



Supplement of

Maximum ozone concentrations in the southwestern US and Texas: implications of the growing predominance of the background contribution

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Contents of this file Tables S1 to S8 Figures S1 to S8 Text S1 to S6 Introduction

- 9 This supporting information collects the parameter values derived from fits of Equations 3 and 4 to all ODV time
- series analyzed in this work in Tables S1 to S5. Figures S1 to S6 illustrate some of these fits and provide additional
- 11 data presentations. Text S1 discusses the uncertainty of observation-based and chemical transport model results, and
- 12 Text S2 to S6 discuss additional issues that may affect the accuracy of the observation-based model.

Table S1. Parameter values (with 95% confidence limits) derived from fits of Equation 1 to time series of ODVs time
 series from the isolated rural CASTNET sites.

Site	a (ppb)	b (ppb yr ⁻¹)	c (ppb yr ⁻²)	year _{max}	RMSD (ppb)
Glacier NP	54.9 ± 1.1	0.09 ± 0.16	$\textbf{-0.010} \pm 0.011$	2004 ± 9	1.2
Yellowstone NP	65.9 ± 2.9	$\textbf{-0.31} \pm 0.67$	$+0.007 \pm 0.032$		1.7
Craters of the Moon NM	62.5 ± 3.8	0.16 ± 0.67	$\textbf{-0.009} \pm 0.038$	2009 ± 51	2.4
Lassen Volcanic NP	72.4 ± 2.7	$\textbf{-0.05} \pm 0.35$	-0.016 ± 0.025	1999 ± 11	3.1
Great Basin NP	71.5 ± 2.1	0.14 ± 0.51	$\textbf{-0.020}\pm0.028$	2004 ± 13	2.0
Canyonlands NP	70.3 ± 2.0	0.17 ± 0.46	-0.024 ± 0.024	2003 ± 10	1.7
Grand Canyon NP	72.5 ± 1.3	0.07 ± 0.21	-0.026 ± 0.014	2001 ± 4	1.4
Chiricahua NM	70.1 ± 1.7	0.19 ± 0.29	$\textbf{-0.020} \pm 0.018$	2005 ± 8	1.8
All sites	67.7 ± 1.9	0.09 ± 0.33	$\textbf{-0.018} \pm 0.020$	2003 ± 10	5.9
All sites - normalized	71.3 ± 0.8	0.07 ± 0.13	$\textbf{-0.015} \pm 0.008$	2002 ± 4	2.4

17 Table S2. Parameter values from fits of Equation 3 to time series of percentiles of maximum MDA8 ozone

18 concentration distributions in the CA air basins and calculated from the ozone sondes launched from Trinidad Head

19 CA. The 98th percentile is not included in Figure 2 of the paper, but is included here as it approximates the ODV.

20 RMSD gives the root-mean-square deviations between the observed ozone concentrations and the derived fits.

Data set	<i>a</i> (ppb)	A (ppb)	RMSD (ppb)
	Maxin	num	
San Diego AB	52.6 ± 13.4	58.6 ± 9.7	16.8
SoCAB	66.6 ± 13.4	95.8 ± 9.7	16.7
SFB AB	75.5 ± 9.6	25.1 ± 6.9	11.9
North Coast AB	65.4 ± 7.7	4.6 ± 6.0	12.0
Ozone sondes	76.5		
	98 th perc	centile	
San Diego AB	58.6 ± 5.7	41.0 ± 4.1	7.1
SoCAB	60.8 ± 8.9	87.7 ± 6.4	11.1
SFB AB	70.2 ± 6.5	21.1 ± 4.7	8.0
North Coast AB	58.1 ± 5.7	4.3 ± 4.5	8.9
Ozone sondes	76.5		
	90 th perc	entile	
San Diego AB	54.2 ± 3.5	32.5 ± 2.5	4.4
SoCAB	53.0 ± 5.6	76.6 ± 4.1	7.0
SFB AB	54.8 ± 5.1	18.5 ± 3.7	6.3
North Coast AB	47.6 ± 3.9	4.1 ± 3.0	6.1
Ozone sondes	52.3		
	75 th nero	entile	
San Diego AB	$\frac{195 + 29}{495 + 29}$	27.9 + 2.1	37
SoCAB	50.0 ± 5.7	27.9 ± 2.1 65.0 + 4.1	71
SFR AR	45.6 ± 3.5	144 + 25	43
North Coast AB	42.4 + 3.2	30+25	5.0
Ozone sondes	45.8	5.0 ± 2.5	
Ozone sondes	medi	an	
San Diego AB	$\frac{458+30}{458+30}$	$\frac{11}{215+22}$	37
SoCAB	46.4 ± 5.0	50.8 ± 4.3	74
SFR AR	388 + 28	10.9 ± 2.0	3.5
North Coast AB	37.6 ± 2.0	13 ± 2.0	4 2
Ozone sondes	393	1.5 ± 2.1	
OZONE SONGES	25 th nero	entile	
San Diego AB	$\frac{23}{432+32}$	149 + 23	4.0
SoCAB	45.2 ± 5.2 45.6 ± 7.1	14.9 ± 2.3 34.4 ± 5.1	8.8
SFR AR	43.0 ± 7.1 33 8 + 2 1	86 ± 15	2.6
North Coast AB	33.0 ± 2.1 33.1 ± 2.7	0.0 ± 1.3 0.5 ± 2.1	4.2
Ozone sondes	31.8	0.5 ± 2.1	ч. 2
Ozone sondes	10 th nero		
San Diego AB	$\frac{10}{404+28}$	10.1 ± 2.0	3.5
SoCAB	46.1 ± 6.9	10.1 ± 2.0 18.0 ± 5.0	8.6
SFR AR	40.1 ± 0.9 29.1 + 2.0	77 ± 14	2.5
North Coast AB	29.1 ± 2.0 29.3 ± 2.4	-0.7 ± 1.9	2.5
Ozone sondes	29.3 ± 2.4 25.7	-0.7 ± 1.9	5.7
Ozone sondes			
San Diago AP	215 ± 4.1		6.4
Sali Diego AD	31.3 ± 4.1 13.1 ± 1.1	4.4 ± 3.2 0 1 ± 3.4	0.4 6 0
SUCAD SED AD	$+3.1 \pm 4.4$	0.1 ± 3.4 5 0 ± 0 1	0.9 A 7
SFD AD North Coast AD	22.7 ± 3.0 20.7 ± 2.2	$\begin{array}{c} J. \angle \pm \angle .4 \\ J \otimes \pm J \end{array}$	++./ 5 1
Ozone sondes	20.7 ± 3.3	-2.0 ± 2.0	5.1
Ozone sonues	5.0		

22	Table S3. Parameter values from all fits of Equation 3 to time series of ODVs recorded in the southwestern US.
23	RMSD gives the root-mean-square deviations between the observed ODVs and the derived fits.

