UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

OFFICE OF
AIR AND RADIATION

MEMORANDUM

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SUBJECT: Interlaboratory Results of the OAQPS 2018 Mega PE Speciation Event

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Introduction

As many of you are aware, the $PM_{2.5}$ Mega performance evaluation (PE) program was suspended for approximately 3 years while the program was transitioned from NAREL to OAQPS. OAQPS resumed the program in late 2017 and completed the first study in early 2018. Draft results were circulated on October 17, 2018; however, one laboratory had yet to analyze their PE samples because their instrumentation was in the process of being updated.

All data have now been received and the results presented here are considered final.

This study was conducted as part of EPA's quality assurance oversight of the $PM_{2.5}$ chemical speciation air monitoring network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) Program. The purpose of the study was to evaluate specific laboratory performance at those laboratories that routinely analyze $PM_{2.5}$ speciation samples. Five laboratories participated in this study: California Air Resources Board (CARB), Desert Research Institute (DRI), the Oregon Department of Environmental Quality (ODEQ), Research Triangle Institute (RTI), and the South Coast Air Quality Management District (SCAQMD).

As in previous studies, each participating laboratory analyzed a set of blind PE filter samples. The PE samples were prepared by the Office of Air Quality Planning and Standards (OAQPS) at the Research Triangle Park (RTP), NC facility. For each analysis type, three sets of collocated ambient air filter samples were collected over varying time periods to ensure sufficient particulate were collected to span

the $PM_{2.5}$ Network average concentrations. The collocated sampling system was designed and fabricated at OAQPS in RTP, NC and is used for both the Mega PE and Gravimetric Round Robin PE events. The sampler can collect up to 32 collocated samples simultaneously and achieves 5% precision between samples (verified though gravimetric QC studies conducted prior to each PE event and flow checks at each cyclone prior to every sampling event). Photos of one of the four sampling manifolds containing eight cyclones, and the collocated sampling system and are shown in Figures 1 and 2, below.

Figure 1. One of four sampling manifolds on the 32-cyclone collocated PE sampler at OAQPS in RTP, NC

Figure 2. PE Sampling system consisting of 32 $PM_{2.5}$ cyclones on four sampling manifolds and one dedicated pump (in pump-box in the foreground)

Each laboratory received the following set of PE speciation samples:

- Anion and Cation Analysis by Ion Chromatography (IC)
    - Five Nylon® filter samples (all labs)
    - Six Teflon® filter samples (one lab)
- Carbon by Thermal Optical Analysis (TOA)
    - Five quartz filter samples
    - Four quartz filter samples (one lab)
- Elemental analysis by X-Ray Fluorescence (XRF)
    - Five 47 mm Teflon® filter samples

Data Analysis

OAQPS does not have its own laboratories and was unable to successfully qualify external referee labs, therefore it was not possible to obtain reference values for the PE samples. Since the lab results could not be evaluated against an assigned value (referee lab result), OAQPS evaluated each result against the results of the other laboratories participating in the study (interlaboratory comparison).

When the draft data were reported, results submitted as either "ND" (not detected) or "<DL" (less than the detection limit) were converted to zero. This was done because non-numerical values included in a statistical analysis skewed the results. Upon reflection, we determined that setting values to zero had more of an impact than excluding these results. For this reason, for this final analysis and report, results reported as "ND" or "<DL" were excluded from the statistical analysis and no scores reported. Results impacted are IC data: one data point from Event 1, and multiple data points from both Blanks.

To avoid this in future studies, all laboratories will be asked to provide the actual numerical value of each result. When laboratories submit "ND" or "<DL", those results will be excluded from the analysis and a z-score will not be reported.

Interlaboratory Comparison Scoring

The interlaboratory comparison was performed by calculating the average and standard deviation of each set of analytical results from distinct sampling events, which were then used to calculate a *z*-score for each individual laboratory result. Each *z*-score indicates how many standard deviations (σ) an analytical result (x) lies from the mean (μ) across all laboratory results for that target compound. A *z*-score, also called a standard score, can be placed on a normal distribution curve to compare results from a test 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.

