Calibration of PM_{2.5} Mass Concentrations Used in the Pittsburgh Aerosol Research and Inhalation Epidemiology Study

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Abstract

Fifteen different types of PM_{2.5} mass concentration samplers were used by seven different monitoring networks at 47 locations in the Pittsburgh, Pennsylvania, region from 1999 to 2008. The samplers included Federal Reference Method (FRM) samplers, speciation samplers, tapered element oscillating microbalance (TEOM) samplers, and others. The different measurement principles used in these designs tended to lead to systematic differences (biases) when measuring the same quantity, and to differences in the typical size of random errors (imprecision) introduced by each type of sampler. Bias can take different forms either as a constant bias or as a non-constant (scale) bias, which depends on the size of the quantity being measured. The objective of the work presented here was to simultaneously calibrate the measurements

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made by these different samplers to remove relative biases (both constant and non-constant) so that all of the available $\text{PM}_{2.5}$ data could be used interchangeably to develop exposure estimates for a retrospective epidemiology study. In order to accomplish this, we used linked temperature-stratified structural equation models, nonlinear regression models, and nonlinear mixed effects models. Applying these methods we constructed a comprehensive measurement error model that included both systematic error and random error components, and derived calibration equations that can be applied to place all of the $\text{PM}_{2.5}$ mass concentration measurements on the same scale. The FRM sampler was used as the reference scale although the parameter estimates are invariant to this choice. Results showed that: (1) 50°C TEOM samplers tended to show a large downward bias relative to the FRM sampler at low temperatures, and the magnitude of this bias decreased according to a nonlinear (sigmoidal) pattern with increasing temperature, (2) speciation samplers and other integrated samplers generally showed smaller biases relative to the FRM sampler that were not temperature-dependent, and (3) FRM samplers tended to be more precise than non-FRM samplers. These results are consistent with our previous work focusing on just a single monitoring site. Results are also presented here for several types of samplers that were not part of our previous study, including 30°C TEOM, FDMS TEOM, and beta attenuation monitors.

Keywords: fine particulate matter, Federal Reference Method, filter samplers, TEOM, structural equation model

1. Introduction

The goal of the Pittsburgh Aerosol Research and Inhalation Epidemiology Study (PARIES) is to determine the extent to which human health outcomes are associated with ambient concentrations of fine particulate matter ($\text{PM}_{2.5}$), its chemical components, and gaseous co-pollutants in the Pennsylvania counties of Allegheny (which includes the city of Pittsburgh), Washington, and Westmoreland. As part of this study, $\text{PM}_{2.5}$ mass concentration data were obtained from 97 samplers located at 47 monitoring sites in the 35 counties surrounding and including the three-county study area, in an effort to fully utilize all available information on the temporal and spatial variability of $\text{PM}_{2.5}$ to derive the best possible exposure estimates and reduce exposure misclassification error [1, 2, 3]. These samplers collectively provided more than 75,000 24-h average $\text{PM}_{2.5}$ mass concentration measurements over the 10-year study period from 1999 to 2008.

The 97 samplers consisted of 15 different types based on designs including the Federal Reference Method (FRM), speciation, dichotomous, beta attenuation, and tapered element oscillating microbalance (TEOM). These types of samplers are prone to differ in systematic ways, and none provides a perfectly accurate measurement of the true ambient concentration of $\text{PM}_{2.5}$. For example, it is well known that TEOM $\text{PM}_{2.5}$ measurements tend to differ from FRM measurements, and the nature of the difference varies with temperature [4, 5, 6, 7, 8, 9]. The FRM sampler also is prone to biases relative to true ambient $\text{PM}_{2.5}$ concentrations because of the loss of semivolatile mate-

rial and the effects of particle-bound water [10, 11, 12, 13]. Nevertheless, we chose to define the FRM as the reference sampler for purposes of presenting our calibration results because of its superior precision and widespread use relative to the other sampler types available for our study, and because it is the measure upon which compliance with the National Ambient Air Quality Standard for $\text{PM}_{2.5}$ is based in the United States. (As such, the results of our epidemiology study can best be interpreted within a regulatory context if they are expressed on an FRM-equivalent basis).

In order to remove bias between any two devices, it is necessary to be able to simultaneously estimate the calibration equation relating the two measurements and determine the imprecision (typical size of the random error) for each device. This requires having suitable collocated measurements. In this study, a comprehensive measurement error model was constructed making it possible to determine the calibration equation linking any two monitor types. The basic methodology was described for a single monitoring site in our previous article [14]. This methodology is extended here to simultaneously calibrate measurements made from all 97 samplers at the 47 monitoring sites used in PARIES.

2. $\text{PM}_{2.5}$ mass concentration data and measurement methods

The $\text{PM}_{2.5}$ mass concentration data used in PARIES were collected by seven ambient air quality monitoring programs that operated in the 35-county study region during some or all of the 1999-2008 period. These

networks included the U.S. Environmental Protection Agency (EPA) Air Quality System (AQS) [15], the Interagency Monitoring of Protected Visual Environments (IMPROVE) network [16], the Clean Air Status and Trends Network (CASTNET) [17], the Upper Ohio River Valley Project (UORVP) [18], the Pittsburgh Air Quality Study (PAQS) [19], the Steubenville Comprehensive Air Monitoring Program (SCAMP) [20], and the National Energy Technology Laboratory Office of Science and Technology (NETL/OST) monitoring site [21]. Data from AQS, IMPROVE, and CASTNET were obtained online from the web sites for each of these monitoring networks; data from UORVP, PAQS, SCAMP, and NETL/OST were obtained directly from the researchers affiliated with those programs.

