

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Air Quality Planning and Standards

Research Triangle Park, NC 27711



MEMORANDUM

DATE: March 29, 2024

SUBJECT: Interlaboratory Results of the 2023 Mega PE Speciation Event

FROM: Colin Barrette (OAQPS)

TO: Research Triangle Institute
University of California, Davis
Desert Research Institute
South Coast Air Quality Management District
California Air Resources Board

Background

The Mega Performance Evaluation (Mega PE) program is a supplemental study designed to evaluate the performance of laboratories routinely analyzing PM_{2.5} speciation samples as part of the PM_{2.5} Chemical Speciation Network (CSN) through the analysis of blind PE filter samples generated by EPA's Ambient Air Monitoring Group (AAMG). The Mega PE program was suspended for approximately 2 years (2020-2022) before being reinitiated by AAMG in late-2022, with the 2023 Mega PE concluding in January 2024. Five laboratories participated in the 2023 Mega PE: Research Triangle Institute (RTI), University of California, Davis (UCD), Desert Research Institute (DRI), California Air Resources Board (CARB), and South Coast Air Quality Management District (SCAQMD). Results were kept anonymous due to Mega PE being a voluntary supplemental study. All program activities were conducted by EPA staff, including flow checks, sample collection, maintenance of the sampling apparatus, and results comparison.

Sample Collection

Blind PE samples were prepared by AAMG at EPA's campus in Research Triangle Park, NC for four separate analyses: anion/cation analysis by ion chromatography (IC), carbon by thermal optical analysis (TOA), metals analysis by x-ray fluorescence (XRF), and total mass analysis by gravimetric weighing. For each analysis type, sets of colocated ambient air filter samples were collected over a single time period during an individual sampling event to ensure sufficient particulates were collected to span the Network's typical concentrations. Samples were collected in December 2023.

The system used for generating colocated sample filters was designed and fabricated at OAQPS in RTP and can collect up to 32 colocated samples simultaneously while maintaining 5% precision

between sample channels (verified though flow checks at each cyclone inlet before and after every sampling event). Photos of the sampling system are shown in Figures 1 and 2, below:

Figure 1. One sampling manifold on the 32-cyclone collocated PE sampler at OAQPS in RTP, NC:



Figure 2. PE Sampling system consisting of 32 PM2.5 cyclones on four sampling manifolds and one dedicated pump (pump-box in the foreground):



Each of the five test laboratories received the following set of PE samples:

- Anion and Cation Analysis by Ion Chromatography (IC): four Nylon® filter samples, and three Nylon® filter blanks (all labs except UCD).
- Carbon by Thermal Optical Analysis (TOA): four quartz filter samples, and three quartz filter blanks (all labs except RTI).
- Elemental analysis by X-Ray Fluorescence (XRF): four 47mm Teflon® filter samples, and three 47mm Teflon® filter blanks.
- Total mass analysis by gravimetric weighing: four 47mm Teflon® filter samples, and three 47mm Teflon® filter blanks (all labs except UCD).