Site(s)	<i>a</i> (ppb)	A (ppb)	Npts ^a	RMSD (ppb)	years			
CASTNET								
CASTNET - normalized	68.5 ± 1.5	2.8 ± 1.9	212	2.3	1990-2021			
	Southwest	tern US - rural						
AZ rural	66.6 ± 1.9	5.4 ± 2.5	116	2.3	1990-2021			
Southern UT, Mesquite NV	64.8 ± 3.6	6.5 ± 5.6	66	2.6	1995-2021			
Four Corners area rural	69.6 ± 4.3	-2.7 ± 6.6	126	4.0	1996-2021			
Southern NM rural	69.4 ± 5.5	-1.3 ± 8.0	76	4.7	1992-2021			
CO rural	69.0 ± 3.1	-1.9 ± 4.4	97	4.0	1986-2021			
Southwestern US - urban								
Phoenix	69.0 ± 1.7	9.4 ± 2.3	658	4.8	1990-2021			
Phoenix max	75.2 ± 4.9	10.2 ± 5.4	32	2.9	1990-2021			
Tucson	63.9 ± 1.4	7.5 ± 1.2	264	3.4	1975-2021			
Tucson max	66.2 ± 2.9	9.7 ± 2.4	38	2.3	1980-2021			
Las Vegas	68.0 ± 2.6	11.6 ± 3.8	230	3.1	2000-2021			
Las Vegas max	69.6 ± 6.6	15.4 ± 9.9	22	2.3	2000-2021			
Reno	66.3 ± 2.2	4.9 ± 2.4	169	3.8	1982-2021			
Reno max	67.1 ± 4.8	6.8 ± 4.1	39	3.8	1982-2021			
Salt Lake City	66.6 ± 1.9	11.8 ± 1.7	351	5.2	1977-2021			
Salt Lake City max	68.9 ± 4.3	15.0 ± 3.2	43	3.8	1979-2021			
Albuquerque-Santa Fe	66.2 ± 1.8	4.0 ± 1.7	275	3.8	1981-2021			
Albuquerque-Santa Fe max	68.4 ± 3.0	5.3 ± 2.4	41	2.5	1981-2021			
Denver	69.0 ± 2.1	8.0 ± 1.7	412	6.2	1974-2021			
Denver max	74.7 ± 2.1	9.4 ± 1.4	47	4.3	1974-2021			

^a Npts gives the number of ODVs included in each fit

28	Table S4. Parameter values from fits of Equation 4 to time series of maximum ODVs recorded in southwestern US,	

30 Texas and two other urban areas, TX, New York City, with the *a* parameter held at that derived for all ODVs in the respective urban area. RMSD gives the root-mean-square deviations between the observed maximum ODVs and the

derived fits.

Site(s)	<i>a</i> (ppb)	Awr (ppb)	WF	RMSD	years			
			(ppb)	(ppb)				
Southwestern US - urban								
Phoenix max	69.0	12.9 ± 3.6	1.6 ± 2.5	3.0	1990-2021			
Tucson max	63.9	10.5 ± 1.6	1.4 ± 1.6	2.2	1980-2021			
Las Vegas max	68.0	16.1 ± 6.6	0.8 ± 3.3	1.8	2000-2021			
Reno max	66.3	7.0 ± 1.3	0.6 ± 1.4	3.8	1982-2021			
Salt Lake City max	66.6	15.6 ± 2.0	1.6 ± 2.5	3.7	1977-2021			
Albuquerque-Santa Fe max	66.2	6.0 ± 1.5	1.4 ± 1.7	2.5	1981-2021			
Denver max	69.0	11.0 ± 1.7	4.0 ± 2.5	4.0	1974-2021			
	Othe	r urban areas	6					
Houston max	53.9	54.4 ± 3.2	1.8 ± 2.0	3.6	1995-2021			
Dallas max	57.7	43.0 ± 2.5	2.6 ± 1.2	1.7	2000-2021			
El Paso max	64.6	14.2 ± 2.1	3.2 ± 2.8	4.3	1977-2021			
New York City max	52.2	39.7 ± 2.3	3.1 ± 1.2	3.7	2000-2021			
Atlanta max	49.1	54.4 ± 9.9	1.2 ± 6.1	5.4	1995-2021			
20								

34 Table S5. Parameter values from all fits of Equation 3 to time series of ODVs recorded in nine Texas regions and 35 neighboring states. RMSD gives the root-mean-square deviations between the observed ODVs and the derived fits.

Site(s)	a (ppb)	A (ppb)	Npts ^a	RMSD	years			
				(ppb)				
CASTNET								
CASTNET - normalized	68.5 ± 1.5	2.8 ± 1.9	212	2.3	1990-2021			
	Tex	as Regions						
Dallas region	57.7 ± 3.1	34.6 ± 4.5	422	5.9	1995-2021			
Houston region	53.9 ± 3.2	43.2 ± 4.2	478	6.7	1995-2021			
El Paso region	64.6 ± 1.8	11.5 ± 1.7	366	4.9	1976-2021			
San Antonio region	58.4 ± 4.1	26.6 ± 6.3	138	3.9	2000-2021			
Beaumont-PA-LC	54.7 ± 3.4	28.0 ± 5.1	230	4.0	2000-2021			
So Coast Texas	52.1 ± 4.1	27.5 ± 6.0	63	2.5	2000-2021			
SW Texas	49.8 ± 4.9	18.2 ± 6.9	72	3.1	2000-2021			
Tyler-LV-SP	50.8 ± 4.6	37.3 ± 6.8	89	3.5	2000-2021			
Western rural region	64.9 ± 5.8	3.2 ± 8.1	50	3.5	1989-2017			
	Other V	Vestern States						
Oklahoma	56.6 ± 2.8	25.1 ± 4.4	365	4.0	2000-2021			
Louisiana	54.3 ± 2.3	29.9 ± 3.3	519	4.2	2000-2021			
Arkansas	48.2 ± 4.7	37.5 ± 7.6	141	4.5	2000-2021			
Kansas	56.6 ± 4.2	20.2 ± 6.6	174	4.3	2000-2021			
Nebraska	56.5 ± 4.0	7.4 ± 3.6	146	6.6	1980-2021			
Montana	58.6 ± 1.6	1.25 ^b	99	4.7	1979-2021			
North Dakota	59.6 ± 0.9	1.25 ^b	181	3.6	1982-2021			
South Dakota	62.2 ± 1.7	1.25 ^b	80	4.4	1990-2021			
Wyoming	64.2 ± 0.6	1.25 ^b	227	2.8	1999-2021			

