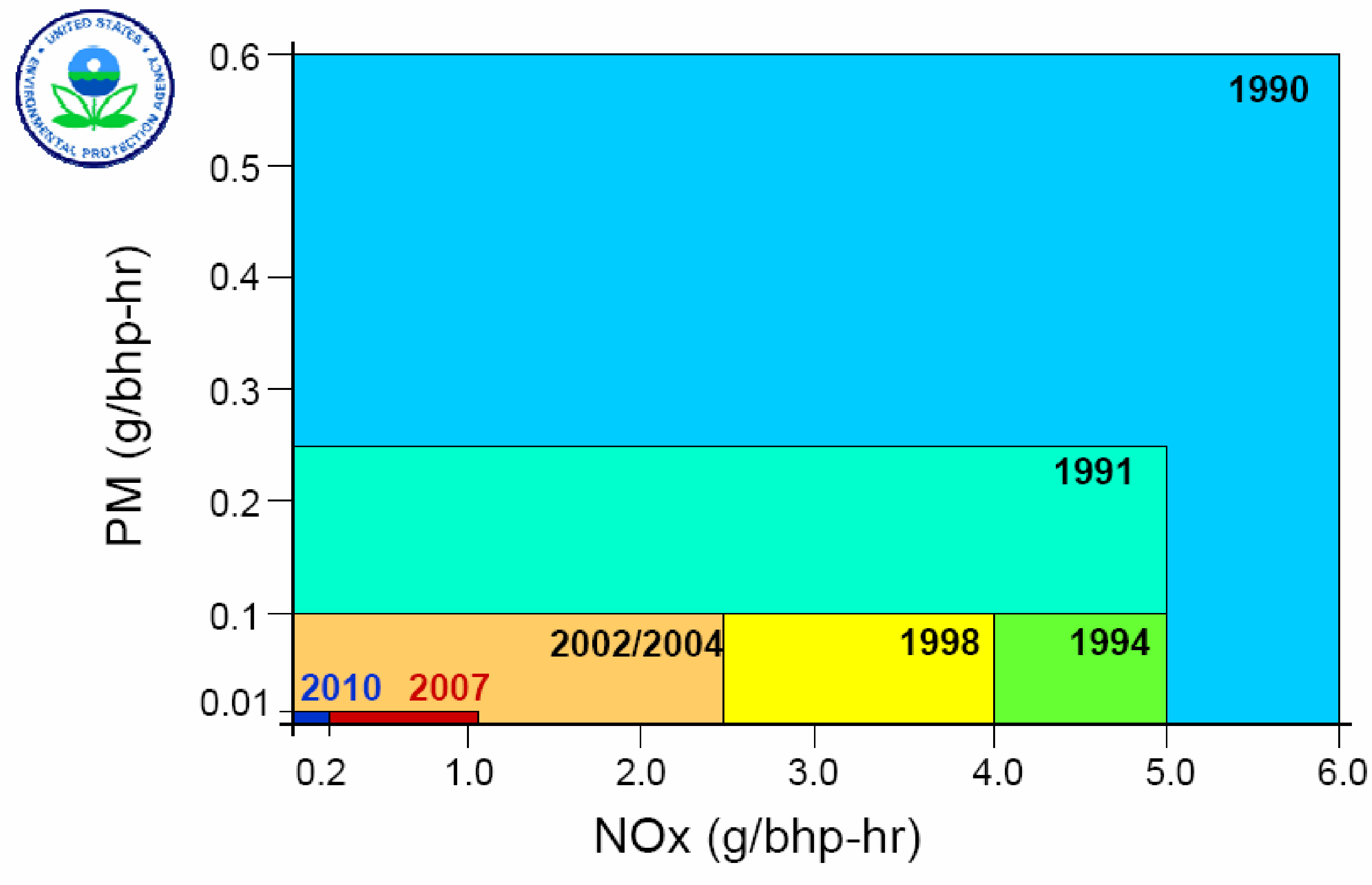
- Karl, et al. (2017), PNAS Article
- **Measured VOCs may be 2-4 times higher than emission inventories**
- More concerns about the accuracy of the emissions inventories and VOC:NO_x ratios underlying ozone modeling
- **Key question: Are we assessing potential targeted NO_x-control measures based on the right ozone-modeling assumptions and projections?**

2. Impact of HDOH NO_x Emissions

2. What's the actual real-world impact of HDOH NO_x emissions?
    - near-zero standards already
    - aggregate in-use performance is robust
    - need for new in-use data to assess potential for further HDOH NO_x reductions
    - significant research efforts are underway

2. Impact of HDOH NO_x Emissions

The Progress Towards Near-Zero HDOH Emission Levels (EPA Standards)



- Current HDOH NO_x standards are already near zero (0.20 g/bhp-hr)
- Another key operative question is: what real-world in-use HDOH NO_x emissions need additional targeted regulatory control to address area-specific ozone concerns?

