Supplement of

Online Measurements Reveal Contrasting Particle-Bound Reactive Oxygen Species and Chemical Composition in Emissions from Six Residential Solid Fuels

Lu Lei[1], Shan Wang[1], Jonas Enarsson[2], Jian Zhao[3], David Nganga[1], Ying Li[4], William Smith[4], Kirsten N. Fossum[1], Aneta Wierzbicka[2], Axel Eriksson[2], Chunshui Lin[1,5], Darius Ceburnis[1], John Wenger[6], Stig Hellebust[6], Colin O'Dowd[1], and Jurgita Ovadnevaite[1]

[1]The Ryan Institute Centre for Climate & Air Pollution Studies, School of Natural Sciences, Physics, University of Galway, Galway, H91 CF50, Ireland

[2]Ergonomics and Aerosol Technology, Lund University, Lund, Sweden

[3] Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Helsinki, 00014, Finland

[4]School of Mechanical and Materials Engineering, University College Dublin, Dublin, Ireland

[5]Chemistry and Physics, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, 710061, China

[6]School of Chemistry and Sustainability Institute, University College Cork, Cork, Ireland

Correspondence to: Lu Lei (lu.lei@universityofgalway.ie) and Jurgita Ovadnevaite (jurgita.ovadnevaite@universityofgalway.ie)

Table S1. Summary of the physicochemical properties of the six residential solid fuels investigated in this study. Moisture content is reported on an as-received basis, while elemental composition is expressed on a dry mass basis. Modified combustion efficiency (MCE) values represent averages obtained from six additional replicate open-fireplace combustion experiments, conducted separately from the ROS measurements in the present study.

Properties	KDHW	WB	GSW	SP	LSMC	HSMC
Moisture (wt%[*1] as received)	**9.50**	**8.72**	**32.3**	**16.5**	**13.1**	**3.68**
C	50.1	51.4	51.3	57.6	79.2	86.3
H	5.70	5.92	5.46	5.28	4.14	4.29
N	0.08	0.28	0.06	1.50	1.47	1.68
O	**44.1**	**42.3**	**43.2**	**35.3**	**6.87**	**2.63**
S	**0.02**	**0.11**	**0.00**	**0.26**	**1.35**	**2.21**
Cl	0.10	0.16	0.10	0.26	0.04	0.02
MCE[*2]	**0.95 ± 0.01**	**0.93 ± 0.02**	**0.89 ± 0.02**	**0.86 ± 0.05**	**0.93 ± 0.01**	**0.94 ± 0.01**

[*1]wt% denotes weight percentage, defined as the mass of a given component divided by the total sample mass, multiplied by 100.

[*2]MCE=modified combustion efficiency, which is calculated as $CO_2/(CO+CO_2)$.

Table S2. Nominal mass-to-charge ratios (UMR m/z) and assigned elemental formulas of the 21 polycyclic aromatic hydrocarbon (PAH)-related ions selected for high-resolution peak fitting of the ToF-ACSM-X data.

No.	UMR m/z	Ion formula	No.	UMR m/z	Ion formula
1	128	$C_{10}H_8^+$	12	264	$C_{21}H_{12}^+$
2	152	$C_{12}H_8^+$	13	266	$C_{21}H_{14}^+$
3	178	$C_{14}H_{10}^+$	14	276	$C_{22}H_{12}^+$
4	202	$C_{16}H_{10}^+$	15	288	$C_{23}H_{12}^+$
5	216	$C_{17}H_{12}^+$	16	290	$C_{23}H_{14}^+$
6	226	$C_{18}H_{10}^+$	17	300	$C_{24}H_{12}^+$
7	228	$C_{18}H_{12}^+$	18	302	$C_{24}H_{14}^+$
8	240	$C_{19}H_{12}^+$	19	316	$C_{25}H_{16}^+$
9	242	$C_{19}H_{14}^+$	20	326	$C_{26}H_{14}^+$
10	250	$C_{20}H_{10}^+$	21	328	$C_{26}H_{16}^+$
11	252	$C_{20}H_{12}^+$	-	-	-



Figure S1. Photographs of the six residential solid fuels during combustion in the open fireplace: kiln-dried hardwood (KDHW), green softwood (GSW), wood briquettes (WB), sod peat (SP), low-sulfur manufactured coal (LSMC), and high-sulfur manufactured coal (HSMC).