36 ^a Npts gives the number of ODVs included in each fit

^b Fit with *A* parameter value held fixed at this value

43	Table S6.	Two-letter	state	abbreviations
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State		State		State	
Alabama	AL	Kentucky	KY	North Dakota	ND
Alaska	AK	Louisiana	LA	Ohio	OH
Arizona	AZ	Maine	ME	Oklahoma	OK
Arkansas	AR	Maryland	MD	Oregon	OR
California	CA	Massachusetts	MA	Pennsylvania	PA
Colorado	CO	Michigan	MI	Rhode Island	RI
Connecticut	CT	Minnesota	MN	South Carolina	SC
Delaware	DE	Mississippi	MS	South Dakota	SD
District of Columbia	DC	Missouri	MO	Tennessee	TN
Florida	FL	Montana	MT	Texas	TX
Georgia	GA	Nebraska	NE	Utah	UT
Hawaii	HI	Nevada	NV	Vermont	VT
Idaho	ID	New Hampshire	NH	Virginia	VA
Illinois	IL	New Jersey	NJ	Washington	WA
Indiana	IN	New Mexico	NM	West Virginia	WV
Iowa	IA	New York	NY	Wisconsin	WI
Kansas	KS	North Carolina	NC	Wyoming	WY





46 Figure S1. Map of southwestern US rural monitoring sites; the symbols are color-coded according to site elevation as

47 annotated. Lines indicate outlines of southwestern US states (black), urban areas (gold) and interstates and selected

48 49 other major highways (violet). ODV time series from rural areas whose sites are analyzed together as separate data

sets are included in Figure S2. Locations of specific CASTNET sites as well as the Four Corners area are annotated.



51 **Figure S2**. Time series of ODVs recorded in four southwestern US rural areas shown in Figure S1. Symbols 52 indicate different sites as annotated. The southern NM sites are identified as western and eastern by different 53 colors. Green dashed curves indicate fits of Equation 3 to all ODVs, with the parameters derived in the fit 54 annotated. The black solid curves with dashed extensions indicate the fit to the baseline data from Figure 1, 55 normalized to the respective *a* parameter values. The light dashed lines indicate the 70 ppb ozone NAAQS.



56 57

Figure S3. (upper graphs) Time series of ODVs recorded in two of the Texas regions shown in Figure 7 of the 58 manuscript. Grey symbols in each graph indicate all recorded Texas ODVs. Colored symbols indicate the ODVs 59 from each respective area. Upper curves indicate fits of Equation 3 to all ODVs in the area; the parameters derived 60 in these fits are annotated. Lower curves with dashed extensions indicate the fit to the baseline data from Figure 61 1, but here normalized to the respective *a* parameter values. (lower graphs) Time series of ODVs recorded in 62 Oklahoma and the four northern rural states. For Oklahoma upper curve indicates fit of Equation 3 to all ODVs 63 in the state for 2000-2021; the parameters derived in this fit is annotated. Lower curve with dashed extension 64 indicates the fit to the baseline data from Figure 1, normalized to the a parameter value derived for Oklahoma.For 65 the northern states the curves indicate fits of Equation 3 to all ODVs recorded in each state; in these fits the A 66 parameter value is fixed at 1.25 ppb. The derived a parameter values are annotated. In all graphs, the light dashed 67 lines indicate the 70 ppb ozone NAAQS.



Figure S4. Analysis of time series of ODVs recorded in four neighboring states. Grey symbols in each graph indicate all recorded ODVs in the states. Upper curves indicate fits of Equation 3 to all ODVs in the respective states. The parameters derived in these fits are annotated. Lower curves with dashed extensions indicate the fit to the baseline data from Figure 1, normalized to the respective *a* parameter values. Colored symbols in Arkansas indicate the ODVs from a single site that appear to be outliers, and are excluded from the fit.





Figure S5. Comparison of percentage of ODVs greater than 70 ppb recorded at all sites in individual states over two 5-year periods: 2017-2021 (hatched and dark blue bars) and a period 20 years earlier - 1997-2001 (light-colored bars). Individual states are indicated by their two letter abbreviations (defined in Table S6). States are arbitrarily divided between eastern and western regions. Southwestern states, Texas and California are indicated by solid dark blue bars. Five states, all in the western region, reported no ODVs greater than 70 ppb. Format is the same as Figure 9 of the manuscript.



Figure S6. Analysis of time series of ODVs recorded in two eastern urban areas – Atlanta GA and New York City NY. In Georgia ODVs from three groups of sites are indicated with different symbols. Grey symbols in lower graph indicate all recorded ODVs in NY. In the GA graph, upper solid curve indicates fit of Equation 3 to all Atlanta ODVs and the dotted curve indicates fit of Equation 4 to maximum Atlanta ODVs indicated by outlined circles. In NY graph, upper solid curve indicates fit of Equation 4 to the ODVs recorded at the sites representing the maxima in New York City. The parameters derived in the fits to Equation 4 are annotated. Lower curves with dashed extensions indicate the fit to the baseline data from Figure 1, normalized to the respective *a* parameter values. The light dashed lines indicate the 70 ppb ozone NAAQS.

90

91 S1. Uncertainty of observation-based and chemical transport model results

92 Equation 3 provides excellent fits to long-term ozone changes in diverse US regions. As written, Equation 3 has 5 adjustable parameters (a, b, c, A, τ); however 3 of these are constants whose values have been determined in previous 93 94 analyses. Parrish et al. (2020) determined values for $b = 0.20 \pm 0.06$ ppb yr⁻¹ and $c = 0.018 \pm 0.006$ ppb yr⁻² that were 95 the same within derived confidence limits throughout northern midlatitudes. Parrish et al. (2021a) show that these 96 results are consistent with results from 28 published quantifications of changes in average surface ozone 97 concentrations at remote and rural western US locations that are thought to represent background ozone transported 98 into North America. Parrish et al. (2017; 2022) determined a value of $\tau = 21.8 \pm 0.8$ years from the time dependence 99 of ODVs in 7 southern California air basins. This same value (within confidence limits) fit ODV time series throughout 100 the western and northern US (Parrish et al., 2022) and in the northeastern US (Parrish and Ennis, 2019). Substitution 101 of these values for b, c and τ into Equation 3 leaves only 2 unknown parameters: a and A. Section 4 of the paper shows 102 that the resulting Equation 3 with varying a and A parameter values provides excellent fits to all percentiles of the 103 distributions of the maximum MDA8 ozone concentrations in 4 urban and rural California air basins (Figure 2), and 104 also to ODV time series recorded at rural and remote western US CASTNET sites (Figure 1), at urban and rural sites 105 throughout the southwestern US and Texas (Figures 5, 6 and 8), and in surrounding and more distant US states (Figures 106 S2-S4 and S6). Previous work (Parrish et al, 2017; 2022; Parrish and Ennis, 2019) demonstrate that same equation (or 107 one closely related) provides excellent fits to ODV time series recorded urban and rural sites along the entire US West 108 Coast, in the northern rural states and in the northeastern US.