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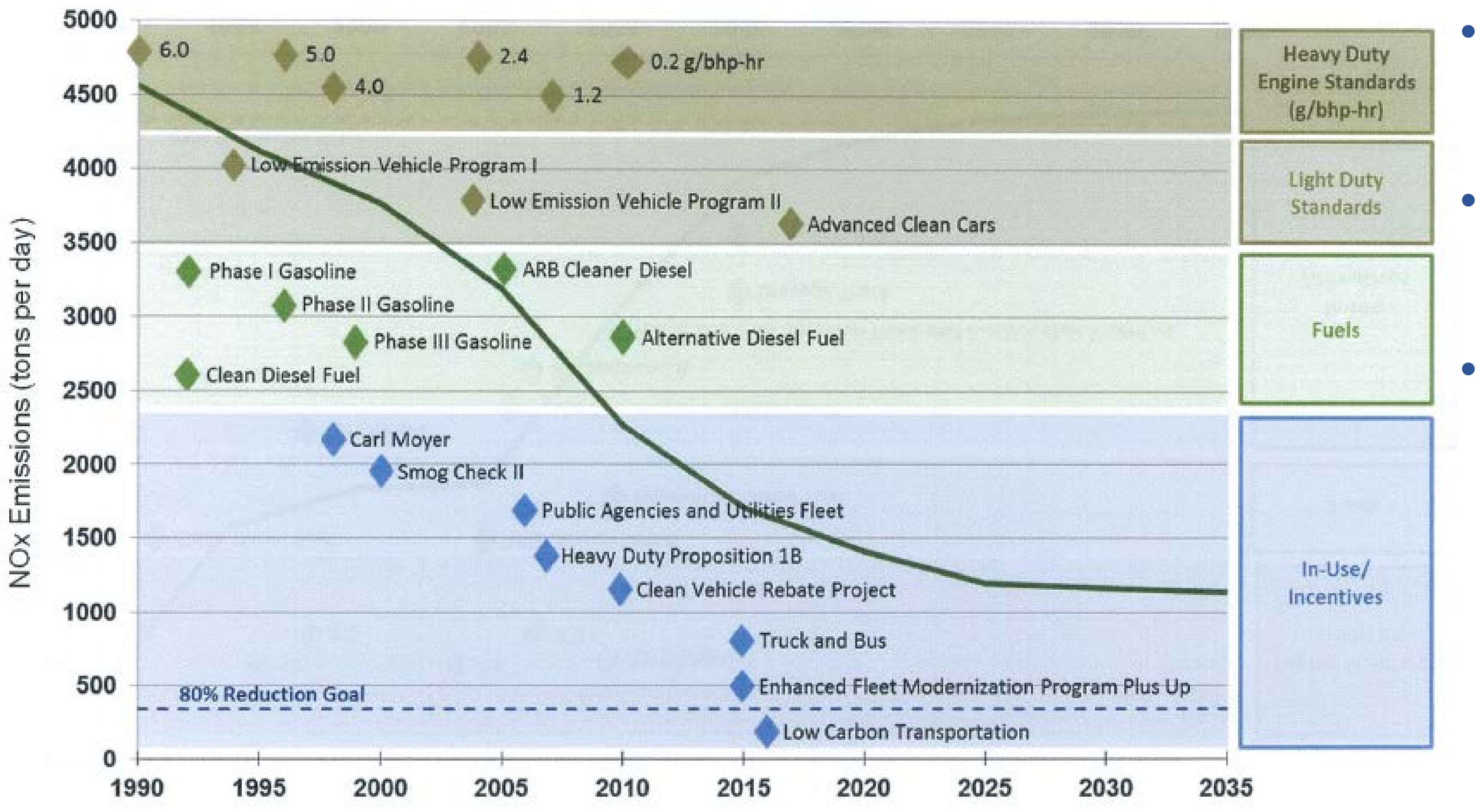
2. Impact of HDOH NO_x Emissions

Programs to Reduce Smog-Forming NOx Emissions (CARB Presentation)



- HDOH NO_x emissions have come down dramatically in the SoCAB
- But after 2023, the era of exponential reductions appears to be over
- Additional incremental HDOH NO_x reductions will need to be more targeted and in-use focused to address region/county-specific attainment issues

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2. Impact of HDOH NO$_x$ Emissions