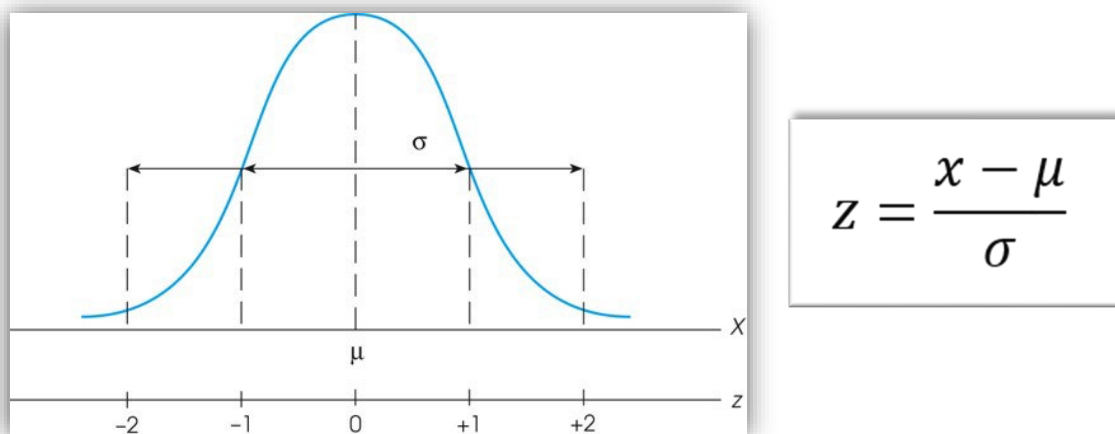
Data Analysis

OAQPS does not have its own speciation laboratories and is unable to serve as a referee lab for all analyses except for mass by gravimetric weighing, therefore it was not possible to provide reference values for the IC, TOA, or XRF samples and blanks. Since these lab results could not be evaluated against a reference value or referee lab result, AAMG evaluated each result through a comparison against the results of other participating labs. Raw values from results submitted as either “ND” (not detected) or “<DL” (less than the detection limit) were not included in the statistical analysis. Values labeled as “NR” (not reported) indicate that the test laboratory did not conduct an analyses for that parameter.

Value Scoring

Interlaboratory comparison was performed by calculating the average and standard deviation of the analytical results from each sampling event, which were then used to calculate a z-score for each individual test laboratory result. Z-scores were calculated using separate averages for sample and blank filters. Each z-score indicates how many standard deviations (σ) an analytical result (x) lies from the mean (μ) of all laboratory results for that target compound/analysis. The z-score can then be compared to a normal distribution curve to compare individual results to a “normal” population. The absolute value of z represents the distance between the raw score and the population mean in units of the standard deviation, as shown in the figure, below:

Figure 3. Relationship between z-score and standard deviation in a normal distribution:



Where:

- z is the z-score;
- x is the value of the individual analytical result;
- μ is the population mean across all laboratories for that analyte; and
- σ is the standard deviation of the population mean of that analyte.

Z-scores range from -3σ (falling to the far left of the normal distribution curve) to $+3\sigma$ (falling to the far right of the normal distribution curve). For this study, when:

- The analytical result is satisfactory when:
 - $-2 < z < 2$ (95% of z-scores are expected to fall in this range for normally distributed data).
- The analytical result is considered questionable when:
 - $-3 < z < -2$ **OR** $2 < z < 3$ (should be investigated by the laboratory).
- The analytical results is unsatisfactory when:
 - $z > 3$ **OR** $-3 > z$ (should be investigated by the laboratory).

Cation/Anion Results

For cation and anion analysis by IC, filters were extracted and analyzed by each participating lab for the cations ammonium (NH_4^+), potassium (K^+), sodium (Na^+), and anions sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-). The z-score result from each filter's ion analysis, in addition to the average measurement for sample and blank filters, are included in the table below. Note that Cl^- was not reported by L4. As shown in red in Table 1, one z-score for SO_4^{2-} exceeded 2 on a single sample filter from RTI, and z-scores for Na^+ and Cl^- exceeded 2 on a separate blank filter from L2.

Table 1. Cations and Anions by IC: Z-Score Results Per Filter

Lab	Replicate	Ammonium	Nitrate	Potassium	Sodium	Sulfate	Chloride
L2	1	1.59	0.60	-0.75	-0.93	2.05	-0.89
L2	2	1.12	0.95	1.01	1.12	1.82	1.28
L2	3	1.01	0.41	-0.59	-0.89	0.06	-0.83
L2	4	0.65	0.26	-0.47	-0.85	0.71	-0.78
L3	1	-0.73	0.43	-0.84	-0.06	-1.52	-0.05
L3	2	0.12	0.64	-0.99	-0.04	-1.30	0.03
L3	3	-1.41	1.15	-1.66	-1.15	-0.38	-1.09
L3	4	-0.31	0.39	0.14	1.46	-1.29	1.52
L4	1	0.18	-1.88	-0.53	-0.96	-0.32	NR
L4	2	ND	-1.54	-0.43	-0.98	0.31	NR
L4	3	ND	-1.18	1.41	1.31	0.21	NR
L4	4	ND	-1.74	0.39	0.29	-0.74	NR
L5	1	-1.58	-0.07	0.42	-0.12	0.42	-0.39
L5	2	-0.16	0.92	1.97	1.44	-0.01	1.25
L5	3	-1.11	0.42	-0.36	-0.86	-0.32	-1.03
L5	4	0.63	0.26	1.27	1.19	0.31	0.98

