

1 *Supplementary Information*

2 **Wildfire Particulate Matter as a Source of Environmentally Persistent Free Radicals and**
3 **Reactive Oxygen Species**

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10 **Table S1.** MOUDI sampling dates and time at highway and urban locations. * collected at the
 11 urban site during wildfire events.

Sample site	Start Date	End Date	Start Local Time	End Local Time
Wildfire*	10/26/2020	10/29/2020	5:00 PM	5:00 PM
	10/29/2020	11/1/2020	5:00 PM	5:00 PM
	11/2/2020	11/5/2020	5:00 PM	5:00 PM
	11/6/2020	11/9/2020	5:00 PM	5:00 PM
	11/10/2020	11/13/2020	5:00 PM	5:00 PM
	11/13/2020	11/16/2020	5:00 PM	5:00 PM
	12/3/2020	12/6/2020	5:00 PM	3:00 PM
	12/6/2020	12/9/2020	3:00 PM	3:00 PM
Urban	2/23/2020	2/23/2020	8:19 AM	6:02 PM
	2/24/2020	2/24/2020	6:27 AM	6:00 PM
	2/25/2020	2/25/2020	6:20 AM	6:02 PM
Highway	1/31/2020	1/31/2020	6:00 AM	6:00 PM
	2/7/2020	2/7/2020	6:08 AM	6:00 PM
	2/8/2020	2/8/2020	6:00 AM	11:37 AM

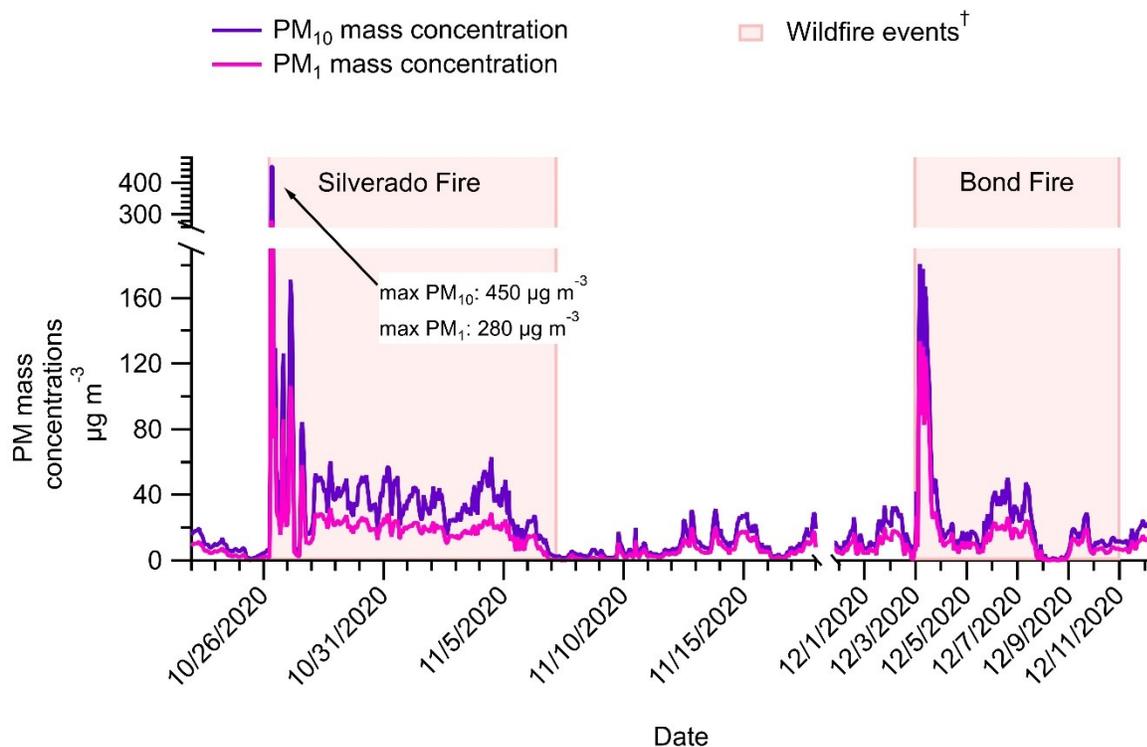
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13 **Table S2.** Hyperfine splitting constants (HFS, mean \pm standard deviation) of the BMPO radical
 14 adducts elucidated from the simulated spectra of the EPR measurement of the aqueous extracts
 15 of size-segregated PM samples collected during wildfire events and at highway and urban sites in
 16 Southern California.