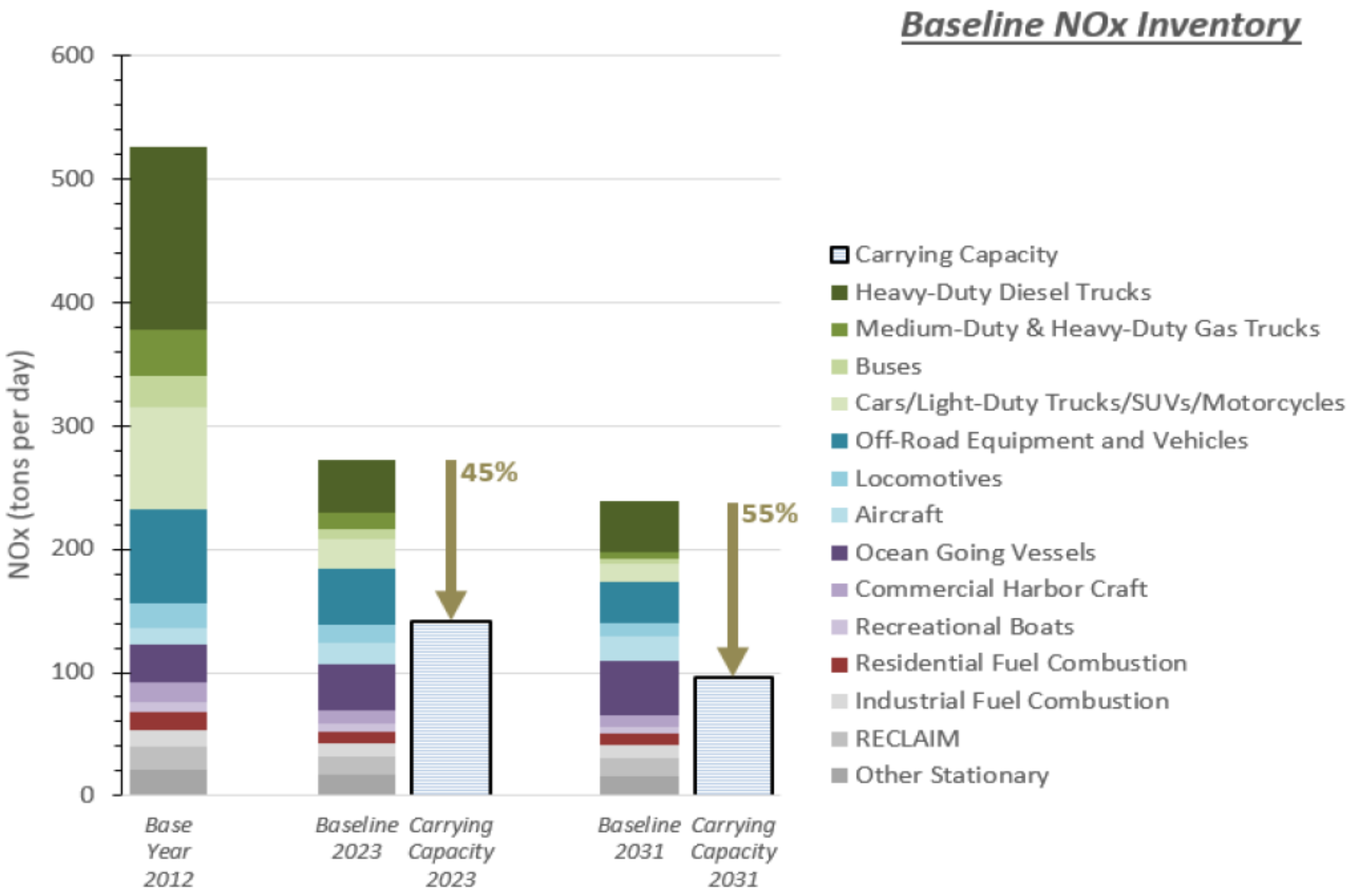

Figure 1-1: NOx Emission Reductions Needed to Achieve Federal 8-Hour Ozone NAAQS (AQMP Data)

- The actual remaining scope of the HDOH NO$_x$ issue (as of 2031) needs to be assessed in context
- Even if all HDOH emissions were eliminated, the county-specific ozone attainment issues in the SoCAB would persist

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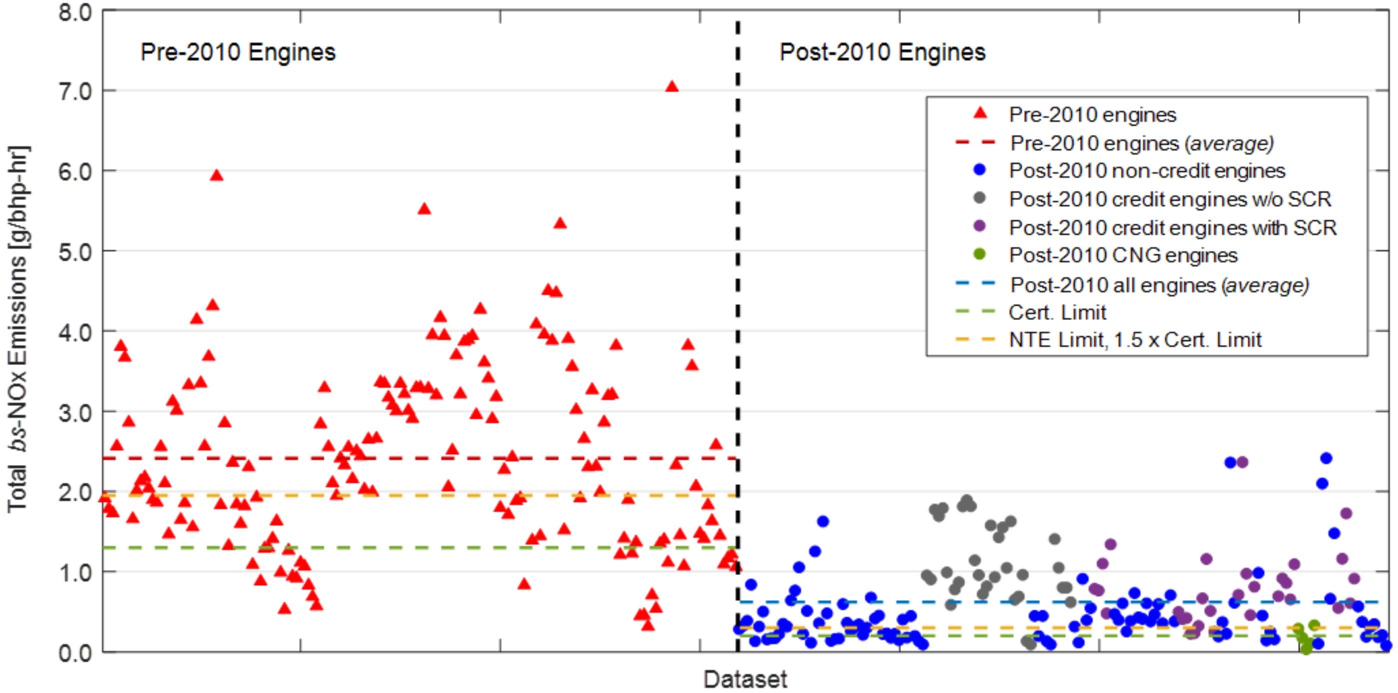
2. Impact of HDOH NO_x Emissions

US 2010 Standards Demonstrating Effectiveness in the Field (WVU HDIUT Data Analysis)



- 100 “non-credit” vehicles; approx. 27,000 VMT
- *Total* day’s NO_x (key-on to key-off, no exclusions)