Average Sample Measurement (ug/filter)		0.63	8.64	1.83	4.03	15.91	4.12
L2	B1	ND	0.33	0.20	0.64	0.20	0.48
L2	B2	ND	1.57	1.752	2.45	ND	2.21
L2	B3	ND	0.52	0.52	1.02	ND	0.83
L3	B1	-0.58	-1.00	-1.15	-0.59	ND	-0.70
L3	B2	1.16	-0.97	-1.12	-0.53	ND	-0.63
L3	B3	-0.58	-0.45	-1.21	-0.69	ND	-0.81
L4	B1	ND	ND	0.75	-1.48	ND	NR
L4	B2	ND	ND	0.07	-0.39	ND	NR
L4	B3	ND	ND	0.18	-0.22	ND	NR
L5	B1	ND	ND	ND	0.09	ND	-0.38
L5	B2	ND	ND	ND	-0.13	ND	-0.45
L5	B3	ND	ND	ND	-0.15	ND	-0.56
Average Blank Measurement (ug/filter)		0.01	0.53	0.53	1.98	0.10	2.45

Carbon Results

Carbon analysis by TOA was conducted by UCD, DRI, CARB, and SCAQMD for organic carbon (OC), elemental carbon (EC), and total carbon (TC) mass. The z-score result from each filter's TOA analysis, in addition to the average measurement for sample and blank filters, are included in the table below. As shown in red in Table 2, no z-scores exceeded 2.

Table 3. Carbon analysis by TOA: Values and Z-Score Results Per Filter

Lab	Replicate	TC z-score	OC z-score	EC z-score
L1	1	0.57	-0.28	1.23
L1	2	0.08	-0.67	0.99
L1	3	-0.38	-1.03	0.77
L1	4	-0.80	-1.40	0.59
L3	1	0.04	-0.45	0.68
L3	2	-0.62	-0.92	0.27
L3	3	-1.14	-1.48	0.17
L3	4	-0.05	-0.10	0.13
L4	1	1.53	1.48	0.60
L4	2	1.59	1.31	0.85
L4	3	1.74	1.59	-0.61
L4	4	0.87	0.80	0.41
L5	1	-0.21	1.05	-1.46
L5	2	-1.26	-0.06	-1.72
L5	3	-0.97	0.04	-1.39

L5	4	-0.99	0.12	-1.51
Average Sample Measurement (ug/cm2)		4.72	3.68	1.01
L3	B1	-0.47	-0.46	ND
L3	B2	-0.73	-0.72	-0.40
L3	B3	-0.33	-0.34	0.50
L4	B1	1.42	1.43	-0.40
L4	B2	1.20	1.24	0.52
L4	B3	1.31	1.28	0.52
L1	B1	-0.62	-0.69	1.48
L1	B2	-0.83	-0.83	-0.33
L1	B3	-0.95	-0.90	-1.89
L5	B1	ND	ND	ND
L5	B2	ND	ND	ND
L5	B3	ND	ND	ND
Average Blank Measurement (ug/cm2)		0.29	0.28	0.004

Elemental Results

Elemental analysis by XRF was conducted by UCD, RTI, DRI, CARB, and SCAQMD for several elemental parameters. Ten parameters with high concentrations measured within CSN and with significant loadings during the MegaPE were selected to evaluate the interlaboratory comparison. The z-score result from each filter's XRF analysis, in addition to the average measurement for sample and blank filters, are included in the table below. As shown in red in Table 3, some z-scores by L1, L2, and L3 exceeded 2 for S, Fe, K, Zn, Br, and Pb. No z-scores exceeded 3.

