Supplement to

Radiocarbon-based source apportionment of carbonaceous aerosols over the Athabasca Oil Sands Region in Alberta, Canada

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Text S1. Routine WBEA gas and meteorological measurements at AMS 1.

The WBEA monitoring network continuously measures 5-minute or hourly integrated ambient concentrations of various gases. All continuous gas analyzers in the WBEA network undergo automatic single-point span calibration and are zeroed daily using Teledyne API Model T700 dynamic dilution calibration systems with U.S. EPA protocol-certified gas standards. Additionally, multi-point span calibrations are performed monthly. More information about calibration can be found here: https://wbea.org/.

Data from AMS 1 were incorporated into this study, including hourly integrated measurements of:

(i) $PM_{2.5}$ mass, monitored using the ThermoScientific (Franklin, MA) Model 5030 Synchronized Hybrid Ambient Real-time Particulate Monitor (SHARP), The SHARP $PM_{2.5}$ instrument is calibrated with certified mass foil sets every six months, and its nephelometers are zeroed monthly,
(ii) Nitrogen dioxide (NO_2) and total oxides of nitrogen (NO_x), measured using a ThermoScientific Model 42i and Teledyne API (San Diego, CA) Model T200 chemiluminescence analyzers, respectively,
(iii) Sulfur dioxide (SO_2), monitored using ThermoScientific Model 43i and Teledyne API Model T100 pulsed fluorescence analyzers,
(iv) O_3 measured using ThermoScientific Model 49i and API Model T400 UV absorption analyzers,
(v) Wind speed measured using Met One Model 010C-1,
(vi) Air temperature and relative humidity measured using Vaisala Model HMP155,
(vii) Precipitation measured using Eppley Radiometer Model 8-48.

Table S1. WBEA ambient monitoring stations in the Regional Municipality of Wood Buffalo and routine-monitoring $PM_{2.5}$ statistics for 1 May-31 October 2017.

ID	OSDP Record ID	Station Name	Latitude	Longitude	$PM_{2.5}$ mean ± sd	$PM_{2.5}$ median	$PM_{2.5}$ max/min
			N	W	µg/m³		
AMS 1*	ECCC-CESI-AIR-1-90801	Bertha Ganter – Fort McKay	57.189428	-111.640583	6.9 ± 4.8	5.3	38.1 / 0.2
AMS 6	ECCC-CESI-AIR-1-90702	Patricia McInnes – Fort McMurray	56.751378	-111.476694	5.8 ± 4.4	4.7	29.0 / 0.4
AMS 7	ECCC-CESI-AIR-1-90701	Athabasca Valley – Fort McMurray	56.73344	-111.39047	6.7 ± 4.0	5.8	23.6 / 1.3
AMS 8	NRCAN-GEOSCAN-1-241912	Fort Chipewyan	58.709236	-111.174994	3.8 ± 3.9	2.6	22.7 / 0.1
AMS 13	ECCC-CESI-AIR-1-90806	Fort McKay South	57.149175	-111.642344	6.1 ± 4.8	4.8	30.1 / 0.4
AMS 14	ECCC-CESI-AIR-1-94601	Anzac	56.448908	-111.037975	5.3 ± 3.4	4.2	19.9 / 1.2
AMS 15	Industrial	CNRL Horizon	57.303681	-111.739486	7.1 ± 5.5	5.6	45.9 / 0.7
AMS 16	NRCAN-GEOSCAN-1-243268	Shell Muskeg River	57.249039	-111.508647	7.8 ± 5.6	6.2	43.6 / 0.7
AMS 17	Industrial	Wapasu	57.259197	-111.038583	5.6 ± 4.1	4.5	23.2 / 0.5
AMS 18	Regional	Stony Mountain	55.621408	-111.172686	5.1 ± 4.3	3.9	40.5 / 0.2
AMS 21	ECCC-CESI-AIR-1-90808	Conklin	55.632331	-111.078872	5.9 ± 4.9	4.8	40.4 / 0.3
AMS 22	Regional	Janvier	55.903242	-110.749744	4.5 ± 4.0	3.3	30.2 / 0.1

*Filter sampling site for this study.

Table S2. Summary statistics for meteorological parameters, gas-phase pollutants, and carbonaceous aerosol species at AMS 1 (Bertha Ganter-Fort McKay) over the study period (1 May-31 October 2017). Continuously monitored variables are reported from the WBEA routine network; laboratory-monitored species are derived from the 29 24-h $PM_{2.5}$ filter samples.

	Minimum	**Maximum**	**Average**	**Std. Dev**
Continuously monitored variables				
WS ($m\ s^{-1}$)	3.4	19.0	8.2	3.8
T (°C)	-1.3	22.8	14.3	5.7
RH %	38.7	97.1	64.7	12.4
Precipitation (mm)	0	0.9	0.05	0.2
$PM_{2.5}$ ($\mu g\ m^{-3}$)	0.75	20.3	6.9	4.7
NO_2 (ppbv)	0.4	16.2	3.6	3.3
SO_2 (ppbv)	0	8.6	1.4	1.9
NO_x (ppbv)	0.5	33.5	5.2	6.2
O_3 (ppbv)	2.4	38.1	21.3	7.3
Laboratory monitored species				
TC ($\mu g\ m^{-3}$)	1.0	11.7	4.2	2.4
EC ($ng\ m^{-3}$)	59.8	591.2	199.3	126.3
OC ($ng\ m^{-3}$)	625.6	9793.0	3763.9	1994.8
EC/$PM_{2.5}$	0.009	0.3	0.04	0.05
OC/EC	6.4	51.7	22.6	12.7