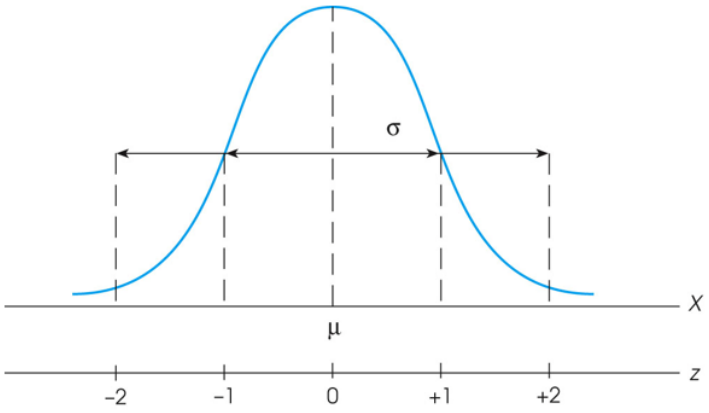

Figure 3. Relationship between *z*-score and standard deviation in a normal distribution

Z-scores range from -3 σ (falling to the far left of the normal distribution curve) to +3 σ (falling to the far right of the normal distribution curve).

$$z = \left|\frac{x - \mu}{\sigma}\right|$$

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.

For this study, when:

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

Happily, all *z*-scores for this study were less than 2. See the tables below for a summary of all results.

Results

For the elemental analysis by XRF, results from the top ten CSN wide average elemental concentrations from June 2016 through May 2018 were included in the interlaboratory comparison. In descending order by average concentration, these elements shown in Figure 2, below, and are sulfur (S), silicon (Si), iron (Fe), potassium (K), sodium (Ns), calcium (Ca), aluminum (Al), chlorine (Cl), magnesium (Mg), and zinc (Z).

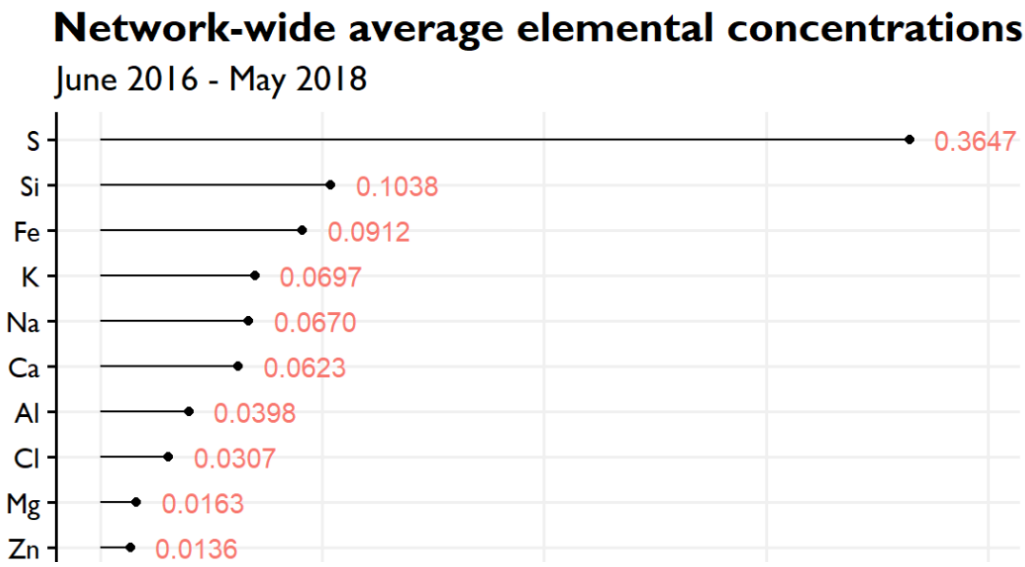

Figure 4. Top-ten CSN-wide average elemental concentrations

As shown in Table 1, below, all *z*-scores for the selected elements by XRF were below 2.