Table 3. Elemental analysis by XRF: Z-Score Results Per Filter

Lab	Replicate	S	Si	Fe	K	Ca	Al	Cl	Zn	Br	Pb
L1	1	-0.09	0.32	0.57	1.18	-0.10	-0.03	-0.89	2.03	-1.25	1.39
L1	2	-0.77	0.16	0.57	0.62	0.66	-0.12	-1.57	0.81	-0.37	1.54
L1	3	0.14	0.06	0.42	0.90	-0.86	0.84	-1.12	0.21	-0.81	1.82
L1	4	-0.49	0.59	2.56	0.34	-0.48	ND	-1.57	1.42	-0.37	2.11
L2	1	-1.28	0.32	-0.88	-1.04	1.74	-1.09	0.15	-1.69	-0.89	-0.51
L2	2	-0.53	0.71	-0.30	0.74	-0.31	-0.95	0.49	-1.20	-0.01	-0.36
L2	3	0.83	0.31	-0.69	2.29	0.03	-1.03	0.92	-0.83	0.89	-0.49
L2	4	-0.78	0.05	-0.93	-0.10	-1.21	-0.86	0.25	-1.54	0.48	-0.55
L3	1	2.06	-1.97	0.21	0.01	ND	-1.37	ND	0.57	-0.74	-0.66
L3	2	1.76	-1.22	-0.68	-1.32	ND	-1.15	ND	-0.61	1.29	ND
L3	3	1.52	-2.15	2.41	-1.35	ND	-1.22	ND	-0.25	-1.35	-0.90
L3	4	0.95	-2.06	0.76	-1.62	ND	-1.17	ND	-0.79	2.53	-0.22
L5	1	-1.29	0.68	-0.49	-0.57	1.21	1.00	ND	0.50	ND	-0.50

L5	2	-0.25	1.26	-0.25	0.89	-0.11	1.12	ND	0.73	ND	-0.47
L5	3	-0.76	0.69	-0.82	-0.34	-1.63	0.98	ND	1.21	ND	-0.62
L5	4	-1.37	0.54	-0.87	-1.25	-1.03	1.16	ND	0.71	ND	-0.46
L4	1	0.18	0.37	-0.19	0.36	0.52	0.92	1.05	-0.54	-0.15	-0.55
L4	2	0.30	0.39	-0.67	0.40	-0.69	0.96	0.81	0.01	0.38	ND
L4	3	0.12	0.53	-0.41	0.18	1.63	1.03	0.84	-0.17	0.09	-0.57
L4	4	-0.25	0.44	-0.32	-0.33	0.65	0.99	0.63	-0.57	0.27	ND
Average Sample Measurement (ug/cm2)		0.91	0.06	0.08	0.11	0.03	0.06	0.01	0.20	0.01	0.01
L1	B1	ND	-0.58	0.63	-0.73	ND	0.33	-0.58	-1.15	ND	0.65
L1	B2	ND	1.15	1.19	1.14	1.13	0.88	1.15	0.58	ND	1.31
L1	B3	ND	-0.58	0.24	-0.41	ND	0.79	-0.58	0.58	ND	0.65
L2	B1	ND	ND	-1.06	ND	-0.75	ND	ND	ND	ND	ND
L2	B2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L2	B3	ND	ND	-1.00	ND	ND	ND	ND	ND	ND	ND
L3	B1	ND	ND	ND	ND	ND	-0.65	ND	ND	ND	-0.99
L3	B2	ND	ND	ND	ND	ND	-1.18	ND	ND	0.71	-1.06
L3	B3	ND	ND	ND	ND	ND	-1.24	ND	ND	-0.71	-0.57
L5	B1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L5	B2	ND	ND	ND	ND	ND	1.07	ND	ND	ND	ND
L5	B3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	B1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
L4	B2	ND	ND	ND	ND	ND	1.07	ND	ND	ND	ND
L4	B3	ND	ND	ND	ND	-0.38	ND	ND	ND	ND	ND
Average Blank Measurement (ug/cm2)		ND	0.01	0.02	0.01	0.01	0.04	0.00	0.00	0.00	0.01