It is widely accepted that photochemical ozone production involves a very complex set of physical and chemical processes, and that complexity causes ambient ozone concentrations to exhibit a highly non-linear dependence upon precursor concentrations (see e.g., Monks et al., 2015). The excellent fits of a 2 parameter equation to a great number of long-term ozone concentration time series recorded in a widely diverse range of environments demonstrates that there is an underlying simplicity to the evolution of ozone concentrations throughout the US, notwithstanding the complexity of ozone photochemistry. Fully understanding the origins of this simplicity may provide a very useful challenge for CTMs studies.

116 In previous papers we have discussed inconsistencies between results of observation-based and chemical transport 117 model (CTM) simulations, and among results from different CTM simulations. Section 3.4 and Figure 6 of Parrish et 118 al. (2017) show seven CTM-derived US background ODV estimates for southern California air basins that varied 119 from ~45 to ~65 ppb, with one outlier of 92 ppb; the observational-derived value of 62 ppb agrees well with one of 120 those model results, although it is larger than most others. In their Section 4.2 Parrish and Ennis (2019) compare 121 results from three CTMs with those from our observational-based approach in five US regions; these comparisons 122 show significant spatial correlation between approaches (r^2 values for different CTMs with the observational-based 123 results vary from 0.31 to 0.90), but the CTMs are, on average, systematically lower by 4 to 13 ppb. Zhang et al. (2020) 124 find disagreements of similar magnitude between CTMs; US background ozone estimates from two state-of-the-art 125 global models differed by 5 ppb on average and up to 15 ppb episodically. These disagreements have led to the 126 increasing recognition that CTMs are not yet able to provide accurate estimates of atmospheric ozone concentrations

- without incorporating additional information from observations; see, e.g., Skipper et al. (2021) and Hosseinpour et al.(2024).
- 129 The results of Hosseinpour et al. (2024) are particularly relevant to the present paper. The authors used a random
- 130 forest machine learning algorithm to improve CTM estimates of US background ozone extreme values (4th largest
- 131 MDA8, i.e., comparable to our US background ODV) in four of the urban areas considered in our analysis (Table S7).
- 132 The original CTM results were lower than the results derived in the present paper from the observation-based model
- 133 by an average of 14 ppb for the three SW US urban areas, and 5 ppb for Houston; after correction the CTM results
- 134 were increased so that they were lower by only to 2 or 3 ppb in all four cities. In the end, the machine learning
- algorithm had forced the CTM to match the observations, so that the CTM was no longer a free running simulation of
- 136 the relevant physical and chemical processes. Instead, the combination of the CTM and the machine learning algorithm
- 137 constituted an elaborate observational-based model. It is encouraging that this alternative observational-based
- approach gave results similar to those derived in this work from our much simpler observational-based model.
- 139 **Table S7.** CAMx simulated 4th highest MDA8 background ozone concentration over April through September 2016
- before and after adjustment by the random forest algorithm reported (Hosseinpour et al., 2024) compared to our
- results for US background ODV in 2016. (Units: ppb)

	Phoenix	Salt Lake City	Denver	Houston
CAMx original simulation (Hosseinpour et al. table 3)	52	51	54	48
Random Forest adjusted CTM (Hosseinpour et al. table 8)	66	63	65	50
US background ODV (this paper)	68	65	67	53

142 Projection of future ozone concentrations by CTM simulation under assumptions regarding the temporal evolution

- 143 of ozone precursor emissions and other relevant model parameters has provided a widely utilized tool for air quality
- 144 policy development. Such projections have also been made by our observational-based model under assumed future
- evolution of the background and anthropogenic ozone contributions; here the parameterized temporal evolution of
- each contribution over the past decades was assumed to continue into the future. Parrish et al. (2017) made such ODV
- 147 projections for seven southern CA air basins (their Figure 8, a portion of which is reproduced here). Those projections
- 148 can now be compared with 8 years of ODVs that have been recorded
- since the projections were made; they are included in the figure to
- 150 the right of the vertical dashed line. The projections had only mixed
- success; there is good agreement with the recent ODVs in the two,

Original Figure 8 of Parrish et al. (2017). Past and projected evolution of the basin ODVs in southern California air basins. The symbols give the annual ODVs for each air basin, and the solid curves indicate the fits of their Equation 1, with the parameters from their Table 4, to the corresponding ODVs with projections to the year 2058. The horizontal dashed line indicates the NAAQS. Added here: Eight more recent years of ODVs are included for each of the 4 coastal air basins; they lie to the right of the vertical dashed line. The results for the 3 inland air basins have been removed for clarity. The larger asterisk symbols indicate CTM-derived ODV projections for the two more urbanized air basins



- 152 less urbanized (North and South Central Coast) air basins, but the projections did not capture the observed increases
- 153 of the recent ODVs in the more urbanized San Diego and South Coast air basins. However, in these two air basins,
- 154 the CTM predictions (indicated in the figure) were even less accurate. The California Air Resources Board (CARB,
- 155 2019) staff report for the Southern California AB predicted that the ODV would be 80 ppb by 2023, some 26 ppb
- below the observed value of 106 ppb, while the Parrish et al. (2017) projection was found to be too low as well, but
- 157 at 90 ppb was 10 ppb closer than the CTM. For the San Diego AB the CARB (2017) staff report predicted that the
- 158 ODV would fall to 75 ppb in the year 2017, Parrish et al. (2017) projected 78 ppb, while 84 ppb was actually recorded.
- 159 The cause of the unexpected increases in the urbanized air basins remains largely unexplained (Wu et al., 2023).
- 160 Parrish and Ennis (2019) projected maximum ODVs in eight northeastern US states (dashed curves in an expanded 161 portion of their Figure 10 reproduced below) following the last year with ODVs available to them (2017). Here we 162 evaluate the fidelity of those projections. For our analysis, ODVs from 2018-2022 or 2023 (depending on the state) 163 had become available; we have added those ODV symbols to the figure shown here. Most of the more recent ODVs 164 agree well with the projections, but in two states (Connecticut and New York) they deviate noticeably. These 165 deviations are due to ODVs from coastal sites on the Long Island Sound, not from the major urban centers in the 166 states. This suggests that photochemical ozone production from precursors trapped within the shallow marine 167 inversion layer significantly impact maximum ozone concentrations in air transported ashore to these sites. Insights 168 such as this make simple observation-based models particularly useful. Parrish and Ennis (2019) also projected the 169 year in which ODVs would drop to the NAAQS (their table reproduced below). We have added a final column to that 170 table indicating when the ODVs actually reached that limit. Again, with the exception of the same two states, 171 reasonable agreement between the projections and reality is found, especially when the 2 to 4 ppb RMSD of the ODVs
- 172 about the fits are considered. Projections of the future
- 173 development of ODVs from our model can provide policy
- 174 relevant information, although (as with any model projection)
- 175 that information must be carefully evaluated.

