

Application of DPPH Assay for Assessment of Particulate Matter Reducing Properties

Maria Agostina Frezzini ^{1,*}, Federica Castellani ¹, Nayma De Francesco ¹, Martina Ristorini ^{2,3} and Silvia Canepari ¹

¹ Department of Chemistry, Sapienza University of Rome, Piazzale Aldo Moro, 5, 00185 Rome, Italy; federica.castellani@uniroma1.it (F.C.); defrancesco.nayma@gmail.com (N.D.F.); silvia.canepari@uniroma1.it (S.C.)

² Research Institute on Terrestrial Ecosystems, National Research Council, Via G. Marconi, 2, 05010 Porano, Italy; m.ristorini@studenti.unimol.it (M.R.)

³ Department of Biosciences and Territory, University of Molise, Via Hertz, 86090 Pesche, Italy

* Correspondence: mariaagostina.frezzini@uniroma1.it; Tel.: +39-06-4991-3742

Supplementary Materials

Table S1: Chemical composition of the total fraction (water-soluble and insoluble) of brake dust (BD), coke (C), Saharan dust (SD) and calcitic soil dust (CSD). Mean ± standard deviation of three replicates is reported.

Technique	UoM	BD	C	SD	CSD	
ICP-MS/XRF	g/Kg	Al	15 ± 0.42	13 ± 2	69 ± 2	11 ± 0.21
ICP-MS	mg/Kg	As	19 ± 1	1.1 ± 0.062	1.4 ± 0.12	96 ± 11
ICP-MS	mg/Kg	B	32 ± 0.073	3.5 ± 0.94	13 ± 0.82	1.6 ± 0.4
ICP-MS	mg/Kg	Cd	1.1 ± 0.051	0.07 ± 0.04	0.91 ± 0.071	0.11 ± 0.003
ICP-MS	mg/Kg	Ce	26 ± 0.12	0.32 ± 0.11	1.2 ± 0.11	10 ± 1.3
ICP-MS	mg/Kg	Co	15 ± 0.54	1.1 ± 0.044	0.73 ± 0.037	1.8 ± 0.11
ICP-MS	mg/Kg	Cr	3107 ± 74	10 ± 0.2	52 ± 1	40 ± 2
ICP-MS	mg/Kg	Cs	3.2 ± 0.036	0.052 ± 0.011	0.025 ± 0.003	2.8 ± 0.32
ICP-MS	mg/Kg	Cu	5051 ± 9	56 ± 12	13 ± 4	14 ± 1
ICP-MS	g/Kg	Fe	204 ± 5	17 ± 4	41 ± 0.31	4 ± 0.11
ICP-MS	mg/Kg	La	13 ± 0.22	0.31 ± 0.23	27 ± 0.11	5.2 ± 1.1
ICP-MS	mg/Kg	Mn	1212 ± 4	46 ± 1	29 ± 0.51	121 ± 5
ICP-MS	mg/Kg	Mo	175 ± 1	77 ± 0.18	0.16 ± 0.021	0.72 ± 0.095
ICP-MS	mg/Kg	Ni	112 ± 3	357 ± 1	7 ± 1	11 ± 1.1
ICP-MS	mg/Kg	Pb	683 ± 4	18 ± 0.14	2.5 ± 0.22	12 ± 2.5
ICP-MS	mg/Kg	Rb	23 ± 1	1.1 ± 0.11	7 ± 0.6	11 ± 2.4
ICP-MS	mg/Kg	Sb	306 ± 1	4 ± 0.011	2.4 ± 0.011	0.41 ± 0.12
ICP-MS	mg/Kg	Se	9.3 ± 0.43	9 ± 0.21	1.5 ± 0.13	11 ± 2.1
ICP-MS	mg/Kg	Sn	1420 ± 3	15 ± 0.32	0.022 ± 0.011	2.8 ± 0.51
ICP-MS	mg/Kg	Sr	257 ± 9	10 ± 7	352 ± 10	525 ± 46
ICP-MS	mg/Kg	Ti	527 ± 9	907 ± 21	4542 ± 111	255 ± 6.2
ICP-MS	mg/Kg	Tl	0.34 ± 0.12	0.032 ± 0.011	0.034 ± 0.012	0.15 ± 0.039
ICP-MS	mg/Kg	V	9 ± 0.47	556 ± 1	6.1 ± 0.41	11 ± 1.1
ICP-MS	mg/Kg	Zn	5317 ± 20	260 ± 17	50 ± 20	110 ± 24
ICP-MS	mg/Kg	Zr	90 ± 1	12 ± 0.14	9.4 ± 0.21	14 ± 1.5
ECOC	g/Kg	EC	17 ± 1	310 ± 15	< 0.001	< 0.001
TOC	g/Kg	WSOC	5.7 ± 0.12	9.5 ± 0.21	0.53 ± 0.02	0.3 ± 0.1
ECOC/TOC	g/Kg	WIOC	30 ± 3	146 ± 5	0.10 ± 0.02	41 ± 3