As stated above, these seven monitoring programs collectively operated 97 $\text{PM}_{2.5}$ samplers, including 15 different types of samplers, at 47 monitoring sites in the study region during 1999-2008. Table 1 provides details on the 15 sampler types, and Table 2 provides information on the 47 monitoring sites used in PARIES, including the location of each site, the types of samplers used at each site, and the number of observations (24-h average $\text{PM}_{2.5}$ mass concentrations) from each sampler type at each site. Site locations are also depicted on a map in Fig. 1. Throughout the rest of this manuscript, the Sampler Type numbers in Table 1 and the Site ID numbers in Table 2 are used as the primary keys for identifying sampler designs and monitoring sites, respectively.

The 15 $\text{PM}_{2.5}$ sampler types used in PARIES include six different models

of FRM samplers (Sampler Types 1, 2, 3, 4, 5, and 8 in Table 1). These samplers, by definition, were manufactured to meet the design and performance requirements set forth in the FRM. [22] As indicated in Section 3.1, they are all treated as a single sampler type (FRM) for the remainder of this paper, and the other nine sampler types are each calibrated using the FRM as a reference. These other sampler types include four types of PM_{2.5} speciation samplers (Sampler Types 6, 9, 10, and 12 in Table 1), a dichotomous sampler (Sampler Type 7 in Table 1), a beta attenuation monitor (BAM) (Sampler Type 17 in Table 1), and three types of TEOM samplers (Sampler Types 14, 16, and 19 in Table 1).

As with the FRM samplers, the speciation and dichotomous samplers collect integrated PM_{2.5} samples on Teflon filters from a stream of sampled air at ambient temperature and pressure, and the mass of PM_{2.5} collected is then determined gravimetrically in the laboratory under controlled conditions of temperature and humidity. Unlike the FRM, however, these samplers are designed to simultaneously collect multiple sample splits for purposes of determining mass concentrations of different PM size fractions or subsequently determining PM_{2.5} chemical speciation, and as a result have certain design characteristics (e.g., sampler inlet, particle size separator, sampling flow rate, flow control scheme, etc.) that deviate from the FRM requirements and can cause differences in performance.

The BAM and the TEOMs are designed to monitor PM_{2.5} mass concentration in the field on an hourly or continuous basis. The BAM does this by

measuring beta ray attenuation through a $\text{PM}_{2.5}$ sample collected on a glass fiber filter tape, and the TEOM does it by measuring the change in frequency of oscillation as $\text{PM}_{2.5}$ is collected on a Teflon-coated glass fiber filter atop an oscillating hollow tube. The three types of TEOM samplers used in PARIES differ in their operating temperature (30°C or 50°C) and their inclusion or exclusion of a Filter Dynamics Measurement System (FDMS), which provides diffusion drying of the sampled air and adds a second, chilled purge filter (maintained at 4°C) to better account for measurement of semi-volatile material. These differences in design and operation can affect the extent of biases resulting from moisture (i.e., condensation and particle-bound water) and from the loss of semi-volatile particulate matter (e.g., ammonium nitrate, semi-volatile organic compounds), which is expected to be most severe at elevated operating temperatures (i.e., above 50°C) and least severe with the FDMS.

The native data obtained from the 97 $\text{PM}_{2.5}$ monitors used in PARIES included 634,130 observations representing sampling intervals ranging from 10 minutes (in the case of certain TEOM measurements) to 24 hours. Prior to aggregation, all data were manually reviewed for quality, and the native data validation flags applied by the data collection agencies were translated to a common set of PARIES validation flags to provide for consistent treatment in the integrated PARIES air monitoring database. Any data that were qualified as "invalid" in the native datasets (including null records) also were qualified as "invalid" in the PARIES database; this affected 14,447 of the

115 634,130 observations. In addition, 8,183 observations were determined to be
116 invalid during the PARIES quality review process because of irregular sam-
117 pling times or sampled volumes, inconsistent or suspicious information in the
118 native data file (without a supporting explanation), or missing information
119 to convert from standard conditions to local conditions. All of these invalid
120 data were excluded from the analysis, as were 116 outliers identified in the
121 native datasets and 126 outliers identified during the PARIES quality review.
122 (Because there were so few outliers - less than 0.04% of the total observations
123 - their inclusion or exclusion was not expected to materially affect the results
124 of our analysis).

125 The remaining 611,258 observations included 588,746 valid measurements,
126 as well as 22,512 measurements that were flagged in the native datasets or
127 during the PARIES quality review but were still included in our analysis
128 because they lacked a sufficient, documented reason for removal. These valid
129 and flagged data were converted from standard temperature and pressure to
130 local conditions, if necessary, and any data collected at intervals shorter than
131 24 hours were aggregated to compute 24-h averages for comparison with the
132 other data. These 24-h averages were considered to be valid only if they
133 included at least 19 hours of valid measurement time. (In most cases, 24-h
134 averages were computed from midnight to midnight, but in some cases they
135 were computed from noon to noon or from 9:00 am to 9:00 am to comport
136 with collocated integrated measurements). This resulted in the 75,927 valid
137 24-h average observations shown in Table 2.