Original Table 3 of Parrish and Ennis (2019). Results of leastsquares fits of Equation 1 to the state maximum ODVs illustrated Figure 10; y_0 and τ were held constant at 45.8 ppb and 21.9 years, respectively. The absolute root-mean-square deviations between the observed ODVs and the derived fits are indicated. Year_{NAAQS} indicates the projected year that the fit to the state maximum ODV drops to the NAAQS of 70 ppb. **Column added here:** Last year of recorded ODV \geq NAAQS.

State	<i>A</i> *(ppb)	RMSD (ppb)	Year _{NAAQs}	Last year ODV ≥
				NAAQS
Connecticut	61 ± 7	5.8	2021	>2023
Maine	48 ± 4	3.2	2015	2010
Massachusetts	53 ± 5	3.9	2017	2019
New Hampshire	43 ± 4	3.0	2013	2012
New Jersey	64 ± 5	3.7	2021	2022
New York	58 ± 4	3.0	2019	>2023
Rhode Island	52 ± 4	3.4	2017	2019
Vermont	35 ± 3	2.1	2008	2009



Original Figure 10 of Parrish and Ennis (2019). Time series of maximum ODVs reported from any site within each of the eight northeastern states. The solid curves are fits of Equation 1 to the respective colored symbols for the 2000-2017 period. The derived *A** values from these latter fits are given in Table 3. The dashed lines are projections of the solid curves. **Added here: 5** or 6 more recent years of ODVs are included in each state.

176 S2. Relationship of US background ODV to ozone exceedance days

177 (Note: A previous version of some of this material was originally included in the Supplement to Parrish et al., 2022 -

178 <u>https://www.tandfonline.com/doi/suppl/10.1080/10962247.2022.2050962?scroll=top&role=tab</u>)

179 One important question lacks a definitive answer: Are the four days that record the highest MDA8 ozone 180 concentrations, i.e., the days that determine the ODV at present, the same four days that correspond to the highest US 181 background, i.e., the days that would determine the ODV in the absence of anthropogenic precursor emissions? In 182 other words, do the present highest ozone days also correspond to the days with the largest background ozone? 183 Photochemical models provide a direct answer, but given the uncertainty associated with modeled background ozone 184 concentrations on specific days (estimated as >10 ppb by Jaffe et al., 2018) this answer is likely not reliable. From our 185 observational perspective, we cannot directly answer this question; however observation-based analyses can 186 illuminate this question. It is useful to consider a heuristic example based on artificial data that illustrates some 187 important considerations when considering this issue.

Figure S7 represents an imaginary world that has no meteorological variability; every day is exactly like every other, except that there are gradual seasonal changes. The upper graph shows how MDA8 ozone might vary seasonally at a particular measurement site (black curves decreasing in amplitude over time due to emission controls.) With no US anthropogenic precursor emissions, ozone would equal the US background ozone (blue curve, assumed to average 40 ppb with a sinusoidal variation of 20 ppb amplitude), and would vary smoothly over the year, repeating identically each year. The US background ODV (i.e., the quantity we estimate in our work, which here is assumed constant) would then be given by the blue symbol very near the peak of the blue curve.

195 US anthropogenic ozone precursor emissions in 2000 are assumed to increase the background ozone by an amount 196 given by the red curve (average 35 ppb with a sinusoidal variation of 40 ppb amplitude). The blue and red curves are 197 3 months out of phase, in approximate accord with observed Northern Hemisphere background free-tropospheric 198 ozone concentrations that peak in the spring (April/May) and many urban areas that peak in mid to late summer. The 199 total ozone measured in 2000 would then be given by the highest black curve, and the site ODV given by the highest 200 black symbol. Subtraction of the US background ODV from the site ODV gives the US anthropogenic ODV 201 enhancement in 2000 as indicated by the red arrow. Notably, that quantity (60 ppb) is smaller than the US 202 anthropogenic contribution to the ODV in 2000 (~71 ppb, given by orange arrow). This illustration lies at the heart of 203 a common misunderstanding: the US background ODVs reported in this work are not the same as the current 204 contributions of background ozone to current ODVs, because the maxima of background ozone and anthropogenic 205 enhancements are offset from each other in the time of year when they occur. Nevertheless, when considering progress 206 in reducing US anthropogenic precursor emissions, the US background ODV is still germane for considerations of 207 compliance with the NAAQS.

209 Now we assume that the US anthropogenic 210 ozone production decreases exponentially with a 211 time constant of 20 years. Consequently, the total 212 measured ozone (black curves) decreases year-by-213 year, with the ODVs (black symbols) also 214 decreasing, and simultaneously shifting to earlier in 215 the year, and approaching the US background ODV 216 (i.e., the blue symbol).

217 As shown in the lower graph of Figure S7, the 218 changes in site ODVs (black symbols in both 219 graphs) are well fit by an exponential decay, as 220 given by Equation 3 of the manuscript. The derived 221 parameter $a = 60.0 \pm 0.4$ ppb agrees with the 60 ppb 222 maximum of the blue curve, and the parameter A =223 59.8 ± 0.3 ppb agrees with the 60 ppb magnitude of 224 the year 2000 US anthropogenic ODV enhancement 225 (red arrow in figure).

226 An important conclusion from this illustrative 227 example is that confusion can arise if a clear 228 distinction is not made between the US 229 anthropogenic ODV enhancement in 2000 (i.e., the 230 red arrow), the anthropogenic contribution to the 231 site ODV (i.e., the orange arrow) and the 232 anthropogenic ozone production (i.e., the red curve, 233 which varies during the year).

234 One implication of this example is that episode 235 days (i.e., those exhibiting the highest ozone) in 236 earlier decades are not seasonally coincident with 237 present episode days, and neither of those sets of 238 episode days is seasonally coincident with future 239 episode days. This is due to the growing relative 240 importance of background ozone (which is larger in 241 spring and early summer) as the magnitude of local 242 and regional photochemical production, which is



Figure S7: Schematic variation of ozone at a measurement site. **(top)** Blue and red curves give the assumed constant US background ozone and the US anthropogenic ozone production in the year 2000, respectively. The black curves are the total observed ozone in the year 2000 and at progressively later 4-year intervals. The US background ODV is given by the blue symbol, and the site ODVs are given by the black symbols at the peak of their respective curves. The year 2000 US anthropogenic ODV enhancement and anthropogenic ODV contribution are given by the red and orange arrows, respectively. **(bottom)** Temporal evolution of site ODVs from upper graph, fit to Equation 3 of the manuscript, with derived parameters annotated.

larger later in the summer, decreases. In actuality, episode days in southern California air basins have been observed to systematically move toward the spring from later in the summer; Parrish et al. (2017) show that when monitoring began in the South Coast Air Basin of California (i.e., the Los Angeles urban area) in the early 1970s, the average ozone episode day occurred in late July, but had progressively moved to early July by 2015. This seasonal shift of episode days adds considerable uncertainty to photochemical modeling for State Implementation Plan (SIP)development. The meteorological conditions (including the background ozone contribution) on the days that will

- 249 require the greatest emission control efforts to lower the MDA8 ozone to the NAAQS is uncertain. The common
- assumption that those days correspond to the present maximum episode days is not valid, since days with higher
- 251 background ozone concentrations may require even greater emission reductions to reach the NAAQS, even if they
- now are not the days when the highest ozone is observed.