Table S1: Chemical composition of the total fraction of brake dust (BD), coke (C), Saharan dust (SD) and calcitic soil dust (CSD). Mean \pm standard deviation of three replicates is reported.

Technique	UoM	BD	C	SD	CSD
ICP-MS/XRF	g/Kg	Al	15 \pm 0.4	13 \pm 2	69 \pm 2
ICP-MS	mg/Kg	As	19.0 \pm 1	1.1 \pm 0.06	1.4 \pm 0.1
ICP-MS	mg/Kg	B	32 \pm 0.07	3.5 \pm 0.9	13 \pm 0.8
ICP-MS	mg/Kg	Cd	1.1 \pm 0.05	0.07 \pm 0.04	0.91 \pm 0.071
ICP-MS	mg/Kg	Ce	26 \pm 0.1	0.32 \pm 0.11	1.2 \pm 0.11
ICP-MS	mg/Kg	Co	15 \pm 0.5	1.1 \pm 0.04	0.73 \pm 0.03
ICP-MS	mg/Kg	Cr	3107 \pm 74	10 \pm 0.2	52 \pm 1
ICP-MS	mg/Kg	Cs	3.2 \pm 0.03	0.05 \pm 0.01	0.025 \pm 0.003
ICP-MS	mg/Kg	Cu	5051 \pm 9	56 \pm 12	13 \pm 4
ICP-MS	g/Kg	Fe	204 \pm 5	17 \pm 4	41 \pm 0.31
ICP-MS	mg/Kg	La	13 \pm 0.2	0.31 \pm 0.2	27 \pm 0.11
ICP-MS	mg/Kg	Mn	1212 \pm 4	46 \pm 1	29 \pm 0.51
ICP-MS	mg/Kg	Mo	175 \pm 1	77 \pm 0.1	0.16 \pm 0.021
ICP-MS	mg/Kg	Ni	112 \pm 3	357 \pm 1	7 \pm 1
ICP-MS	mg/Kg	Pb	683 \pm 4	18 \pm 0.1	2.5 \pm 0.22
ICP-MS	mg/Kg	Rb	23 \pm 1	1.1 \pm 0.1	7 \pm 0.6
ICP-MS	mg/Kg	Sb	306 \pm 1	4 \pm 0.01	2.4 \pm 0.011
ICP-MS	mg/Kg	Se	9.3 \pm 0.4	9 \pm 0.2	1.5 \pm 0.13
ICP-MS	mg/Kg	Sn	1420 \pm 3	15 \pm 0.3	0.022 \pm 0.011
ICP-MS	mg/Kg	Sr	257 \pm 9	10 \pm 7	352 \pm 10
ICP-MS	mg/Kg	Ti	527 \pm 9	907 \pm 21	4542 \pm 111
ICP-MS	mg/Kg	Tl	0.34 \pm 0.1	0.032 \pm 0.011	0.034 \pm 0.012
ICP-MS	mg/Kg	V	9 \pm 0.4	556 \pm 1	6.1 \pm 0.41
ICP-MS	mg/Kg	Zn	5317 \pm 20	260 \pm 17	50 \pm 20
ICP-MS	mg/Kg	Zr	90 \pm 1	12 \pm 0.1	9.4 \pm 0.21
ECOC	g/Kg	EC	17 \pm 1	310 \pm 15	< 0.001
TOC	g/Kg	WSOC	5.7 \pm 0.1	9.5 \pm 0.2	0.53 \pm 0.02
ECOC/TOC	g/Kg	WIOC	30 \pm 3	146 \pm 5	0.10 \pm 0.02
					41 \pm 3