Type	Description	Model	Filter	Inlet	Resolution
1	PM _{2.5} Federal Reference Method Sampler	R&P Partisol-Plus Model 2025 Sequential Air Sampler	Teflon	WINS Impactor	24 h
2	PM _{2.5} Federal Reference Method Sampler	Andersen RAAS 2.5-300 PM _{2.5} Sequential Sampler	Teflon	WINS Impactor	24 h
3	PM _{2.5} Federal Reference / Equivalent Method Sampler	R&P Model 2000 PM _{2.5} Air Sampler with BGI VSCC	Teflon	Very Sharp Cut Cyclone	24 h
4	PM _{2.5} Federal Reference / Equivalent Method Sampler	R&P Model 2025 PM _{2.5} Sequential Sampler with BGI VSCC	Teflon	Very Sharp Cut Cyclone	24 h
5	PM _{2.5} Federal Reference / Equivalent Method	Unspecified	Teflon	Unspecified	24 h
6	PM _{2.5} Speciation Sampler	Desert Research Institute Sequential Filter Sampler	Teflon	Cyclone	6-24 h
7	Dichotomous Sampler	Andersen Dichotomous Sampler	Teflon	Impactor-virtual/concentrator	24 h
8	PM _{2.5} Federal Reference Method Sampler	R&P Partisol FRM	Teflon	Impactor-virtual/concentrator	24 h
9	PM _{2.5} Speciation Sampler	IMPROVE Module A	Teflon	Cyclone	24 h
10	PM _{2.5} Speciation Sampler	Met One SASS Speciation Sampler	Teflon	Very Sharp Cut Cyclone	24 h
12	PM _{2.5} Speciation Sampler	CASTNET Sampler	Teflon	Cyclone	24 h
14	TEOM - 50°C Operation	Rupprecht & Patashnick Tapered Element Oscillating Microbalance - 50°C	Teflon-Coated Glass Fiber	Sharp Cut Cyclone	Continuous
16	TEOM - 30°C Operation	Rupprecht & Patashnick Tapered Element Oscillating Microbalance - 30°C	Teflon-Coated Glass Fiber	Sharp Cut Cyclone	Continuous
17	Beta Attenuation Monitor	Met One Beta Attenuation Monitor	Glass Fiber Tape	Sharp Cut Cyclone	1 h
19	TEOM - FDMS	Rupprecht & Patashnick Tapered Element Oscillating Microbalance with Filter Dynamics Measurement System	Teflon-Coated Glass Fiber	Sharp Cut Cyclone	Continuous

Table 1: Description of PM_{2.5} mass concentration samplers from the seven monitoring networks used in PARIES.