	2007	2010	%change
Standard (g/bhp-hr)	1.3	0.20	-84.6%
Average NO_x	2.14	0.365	-83.0%

- **Significantly, aggregate real-world in-use HDOH NO_x performance is 0.37 g/bhp-hr across all operations**
- **Percentage reduction of in-use emissions has matched percentage reduction in standards (83%/85%)**
- An additional cost-effective 83% reduction in real-world in-use NO_x (through incremental improvements in SCR conversion efficiencies) across the board is not realistic
- Limited “low-hanging” fruit
- **Additional reductions will need to be incremental and targeted**

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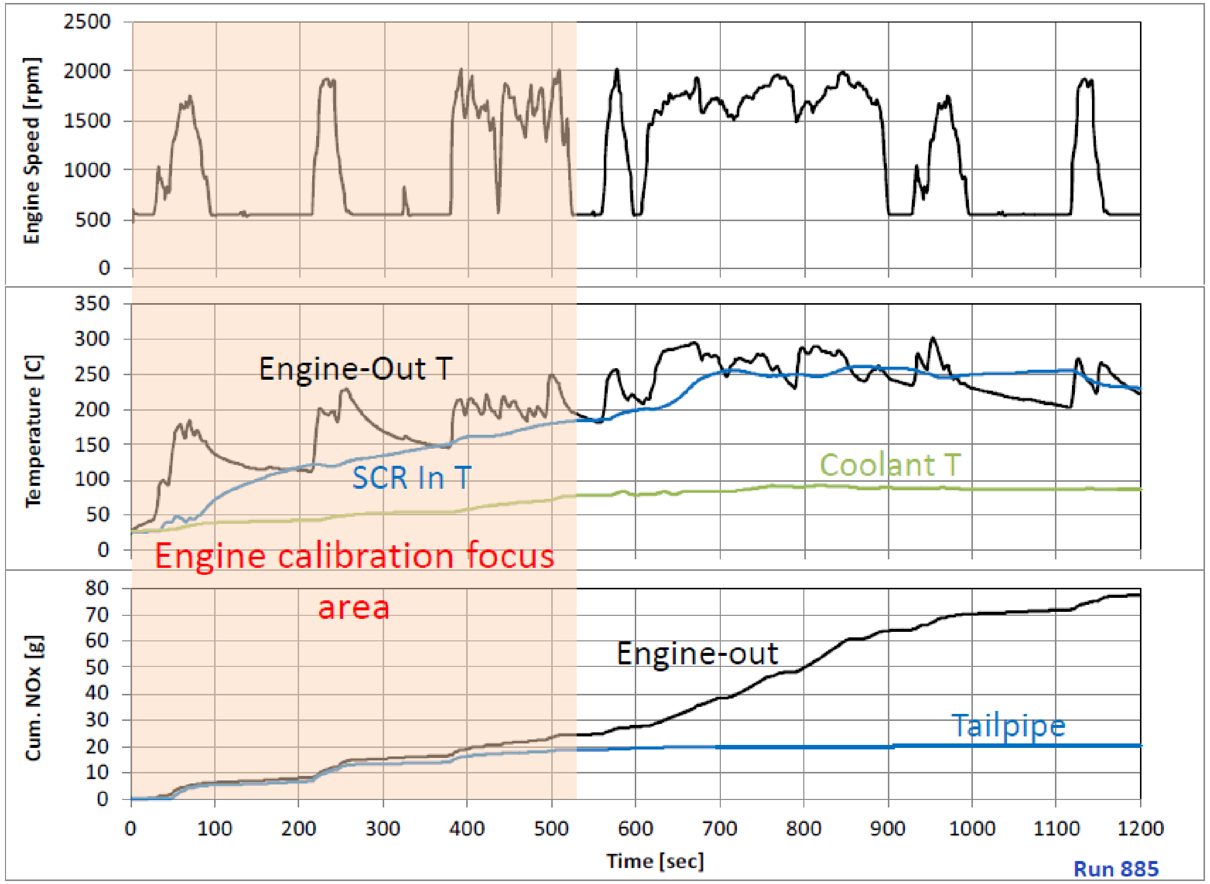
3. The Best Path Forward?

3. What’s the best path forward?
    - FTP-oriented development efforts?
    - focus on cold-start emissions? light-load emissions?
    - need to preserve feasibility of GHG targets
    - focus on real-world real-time emissions data
    - establish actual relevant in-use baseline emissions from which to assess potential targeted in-use emissions improvements
    - consider role for NO_x sensors and telematics
    - vehicle/engines families as the new “lab” to generate aggregated in-use emissions data

3. The Best Path Forward?

Low-NOx Technology Issues (SwRI Presentation)

Baseline Cold-start FTP



Note: typical FTP work is 27 HP-hr

- Additional FTP-based standards and optimization may not be the best strategies for achieving targeted real-world in-use HDOH NO_x reductions
- "Cold-Start" NO_x reduction is the focus of the FTP engine-calibration efforts that are a part of the low-NO_x research project pending at SwRI