Table 1. Selected Elements by XRF: Interlaboratory *z*-score Results

Lab	Event	S	Si	Fe	K	Na	Ca	Al	Cl	Mg	Zn
DRI	1	0.82	1.14	0.85	0.50	1.48	0.68	0.70	1.19	0.77	1.26
ODEQ		1.43	0.52	1.44	1.14	0.70	1.44	1.46	0.19	0.77	1.19
SCAQMD		0.10	1.02	0.37	1.06	0.48	0.67	0.59	1.23	1.33	0.04
UCD		0.51	0.63	0.22	0.58	0.30	0.08	0.16	0.15	0.22	0.04
DRI	2	0.71	1.28	0.39	0.17	1.50	0.30	0.81	1.12	0.85	0.62
ODEQ		1.47	0.31	1.47	1.44	0.59	1.49	1.23	0.97	0.85	1.49
SCAQMD		0.22	0.91	0.77	0.85	0.46	0.63	0.81	0.70	1.11	0.43
UCD		0.53	0.67	0.31	0.41	0.45	0.55	0.39	0.55	0.58	0.45
DRI	3	0.90	0.78	0.45	0.58	1.50	0.39	1.50	0.61	0.87	0.77
ODEQ		1.40	0.85	1.49	1.49	0.53	1.49	0.55	1.50	0.87	1.47
SCAQMD		0.01	1.23	0.65	0.32	0.47	0.61	0.52	0.44	0.87	0.35
UCD		0.49	0.40	0.40	0.59	0.50	0.49	0.43	0.45	0.86	0.34
DRI	B1	0.00	1.22	0.50	0.45	1.50	1.12	0.06	0.58	0.02	0.87
ODEQ		0.00	0.40	0.50	0.52	0.52	0.84	0.69	0.58	0.81	0.87
SCAQMD		0.00	0.90	0.50	0.52	0.52	0.84	0.69	1.49	1.40	0.88
UCD		0.00	0.73	1.50	1.50	0.46	0.57	1.43	0.33	0.61	0.85
DRI	B2	0.00	1.12	0.43	0.39	0.50	1.43	0.50	0.62	0.82	1.37
ODEQ		0.00	0.57	0.54	0.55	0.50	0.88	0.50	0.62	0.82	0.74
SCAQMD		0.00	0.83	0.54	0.55	0.50	0.42	0.50	1.48	1.21	0.74
UCD		0.00	0.86	1.50	1.50	1.50	0.13	1.50	0.24	0.43	0.12

For cation and anion analysis by IC, filters were extracted and analyzed for the cations sodium (Na), ammonium (NH_4^+), potassium (K), and anions chloride (Cl^-), nitrate (NO_3^-), and sulfate (SO_4^{2-}). Note that Cl^- was added to the analyte list several years ago because there was an interest in quantifying the impact of sea spray on $PM_{2.5}$. Desert Research Institute (DRI) has additional samples because they perform these analyses on both nylon and Teflon filters, so both filter types were included with their PE samples. Additionally, the DRI B2 Teflon PE sample was found to have two filters adhered together. DRI extracted these samples separately and reported both results, which were included in the data analysis. As shown in Table 2, below, all *z*-scores were below 2.

Results reported by laboratories as "ND" or "<DL" were excluded from the statistical analysis and scores are not reported, instead they are noted as "NS". Two laboratories, CARB and ODEQ, do not routinely include Cl^- in their analyses suite so they did not analyze the PE filters for this analyte. An "NR" in the table indicates that data for this analyte was not reported by the laboratory.

