Table S1. Information for EPA AQS sites, including site number, location, site name, and urban setting. Locations are shown on the map in Figure 1. Urban settings are classified into three categories: suburban, urban, and rural.

Site #	AQS Site	Location	AQS Site Name	Location
	Number			Setting
1	04-013-1003	33.41018, 111.865	Mesa	Suburban
2	04-013-1004	33.56031, -112.066	North Phoenix	Urban
3	04-013-1010	33.45244, -111.733	Falcon Field	Rural
4	04-013-19	33.48378, -112.143	West Phoenix	Suburban
5	04-013-2001	33.57453, -112.192	Glendale	Rural
6	04-013-2005	33.70639, -111.856	Pinnacle Peak	Suburban
7	04-013-3002	33.45797, -112.047	Central Phoenix	Urban
8	04-013-3003	33.47968, -111.917	South Scottsdale	Suburban
9	04-013-4003	33.40314, -112.075	South Phoenix	Urban
10	04-013-4004	33.29896, -111.884	West Chandler	Suburban
11	04-013-4005	33.41123, -111.935	Tempe	Urban
12	04-013-4008	33.82169, -112.017	Cave Creek	Rural
13	04-013-4010	33.63718, -112.342	Dysart	Suburban
14	04-013-4011	33.36985, -112.621	Buckeye	Rural
15	04-013-7003	33.29023, -112.161	St Johns Station	Rural
16	04-013-7020	33.48813, -111.855	Senior Center Station	Rural
17	04-013-7021	33.50799, -111.755	Red Mountain Station	Rural
18	04-013-7022	33.47461, -111.806	Lehi Station	Rural
19	04-013-7024	33.50813, -111.839	High School Station	Rural
20	04-013-9508	33.9828, -111.799	Humboldt Mountain	Rural
21	04-013-9702	33.54558, -111.61	Blue Point	Rural
22	04-013-9704	33.61092, -111.725	Fountain Hills	Suburban
23	04-013-9997	33.50383, -112.096	JLG Supersite	Urban

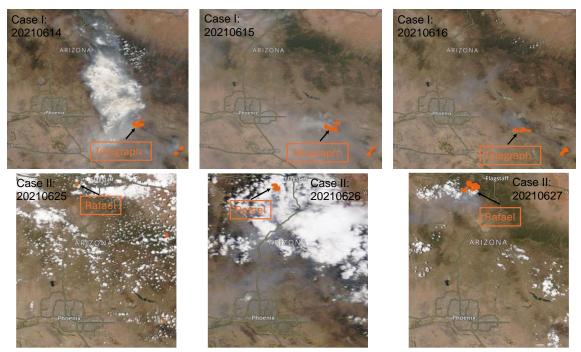


Figure S1. Screenshots from the MODIS Terra Corrected Reflectance map overlaid with MODIS fires and thermal anomaly products (orange area), generated using Worldview available at worldview.earthdata.nasa.gov. The top panel shows Case I from June 14 to 16 (2021), and the bottom panel shows Case II from June 25 to 27 (2021).

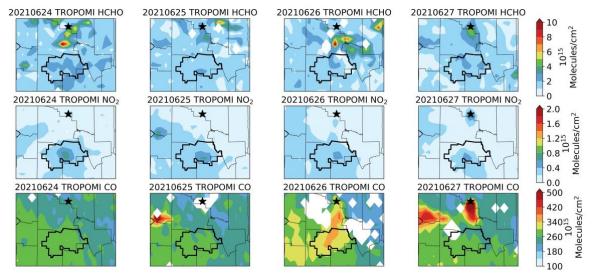


Figure S2. TROPOMI tropospheric columnar HCHO (top), NO<sub>2</sub> (middle), and CO (bottom) concentrations during the smoke periods for Case II over Phoenix area. The black polygon lines represent the EPA designated Phoenix-Mesa nonattainment area. The grid resolution is 0.2°. Grids without available data are marked as white space.

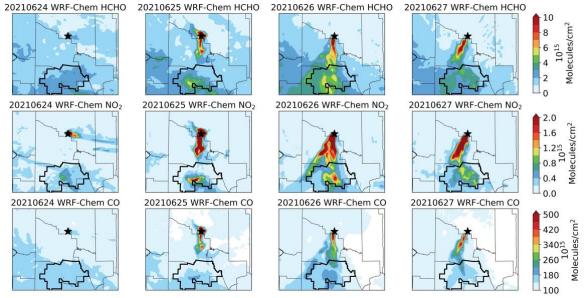


Figure S3. WRF-Chem simulated tropospheric columnar HCHO, NO<sub>2</sub>, and CO concentrations at local time 18:00 for Case II over Phoenix area.