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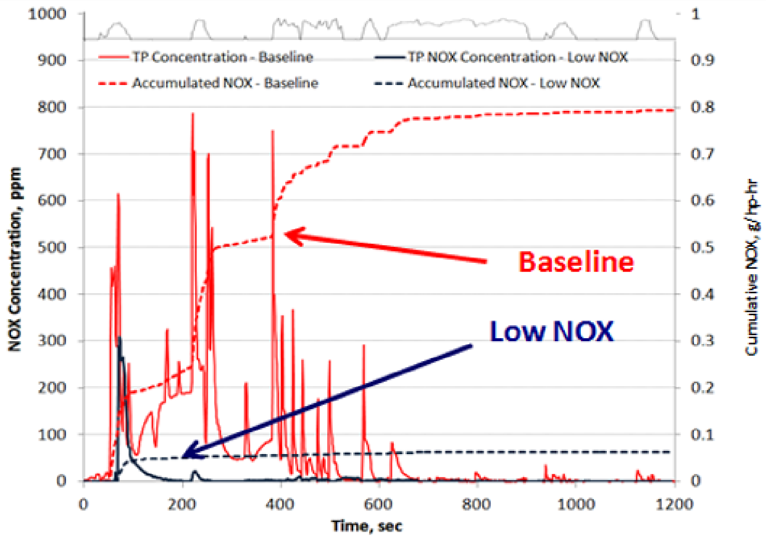
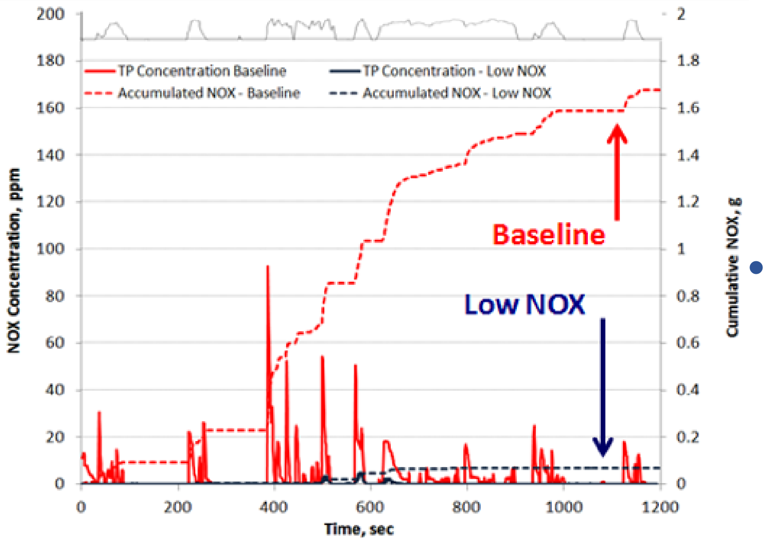
3. The Best Path Forward?

(Figs from SAE Paper 2017-01-0958)



Cold-FTP



Hot-FTP

Aftertreatment NO_x Conversion Efficiency, %

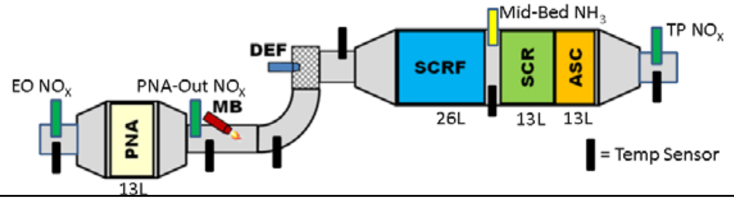
Test Config	FTP Transient			RMC-SET	WHTC
	Cold	Hot	Composite		
Baseline	75%	98.5%	95%	97%	97%
Devel Aged	98%	99.7%	99.5%	99.3%	99.4%
Final Aged	96%	99.3%	98.8%	98.2%	98.8%

- Focusing on the first 500 seconds of the FTP cycle may not translate into corollary effective real-world in-use NO_x reductions
- **Cold-start emissions account for only 0.4% of aggregate in-use real-world HDOH NO_x emissions** (WVU analysis of HDIUT data)
- Cold-start-focused technologies (e.g., PNAs) do not yield significant real-world NO_x reductions, but do add significant costs and complexity

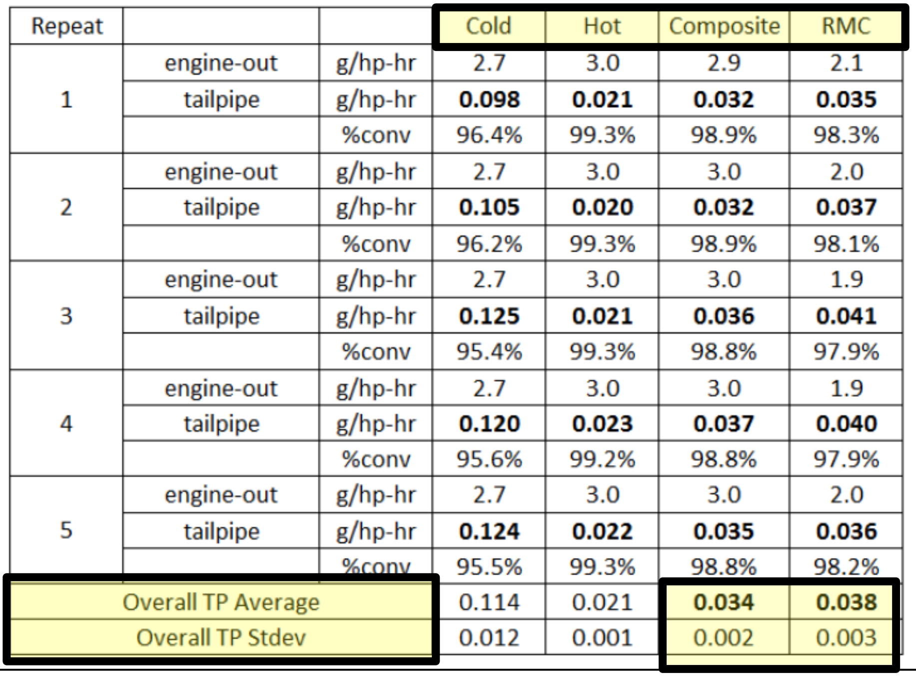
3. The Best Path Forward?