Site			Sampler Type																	
Label	ID	Latitude	Longitude	Collocation	1	2	3	4	5	6	7	8	9	10	12	14	16	17	19	Total
24-23-2	8	39.70595	-79.01200	9,17	0	0	0	0	0	0	0	0	553	0	0	0	0	1384	0	1937
39-121-9000	19	39.94283	-81.33761	9,12,12	0	0	0	0	0	0	0	0	913	0	177	0	0	0	0	10909
39-155-7	10	41.21417	-80.78750	2,14	0	2483	0	0	0	0	0	0	0	0	0	1130	0	0	0	3613
39-67-HOP	42	40.32000	-80.90000		0	586	0	0	0	0	0	0	0	0	0	0	0	0	0	586
39-81-1001	30	40.32194	-80.60639	2,2,10	0	1908	0	0	0	0	0	0	0	92	0	0	0	0	0	200
39-81-16	23	40.36278	-80.61556		0	536	0	0	0	0	0	0	0	0	0	0	0	0	0	536
39-81-17	46	40.36610	-80.61500	2,10	0	547	0	0	0	0	0	0	0	125	0	0	0	0	0	672
39-81-FRA	6	40.38000	-80.62000	2,14	0	640	0	0	0	0	0	0	0	0	0	587	0	0	0	1227
39-99-14	7	41.09587	-80.65843	2,10,14	0	1491	0	0	0	0	0	0	0	391	0	2277	0	0	0	4159
39-99-5	13	41.11111	-80.64528	2,2	0	2366	0	0	0	0	0	0	0	0	0	0	0	0	0	2366
42-125-200	22	40.17056	-80.26139		1112	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1112
42-125-5	12	40.14667	-79.90222	1,1,17	1340	0	0	0	0	0	0	0	0	0	0	0	0	809	0	2149
42-125-5001	21	40.44528	-80.42083	1,10,4,10	1510	0	0	1633	0	0	0	0	0	449	0	0	0	0	0	3592
42-129-8	31	40.30469	-79.50567	1,10,4,10	512	0	0	582	0	0	0	0	0	466	0	0	0	0	0	1560
42-129-SVC	40	40.29000	-79.40000		0	674	0	0	0	0	0	0	0	0	0	0	0	0	0	647
42-21-11	9	40.30972	-78.91500	1,17	1108	0	0	0	0	0	0	0	0	0	0	0	0	1510	0	2618
42-3-1008	32	40.61861	-79.72722		1037	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1037
42-3-116	27	40.47361	-80.07722		718	0	0	0	0	0	0	0	0	0	0	0	0	0	0	718
42-3-1301	25	40.40250	-79.86028	1,1	1246	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1246
42-3-131	29	40.28944	-80.00500		180	0	0	0	0	0	0	0	0	0	0	0	0	0	0	180
42-3-133	45	40.26013	-79.88650		156	0	0	0	0	0	0	0	0	0	0	0	0	0	0	156
42-3-21	33	40.41361	-79.94139	1,10	732	0	0	0	0	0	0	0	0	143	0	0	0	0	0	875
42-3-3007	44	40.29444	-79.88667		455	0	0	0	0	0	0	0	0	0	0	0	0	0	0	455
42-3-64	4	40.32361	-79.86833	1,1,10,14	3562	0	0	0	0	0	0	0	0	285	0	3210	0	0	0	7057
42-3-67	36	40.38194	-80.18556		971	0	0	0	0	0	0	0	0	0	0	0	0	0	0	971
42-3-8	5	40.46556	-79.96111	1,1,5,6,9,10,14	3355	0	0	0	129	439	0	0	122	767	0	3057	0	0	0	7869
42-3-9002	24	40.54694	-79.78389		369	0	0	0	0	0	0	0	0	0	0	0	0	0	0	369
42-3-93	35	40.60722	-80.02083		412	0	0	0	0	0	0	0	0	0	0	0	0	0	0	412
42-3-95	26	40.48694	-80.18806		433	0	0	0	0	0	0	0	0	0	0	0	0	0	0	433
42-3-97	28	40.55306	-80.20333		56	0	0	0	0	0	0	0	0	0	0	0	0	0	0	56
42-3-BRU	2	40.30650	-79.97940	1,14,16	1597	0	0	0	0	0	0	0	0	0	0	1056	436	0	0	3089
42-3-SCH	1	40.43950	-79.94050	7,8,16	0	0	0	0	0	0	319	348	0	0	0	0	378	0	0	1045
42-5-1	3	40.81418	-79.56475		0	0	0	0	0	0	0	0	0	0	0	0	2727	0	0	2727
42-59-2	34	39.80933	-80.26567	5,6	0	0	0	0	129	286	0	0	0	0	0	0	0	0	0	415
42-7-14	37	40.74780	-80.31644	1,1	1212	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1212
42-85-100	39	41.21501	-80.48478		1021	0	0	1657	0	0	0	0	0	0	0	0	0	0	0	2678
42-85-9000	20	41.42691	-80.14507	9,12	0	0	0	0	0	0	0	0	924	0	143	0	0	0	0	1067
54-29-1004	14	40.42154	-80.58072		740	0	0	392	0	0	0	0	0	0	0	0	0	0	0	1132
54-29-TOM	41	40.54000	-80.58000		0	662	0	0	0	0	0	0	0	0	0	0	0	0	0	662
54-49-6	38	39.48148	-80.13467		661	0	371	0	0	0	0	0	0	0	0	0	0	0	0	1032
54-51-1002	11	39.91596	-80.73386	1,10,19	784	0	0	860	0	0	0	0	0	264	0	0	0	0	1031	2939
54-61-3	15	39.64937	-79.92087	1,6	869	0	295	14	0	121	0	0	0	0	0	0	0	0	0	1299
54-69-10	47	40.11488	-80.70097		78	0	0	400	0	0	0	0	0	0	0	0	0	0	0	478
54-69-8	16	40.06383	-80.72050		687	0	0	0	0	0	0	0	0	0	0	0	0	0	0	687
54-69-WJU	43	40.07000	-80.69000		0	416	0	0	0	0	0	0	0	0	0	0	0	0	0	416
54-9-11	17	40.39458	-80.61202	1,1,4,4	1532	0	0	632	0	0	0	0	0	0	0	0	0	0	0	2164
54-9-5	18	40.34102	-80.59664		760	0	0	400	0	0	0	0	0	0	0	0	0	0	0	1160
Total					29205	12309	666	6570	258	846	319	348	2512	2982	320	11317	3541	3703	1031	75927

Table 2: Total numbers of 24-h averaged PM_{2.5} mass concentration measurements by site, sampler type, and collocation status. The first two digits of the site label indicate the state in which the site was located, as follows: 24 = Maryland, 39 = Ohio, 42 = Pennsylvania, and 54 = West Virginia. The *Collocation* column indicates which samplers were collocated. For example, for site *39-121-9000*, samplers of types 9 and 12 were collocated and two samplers of type 12 were collocated. This does not necessarily mean that all three samplers operated on the same days, but there was overlap so that a separate calibration model could be fitted. For site *42-125-5001*, samplers of type 1 and 10 were collocated and, separately, samplers of type 4 and 10 were collocated. For site *39-99-5*, two samplers of type 2 both operated on some days.

Figure 1: Locations of the 47 monitoring sites (+) in Pennsylvania, Ohio, West Virginia, and Maryland. Boundaries of the counties constituting the three-county study area are outlined.

138 3. Nonlinear measurement error model

139 3.1. Building blocks

140 In our previous study [14], the classic measurement error model was thor-
 141 oughly described and was applied to calibrate collocated measurements made

142 by multiple PM_{2.5} samplers at a single site. Fig. 2 shows the path diagram
 143 for a single site with three collocated samplers. This is the simplest case in
 144 which it is possible for a calibration model to simultaneously estimate both
 145 systematic error (bias) and random error (imprecision) without making ar-
 146 bitrary assumptions. Because the true PM_{2.5} mass concentrations (μ) are
 147 unknown, measurements from the first device (X_1) are arbitrarily used as
 148 the reference so that β_1 is constrained to equal one, α_1 (not shown in Fig.
 149 2) is constrained to equal zero, and the biases for samplers 2 and 3 are then
 150 estimated relative to sampler 1. The imprecision standard deviations (σ_i)
 151 for each sampler are also estimated by the model. In this study, as in our
 152 previous study, we arbitrarily use the FRM as the reference sampler. (The
 153 relative biases and differences in imprecision among the various models of
 154 FRM samplers are assumed to be negligible). This basic design is then used
 155 as a building block to handle a more complex analysis. For example, in our
 156 previous work [14], the classic model was extended, using stratification, to
 157 account for the nonlinear effect of temperature on PM_{2.5} mass concentration
 158 measurements made using a 50°C TEOM monitor. Here we extend the
 159 model further to also include samplers located at multiple monitoring sites.