It should also be noted that an observation-based analysis has indicated a significant positive correlation between maximum observed ozone concentrations and high background ozone concentrations. Parrish et al. (2010) show that MDA8 ozone measured at surface sites in California's Northern Sacramento Valley correlates positively (correlation coefficients as large as +0.53 at valley sites and +0.71 at an elevated surface site) with baseline ozone concentrations measured by sondes launched from the upwind location at Trinidad Head on the northern California coast. This analysis suggests that the days that determine the ODV will progressively tend to be the days of highest US background ozone concentration as anthropogenic ozone contributions are further reduced.

260 It has been argued (e.g., see Section 1.8 of US EPA, 2020) that the highest US ozone concentrations occur during 261 periods of low background ozone contributions. This argument is based on the reasoning that the largest background 262 ozone contributions occur on spring days with strong convective mixing when ozone generated in the stratosphere or 263 during long-range transport of Asian or natural precursors in the upper troposphere are more readily mixed to the 264 surface. In contrast, the highest US ozone concentrations are thought to occur during multiday episodes under stagnant 265 conditions when an air mass remains stationary over a region abundant in anthropogenic ozone precursor sources. 266 However, this reasoning does not apply to the southwestern US, because surface ozone concentrations are strongly 267 correlated with higher ambient temperatures, and higher temperatures are correlated with deeper atmospheric 268 boundary layers (ABL) in this area. Examination of the climatology of ABL heights over western North America 269 shows that in summer, when most ozone NAAQS violations occur, boundary layers tend to be deepest (see figure 5 270 of von Engeln and Teixeira, 2013). Deeper boundary layers develop due to greater vertical mixing driven by strong 271 surface heating (i.e., entrainment). A recent paper (Langford et al., 2022) emphasizes that layers with elevated ozone 272 concentrations above Las Vegas were commonly entrained into the ABL and thereby contributed to mean MDA8 273 regional background ozone concentrations of 50-55 ppb; note that our paper analyzes ODVs, which represent ~98th 274 percentile MDA8 concentrations, and, as expected, the US background ODVs that we quantify are substantially larger 275 than the 50–55 ppb mean background ozone discussed by Langford et al. (2022).

276 Photochemical modeling in support of air quality policy development has generally focused on days exhibiting

the largest MDA8 ozone concentrations. This choice is based on the implicit assumption that such days represent the

278 meteorological conditions under which it will be most difficult to reduce the MDA8 to the NAAQS. Importantly, the

- 279 US background ODV that is the focus of our analysis may not occur on those same days. Photochemical modeling
- 280 on days with larger US background ODVs will be very informative, but such days are difficult to specifically

identify.

282 S3. Approximation of long-term change of US anthropogenic ODV enhancements by an exponential decrease

An exponential function is chosen to approximate the long-term decrease of US anthropogenic ODV enhancements because it a) is consistent with our physical understanding of the drivers of urban and rural ozone concentrations, b)

- is a continuous function, c) is mathematically as simple as possible (i.e., has the fewest possible unknown parameters),
- and d) successfully accounts for a large fraction of the variance in recorded ODV time series throughout the US.
- 287 Any functional form selected for interpretation of an ODV time series must be consistent, first, with a background 288 contribution below which ODVs cannot be reduced by U.S. precursor emission controls alone, and second, with ODVs 289 that have been enhanced above that background due to a pollution contribution, an enhancement that has continually 290 decreased due to decades-long precursor emission reduction efforts. Equation 3 of the manuscript is designed to follow 291 this physical picture. More generally, examination of ozone observations in US urban areas reveals similar trends 292 throughout the country, with general decreases in all areas. A simple intuitive argument suggests that an exponential 293 decrease in the pollution ozone contribution is to be expected. When emission controls are initiated, early progress 294 can be rapid, since there are large emission sources that evolved initially with no plans for their control. As an 295 illustrative example, when emission controls are first initiated it might be possible to reduce the pollution ozone 296 contribution by half in the first 15 years of control efforts. After that period reducing emissions will be harder, since 297 the most easily controlled emissions have been addressed. During the next 15 years, it might be possible to again 298 reduce the remaining pollution ozone contribution by half (i.e., reduction of 25% of the original). A similar argument 299 can be applied to each successive 15-year period. If this example were realistic, then the emission reductions would 300 follow an exponential function, with $\tau = 21.6$ years, close to the value of $\tau = 21.8 \pm 0.8$ years reported by Parrish et 301 al. (2022). Simply put, the expected increasing difficulty of reducing emissions by an absolute amount implies an 302 approximately exponential decrease in the impact of those emissions.
- Despite the large variability of tropospheric ozone on a wide spectrum of temporal scales, the underlying longterm changes in ODVs are expected to be continuous, since they are determined by slowly varying drivers such as changes in anthropogenic precursor emissions, land use (which affects natural precursor emissions), and climate. Exceptions might include rapid societal changes, such as occurred during the COVID-19 epidemic response, and volcanic eruptions; however, no discontinuous long-term changes have been encountered in all of the US ODV time series we have analyzed. Thus, the choice of the exponential function, which is continuous, is again indicated.
- 309 The exponential term of Equation 3 $A \exp(-t/\tau)$ with two parameters is the simplest possible functional form
- 310 that can capture the behavior of the pollution enhancement. Each ODV is a three-year average; hence a three-decade
- 311 ODV time series provides only 10 independent data. The ODVs have significant short-term variability (e.g., Guo et
- al., 2018), so an attempt to quantify systematic, long-term changes from available ODV time series requires fitting
- 313 to no more than a simple mathematical function for that quantification. That is, to yield precise determinations of the
- 314 values of the function's parameters the function must have as few unknown parameters as possible. A linear
- 315 function, also with two parameters slope and intercept is often utilized for time series fits; it is as mathematically
- 316 simple as an exponential function, but a linear fit to a decreasing trend will eventually become negative, and
- therefore cannot generally be consistent with a positive background contribution. A linear decrease that ends when it
- 318 intersects a background function, such as a constant or the function given by the first three terms of Equations 3 and