Table S3. Sample-resolved radiocarbon and stable carbon isotope data for total carbon (TC, n = 29) and elemental carbon (EC, n = 2) in 24-h $PM_{2.5}$ filter samples collected at AMS 1, with apportioned source contributions (*f*) from biomass burning ($_{bb}$), fossil ($_{ff}$) or contemporary ($_{con}$) sources. For smoke-free samples (f_{bb} = 0), f_{con} and f_{ff} were derived from a two-source isotopic mass balance on $F^{14}C$; for smoke-impacted samples, contributions were derived from a three-source dual-isotope Monte Carlo simulation (100,000 iterations per sample) using $F^{14}C$ and $\delta^{13}C$ jointly. Air mass is the dominant 10-day HYSPLIT back-trajectory (N = northerly, W = westerly, Mix = mixed).

Date	Air mass	TC									EC					
		Concen-tration	KC AMS[1]	$F^{14}C$	$F^{14}C_{error}$	$\delta^{13}C$	$\delta^{13}C$[2]	f_{con}	f_{bb}	f_{ff}	Concen-tration	KC AMS[1]	$F^{14}C$	$F^{14}C_{error}$	f_{con}	f_{ff}
		µg/m³				‰			%		ng/m³				%	
5/7/17	N	1.95	228832	0.5807	0.0039	-25.67	n.m.	57	0	43	98.44			n.m.		
5/13/17	Mix	1.47	228829	0.5294	0.0050	-25.16	n.m.	52	0	48	71.87			n.m.		
5/19/17	N	3.88	228830	0.7177	0.0028	-24.92	n.m.	70	0	30	127.42			n.m.		
5/25/17	W	3.46	223653	0.3959	0.0030	-20.23	-20.35	39	0	61	146.75			n.m.		
5/31/17	W	11.65	228831	0.3673	0.0013	-22.41	n.m.	36	0	64	591.23	295229	0.4149	0.1172	41	59
6/6/17	W	4.7	228834	0.5649	0.0019	-25.05	-26.83	56	0	44	156.41			n.m.		
6/12/17	W	5.39	228835	0.4431	0.0019	-24.69	n.m.	44	0	56	279.61			n.m.		
6/18/17	N	3.12	228833	0.7526	0.0038	-25.67	n.m.	74	0	26	214.39			n.m.		
6/24/17	W	5.11	228838	0.4180	0.0020	-27.66	n.m.	27	52	22	228.88			n.m.		
6/30/17	N	3.74	223655	0.7117	0.0030	-27.40	-26.85	26	59	16	141.92			n.m.		
7/6/17	Mix	2.02	223656	0.6118	0.0041	-25.60	n.m.	28	34	38	59.79			n.m.		
7/12/17	W	6.42	228836	0.4715	0.0016	-25.24	n.m.	28	26	46	352.08			n.m.		
7/18/17	N	1.88	228837	0.7907	0.0067	-28.27	n.m.	31	56	13	132.26			n.m.		
7/24/17	Mix	7.59	228839	0.7941	0.0023	-27.04	n.m.	23	61	16	154.00	295228	0.6969	0.0204	70	30
7/30/17	Mix	4.11	223657	0.7159	0.0028	-25.68	n.m.	29	38	32	289.27			n.m.		
8/5/17	Mix	5.55	230126	0.5038	0.0017	-27.55	n.m.	29	48	23	219.22			n.m.		
8/11/17	N	7.04	230127	0.5320	0.0015	-26.72	n.m.	27	46	28	190.23			n.m.		
8/17/17	W	5.39	230128	1.0010	0.0040	-26.50	n.m.	23	67	11	96.02			n.m.		
8/23/17	W	4.93	223658	0.4727	0.0022	-25.23	n.m.	29	27	44	371.40			n.m.		
8/29/17	W	4.95	230129	0.4134	0.0020	-19.29	-20.51	32	9	58	64.62			n.m.		
9/4/17	W	1.12	223659	0.5943	0.0066	-27.28	n.m.	28	51	21	112.93			n.m.		
9/10/17	W	3.74	230130	0.9851	0.0055	-26.84	n.m.	15	76	9	93.61			n.m.		
9/16/17	Mix	5.72	230131	0.3030	0.0023	-23.92	-25.50	30	16	55	417.30			n.m.		
9/22/17	N	0.99	230132	0.6324	0.0081	-26.01	n.m.	62	0	38	98.44			n.m.		
9/28/17	N	6.43	230133	0.3483	0.0019	-21.80	-21.85	35	0	65	282.03			n.m.		
10/5/17	W	3.57	230134	0.8765	0.0044	-25.85	n.m.	29	47	24	100.85			n.m.		
10/10/17	Mix	1.37	230135	0.2183	0.0120	-27.21	n.m.	23	0	77	216.80			n.m.		

10/22/17	W	3.05	230136	0.4275	0.0031	-28.06	n.m.	42	0	58	366.57	n.m.
10/28/17	W	1.7	230137	0.7298	0.0061	-26.88	-27.13	25	55	21	105.68	n.m.

[1]Laboratory identifier; [2]acidified; n.m. = not measured

Table S4. Monte Carlo posterior statistics for three-source apportionment of $PM_{2.5}$ total carbon (TC) collected at AMS 1, Fort McKay, Alberta (May-October 2017). For each sample, the mean and 90% credible interval (5th percentile, p5; 95th percentile, p95) of the retained Monte Carlo iteration distributions are reported for contributions f_{con}, f_{bb} , f_{ff}. Iterations yielding negative source fractions or fractions exceeding unity were rejected; n retained indicates the number of physically valid solutions (see Method 2.3.2). Wide credible intervals and/or low n retained values indicate that the measured isotopic composition is poorly constrained within the defined endmember space, reflecting overlap between the contemporary biogenic and biomass burning endmembers in dual-isotope space.