160 3.2. Structural equation model

161 Each path diagram represents a structural equation model (SEM), which
 162 is a set of simultaneous equations that include one or more latent variables.
 163 As shown in more detail in our previous study [14], the relationship between

Figure 2: Path diagram for the measurement error model describing three collocated PM_{2.5} samplers. Here μ denotes the square-root transformed true but unobserved 24-h averaged PM_{2.5} mass concentrations and is assumed to be normally distributed with mean $\bar{\mu}$ and standard deviation σ . Each sampler provides a measurement, X_1 , X_2 , and X_3 . The single-ended arrows indicate the direction of influence - each X_i is a linear function of μ with intercept α_i (not shown) and scale (slope) β_i . The curved, double-ended arrows denote standard deviations. The residual standard deviation for the i^{th} sampler is σ_i and denotes the imprecision. Not including intercepts, there are six parameters to be estimated: β_2 , β_3 , σ_1 , σ_2 , σ_3 , and σ .

164 any pair of devices can be derived. By taking expectations (averaging out
 165 the random error using expected values), the calibration equations can be
 166 determined. The calibration equations corresponding to the path diagram in

Fig. 2 are:

$$1 : 2 \quad E[X_1] = \left[\alpha_1 - \alpha_2 \frac{\beta_1}{\beta_2} \right] + \frac{\beta_1}{\beta_2} E[X_2], \quad E[X_2] = \left[\alpha_2 - \alpha_1 \frac{\beta_2}{\beta_1} \right] + \frac{\beta_2}{\beta_1} E[X_1]$$

$$1 : 3 \quad E[X_1] = \left[\alpha_1 - \alpha_3 \frac{\beta_1}{\beta_3} \right] + \frac{\beta_1}{\beta_3} E[X_3], \quad E[X_3] = \left[\alpha_3 - \alpha_1 \frac{\beta_3}{\beta_1} \right] + \frac{\beta_3}{\beta_1} E[X_1]$$

$$2 : 3 \quad E[X_2] = \left[\alpha_2 - \alpha_3 \frac{\beta_2}{\beta_3} \right] + \frac{\beta_2}{\beta_3} E[X_3], \quad E[X_3] = \left[\alpha_3 - \alpha_2 \frac{\beta_3}{\beta_2} \right] + \frac{\beta_3}{\beta_2} E[X_2]$$

The calibration intercepts and slopes are invariant to the choice of constraints in the SEM. The observed covariance matrix $\mathbf{S}$ is:

$$\begin{pmatrix} S_1^2 & S_{12} & S_{13} \\ & S_2^2 & S_{23} \\ & & S_3^2 \end{pmatrix}$$

where S_i^2 is the variance of the measurements X_i , and S_{ij} is the covariance between measurements X_i and X_j .

A simple approach to providing estimates of the model parameters is to use the method of moments. In the method of moments, the theoretical covariance matrix of the measurements is derived from the model and equated to the observed covariance matrix. The theoretical covariance matrix is a function of the model parameters $\beta_2, \beta_3, \sigma_1, \sigma_2, \sigma_3$, and σ , and the solution of the simultaneous equations provides the parameter estimates. (If the sample means are included, α_2, α_3 , and $\bar{\mu}$ can also be estimated.) With three different

179 types of measurements in the simple one-factor model shown in Fig. 2, there
 180 are as many equations as unknown parameters, and thus a unique solution
 181 results. To illustrate, first note that the theoretical covariance matrix Σ for
 182 this model is:

$$\Sigma = \mathbf{B}\sigma^2\mathbf{B}' + \mathbf{E} \quad (1)$$

183 where $B = [\beta_1 \ \beta_2 \ \beta_3]$ and $\mathbf{E}$ denotes the 3×3 residual variance matrix:

$$\begin{pmatrix} \sigma_1^2 & 0 & 0 \\ & \sigma_2^2 & 0 \\ & & \sigma_3^2 \end{pmatrix}$$

184 In this case, Σ is given by:

$$\begin{pmatrix} \beta_1^2\sigma^2 + \sigma_1^2 & \beta_1\beta_2\sigma^2 & \beta_1\beta_3\sigma^2 \\ & \beta_2^2\sigma^2 + \sigma_2^2 & \beta_2\beta_3\sigma^2 \\ & & \beta_3^2\sigma^2 + \sigma_3^2 \end{pmatrix}$$

The method of moments equates the observed covariance matrix $\mathbf{S}$ to the theoretical covariance matrix Σ resulting in six equations (setting $\beta_1 = 1$) in

six unknowns:

$$S_1^2 = \sigma^2 + \sigma_1^2$$

$$S_2^2 = \beta_2^2 \sigma^2 + \sigma_2^2$$

$$S_3^2 = \beta_3^2 \sigma^2 + \sigma_3^2$$

$$S_{12} = \beta_2 \sigma^2$$

$$S_{13} = \beta_3 \sigma^2$$

$$S_{23} = \beta_2 \beta_3 \sigma^2$$

This easily leads to the solution for the method of moments parameter estimates:

$$\beta_2 = S_{23}/S_{13}$$

$$\beta_3 = S_{23}/S_{12}$$

$$\sigma_1^2 = S_1^2 - \frac{S_{12}S_{13}}{S_{23}}$$

$$\sigma_2^2 = S_2^2 - \frac{S_{12}S_{23}}{S_{13}}$$

$$\sigma_3^2 = S_3^2 - \frac{S_{13}S_{23}}{S_{12}}$$

$$\sigma^2 = \frac{S_{12}S_{13}}{S_{23}}$$

185 The solution depends on the constraint used to ensure a unique solution
 186 (i.e., identifiability) and will change, for example, if β_2 , instead of β_1 , is set
 187 to 1. Other constraints are possible. If $\beta_1\beta_2\beta_3$ is constrained to 1 (effectively

188 constraining the geometric average of the β s), the estimate for σ^2 will be
189 $\sqrt[3]{S_{12}S_{13}S_{23}}$ and the estimates for the β s will also differ from the current
190 solution. The ratio of the β s and the ratio of the imprecision variances are,
191 however, invariant to the choice of these constraints.