Total Mass Results

Total mass analysis by gravimetric weighing was conducted by UCD, RTI, DRI, CARB, and SCAQMD for samples and blanks. Z-scores for total mass were calculated using the average and standard deviations of difference between OAQPS' observed value and the test laboratory's observed value. One filter for L3 was labeled "NA" and disqualified from evaluation due to filter handling issues by EPA. Table 4 shows that no z-scores exceeded 2.

Table 4. Total Mass by Gravimetric Weighing: Z-Score Results Per Filter

LAB	Replicate	OAQPS Weight (ug)	Lab Weight (ug)	Difference (ug)	Difference Z-Score
L2	1	168.838	168.828	-0.010	-0.68
L2	2	170.779	170.766	-0.013	-0.88
L2	3	164.648	164.636	-0.012	-0.81
L2	4	171.819	171.803	-0.016	-1.08

L3	1	167.121	167.14	0.019	1.26
L3	2	170.518	170.532	0.014	0.93
L3	3	162.636	162.666	0.030	NA
L3	4	172.371	172.398	0.027	1.80
L4	1	164.240	164.239	-0.001	-0.08
L4	2	164.530	164.522	-0.008	-0.54
L4	3	169.589	169.577	-0.012	-0.81
L4	4	172.453	172.436	-0.017	-1.14
L5	1	164.178	164.176	-0.002	-0.14
L5	2	165.807	165.809	0.002	0.13
L5	3	169.153	169.153	0	-0.01
L5	4	171.792	171.793	0.001	0.06
L2	B1	149.634	149.62	-0.014	-0.78
L2	B2	149.153	149.136	-0.017	-0.96
L2	B3	148.316	148.302	-0.014	-0.78
L3	B1	146.141	146.169	0.028	1.79
L3	B2	148.632	148.657	0.025	1.61
L3	B3	149.937	149.958	0.021	1.36
L4	B1	146.729	146.721	-0.008	-0.41
L4	B2	149.482	149.468	-0.014	-0.78
L4	B3	168.331	168.32	-0.011	-0.60
L5	B1	144.663	144.661	-0.002	-0.05
L5	B2	147.794	147.789	-0.005	-0.23
L5	B3	147.682	147.678	-0.004	-0.17

Discussion

The results in the questionable z-score range for cation/anion and elemental analyses do not track with any sampler inlet/position and cannot be explained by flow variations in the sampling apparatus (confirmed via flow checks conducted prior to each event).

Cation/anion analysis revealed abnormally high z-score values for Na^+ , SO_4^{2-} , and Cl^- for sampled and blank filters analyzed by lab L2. EPA found that some Nylon filters used in this MegaPE had failed acceptance testing for Na, thereby explaining abnormally high Na values detected on lab L2's B2 blank filter. EPA may further investigate the cause of abnormally high z-score values of SO_4^{2-} and Cl^- . Furthermore, elemental analyses revealed abnormally high z-score values for S, Fe, K, Zn, Br, and Pb for sampled filters analyzed by labs L1, L2, and L3. EPA may further investigate the cause of abnormally high z-score values for S, Fe, K, Zn, Br, and Pb.

Findings from this Mega PE will be used by EPA in assessing irregular or questionable results from laboratories participating in CSN and in validating the performance of the sampling apparatus in subsequent evaluations.

Appendix: OAQPS flow verification and sample collection notes from samples used in the 2023 Mega PE.