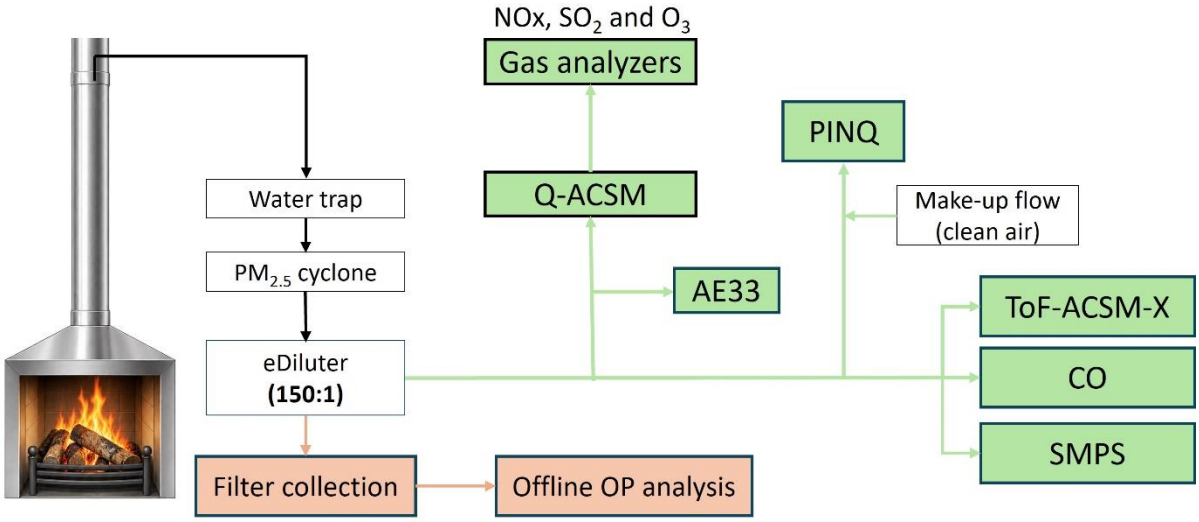


Figure S2. Schematic plot of the open fireplace combustion experimental setup, including the aerosol sampling system, dilution arrangement, and online and offline instruments used for characterizing particle emissions and particle-bound ROS.

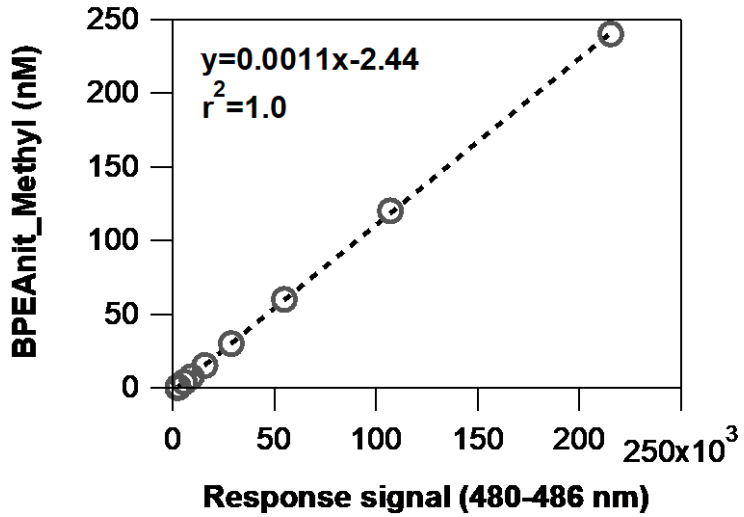


Figure S3. Calibration of the PINQ fluorescence response using standard solutions containing different concentrations of BPEAnit-Me. The slope of the linear regression was used to convert the measured fluorescence response into BPEAnit-Me-equivalent concentration in the collection liquid, which was subsequently converted to ROS concentration using the liquid-to-aerosol flow ratio.