192 In practice, the method of maximum likelihood [23] is preferred to the
193 method of moments for both simple and complex models because the method
194 of maximum likelihood usually provides superior estimates. If there are no
195 missing values, the model parameter estimates are easily computed using
196 the method of maximum likelihood. Otherwise, full information maximum
197 likelihood accommodates missing values.

198 3.3. *Linked sub-models for multiple sites*

199 Sites 42-3-8 (ID = 5) and 42-85-9000 (ID = 20) will be used to illus-
200 trate linking sub-models and stratification by temperature. Site ID = 20
201 had only two collocated samplers of type 9 (Met One SASS speciation) and
202 type 12 (CASTNet speciation). Site ID = 5 had six samplers, but for this
203 illustration we will only consider the type 1 (R & P Partisol-Plus Model
204 2025 Sequential Air Sampler FRM), type 9 (IMPROVE), and type 14 (Rup-
205 precht & Patashnick 50°C TEOM) samplers. The first step in developing
206 a comprehensive model to calibrate all measurement devices that are spread
207 across multiple sites is to construct individual models for each site. The top
208 leftmost path diagram shown in Fig. 3 illustrates the measurement error
209 model for Site ID = 5 for the lowest temperature stratum. The circle la-

beled with μ represents the unknown true $\text{PM}_{2.5}$ concentrations where the
 first subscript denotes the site ID and the second subscript describes the
 temperature stratum. The double-ended curved arrow pointing at the circle
 denotes the standard deviation of the true values labeled as σ_{5-1} . There are
 three single-arrow paths pointing to the three collocated measurements each
 denoted by an X in a square box. The third subscript for each X denotes the
 sampler type. The path labels are the systematic bias β parameters with the
 FRM sampler used as a reference by constraining its coefficient to equal 1.
 The imprecision standard deviations for each sampler are denoted by the σ s
 labeling the double-ended curved arrows pointing to each yellow square box.
 The intercept parameters (mean of the true values and the α intercepts) are
 not shown for simplification. With just these three samplers at this site for
 this temperature stratum, there is sufficient information to fully estimate all
 of the model parameters. Site ID = 20 for the first temperature stratum is
 shown as the leftmost path diagram on the bottom row. At this site there are
 only two samplers so that by itself, there would not be sufficient information
 to fully estimate all of the model parameters without additional constraints.
 The constraint used to *link* the two sub-models is to equate the β parameters
 for the type 9 samplers at each site. This is accomplished simply by using
 the same label $\beta_{\#-\#-9}$ for both samplers. The first $\#$ indicates that the
 label is independent of the site. This approach allows sampler type 9 to be
 calibrated against the FRM at site ID = 5, and sampler type 12 at site ID =
 20 can then be calibrated indirectly against the FRM through sampler type

233 9. This represents the assumption that the two samplers of type 9 at each
 234 site operate in the same manner.

Figure 3: Simplified illustration of temperature stratification for linked set 3 with eight strata (1, 2, ... 8) across two sites (5 and 20) in order to determine the dependency of TEOM sampler $\text{PM}_{2.5}$ mass concentration measurements on temperature relative to the Federal Reference Method samplers. Only three sampler types are illustrated at site 5 (sampler types 1, 9, and 14). Note that μ_{5-1} denotes the true values at site 5 for the first (lowest) temperature stratum (stratum 1). X_{5-1-9} denotes the measured $\text{PM}_{2.5}$ concentration at site 5, first temperature stratum, and sampler type 9. By using the same label $\beta_{\#-\#-9}$ for all temperature strata for site 5, the coefficient is assumed not to depend on temperature. By using the same label at site 20, this provided a reference for sampler 12 at this site. Otherwise, there would be no way to calibrate sampler 12 because there were only two collocated samplers at this site. Conversely, the β coefficients for sampler type 14 (TEOM 50°C) have different labels for each temperature stratum for site 5 in order to determine how the relationship between the FRM and TEOM changes with temperature.

235 3.4. *Temperature stratification needed for TEOM samplers*

236 The final step in model construction is to extend the linking across all
237 temperature strata as shown in Fig. 3. In each path diagram, the second
238 subscript denoting the temperature stratum changes from column to column
239 for μ , the measurements X and the standard deviation parameters. For
240 the TEOM sampler (type = 14), the bias parameter label also changes with
241 temperature. For samplers that do not depend on temperature (samplers of
242 type 1, 9 and 12), the β labels are the same across all temperature strata,
243 i.e., the second subscript is always a #. The method used to define the eight
244 temperature strata was described in [14].