Date	n retained	f_{con} mean	f_{con} p5	f_{con} p95	f_{bb} mean	f_{bb} p5	f_{bb} p95	f_{ff} mean	f_{ff} p5	f_{ff} p95
5/7/17	100000	0.58	0.57	0.58	0	0	0	0.43	0.42	0.43
5/13/17	100000	0.52	0.52	0.53	0	0	0	0.48	0.47	0.48
5/19/17	100000	0.71	0.71	0.72	0	0	0	0.29	0.29	0.29
5/25/17	100000	0.39	0.39	0.40	0	0	0	0.61	0.60	0.61
5/31/17	100000	0.36	0.36	0.37	0	0	0	0.64	0.63	0.64
6/6/17	100000	0.56	0.56	0.56	0	0	0	0.44	0.44	0.44
6/12/17	100000	0.44	0.44	0.44	0	0	0	0.56	0.56	0.56
6/18/17	100000	0.75	0.74	0.75	0	0	0	0.26	0.25	0.26
6/24/17	6947	0.30	0.02	0.39	0.48	0.02	0.36	0.21	0.59	0.62
6/30/17	21362	0.27	0.04	0.67	0.58	0.04	0.61	0.15	0.30	0.36
7/6/17	19171	0.29	0.03	0.57	0.33	0.03	0.53	0.38	0.40	0.45
7/12/17	12408	0.29	0.02	0.44	0.26	0.02	0.40	0.45	0.54	0.58
7/18/17	12987	0.31	0.07	0.76	0.57	0.03	0.65	0.12	0.22	0.29
7/24/17	32200	0.23	0.04	0.72	0.62	0.06	0.68	0.15	0.22	0.29
7/30/17	23489	0.30	0.03	0.66	0.38	0.04	0.62	0.32	0.30	0.36
8/5/17	9797	0.31	0.03	0.47	0.48	0.02	0.43	0.21	0.50	0.55
8/11/17	15158	0.28	0.03	0.50	0.44	0.02	0.46	0.28	0.48	0.52
8/17/17	36903	0.23	0.03	0.86	0.67	0.12	0.87	0.11	0.02	0.11
8/23/17	12162	0.29	0.02	0.44	0.26	0.02	0.41	0.45	0.53	0.58
8/29/17	47	0.27	0.02	0.38	0.10	0.03	0.35	0.63	0.59	0.63
9/4/17	15570	0.26	0.03	0.56	0.54	0.03	0.51	0.20	0.41	0.47
9/10/17	45572	0.15	0.02	0.78	0.76	0.18	0.87	0.09	0.04	0.12
9/16/17	5226	0.28	0.02	0.29	0.14	0.01	0.26	0.55	0.70	0.73
9/22/17	100000	0.63	0.61	0.64	0	0	0	0.37	0.36	0.39
9/28/17	100000	0.35	0.34	0.35	0	0	0	0.66	0.65	0.66
10/5/17	25290	0.29	0.04	0.81	0.48	0.05	0.75	0.23	0.14	0.22
10/10/17	100000	0.22	0.20	0.24	0	0	0	0.78	0.76	0.80
10/22/17	100000	0.42	0.42	0.43	0	0	0	0.58	0.57	0.58
10/28/17	28119	0.27	0.03	0.67	0.54	0.05	0.63	0.20	0.28	0.35