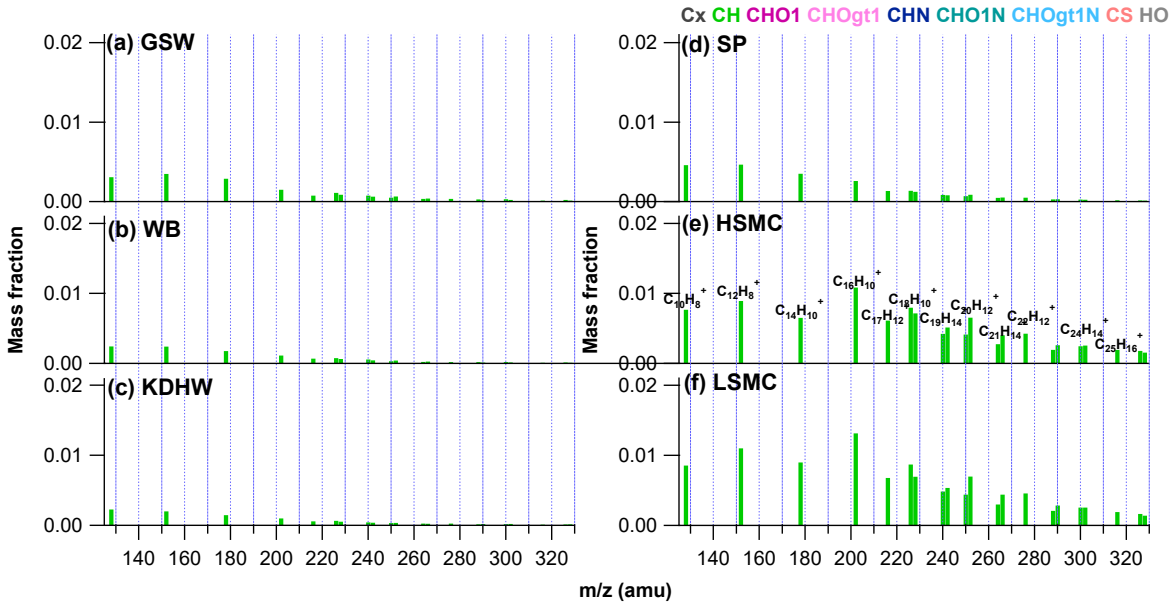


Figure S4. Enlarged high-resolution mass spectra (m/z 120-330) of organic aerosol emissions from the six residential solid fuels, mainly PAH-related ions.

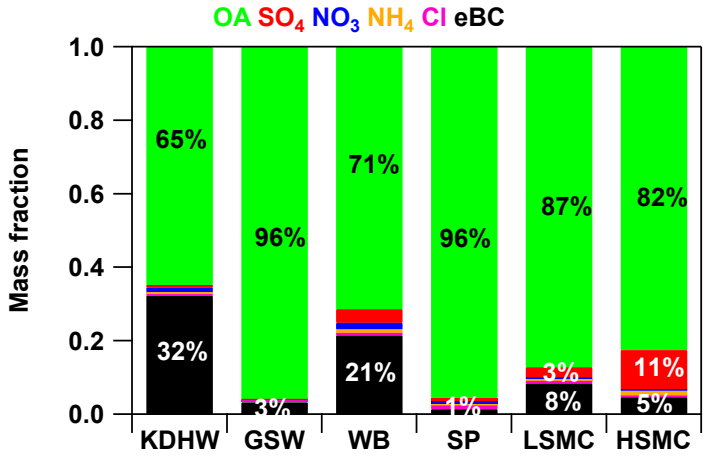


Figure S5. Average PM_1 chemical composition of emissions from six residential solid fuels during independent replicate open-fireplace combustion experiments (at least six burns per fuel).