Ultra Low NOx Engine Demonstration at SwRI (SwRI Presentation)

Final ARB Low NO_X Configuration

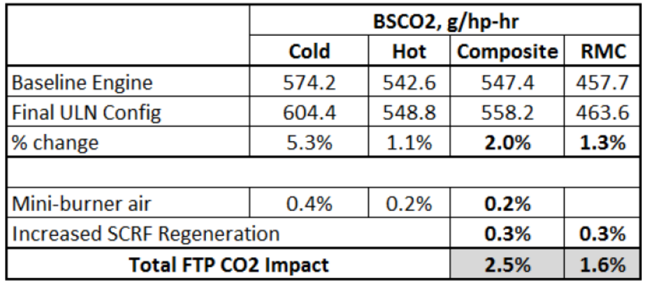


FTP and RMC Results for Final Aged Parts



Repeat			Cold	Hot	Composite	RMC
1	engine-out	g/hp-hr	2.7	3.0	2.9	2.1
	tailpipe	g/hp-hr	**0.098**	**0.021**	**0.032**	**0.035**
		%conv	96.4%	99.3%	98.9%	98.3%
2	engine-out	g/hp-hr	2.7	3.0	3.0	2.0
	tailpipe	g/hp-hr	**0.105**	**0.020**	**0.032**	**0.037**
		%conv	96.2%	99.3%	98.9%	98.1%
3	engine-out	g/hp-hr	2.7	3.0	3.0	1.9
	tailpipe	g/hp-hr	**0.125**	**0.021**	**0.036**	**0.041**
		%conv	95.4%	99.3%	98.8%	97.9%
4	engine-out	g/hp-hr	2.7	3.0	3.0	1.9
	tailpipe	g/hp-hr	**0.120**	**0.023**	**0.037**	**0.040**
		%conv	95.6%	99.2%	98.8%	97.9%
5	engine-out	g/hp-hr	2.7	3.0	3.0	2.0
	tailpipe	g/hp-hr	**0.124**	**0.022**	**0.035**	**0.036**
		%conv	95.5%	99.3%	98.8%	98.2%
Overall TP Average			0.114	0.021	**0.034**	**0.038**
Overall TP Stdev			0.012	0.001	0.002	0.003

GHG Impact Summary



	BSCO2, g/hp-hr			
	Cold	**Hot**	**Composite**	**RMC**
Baseline Engine	574.2	542.6	547.4	457.7
Final ULN Config	604.4	548.8	558.2	463.6
% change	5.3%	1.1%	**2.0%**	**1.3%**
Mini-burner air	0.4%	0.2%	**0.2%**	
Increased SCRF Regeneration			**0.3%**	**0.3%**
Total FTP CO2 Impact			**2.5%**	**1.6%**

- The FTP-based approach also would necessitate early-cycle added heat (e.g., with a 10+kW mini-burner system) and a fuel penalty (2.5%) to achieve higher conversion efficiencies over the first 500 seconds of the test
- **Is it time to think outside the certification testing laboratory?**

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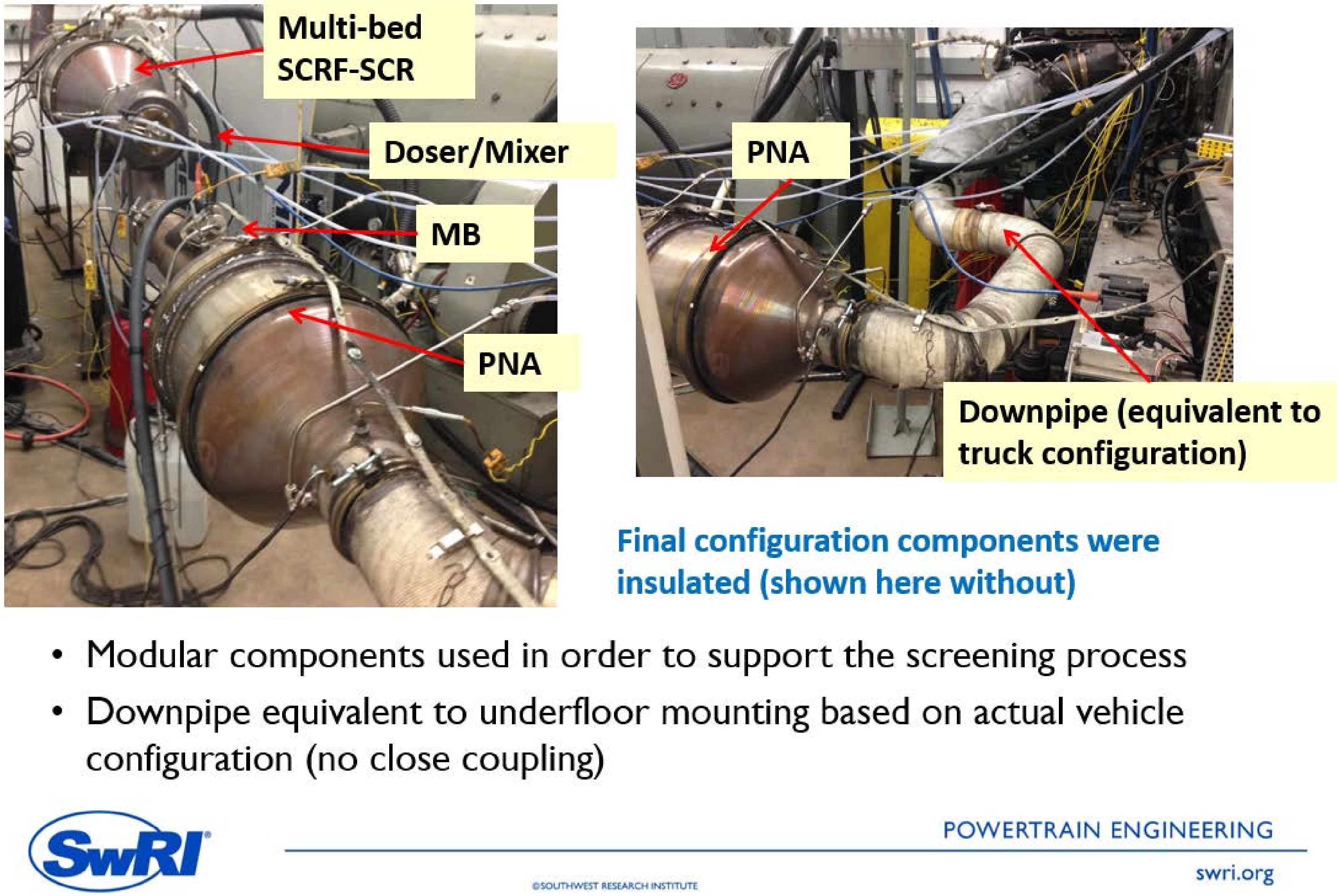
3. The Best Path Forward?