- 319 4 of the manuscript, requires only two parameters, but the resulting function is not continuous. Likewise, piece-wise
- 320 linear fits are not continuous, and generally require at least four parameters to specify. Any other function that might
- 321 be applied (e.g., a polynomial fit) would require more than two parameters. From a simplicity and continuity
- 322 perspective, the chosen exponential function is uniquely suited for quantifying a decreasing ODV time series.
- 323 Finally, experience has shown that an exponential function gives excellent fits to the last two to five decades of
- 324 ozone observed in US urban areas. In their section 2.4 Parrish et al. (2017) present a multivariate fit of Equation 3
- 325 (but with a constant background term) to maximum ODV time series in seven southern California air basins over 35
- 326 years; the r^2 value for that fit is 0.984. In a similar analysis Parrish and Ennis (2019) find an r^2 value of 0.89 for a
- 327 shorter (17 year) period of time series of maximum ODVs recorded in eight northeastern states. Section S6 below
- 328 discusses similar analyses for ODV time series analyzed in this manuscript, and again find large r^2 values 0.94 for
- 329 eight Texas regions and 0.79 for the maximum ODV time series in eight southwestern US urban areas. These large
- r^2 values demonstrate that an exponential function accurately captures a large fraction (approximately equal to the
- respective r^2 values) of the variance in the ODV time series in all US regions that we have investigated. These
- 332 considerations demonstrate that an exponential function is a very effective choice for analysis of long-term ozone
- time series.

334 S4. Differing rates of decrease of anthropogenic precursor emissions are not directly treated

Equation 3 includes only a single term to account for the influence of decreasing anthropogenic emissions on ODVs; that term depends on a single exponential time constant, τ . However, different anthropogenic emission sectors may have differing time evolution of emissions, which may be expected to be reflected in the temporal evolution of ODVs. In effect, τ in Equation 3 is assumed to represent an average, overall response of ODVs to decreasing anthropogenic emissions.

340 In this and previous work we discuss the impact of two anthropogenic emission sectors that have not decreased. 341 First, southern California has regions of very intensive agricultural activity - the Imperial Valley in the Salton Sea Air 342 Basin, the San Joaquin Valley Air Basin, and the Salinas Valley in the North Central Coast Air Basin; Parrish et al. 343 (2017; 2022) note that derived a parameter values are biased high by ~ 5 to 12 ppb in these locations, and thus cannot 344 be interpreted as direct determinations of the US background ODV. Second, the development of Equation 4 provides 345 an approximate treatment of the increasing influence of wildfires on ODVs; a small wildfire influence (WF up to 4 346 ppb) could be discerned in the region studied in this work, and a larger influence (~10-15 ppb) was approximately 347 quantified in urban areas of the Pacific Northwest (Parrish et al., 2022).

There are additional anthropogenic emission sectors that may not have decreased over time, and hence could possibly bias our estimate of US background ODVs. These sources include emissions associated with oil and gas (O&G) exploration, drilling and production, which have increased over the past two decades in some regions of the Western US. In addition, nonroad equipment, such as construction equipment, lawn and garden equipment, and VCP emissions (Coggon et al., 2021) may be important in urban areas, and they have not received as much regulatory attention as anthropogenic emissions. The Supplement Section S5 of Parrish et al. (2022) analyzes time series of ozone observations in the Bakken O&G basin located in North Dakota, and examines correlations of derived *a* and *A* 355 parameter values in West Coast urban areas. That discussion found no indications of a significant bias arising from 356 these emissions sectors.

S5. Value of exponential decrease time constant, τ, determined in Southern California, applied to the entire southwestern US

We have not found it possible to precisely determine the three parameters (*a*, *A* and τ) of Equation 3 from a fit to most available US ODV time series. The analysis in the manuscript assumes that τ in the southwestern US and Texas (as well as other states considered) is the same value as derived for southern California ($\tau = 21.8 \pm 0.8$ years). This assumption follows from the perspective of other states closely following the lead of California in emission control efforts, and is supported by the excellent fits provided by Equation 3 to ODV time series throughout the US, as discussed above in Section S4.

365 Generally, it is not possible to precisely determine the three parameters (a, A and τ) of Equation 3 from a fit to 366 most available US ODV time series. Here, however we conduct two iterative, multivariate regression analyses, 367 similar to that described in Section 2.4 of Parrish et al. (2017) and applied by Parrish and Ennis (2019) to the 368 northeastern US. Simultaneous fits to several ODV time series improve the precision of the parameter 369 determinations, allow alternate derivation of some parameter values, and provide alternate estimates of confidence 370 limits for the derived parameter values. Two separate analyses, each analyzing eight ODV time series, are presented. 371 The first analysis fits Equation 3 to ODV time series from the first eight Texas regions listed in Table S5 and 372 illustrated in Figures 8 and S4; the western rural region is omitted due to its small range of recorded ODVs. An 373 ODV time series for each region is obtained by averaging all ODVs collected in that region for each year of the 374 temporal ranges indicated in Table S5. A separate exponential time constant, τ_{Ho} , is derived for the Houston region, 375 and a single parameter value for τ is derived for the other seven regions. Values of these two τ values and 16 total 376 separate *a* and *A* parameter values for each of the eight regions are optimized in an iterative process that minimizes 377 the sum of the squares of the deviations between the fit and the original mean ODV time series. The second analysis 378 fits Equation 4 to the maximum ODV time series in the seven southwestern US urban areas discussed in Section 4.3 379 and plotted as light red solid circles in Figures 5 and 6, and the maximum El Paso ODV time series plotted in Figure 380 8. A similar iterative process attempts to optimize single common parameter values for τ and the wildfire 381 proportionality constant (i.e., the factor of 0.03 in Equation 4) for all areas, and separate a and A parameter values of 382 each of the eight regions. For both analyses the 18 derived parameter values are given in Table S8, and Figure S8 383 compares the fits of Equations 3 and 4 to the original ODV time series, both for the original fits discussed in the 384 manuscript (upper graphs) and for the multivariate analyses (lower graphs).

The three derived τ values (18.4 to 19.1 years) are up to 16% smaller than the southern California value of 21.8 ± 0.8 years, and are outside the 95% confidence limit of the California value. However, it is very difficult to force convergence of the Texas multivariate fit, and not possible for the southwestern US analysis due to anti-correlations between parameters. Notably, the agreement between the *a* and *A* parameter values between the original analysis (assuming derived $\tau = 21.8 \pm 0.8$ years) and the multivariate analysis (83% overall) is usually within the confidence limits of the original analysis, and these multivariate fits provided only very modest improvements over the original

- 391 fits in the overall r² and RMSD values (compare final two rows in Table S8). Given this overall agreement, we are
- 392 confident in our application of the southern California value of τ throughout the entire region studied in this work.
- 393 Table S8. Parameter values derived from multi-variate fits described in Section S3. All units are ppb ozone unless
- 394 otherwise noted, except for the dimensionless parameter, r^2 .