Table 2. Cations and Anions by IC: Interlaboratory *z*-score Results

Lab	Event	Na	$NH4^+$	K	Cl^-	NO_3^-	SO_4^{2-}
CARB	1	*NS*	0.90	0.03	*NR*	0.85	0.07
DRI		0.86	1.27	0.96	0.70	0.08	0.41
DRI		1.16	0.05	1.36	0.95	1.96	1.65
ODEQ		0.63	1.54	0.33	*NR*	0.44	1.10
RTI		0.17	0.21	0.67	0.48	0.50	0.10
SCAQMD		1.22	0.38	1.30	1.17	0.08	0.94
CARB	2	1.47	0.28	0.49	*NR*	0.96	0.13
DRI		0.10	0.55	1.05	0.37	0.03	1.02
DRI		1.55	1.92	1.38	1.49	1.89	1.52
ODEQ		0.12	0.49	0.39	*NR*	0.59	0.23
RTI		0.26	0.56	0.32	0.62	0.36	0.35
SCAQMD		0.57	0.61	1.22	0.50	0.01	1.21
CARB	3	0.09	0.25	0.28	*NR*	0.77	0.33
DRI		0.39	0.37	0.74	0.03	0.12	0.08
DRI		1.95	1.52	1.38	1.34	1.94	1.49
ODEQ		0.03	1.50	0.26	*NR*	0.58	0.88
RTI		0.61	0.17	0.79	1.06	0.50	0.44
SCAQMD		0.83	0.47	1.34	0.25	0.21	1.30
CARB	B1	*NS*	*NS*	*NS*	*NR*	*NS*	*NS*
DRI		1.03	0.58	0.48	0.71	0.59	0.52
DRI		0.66	0.58	0.67	0.98	0.56	1.15
ODEQ		*NS*	*NS*	*NS*	*NR*	*NS*	*NS*
RTI		0.64	*NS*	*NS*	0.59	*NS*	*NS*
SCAQMD		1.05	1.15	1.15	1.09	1.15	0.64
CARB	B2	*NS*	*NS*	*NS*	*NR*	*NS*	*NS*
DRI		0.43	0.00	0.02	0.37	0.38	0.50
DRI		0.44	0.00	1.11	0.56	0.87	0.50
DRI		1.14	0.00	0.23	0.56	0.76	0.50
ODEQ		*NS*	*NS*	*NS*	*NR*	*NS*	*NS*
RTI		*NS*	*NS*	*NS*	*NS*	1.50	*NS*
SCAQMD		0.00	0.00	0.00	0.00	0.00	0.00

NS: Not scored because reported result was either ND or <DL.

NR: This laboratory does not routinely report Cl^- and did not report this analyte for this study.

For organic carbon analysis, results for organic carbon (OC), elemental carbon (EC), and total carbon (TC) were analyzed and compared across laboratories. Note that one lab was not provided a filter for Event 1, so was not included in that comparison. As shown in Table 3, below, all *z*-scores were below 2.

Table 3. Carbon by TOA: Interlaboratory *z*-score Results

Lab	Event	OC	EC	TC
CARB	1	0.77	1.40	0.22
DRI		1.23	0.11	1.18
SCAQMD		0.86	0.96	1.22
UCD		0.40	0.33	0.26
CARB	2	0.52	0.87	0.32
DRI		1.72	1.48	1.59
ORD		0.53	0.45	0.80
SCAQMD		0.70	0.16	0.80
UCD		0.01	0.90	0.32
CARB	3	0.32	1.41	1.13
DRI		1.35	1.41	0.60
ORD		1.42	0.09	1.52
SCAQMD		0.04	0.11	0.02
UCD		0.21	0.02	0.23
CARB	B1	0.05	0.59	0.06
DRI		0.92	1.72	0.91
ORD		0.92	0.59	0.93
SCAQMD		0.44	0.59	0.44
UCD		1.45	0.05	1.45
CARB	B2	0.62	0.45	0.62
DRI		0.96	0.45	0.96
ORD		0.44	0.45	0.44
SCAQMD		1.44	0.45	1.44
UCD		0.66	1.79	0.65