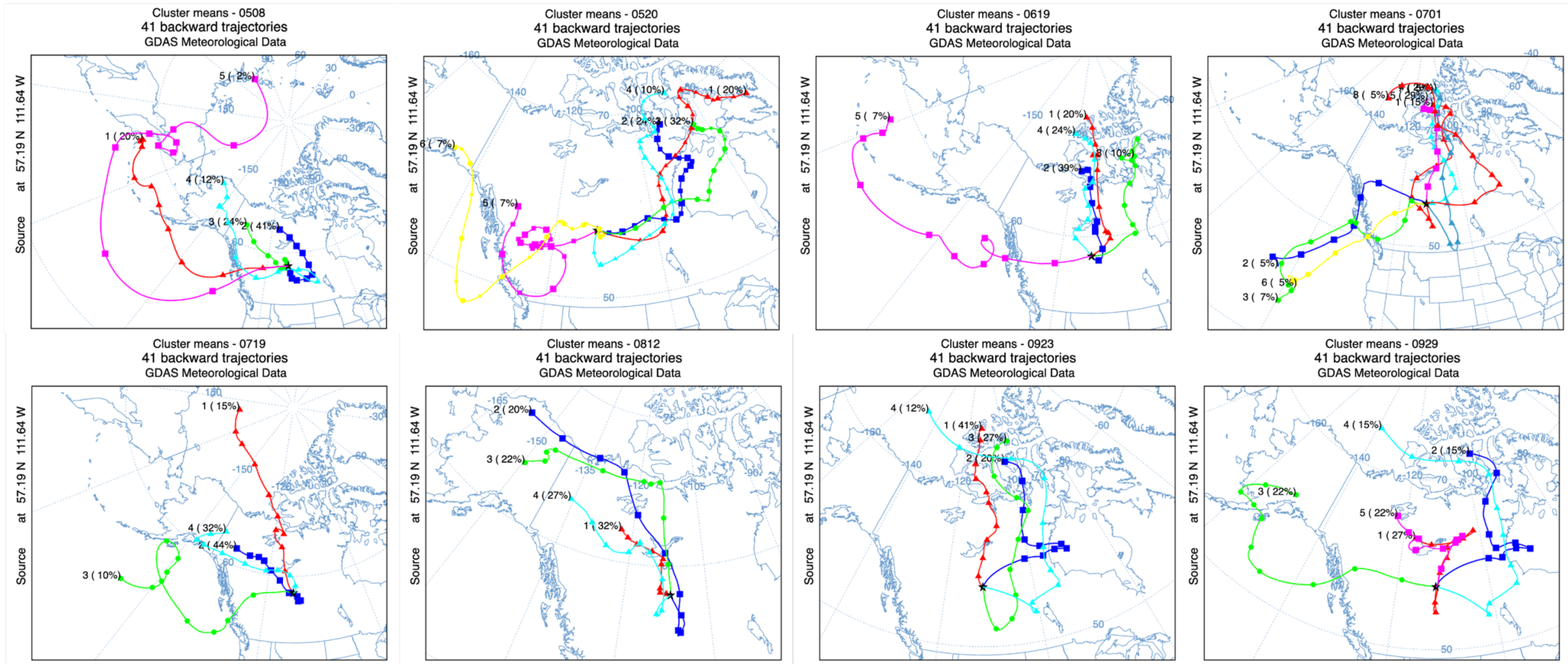


Figure S1. Ten-day HYSPLIT back-trajectories arriving at AMS 1 (Bertha Ganter-Fort McKay) for northerly-dominated sampling periods (n = 8), defined as periods in which northerly flow accounted for more than 60% of the trajectory cluster distribution. Trajectories were computed using NOAA HYSPLIT v5.2.0 driven by GDAS 1° meteorology, with a 240 h backward window initialized at 270 m a.g.l. and a model top of 10,000 m a.g.l., at 6 h intervals across each weekly sampling event. Cluster lines are colored by mean direction; percentages give the fractional contribution of each cluster to total trajectory mass.