Table S2: Correlation matrix among elemental concentrations, PM mass concentration (PM), 2,2-diphenyl-1-picrylhydrazyl assay (RP) and oxidative potential assays (ascorbic acid, AA; dithiothreitol, DTT; 2',7'-dichlorofluorescin, DCFH) of extracted fraction of PM_{2.5} filters collected in Cassana (FE), Italy.

	Al	As	Bi	Cd	Ce	Co	Cr	Cs	Cu	Fe	La	Li	Mg	Mn	Mo	Na	Ni	Pb	Rb	Sb	Sn	Sr	Ti	V	Zn	Zr	PM	RP	AA	DTT	DCFH	
Al	-																															
As	0.59	-																														
Bi	0.59	0.77	-																													
Cd	0.25	0.29	0.37	-																												
Ce	0.56	0.49	0.47	0.64	-																											
Co	0.67	0.62	0.49	0.33	0.64	-																										
Cr	0.50	0.77	0.81	0.55	0.51	0.45	-																									
Cs	0.64	0.52	0.41	0.47	0.56	0.41	0.46	-																								
Cu	0.62	0.78	0.84	0.67	0.59	0.57	0.91	0.54	-																							
Fe	0.70	0.61	0.72	0.33	0.70	0.78	0.63	0.49	0.68	-																						
La	0.10	-0.04	-0.013	0.63	0.67	0.21	0.13	0.19	0.25	0.25	-																					
Li	0.62	0.65	0.74	0.69	0.64	0.51	0.87	0.66	0.93	0.65	0.28	-																				
Mg	0.77	0.45	0.52	0.32	0.73	0.79	0.48	0.46	0.56	0.89	0.39	0.58	-																			
Mn	0.63	0.75	0.79	0.67	0.56	0.52	0.91	0.61	0.94	0.61	0.15	0.96	0.55	-																		
Mo	0.46	0.64	0.78	0.58	0.66	0.52	0.85	0.41	0.85	0.71	0.35	0.86	0.64	0.84	-																	
Na	0.44	0.16	0.16	0.34	0.64	0.64	0.21	0.18	0.32	0.59	0.63	0.34	0.83	0.28	0.44	-																
Ni	0.007	0.20	0.048	-0.066	0.038	0.51	0.076	-0.13	-0.002	0.26	0.10	-0.15	0.27	-0.070	0.058	0.33	-															
Pb	0.58	0.59	0.63	0.51	0.53	0.56	0.62	0.65	0.67	0.68	0.05	0.65	0.48	0.64	0.43	0.17	0.052	-														