Texas region	Original fits ^a	Multi-var fit	SW US urban area	Original fits ^b	Multi-var fit°
τ (years)	21.8 ± 0.8	18.9 ± 0.9	τ (years)	21.8 ± 0.8	18.4 ± 0.7
$ au_{Ho}$ (years)	21.8 ± 0.8	19.1 ± 2.2	prop. const. (year ⁻¹)	0.03	0.116 ± 0.19
Dallas - A	34.6 ± 4.5	30.3 ± 1.7	Phoenix $-A_{WF}$	12.9 ± 3.6	12.8 ± 1.9
Dallas - <i>a</i>	57.7 ± 3.1	61.6 ± 1.3	Phoenix - a	69.0 ± 1.7	70.5 ± 1.7
Houston - A	43.2 ± 4.2	39.1 ± 1.7	Tucson - A_{WF}	10.5 ± 1.6	10.6 ± 1.3
Houston - a	53.9 ± 3.2	57.9 ± 1.3	Tucson - <i>a</i>	63.9 ± 1.4	63.1 ± 1.6
El Paso - A	11.5 ± 1.7	9.2 ± 0.6	Las Vegas - AWF	16.1 ± 6.6	16.8 ± 3.3
El Paso - a	64.6 ± 1.8	66.6 ± 1.0	Las Vegas - <i>a</i>	68.0 ± 2.6	67.6 ± 2.1
San Antonio - A	26.6 ± 6.3	25.0 ± 2.2	Reno - AWF	7.0 ± 1.3	6.8 ± 1.2
San Antonio - a	58.4 ± 4.1	60.4 ± 1.4	Reno - <i>a</i>	66.3 ± 2.2	66.1 ± 1.6
BeauPA-LC - A	28.0 ± 5.1	25.5 ± 2.2	Salt Lake City - AWF	15.6 ± 2.0	14.9 ± 1.0
BeauPA-LC - a	54.7 ± 3.4	57.2 ± 1.4	Salt Lake City - a	66.6 ± 1.9	66.3 ± 1.5
So Coast Texas - A	27.5 ± 6.0	25.6 ± 2.2	AlbuquerSF - A_{WF}	6.0 ± 1.5	6.9 ± 1.1
So Coast Texas - a	52.1 ± 4.1	54.2 ± 1.4	AlbuquerSF - a	66.2 ± 1.8	64.7 ± 1.5
SW Texas - A	18.2 ± 6.9	16.7 ± 2.1	Denver - AwF	11.0 ± 1.7	13.4 ± 0.8
SW Texas - a	49.8 ± 4.9	51.6 ± 1.4	Denver - <i>a</i>	69.0 ± 2.1	64.5 ± 1.5
Tyler-LV-SP - A	37.3 ± 6.8	33.8 ± 2.2	El Paso - A_{WF}	14.2 ± 2.1	15.1 ± 0.9
Tyler-LV-SP - a	50.8 ± 4.6	54.2 ± 1.4	El Paso - <i>a</i>	64.6 ± 1.8	62.3 ± 1.5
$r^{2 d}$	0.934	0.936	$r^{2 d}$	0.770	0.794
RMSD ^d	2.65	2.61	RMSD ^d	3.42	3.24

^a Fits described in Section 4 of the paper. Values are reproduced from Table S5.

^b Fits described in Section 4 of the paper. Values are reproduced from Tables S3 and S4.

^c Multivariate fit did not converge; these results were obtained after a large number of iterations of the fitting
 routine.

 $\frac{d}{r^2} \text{ and RMSD are the parameters for the linear regression fit between the actual ODVs and the fit function, as shown in Figure S8.$





402

Figure S8. Comparison of observed ODVs with those from fits. The Texas regional and southwestern US urban time series are on the left and right, respectively. The fits to individual time series from the paper are at the top and the simultaneous multivariate fits to all of the time series are at the bottom. Black lines give the linear fit to all points with the intercept held at zero; the slopes of all lines are within 0.0013 of unity, the value expected for a perfect fit. The iterative process was not able to locate a unique minimum for the sum of the squares of the deviations for the 18 parameter fit to the southwestern US urban time series; this is attributed to poor constraints on all 18 parameters in the that data set.

410 S6. Effect of not considering the US Exceptional Event Rule

411 In this work we utilize the ODVs tabulated in the data archive of the US EPA to quantify the maximum ozone

- 412 concentrations impacting surface monitoring sites, and to determine whether a site is approaching or exceeding the
- 413 NAAQS. It should be noted that if measurement data are influenced by exceptional events, such as wildfires (e.g.,

- 414 Jaffe et al., 2013) or stratospheric ozone intrusions (e.g., Langford et al., 2017), those data can, in principle, be
- 415 removed from the MDA8 monitoring record, as uncontrollable "exceptional events", thereby affecting the ODV
- 416 archive. More details of the Exceptional Events Rule can be found on the US EPA website: <u>https://www.epa.gov/air-</u>
- 417 quality-analysis/treatment-air-quality-data-influenced-exceptional-events-homepage-exceptional. If a significant
- 418 number of ODVs were affected by excluded data, then the ODV archive would not faithfully reflect the actual time
- 419 series of maximum ozone concentrations, or the true relationship of the ozone concentrations at a site to the
- 420 NAAQS. Data are excluded when the US EPA concurs with a state's exceptional event demonstration.
- 421 The US EPA apparently does not maintain a data base of exceptional event concurrences, but so far as we can
- 422 determine from an internet search, at the time of this writing, the US EPA has concurred with only one ozone
- 423 exceptional event demonstration in the five southwestern US states plus TX and CA examined in this paper since the
- 424 implementation of the 2016 Exceptional Events Rule. That event was on September 2 and 4, 2017 when wildfires in
- 425 the Pacific Northwest impacted the National Renewable Energy Laboratory (NREL) ozone monitoring site operated
- 426 in the greater Denver urban area. As a result of this concurrence the ODV at that site would be reduced by 1 ppb for
- 427 the years 2017 (from 80 to 79 ppb) and 2019 (from 77 to 76 ppb). In 2017, but not in 2019, this site recorded the
- 428 maximum ODV in the Denver area, so the urban maximum ODV would be reduced by 1 ppb in 2017, but not
- 429 affected in 2019. According to the statistics compiled by David et al. (2021), there were 5 other exceptional events
- 430 totalling 14 days to which the EPA concurred in 2000-2015 under an earlier exceptional event rule; thus, there has
- 431 been on average only 1 exceptional event every 3 years successfully removed from nonattainment consideration
- 432 within the seven state region.
- 433 In summary, archived ODVs can be reduced by US EPA exceptional event concurrences; however, to date
- 434 concurrences have been extremely limited, and therefore have not significantly affected the analysis presented in
- 435 this paper. However, future concurrences may possibly affect application of the present analysis approach to coming
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