Final ARB Low-NO_x Aftertreatment Configuration (SwRI Presentation)



Final configuration components were insulated (shown here without)

- Modular components used in order to support the screening process
- Downpipe equivalent to underfloor mounting based on actual vehicle configuration (no close coupling)

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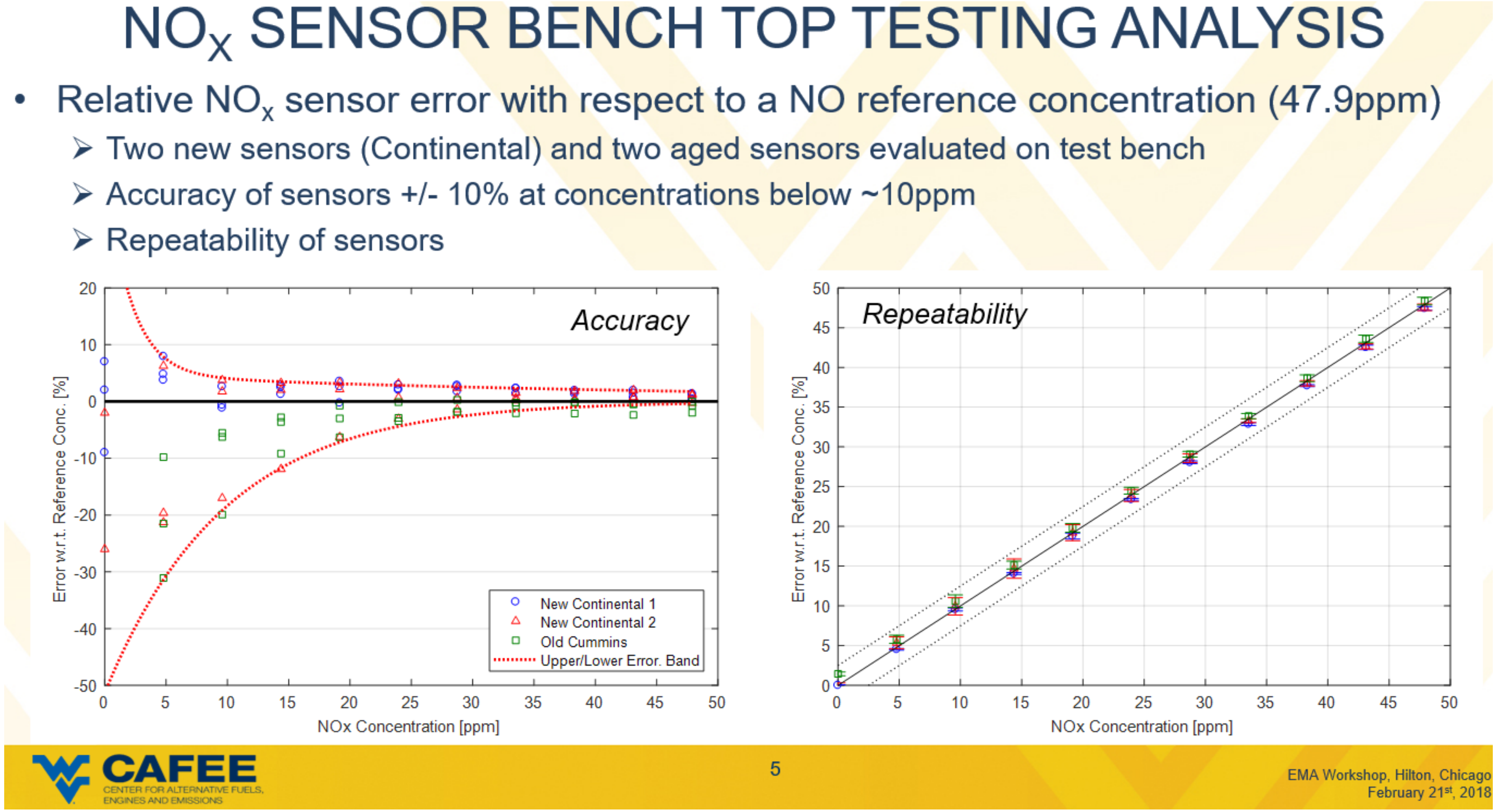
- Is it time to move beyond these types of additional lab-based certification cycles, complexities and configurations?