Rb	0.64	0.36	0.35	0.40	0.36	0.47	0.48	0.58	0.53	0.49	0.09	0.61	0.52	0.61	0.38	0.26	-0.006	0.43	-													
Sb	0.49	0.72	0.72	0.67	0.44	0.51	0.86	0.55	0.91	0.56	0.10	0.83	0.38	0.87	0.64	0.13	0.04	0.78	0.55	-												
Sn	0.61	0.76	0.75	0.61	0.41	0.56	0.84	0.65	0.89	0.61	0.04	0.82	0.45	0.87	0.63	0.15	0.12	0.81	0.57	0.97	-											
Sr	0.77	0.54	0.60	0.26	0.74	0.81	0.52	0.50	0.58	0.96	0.28	0.59	0.96	0.54	0.66	0.71	0.26	0.59	0.47	0.41	0.49	-										
Ti	0.54	0.52	0.58	0.41	0.56	0.79	0.48	0.42	0.58	0.82	0.14	0.48	0.69	0.47	0.44	0.44	0.34	0.78	0.41	0.65	0.66	0.75	-									
V	0.004	-0.11	-0.37	-0.21	-0.17	0.31	-0.31	-0.16	-0.31	-0.19	0.01	-0.34	-0.022	-0.29	-0.35	0.16	0.65	-0.19	-0.017	-0.19	-0.14	-0.078	-0.044	-								
Zn	0.72	0.52	0.65	0.34	0.69	0.73	0.59	0.55	0.64	0.97	0.26	0.68	0.91	0.61	0.69	0.61	0.19	0.68	0.52	0.51	0.58	0.96	0.76	-0.21	-							
Zr	0.45	0.59	0.73	0.64	0.51	0.53	0.66	0.42	0.79	0.55	0.09	0.69	0.37	0.71	0.56	0.13	-0.002	0.72	0.36	0.85	0.81	0.44	0.72	-0.24	0.49	-						
PM	0.59	0.77	0.79	0.42	0.59	0.49	0.79	0.64	0.76	0.61	-0.05	0.78	0.43	0.81	0.71	0.043	-0.15	0.68	0.44	0.73	0.73	0.54	0.52	-0.35	0.56	0.71	-					
RP	0.31	0.43	0.63	0.59	0.46	0.26	0.65	0.35	0.62	0.38	0.06	0.59	0.21	0.62	0.56	-0.058	-0.16	0.56	0.25	0.68	0.64	0.28	0.50	-0.38	0.33	0.82	0.77	-				
AA	0.22	0.31	0.40	0.31	0.25	0.16	0.43	0.061	0.59	0.36	0.32	0.56	0.33	0.48	0.61	0.35	-0.16	0.15	0.078	0.33	0.32	0.31	0.067	-0.32	0.38	0.22	0.19	0.052	-			
DTT	0.69	0.66	0.60	0.31	0.43	0.66	0.65	0.57	0.65	0.71	-0.01	0.59	0.67	0.67	0.56	0.31	0.23	0.64	0.67	0.73	0.71	0.73	-0.008	0.71	0.53	0.63	0.47	0.14	-			
DCFH	0.18	0.31	0.43	0.18	0.14	0.23	0.23	0.21	0.26	0.39	-0.20	0.11	0.11	0.15	0.003	-0.16	0.14	0.66	0.19	0.45	0.46	0.23	0.65	-0.24	0.31	0.62	0.33	0.51	-0.23	0.34	-	