Filter ID	Filter Media	Start Sample Flow	End Sample Flow	Analysis Type	Lab Assign
W20204901	Teflon	7.020	6.670	XRF	UCD
W20204902	Teflon	6.850	6.640	XRF	DRI
W20204903	Teflon	6.780	6.500	Grav	RTI
W20204904	Teflon	6.360	6.180	Grav	DRI
W20204905	Teflon	6.750	6.520	XRF	SCAQMD
W20204906	Teflon	6.860	6.610	XRF	CARB
W20204907	Teflon	6.740	6.570	Grav	SCAQMD
W20204908	Teflon	6.650	6.370	Grav	CARB
W20204909	Teflon	6.820	6.620	XRF	UCD
W20204910	Teflon	6.770	6.580	Grav	RTI
W20204911	Teflon	6.720	6.540	XRF	DRI
W20204912	Teflon	6.850	6.670	Grav	DRI
W20204913	Teflon	6.840	6.660	XRF	SCAQMD
W20204914	Teflon	6.950	6.730	XRF	CARB
W20204915	Teflon	6.930	6.730	XRF	UCD
W20204916	Teflon	6.770	6.610	XRF	DRI
W20204917	Teflon	6.890	6.760	XRF	SCAQMD
W20204918	Teflon	6.860	6.730	Grav	SCAQMD
W20204919	Teflon	6.860	6.700	XRF	CARB
W20204920	Teflon	6.880	6.750	Grav	CARB
W20204921	Teflon	6.830	6.680	XRF	UCD
W20204922	Teflon	6.670	6.530	XRF	DRI
W20204923	Teflon	6.640	6.520	XRF	SCAQMD
W20204924	Teflon	6.940	6.800	Grav	RTI
W20204925	Teflon	6.860	6.690	Grav	DRI
W20204937	Teflon	6.750	6.580	XRF	CARB
W20204931	Teflon	6.510	6.340	Grav	SCAQMD
W20204936	Teflon	6.850	6.670	Grav	CARB
W20204939	Teflon	6.870	6.720	Grav	RTI
W20204942	Teflon	6.560	6.390	Grav	DRI
W20204944	Teflon	6.600	6.430	Grav	SCAQMD
W20204945	Teflon	6.580	6.390	Grav	CARB
Q1	Quartz	6.810	6.960	Carbon	UCD
Q2	Quartz	6.750	6.880	Carbon	UCD
Q3	Quartz	6.620	6.740	Carbon	UCD
Q4	Quartz	6.420	6.500	Carbon	UCD

Q5	Quartz	6.660	6.750	Carbon	DRI
Q6	Quartz	6.720	6.820	Carbon	DRI
Q7	Quartz	6.690	6.790	Carbon	DRI
Q8	Quartz	6.510	6.630	Carbon	DRI
Q9	Quartz	6.680	6.680	Carbon	SCAQMD
Q10	Quartz	6.640	6.650	Carbon	SCAQMD
Q11	Quartz	6.590	6.620	Carbon	SCAQMD
Q12	Quartz	6.740	6.750	Carbon	SCAQMD
Q13	Quartz	6.710	6.690	Carbon	CARB
Q14	Quartz	6.740	6.720	Carbon	CARB
Q15	Quartz	6.770	6.750	Carbon	CARB
Q16	Quartz	6.650	6.610	Carbon	CARB
N1	Nylon	6.950	6.780	Ions	RTI
N2	Nylon	6.900	6.750	Ions	RTI
N3	Nylon	6.830	6.740	Ions	RTI
N4	Nylon	6.400	6.280	Ions	RTI
N5	Nylon	6.830	6.740	Ions	DRI
N6	Nylon	6.770	6.670	Ions	DRI
N7	Nylon	6.740	6.610	Ions	DRI
N8	Nylon	6.670	6.570	Ions	DRI
N9	Nylon	6.670	6.430	Ions	SCAQMD
N10	Nylon	6.580	6.340	Ions	SCAQMD
N11	Nylon	6.480	6.250	Ions	SCAQMD
N12	Nylon	6.620	6.390	Ions	SCAQMD
N13	Nylon	6.580	6.340	Ions	CARB
N14	Nylon	6.720	6.500	Ions	CARB
N15	Nylon	6.620	6.390	Ions	CARB
N16	Nylon	6.500	6.300	Ions	CARB