4. Next Steps?

4. What’s next?
   - develop data-driven real-world in-use NO_x-emissions baseline for “non-credit” HDOH engines/vehicles
   - develop data-driven real-world in-use targeted NO_x reductions
   - develop appropriate in-use metric for compliance
   - develop targeted in-use standards assessed against aggregated in-use emissions data
   - streamline outmoded regulatory requirements and procedures
   - implement a new in-use-focused regulatory paradigm

4. Next Steps?



NO$_X$ SENSOR BENCH TOP TESTING ANALYSIS

- Relative NO$_x$ sensor error with respect to a NO reference concentration (47.9ppm)
  - ➢ Two new sensors (Continental) and two aged sensors evaluated on test bench
  - ➢ Accuracy of sensors +/- 10% at concentrations below ~10ppm
  - ➢ Repeatability of sensors

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EMA Workshop, Hilton, Chicago
February 21st, 2018

- Current and emerging NO$_x$ sensors may be reliable enough (with continued improvements) to enable robust in-use standards and metrics
- Development of the appropriate aggregate in-use compliance standard and the necessary in-use compliance metric for assessing conformity with that standard are core research objectives
- EMA is pursuing that core research

4. Next Steps?

- EMA is funding WVU to equip 100 in-use HDOH 2013 and later MY vehicles operating in California (representing a broad range of applications) with NO_x sensors and data-loggers (with telematic capabilities)
- Real-time in-use emissions data will be gathered for 2-4 weeks from each vehicle
- Those data (perhaps the largest such data set) will be analyzed and aggregated to assess which types of vehicle operations/applications may be associated with potentially “excess” NO_x emissions, and to assess what level of targeted in-use NO_x reductions (and what form of in-use compliance metric) might be warranted and feasible through better optimization of technologies

4. Next Steps?

- Currently, approximately 30 vehicles are being tested, and preliminary data are being assessed

- The WVU research program should be complete within the next several months

4. Next Steps?

The WVU research potentially will inform an initiative to:

i. assess in-use emissions performance over shift-days (or longer?) based on aggregated emissions data from similar vehicle applications/engine families

ii. assess what targeted percentage reduction of aggregate in-use emissions performance might be warranted and feasible (taking the area-specific scope of the non-attainment issue into account)

iii. develop an appropriate in-use sensor-based emissions-compliance metric for assessing aggregate compliance (over shift-days or longer) with the targeted in-use percentage emissions reduction

4. Next Steps?

- To the extent such an in-use focused sensor-based regulatory paradigm can be developed, current regulations derived from and oriented toward laboratory-based compliance programs can be identified for eventual amendment, replacement, phase-out and/or repeal
- This would enable a cost-effective paradigm shift from laboratory-based compliance programs to compliance programs centered around real-world in-use emissions assessments premised on an aggregate in-use compliance metric

Conclusions

- Remaining ozone issues are county/area-specific
- Many factors are influencing the rate of progress for the remaining non-attainment sites, including “ridgeline” conditions, background ozone levels, underestimated VOCs, fertilizer/soil-derived NO_x, and more extreme meteorology
- Current modeling and policies will need to account for those factors

Conclusions

- HDOH NO_x emissions have been reduced dramatically and the relevant in-use fleet (2013 and later MY vehicles) is performing at an aggregate NO_x emissions rate of 0.37 g/bhp-hr (or even lower on a VMT-weighted basis)
- A new additional FTP-based HDOH NO_x standard does not seem well-suited to achieving the type of cost-effective reductions of real-world in-use NO_x emissions that may be warranted and feasible based on a thorough assessment of real-world in-use HDOH NO_x data
- Cold-start emissions account for only 0.4% of aggregate in-use real-world HDOH NO_x emissions, and a cold-start FTP focus can engender a 2.5% fuel penalty

Conclusions

- Next-tier standards need to start with a clear and data-driven understanding of the nature and magnitude of actual real-world HDOH NO_x emissions, and need to be premised on the utilization of real-world data to identify real-world opportunities for additional cost-effective NO_x reductions
- Additional HDOH NO_x reductions will be incremental given the already-low level of in-use emissions, and should be targeted to yield the greatest benefits for the few remaining (yet densely populated) non-attainment counties
- NO_x sensors can be used to measure, track and aggregate the in-use NO_x emissions of manufacturers' HDOH engine/vehicle families and/or manufacturers' specified HDOH vehicle applications

Conclusions

It may be feasible to develop national next-tier HDOH low-NO_x regulations that:

i. are premised on the aggregate in-use NO_x performance of an engine/vehicle family over a shift-day (or work-week or longer)

ii. establish an aggregate in-use NO_x performance standard that is a data-driven percentage lower than the current level of aggregate HDOH in-use NO_x performance (e.g., some percentage below 0.37 g/bhp-hr)

iii. establish a new in-use compliance metric to assess aggregate conformity with the new aggregate in-use NO_x standard

iv. phase-in compliance with the new in-use aggregate NO_x standard to allow for an appropriate transition to the new in-use regulatory paradigm

v. potentially incorporate geofencing where appropriate to maximize NO_x reductions in the few remaining non-attainment counties

vi. include a phase-out of outmoded regulations derived from and oriented toward laboratory-based and cycle-based compliance programs

Conclusions

- Research is underway to inform the potential development of this type of regulatory paradigm shift
- All stakeholders are encouraged to join in assessing the feasibility of this important initiative
- Collaboration can yield a national program that can achieve meaningful and cost-effective nationwide benefits with potential additional targeted in-use NO_x reductions in key nonattainment areas