Table S3: Correlation matrix among elemental concentrations, PM mass concentration (PM), 2,2-diphenyl-1-picrylhydrazyl assay (RP) and oxidative potential assays (ascorbic acid, AA; dithiothreitol, DTT; 2',7'-dichlorofluorescin, DCFH) of residual fraction of PM_{2.5} filters collected in Cassana (FE), Italy.

	Al	Bi	Cd	Ce	Cr	Cs	Cu	Fe	La	Li	Mg	Mn	Mo	Ni	Pb	Sb	Sn	Sr	Ti	Tl	V	Zn	Zr	PM	RP	AA	DTT	DCFH	
Al	-																												
Bi	-0.11	-																											
Cd	0.56	-0.11	-																										
Ce	0.065	0.17	-0.12	-																									
Cr	0.57	0.081	0.61	-0.07	-																								
Cs	0.012	0.17	0.18	-0.14	0.17	-																							
Cu	-0.013	0.89	-0.091	0.00	0.16	0.14	-																						
Fe	0.25	0.68	0.23	-0.10	0.53	0.21	0.77	-																					
La	-0.21	-0.013	-0.19	0.87	-0.24	-0.079	-0.18	-0.22	-																				
Li	0.037	0.39	0.28	-0.21	0.19	0.75	0.44	0.56	-0.19	-																			
Mg	0.69	-0.008	0.69	-0.13	0.71	0.31	0.059	0.45	-0.35	0.29	-																		
Mn	0.0004	0.76	0.18	-0.15	0.22	0.42	0.74	0.74	-0.24	0.62	0.15	-																	
Mo	-0.19	0.57	-0.069	0.12	0.013	0.21	0.55	0.37	0.088	0.34	-0.002	0.44	-																
Ni	0.14	-0.04	0.29	-0.37	0.56	0.13	0.21	0.54	-0.24	0.27	0.44	0.11	0.27	-															
Pb	-0.075	0.38	0.058	-0.11	-0.32	0.22	0.21	0.14	-0.04	0.45	-0.22	0.53	0.16	-0.32	-														
Sb	0.19	0.36	0.47	-0.28	0.19	-0.013	0.42	0.55	-0.33	0.43	0.33	0.57	0.48	0.33	0.34	-													
Sn	-0.017	0.85	-0.18	0.06	-0.015	0.18	0.81	0.63	-0.14	0.41	0.039	0.72	0.56	0.032	0.45	0.38	-												
Sr	0.32	-0.13	0.53	0.06	0.66	0.31	-0.16	0.11	-0.02	0.16	0.61	-0.017	-0.008	0.32	-0.23	0.052	-0.34	-											
Ti	0.19	0.42	-0.12	-0.04	0.069	0.078	0.57	0.66	-0.17	0.51	0.22	0.34	0.24	0.35	0.15	0.32	0.63	-0.29	-										
Tl	0.22	0.12	0.61	-0.10	0.32	0.62	0.17	0.21	-0.07	0.61	0.35	0.37	-0.061	0.072	0.26	0.18	-0.075	0.47	-0.14	-									
V	0.13	-0.35	0.61	-0.30	0.59	0.077	-0.27	0.11	-0.21	0.22	0.34	-0.085	-0.18	0.53	-0.23	0.21	-0.45	0.55	-0.16	0.31	-								
Zn	0.44	-0.13	0.48	-0.02	0.46	0.41	-0.17	0.041	-0.21	0.14	0.73	0.093	-0.025	0.062	-0.11	0.11	-0.15	0.79	-0.25	0.37	0.22	-							
Zr	-0.056	0.49	-0.17	0.13	-0.018	-0.24	0.31	0.28	-0.05	-0.025	0.036	0.13	0.28	-0.11	0.14	0.17	0.59	-0.34	0.32	-0.35	-0.34	-0.25	-						
PM	0.024	0.63	-0.25	0.00	-0.25	0.026	0.54	0.19	-0.29	0.17	-0.074	0.43	0.18	-0.53	0.53	0.18	0.64	-0.25	0.24	0.020	-0.58	0.029	0.43	-					
RP	0.30	0.47	0.13	-0.04	0.030	-0.11	0.41	0.31	-0.39	0.15	0.32	0.38	0.23	-0.24	0.45	0.39	0.59	0.015	0.36	-0.027	-0.33	0.31	0.46	0.77	-				
AA	-0.21	0.55	-0.42	0.40	-0.27	-0.29	0.47	0.28	0.42	-0.25	-0.34	0.22	0.25	-0.071	0.093	-0.092	0.51	-0.49	0.26	-0.33	-0.64	-0.52	0.39	0.19	0.052	-			
DTT	-0.13	0.38	-0.003	-0.13	-0.25	-0.18	0.41	0.061	-0.28	0.011	-0.18	0.29	0.041	-0.37	0.31	0.17	0.31	-0.29	0.033	0.13	-0.18	-0.23	0.21	0.63	0.46	0.14	-		
DCFH	0.19	0.12	0.24	0.07	0.012	0.13	0.092	0.12	-0.072	0.27	0.16	0.38	0.14	-0.27	0.46	0.29	0.061	0.26	0.035	0.21	-0.011	0.38	-0.27	0.33	0.51	-0.23	0.34	-	