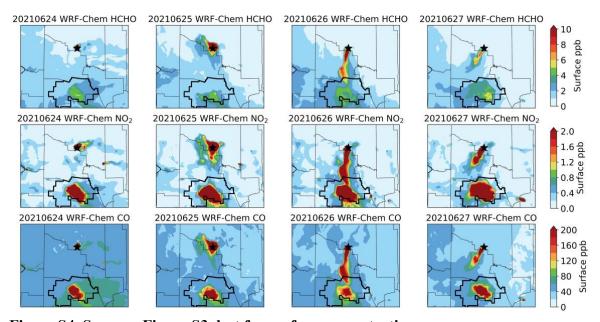


Figure S4. Same as Figure S3, but for surface concentrations.

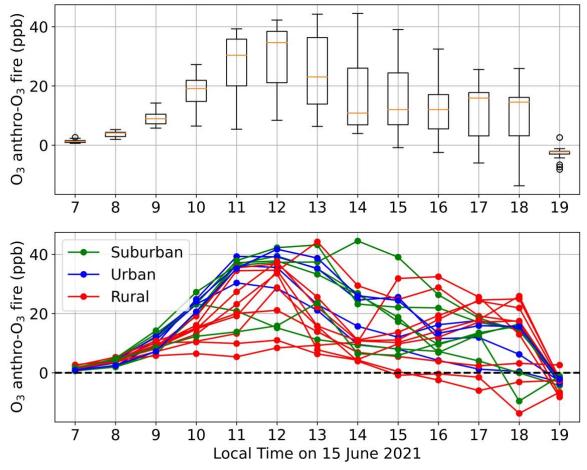


Figure S5. Comparison of O<sub>3</sub> concentrations contributed by Arizona anthropogenic and fire emissions on June 15, 2021. The top panel presents boxplots of their difference through the daytime. The bottom panel shows the hourly variation of O<sub>3</sub> difference across different site types: Suburban (green), Urban (blue), and Rural (red) as listed in Table S1.

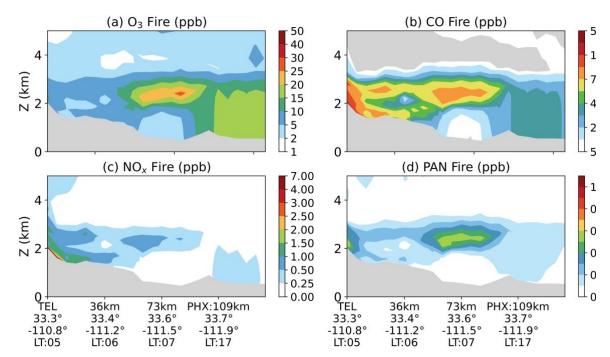


Figure S6. Cross-sectional analysis of a smoke plume traveling towards Phoenix during case I, showing vertical and horizontal distribution of various pollutants. The subplots represent concentrations of (a)  $O_3$ , (b) CO, (c)  $NO_x$ , (d) HCHO, (e)  $PM_{2.5}$ , and (f) PAN (Peroxyacetyl Nitrate) across different altitudes and distances from the fire. The grey shading represents the topography heights.

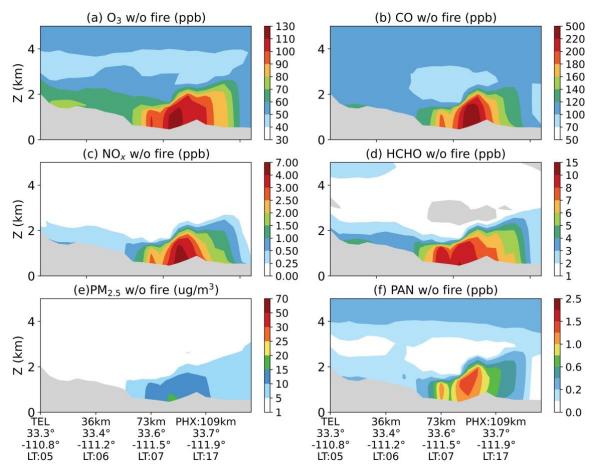


Figure S7. Same as Figure 15, but for scenario without fire emissions.