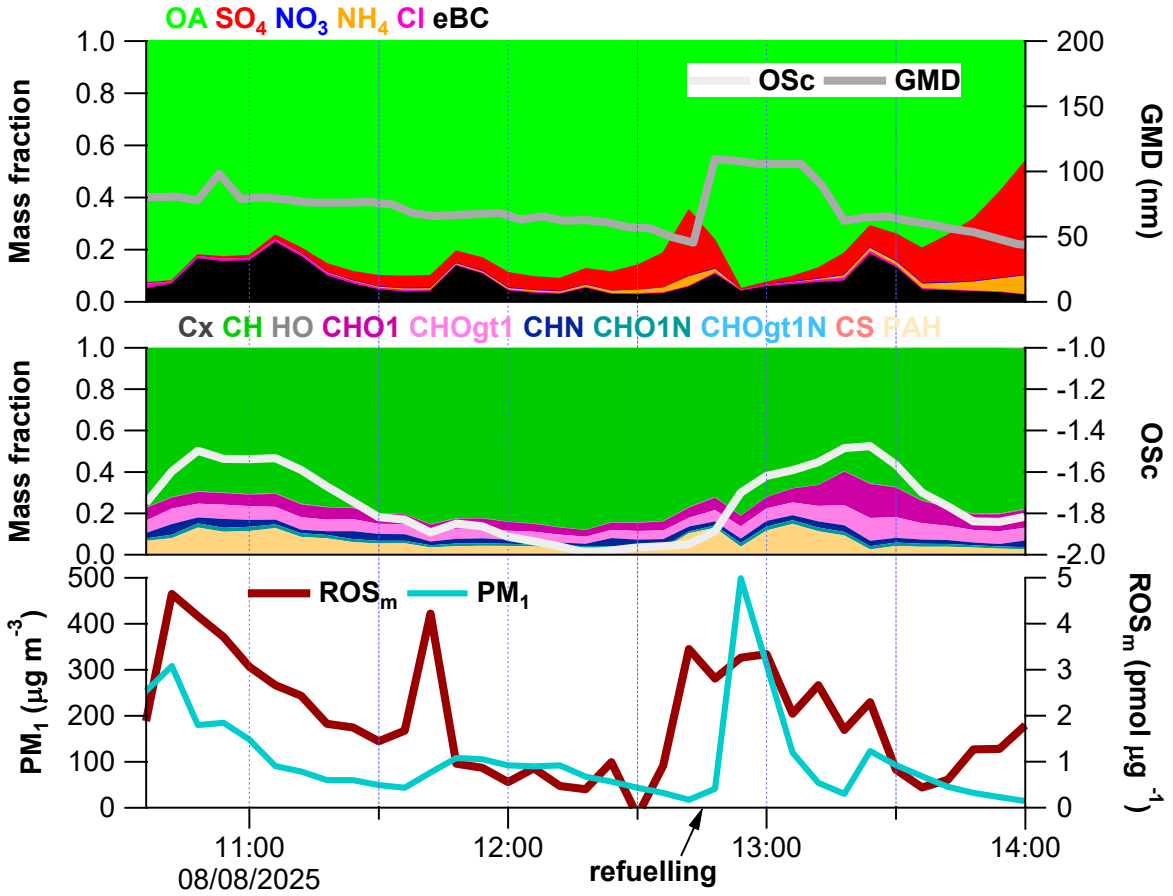


Figure S6. Time-resolved evolution of particle physicochemical properties and mass-normalized particle-bound ROSm during an illustrative LSMC combustion experiment. The panels show (top) PM_1 chemical composition and particle geometric mean diameter (GMD), (middle) high-resolution OA composition and average carbon oxidation state (OSc), and (bottom) PM_1 mass concentration and ROS_m.