245 3.5. *Linked sites*

246 As previously discussed, some sites with collocated samplers of different
247 types had only two samplers and/or lacked an FRM. Thus, in order to pro-
248 duce calibration equations relating all of the non-FRM samplers to the FRM
249 sampler, it was necessary to construct subsets of sites as shown in Table 3.
250 The seven linked sets shown in this table cover all of the types of samplers
251 and all of the sites with collocated samplers, except for sites that only had
252 collocated FRM samplers for which calibration was not needed. Fortunately,
253 there were no sites in this study that had only one non-FRM sampler.

254 4. **Measurement error model fitting**

255 The R statistical language and environment (Version 2.13.1) [24] was
256 used for statistical analysis and graphics. The OpenMx R package (Version

Set	Site ID	Sampler Types				FRM Imprecision SD			
1	1	7	8	16	0.201				
	2	1	14	16					
	33	1	10						
2	4	1	10	14	0.100				
	9	1	17						
	31	1	4	10					
3	5	1	5	6	<u>9</u>	10	14	0.103	
	19	<u>9</u>	<i>12</i>						
	20	<u>9</u>	12						
4	6	2	14		0.216				
	21	1	4	10					
	30	2	10						
	46	2	10						
5	7	2	10	14	0.148				
	10	2	14						
6	11	1	4	10	19	0.117			
	15	1	6						
	34	5	6						
7	8	9	<u>17</u>		0.155				
	12	1	<u>17</u>						
Root Mean Sq.						0.155			

Table 3: Sets of linked monitoring sites. In order to be able to calibrate all sampler types, it was necessary to group individual sites with collocated samplers into seven sets according to available overlap in the sampler types. FRM samplers (1-5 and 8) are in **bold** and whenever possible were used to link sites. If FRMs were not available, the linked samplers are underlined. Duplicated samplers of the same type are in *italics*.

257 1.0.6-1581) [25, 26] was used to estimate the SEM parameters using full infor-
258 mation maximum likelihood. Modeling of the temperature relationship using
259 nonlinear regression was performed using the **nls** R function, and the **nlme**
260 R package (Version 3.1-11) was used to fit nonlinear mixed effects models
261 [27]. It was necessary to square root transform the PM_{2.5} concentrations to
262 ensure approximate normality.

263 5. Non-TEOM sampler results

264 5.1. Parameter Estimates

265 In our initial modeling, we determined that the TEOM was the only
266 sampler type for which bias (relative to the FRM sampler) tended to show
267 a dependency with temperature. Therefore, the final models used assumed
268 that the bias parameters for all non-TEOM samplers were not temperature-
269 dependent, and only bias parameters for TEOMs were allowed to vary with
270 temperature. The parameter estimates for the non-TEOM samplers are
271 shown in Table 4. Except for the single dichotomous sampler (type 7), each
272 sampler type was used at multiple sites. Summary measures for multiple
273 sites were computed as the simple arithmetic mean for α , as the geometric
274 mean for β , and as the root mean squared for σ_i/β_i . For β , the range of
275 estimates for each sampler type tends to be relatively narrow. The one ex-
276 ception occurs for the Met One SASS speciation sampler (type 10) at site 46
277 (39-81-17), which has an unusually low estimate for β . The confidence in-
278 tervals for β in general were reasonably narrow indicating reasonably precise
279 estimates.

280 For the Desert Research Institute Sequential Filter Sampler (type 6), the
281 estimated β is below 1 for all three sites and is statistically significantly
282 below 1 for two of the three sites. For the dichotomous sampler (type 7),
283 the estimated β is very close to 1 and not statistically significantly different
284 from 1. For the IMPROVE speciation sampler (type 9), the β at site 5
285 is slightly above 1 and the β at site 8 is slightly below 1, and neither is

Sampler	β		α		σ_i/β_i
	Type	Site ID	Estimate	Lower	Upper
DRI SFS	6	5	0.889	0.846	0.932
		15	0.877	0.759	0.994
		34	0.927	0.817	1.036
		Mean	0.897		
Dichotomous IMPROVE	7	1	1.003	0.965	1.042
		5	1.016	0.977	1.055
		8	0.951	0.889	1.017
		Mean	0.982		
Met One SASS	10	4	0.977	0.946	1.008
		5	0.983	0.968	0.999
		7	0.997	0.972	1.023
		11	0.954	0.923	0.985
		21	1.050	1.014	1.087
		30	0.935	0.835	1.034
		31	0.968	0.944	0.992
		33	1.039	0.975	1.103
CASTNet	12	46	0.785	0.705	0.866
		Mean	0.962		
		19	1.100	0.962	1.261
		20	1.163	1.030	1.320
BAM	17	Mean	1.131		
		9	1.078	1.053	1.104
		8/12	0.949	0.902	0.997
		Mean	1.012		
			0.249	0.078	0.421
			0.689	0.233	1.143
			0.575	0.182	0.973
			0.504		0.654
			-0.139	-0.294	0.017
			-0.087	-0.239	0.065
			-0.165	-0.404	0.060
			-0.126		0.154
			0.328	0.192	0.464
			0.243	0.182	0.304
			0.127	0.029	0.226
			0.273	0.153	0.392
			-0.024	-0.158	0.105
			0.697	0.304	1.092
			0.231	0.140	0.321
			0.006	-0.262	0.270
			0.556	0.214	0.894
			0.271		0.357
			-0.142	-0.686	0.328
			-0.270	-0.765	0.170
			-0.206		0.205
			-0.220	-0.319	-0.121
			0.126	-0.055	0.305
			-0.047		0.377

Table 4: Calibration parameter estimates on the square root transformed scale for speciation, dichotomous, and beta attenuation monitor samplers. For β , the mean is the geometric mean. For α , the mean is the arithmetic mean. For the scale-adjusted imprecision standard deviation (σ_i/β_i), the mean is the root mean square.