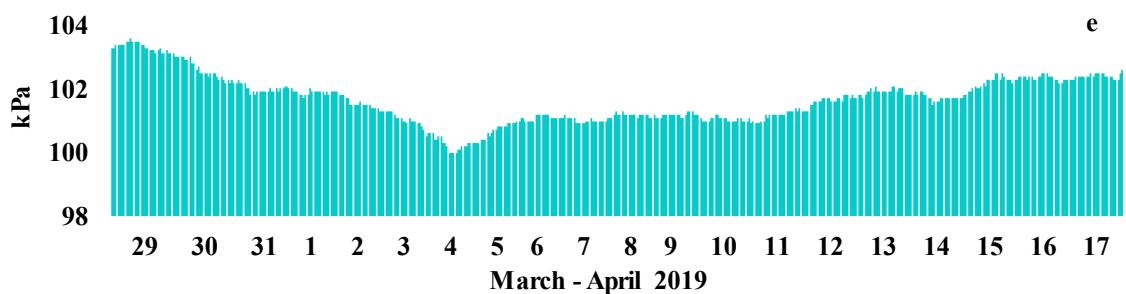
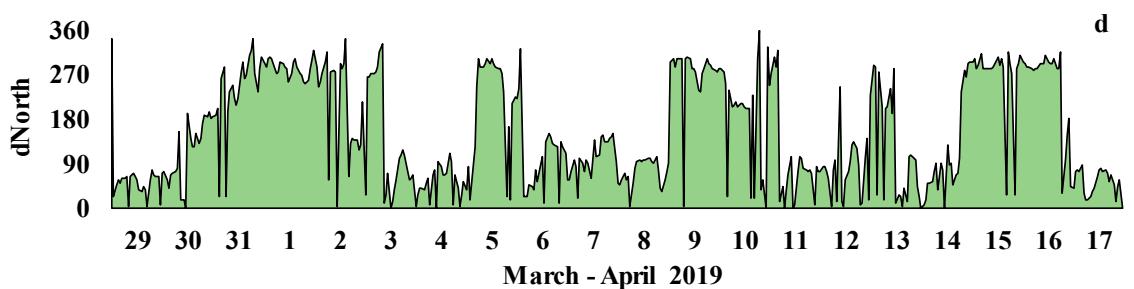
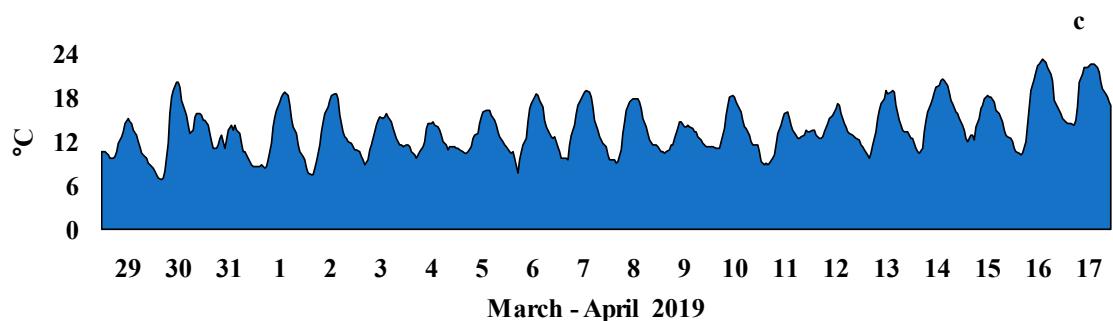
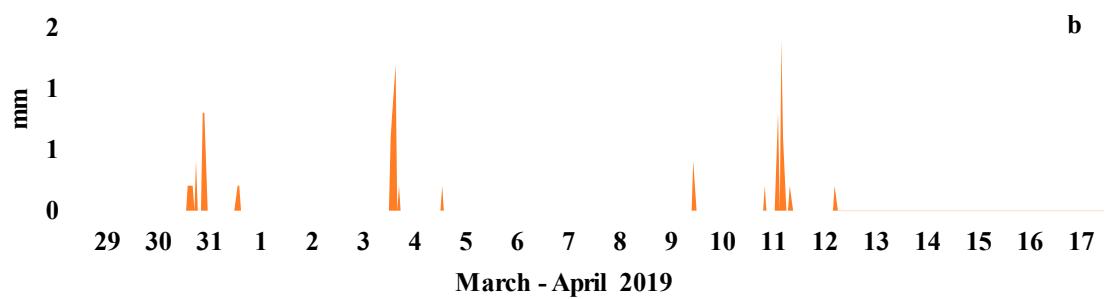
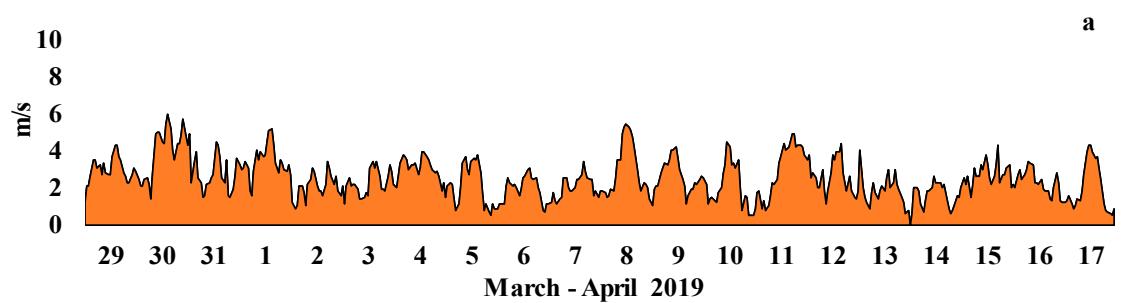