BMPO radical adducts	HFS	Wildfire	Highway & Urban
BMPO-OH conformer I	α^N, G	14.1 ± 0.1	14.1 ± 0.02
	α^H_{β}, G	12.6 ± 0.2	12.6 ± 0.06
	α^H_{γ}, G	0.4 ± 0.1	0.7 ± 0.04
BMPO-OH conformer II	α^N, G	14.2 ± 0.2	14.2 ± 0.05
	α^H_{β}, G	15.4 ± 0.4	15.2 ± 0.2
	α^H_{γ}, G	0.7 ± 0.1	0.8 ± 0.2
BMPO-R	α^N, G	15.2 ± 0.1	15.1 ± 0.2
	α^H_{β}, G	21.7 ± 0.3	21.7 ± 0.2
BMPO-OR	α^N, G	14.6 ± 0.2	-
	α^H_{β}, G	16.7 ± 0.4	-
BMPO-OOH	α^N, G	14.1 ± 0.5	-
	α^H_{β}, G	8.3 ± 1.0	-

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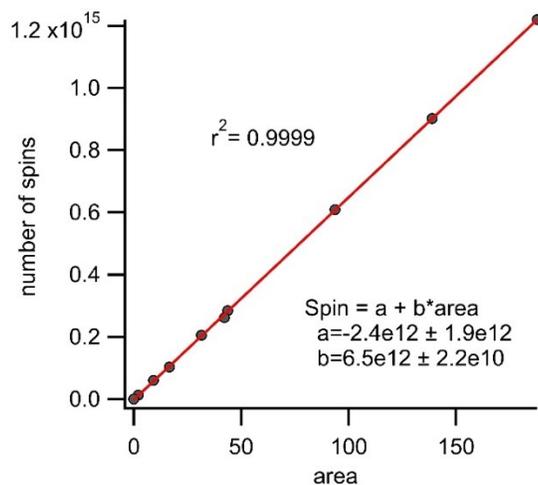


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20 **Figure S1.** PM₁ and PM₁₀ mass concentrations at the sampling site during wildfire events.

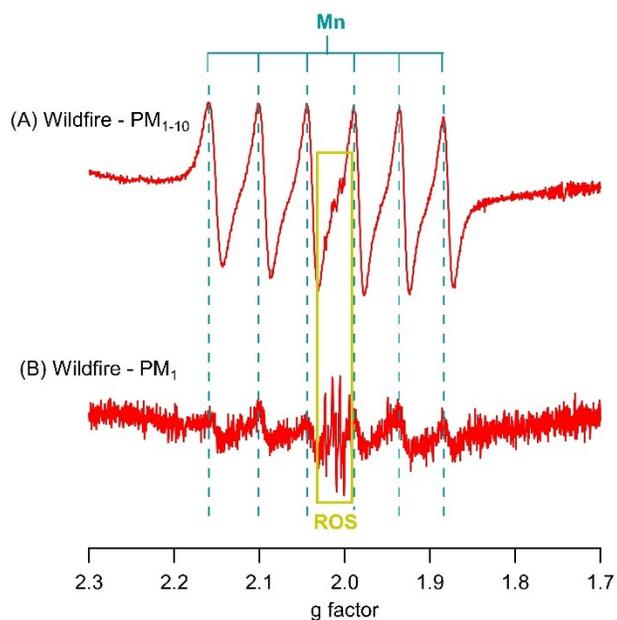
21 †wildfire events – box indicates the dates of fire start and containment reported by CAL FIRE.

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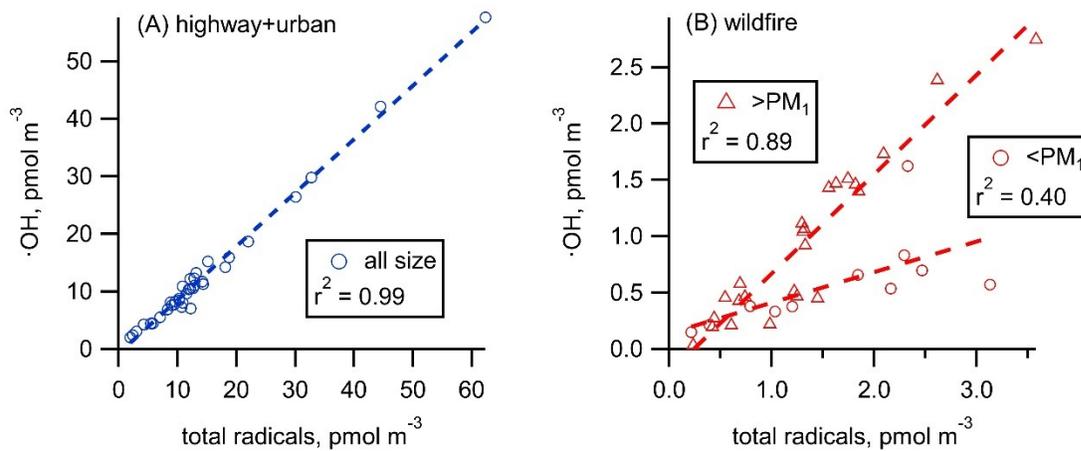
24 **Figure S2.** EPR calibration using 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPOL)
 25 standard solutions. TEMPOL stock was made by dissolving TEMPOL powders in water and
 26 different TEMPOL standard solutions were diluted from the stock for different number of spins
 27 and inserted in EPR 50 µL capillary tubes for EPR analysis. The area under the EPR peaks were
 28 calculated using the Xenon software. The stock and the standard solutions were made on the same
 29 day of experiments.



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31 **Figure S3.** Large scan range of EPR spectra of PM_{1-10} and PM_1 collected at an urban site during
 32 wildfire events in winter 2020. The yellow box highlights the BMPO radical adducts (Fig. 2)
 33 atop Mn EPR signals.

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36 **Figure S4.** Correlations of $\cdot OH$ with total radical forms of ROS.