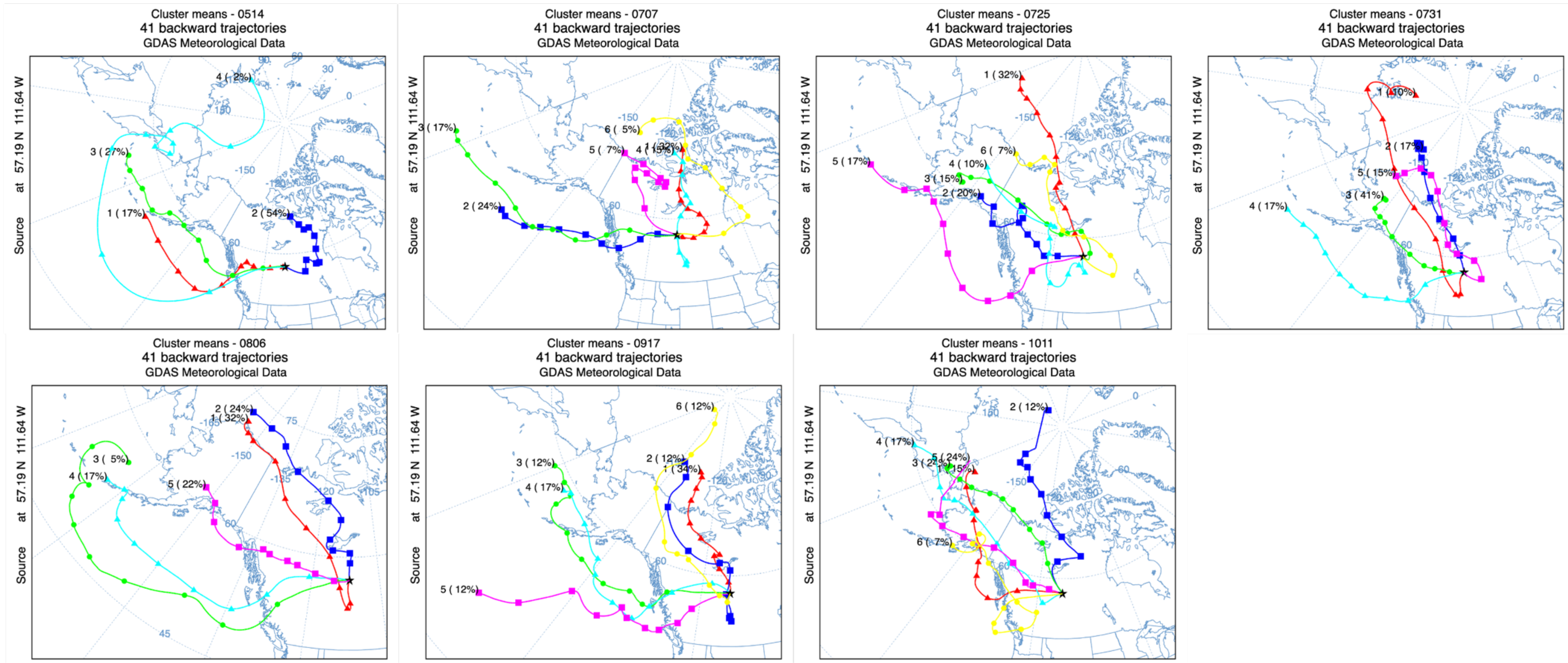
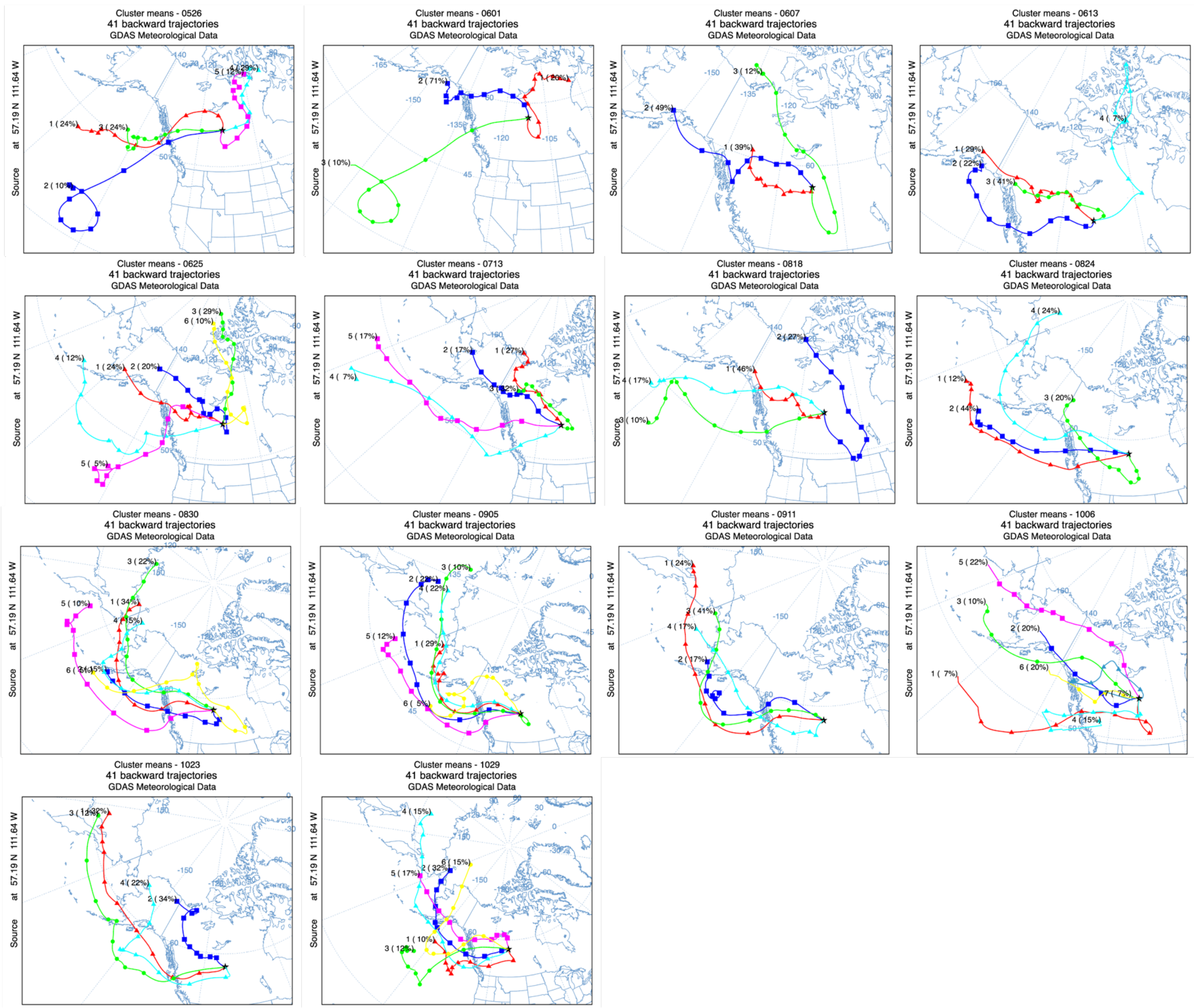


Figure S2. Ten-day HYSPLIT back-trajectories arriving at AMS 1 for mixed sampling periods (n = 7), defined as periods in which northerly, westerly, and other directional components each contributed comparably to the cluster distribution. Trajectories were computed using NOAA HYSPLIT v5.2.0 driven by GDAS 1° meteorology, with a 240 h backward window initialized at 270 m a.g.l. and a model top of 10,000 m a.g.l., at 6 h intervals across each weekly sampling event. Cluster lines are colored by mean direction; percentages give the fractional contribution of each cluster to total trajectory mass.


Cluster means - 0526
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0601
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0607
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0613
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0625
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0713
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GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0818
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GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0824
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GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0830
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0905
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 0911
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 1006
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 1023
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W
Cluster means - 1029
41 backward trajectories
GDAS Meteorological Data
Source at 57.19 N 111.64 W

Figure S3. Ten-day HYSPLIT back-trajectories arriving at AMS 1 for westerly-dominated sampling periods (n = 14), defined as periods in which westerly flow accounted for more than 60% of the trajectory cluster distribution. Trajectories were computed using NOAA HYSPLIT v5.2.0 driven by GDAS 1° meteorology, with a 240 h backward window initialized at 270 m a.g.l. and a model top of 10,000 m a.g.l., at 6 h intervals across each weekly sampling event. Cluster lines are colored by mean direction; percentages give the fractional contribution of each cluster to total trajectory mass.