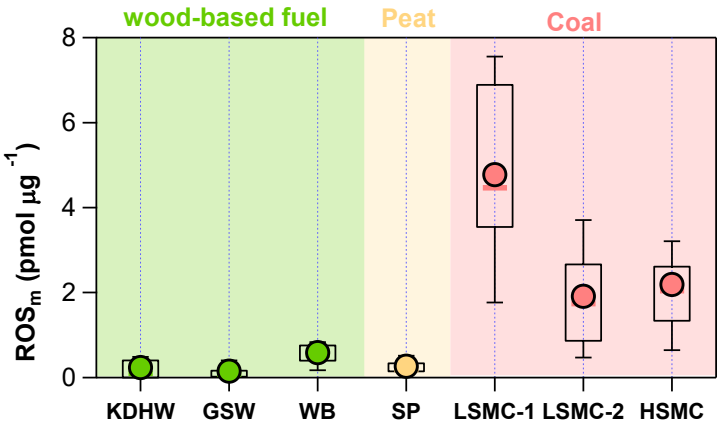


Figure S7. Distributions of mass-normalized particle-bound ROS (ROS_m) across the seven combustion experiments, with the two independent LSMC burns (LSMC-1 and LSMC-2) presented separately to illustrate between-burn variability.

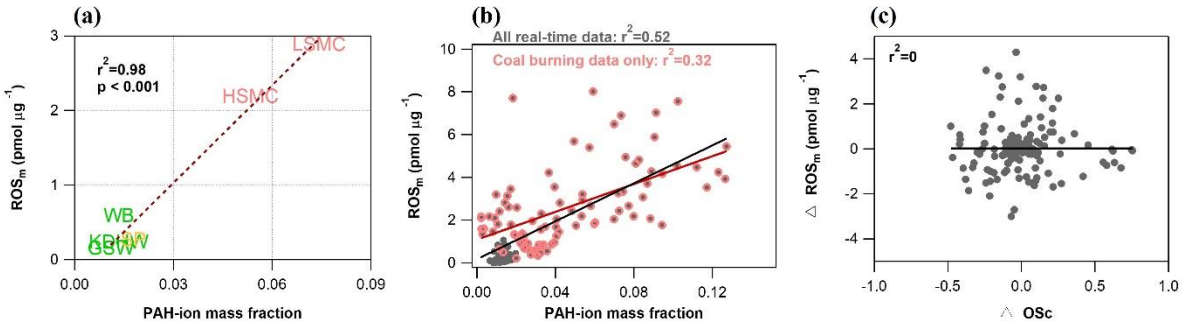


Figure S8. Relationships between mass-normalized particle-bound ROS (ROS_m) and aerosol chemical properties: (a) burn-averaged ROS_m versus the PAH-related ion mass fraction for the six residential solid fuels, with the two LSMC experiments combined to obtain a single fuel-average value ($r^2 = 0.98$, $p < 0.001$); (b) time-resolved ROSm versus the PAH-related ion fraction for all aligned measurements ($r^2 = 0.52$) and manufactured-coal measurements alone ($r^2 = 0.32$); and (c) changes in ROSm (ΔROS_m) versus changes in average carbon oxidation state (ΔOSc), showing no apparent linear correlation ($r^2 = 0$). Lines represent the corresponding linear regression fits.

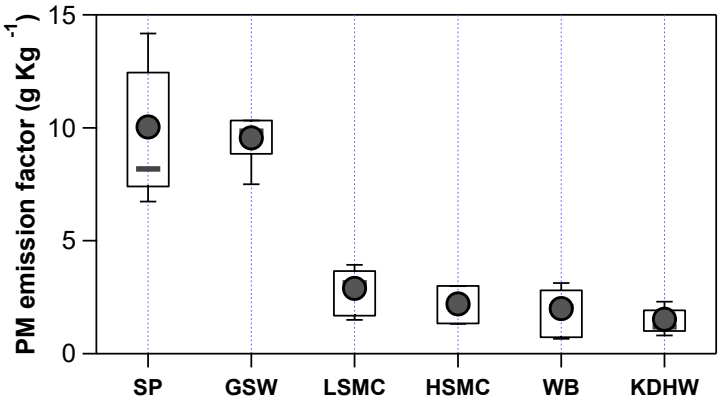


Figure S9. Distributions of particulate matter (PM) mass emission factors for the six residential solid fuels, derived from a separate series of repeated open-fireplace combustion experiments, with at least six independent burns conducted for each fuel. Boxplots illustrate the variability among replicate experiments, and black circles indicate the mean emission factors. These measurements were conducted independently of the seven combustion experiments used for the PINQ ROS analysis.