Figure S1: Meteorological data collected from 29th to 17th March-April 2019 at Cassana (FE), Italy: wind speed (a), rainfall (b), temperature (c), wind direction (d) and pressure (e).

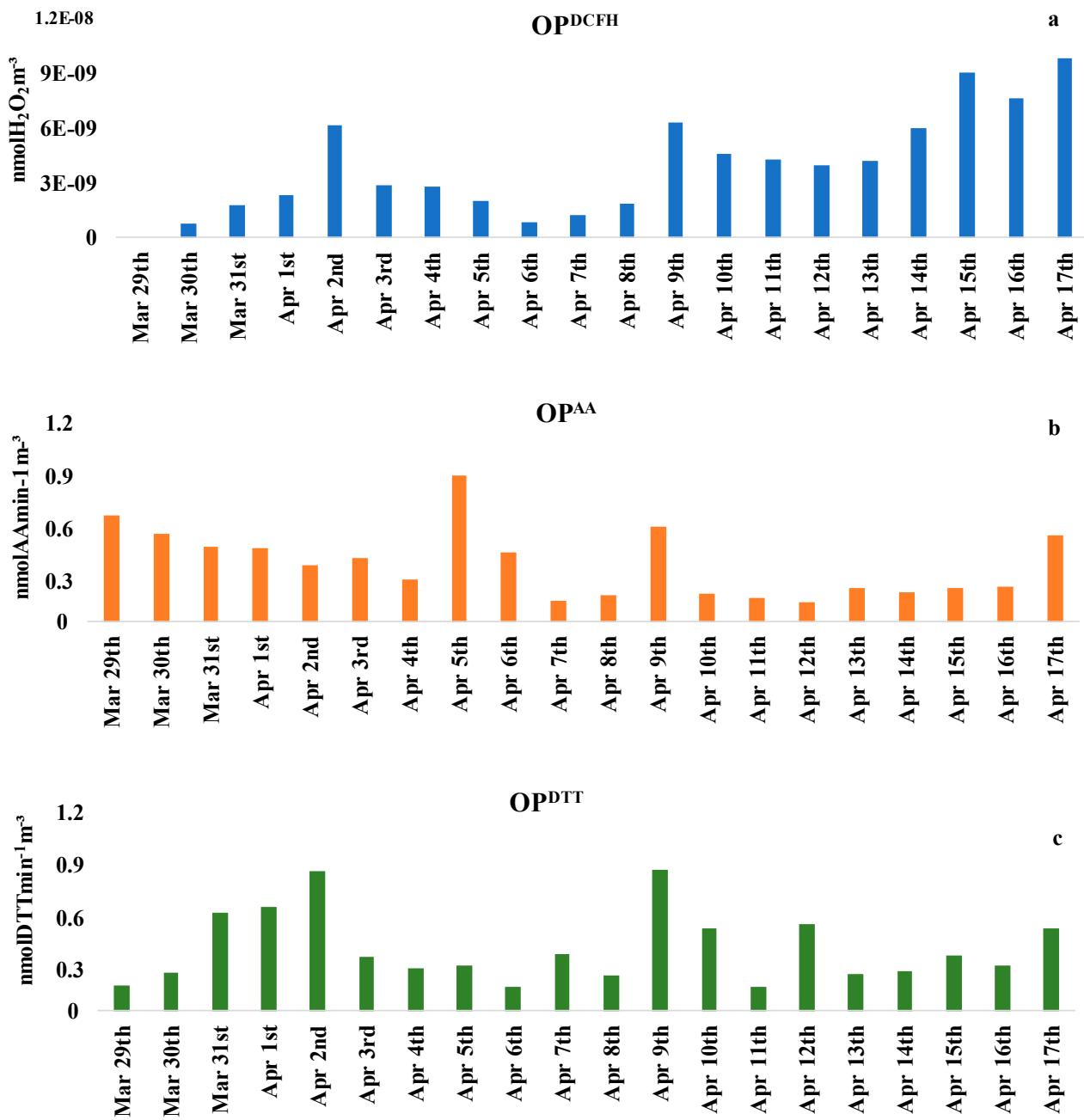


Figure S2: Oxidative potential obtained through 2',7'-dichlorofluorescin (OP^{DCFH}), ascorbic acid (OP^{AA}) and dithiothreitol (OP^{DTT}) assays on $\text{PM}_{2.5}$ filters collected at Cassana (FE), Italy, from 29th to 17th March-April 2019. Values below limits of detection (LODs) are not reported.

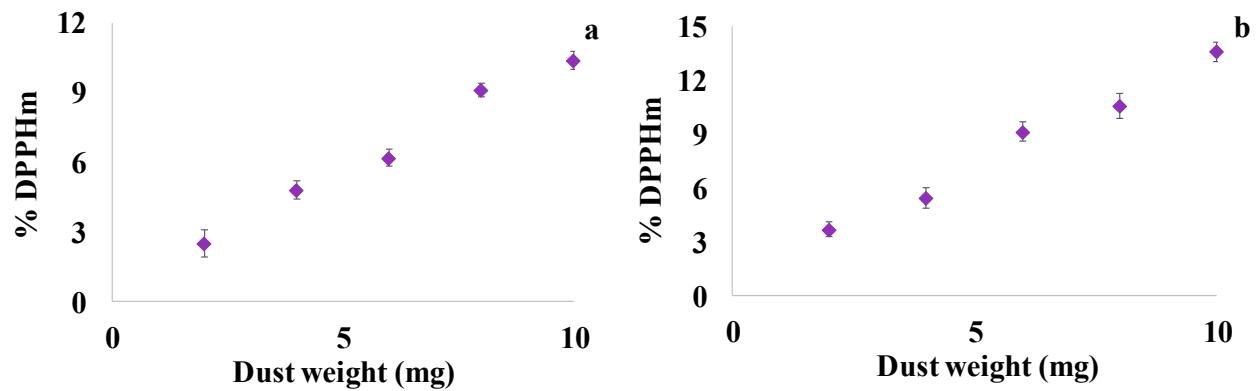


Figure S3: Reducing potential (%DPPHm) linearity of response of (a) UD (urban particulate matter certified material, NIST168a) and (b) D (diesel particulate matter certified material, NIST1650b).