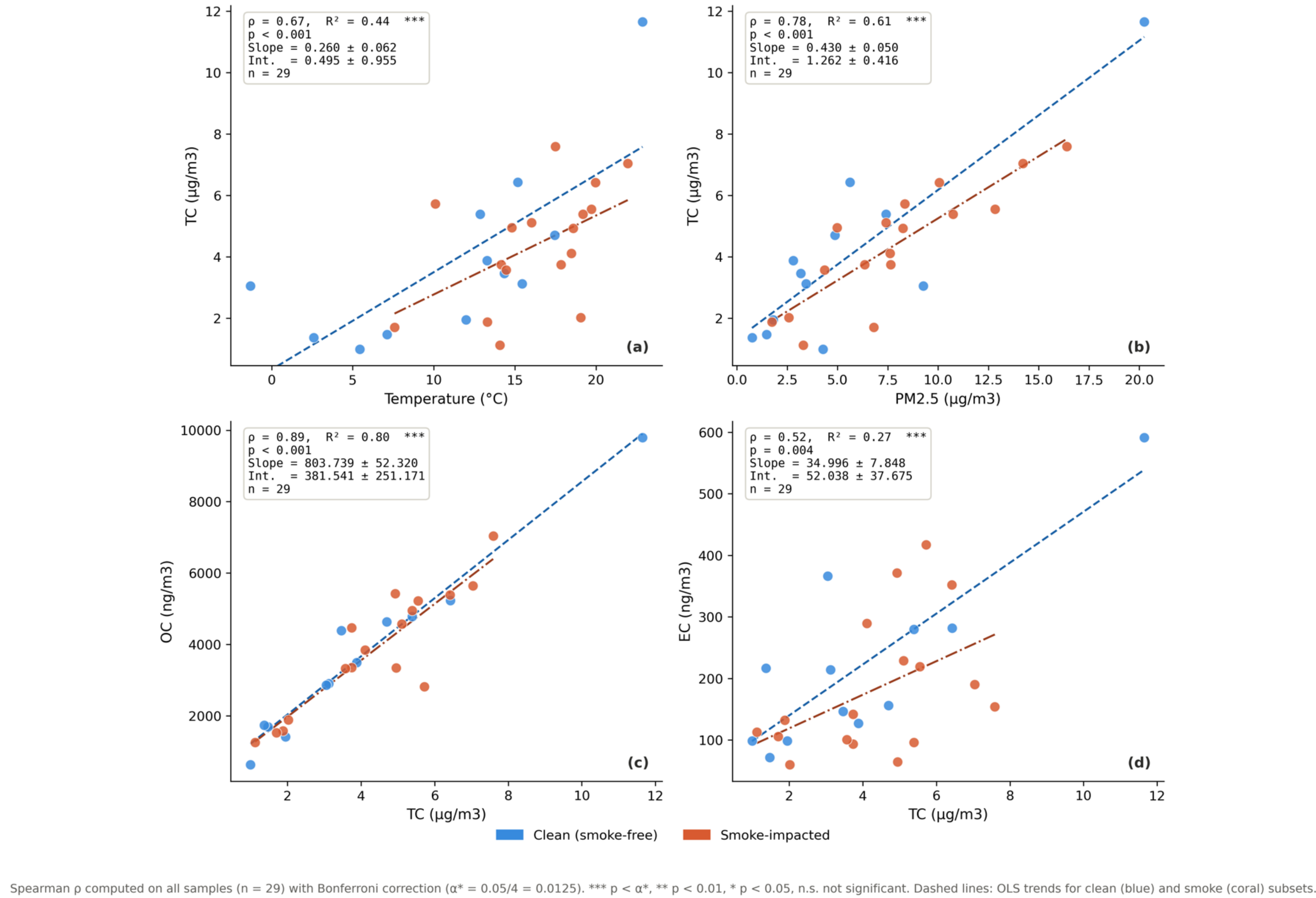


Figure S4. Spearman rank correlations of total carbon (TC) with meteorological variables and trace gases in weekly $PM_{2.5}$ samples at AMS 1, May-October 2017 (n = 29). Marker color distinguishes smoke-impacted (red, n = 17) from smoke-free (blue, n = 12) sampling periods.

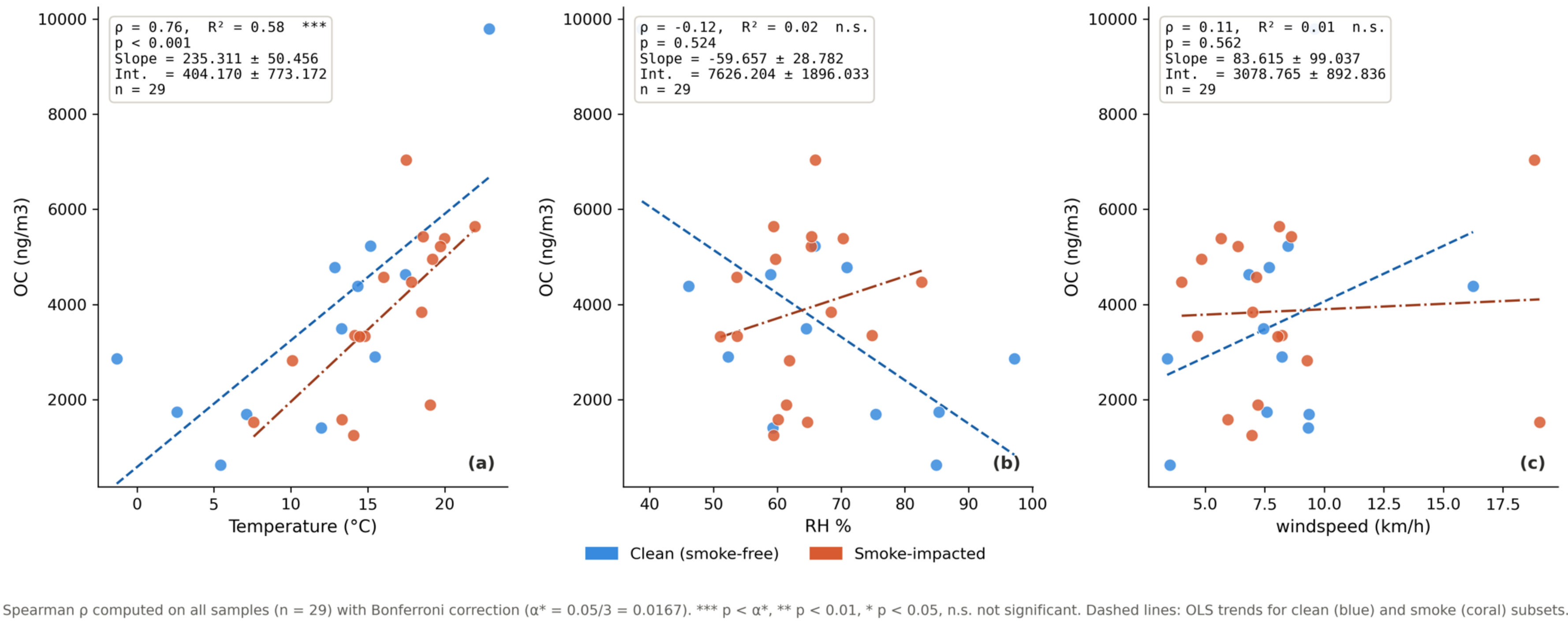
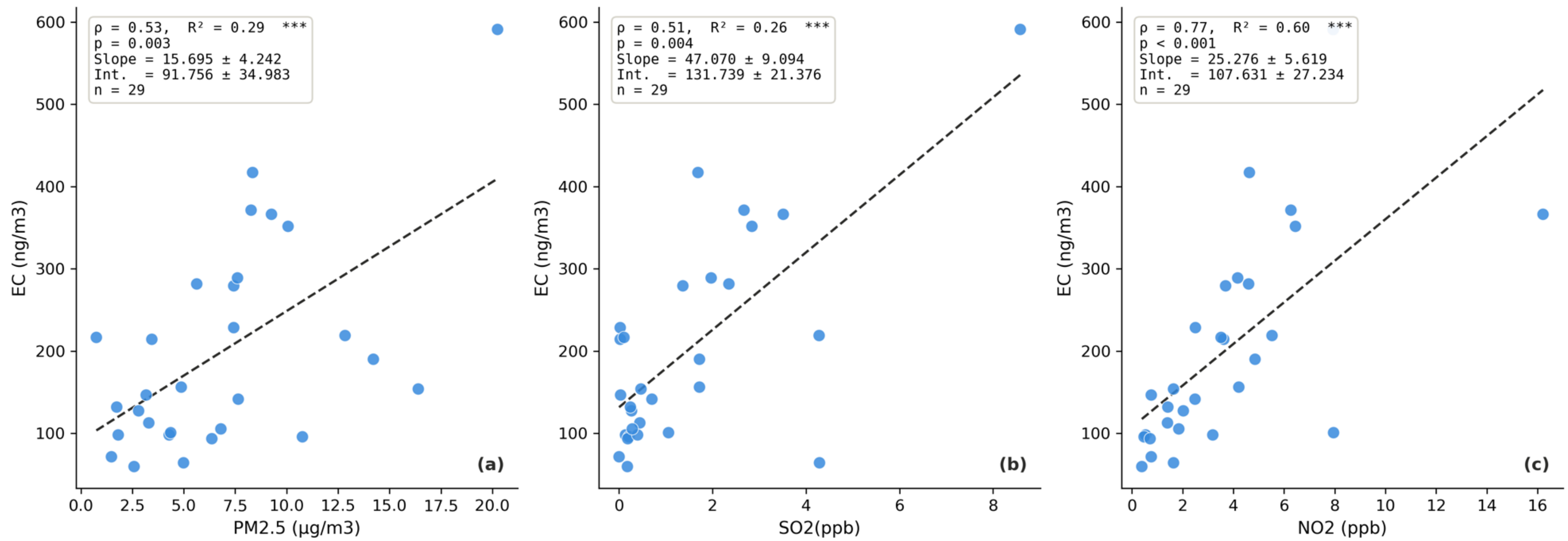


Figure S5. Spearman rank correlations of organic carbon (OC) with meteorological variables and trace gases in weekly $PM_{2.5}$ samples at AMS 1, May-October 2017 (n = 29). Marker color distinguishes smoke-impacted (red, n = 17) from smoke-free (blue, n = 12) sampling periods.



Spearman ρ computed on all samples (n = 29) with Bonferroni correction (α* = 0.05/3 = 0.0167). *** p < α*, ** p < 0.01, * p < 0.05, n.s. not significant. Dashed line: OLS trend for all samples (visual guide only).

Figure S6. Spearman rank correlations of elemental carbon (EC) with meteorological variables and trace gases in weekly $PM_{2.5}$ samples at AMS 1, May-October 2017 (n = 29). Marker color distinguishes smoke-impacted (red, n = 17) from smoke-free (blue, n = 12) sampling periods.

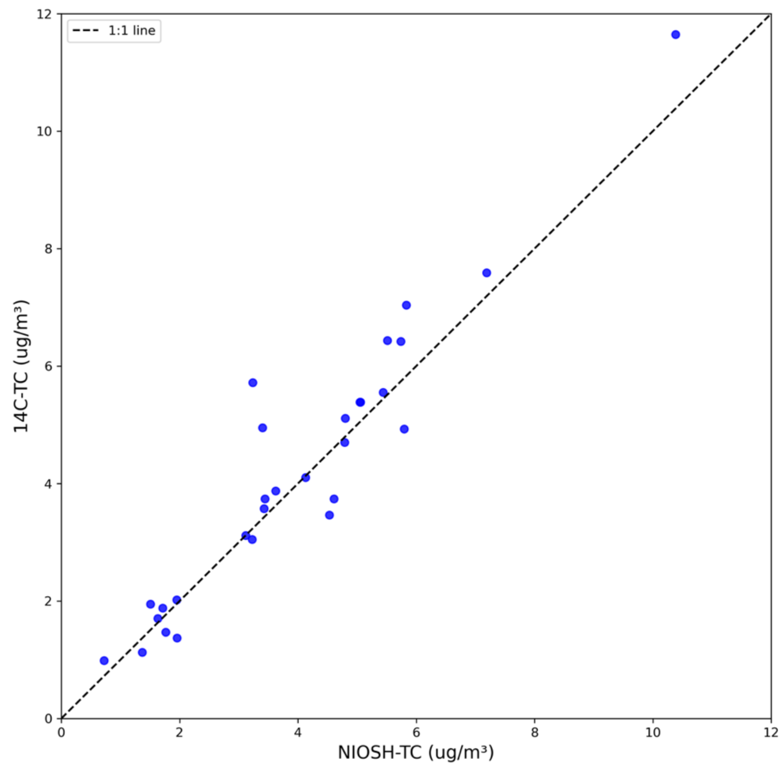


Figure S7. Comparison of total carbon (TC) concentrations measured by two independent methods on $PM_{2.5}$ filter samples from AMS 1. The combustion-based TC (y-axis; multiple 1.5 cm^2 punches sealed-tube combusted at 900°C with CuO and quantified manometrically) is compared against TC from the NIOSH 5040 thermal-optical transmittance method (x-axis; single 1.5 cm^2 punch on a Sunset Laboratory carbon analyzer, reported as TC = OC + EC). The 1:1 line is shown for reference. Combustion-based TC was used for the ^{14}C source apportionment; NIOSH 5040 TC supports comparison with long-term WBEA monitoring records.

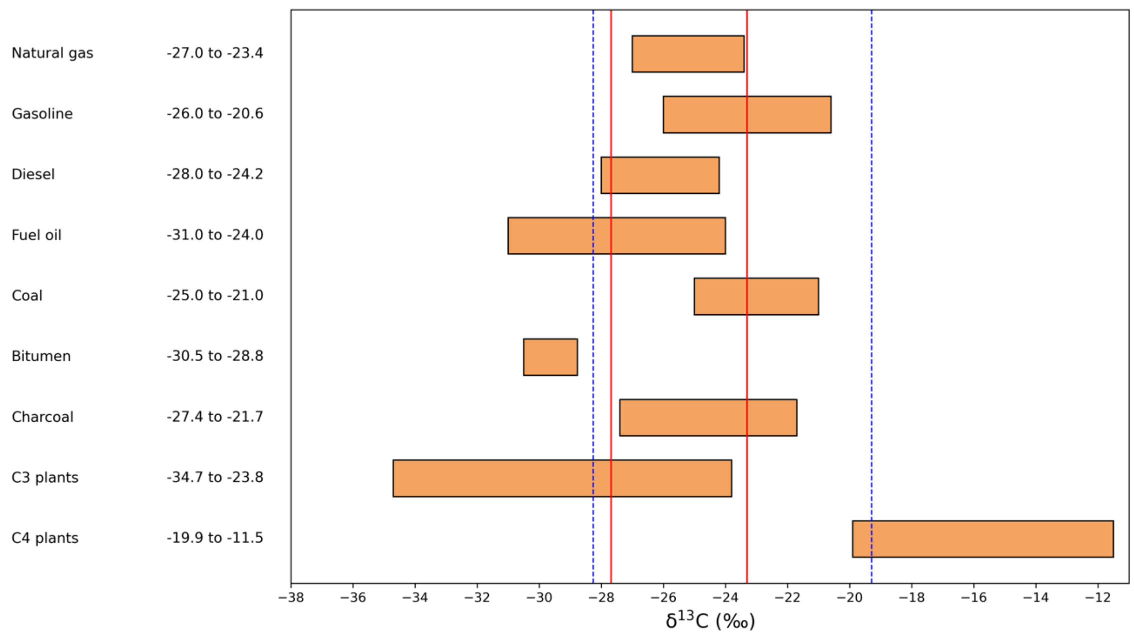


Figure S8. Literature $\delta^{13}C$ ranges of candidate carbonaceous aerosol source endmembers used to interpret samples from the AOSR. Orange bars represent the reported isotopic range for each source material; references for individual sources can be found in Martinsson et al. (2017). Vertical red lines indicate the mean ± 1σ of $\delta^{13}C$ values measured in AOSR carbonaceous aerosol samples in this study, and the blue dashed line denotes the full range of observed sample $\delta^{13}C$ values.

References

Martinsson, J., Andersson, A., Sporre, M. K., Friberg, J., Kristensson, A., Swietlicki, E., Olsson, P.-A., and Stenström, K. E.: Evaluation of δ13C in Carbonaceous Aerosol Source Apportionment at a Rural Measurement Site, Aerosol Air Qual. Res., 17, 2081–2094, https://doi.org/10.4209/aaqr.2016.09.0392, 2017.