286 statistically significantly different than 1. For the Met One SASS speciation
 287 sampler (type 10), eight of the nine sites had β s very near 1 although four
 288 had narrow enough 95% confidence intervals to be statistically significantly
 289 different than 1 (three of these were above 1 and one was below 1). As noted
 290 above, the estimate for β at site 46 was substantially lower than 1 and was
 291 statistically significantly different than 1 with an upper bound of just 0.866.
 292 For the CASTNET speciation sampler (type 12), both estimates for β were
 293 above 1, with one site having a statistically significant difference from 1.
 294 Finally, for the Beta Attenuation Monitor (type 17), the β for one site was
 295 somewhat above 1 and the β for the other was somewhat below 1, with both
 296 statistically significantly different from 1.

297 In general, the bias parameter α , while needed for calibration, is difficult
 298 to interpret. The exception occurs when the corresponding parameter β
 299 equals (or at least is near) 1. When $\beta = 1$, the parameter α represents the
 300 constant bias between the sampler and the FRM sampler. For example, the
 301 Dichotomous sampler at site 1 and the Met One SASS sampler at site 7 have
 302 estimated β s very nearly equal to 1. Thus, these samplers at these sites had
 303 a nearly constant bias relative to the FRM sampler. When β differs from 1,
 304 the bias changes with the true $\text{PM}_{2.5}$ concentration. Calibration is discussed
 305 in more detail in the next section.

306 The typical value for the FRM imprecision standard deviation (σ_i) is
 307 given in Table 3 as $0.155 (\mu\text{g m}^{-3})^{0.5}$. Table 4 shows that non-FRM / non-
 308 TEOM samplers tended to have higher scale-adjusted imprecision standard

309 deviations (σ_i/β_i). The exception was the IMPROVE sampler, which had a
 310 scale-adjusted imprecision standard deviation that was similar to the FRM
 311 samplers.

312 5.2. Calibration Results

313 The calibration parameter estimates shown in Table 4 can be used to
 314 write the calibration equation relating each sampler at a site to the FRM
 315 sampler. For example, for the CASTNET speciation sampler (type 12) at
 316 site 20:

$$E[X_{20-CASTNet-\#}] = \left(-0.270 + 1.163\sqrt{E[X_{20-FRM-\#}]} \right)^2 \quad (2)$$

317 Equivalently, to predict the FRM equivalent value from the observed speci-
 318 ation sampler measurement:

$$E[X_{20-FRM-\#}] = \left(\frac{0.270}{1.163} + \frac{1}{1.163}\sqrt{E[X_{20-CASTNet-\#}]} \right)^2 \quad (3)$$

319 In a similar fashion, a calibration equation is available for each non-TEOM
 320 sampler at each site to convert the observed measurement to an FRM-
 321 equivalent value. Although a site-specific calibration equation is available for
 322 all of the non-TEOM samplers in this study, had there been a site without

Site ID	°C	β			α			σ_i/β_i
		Estimate	Lower	Upper	Estimate	Lower	Upper	
2	-6.026	0.585	0.473	0.690	0.965	0.594	1.361	0.828
	0.547	0.595	0.507	0.681	1.010	0.705	1.325	0.867
	5.344	0.730	0.601	0.855	0.686	0.279	1.105	0.838
	10.016	0.841	0.707	0.971	0.464	0.027	0.911	0.627
	14.554	0.871	0.730	1.006	0.435	-0.072	0.959	0.747
	17.999	0.909	0.752	1.058	0.308	-0.273	0.917	0.722
	21.114	0.848	0.707	0.984	0.499	-0.109	1.135	0.735
	24.333	0.827	0.708	0.946	0.569	-0.069	1.204	0.685
4	-5.834	0.801	0.768	0.834	0.220	0.094	0.346	0.416
	0.666	0.783	0.754	0.812	0.401	0.286	0.516	0.463
	5.360	0.841	0.817	0.866	0.303	0.200	0.405	0.427
	10.018	0.856	0.834	0.878	0.387	0.294	0.480	0.376
	14.355	0.890	0.869	0.890	0.352	0.261	0.443	0.326
	18.054	0.960	0.935	0.984	0.147	0.034	0.259	0.346
	21.127	1.026	1.003	1.049	-0.115	-0.230	-0.000	0.274
	24.396	1.028	1.003	1.053	-0.156	-0.299	-0.014	0.285
5	-5.829	0.700	0.627	0.774	0.454	0.190	0.717	0.718
	0.671	0.722	0.672	0.772	0.519	0.340	0.698	0.565
	5.345	0.777	0.724	0.830	0.458	0.277	0.638	0.541
	10.013	0.860	0.793	0.927	0.311	0.092	0.530	0.542
	14.353	0.942	0.888	0.996	0.119	-0.073	0.310	0.446
	18.060	1.011	0.960	1.062	-0.047	-0.244	0.149	0.416
	21.146	1.050	1.006	1.093	-0.282	-0.472	-0.093	0.375
	24.394	1.020	0.987	1.053	-0.180	-0.351	-0.009	0.302
6	-5.644	0.937	0.812	1.072	-0.782	-1.251	-0.344	0.224
	0.681	0.971	0.905	1.039	-0.790	-1.046	-0.540	0.193
	5.202	0.996	0.907	1.086	-0.873	-1.238	-0.513	0.349
	10.228	0.996	0.934	1.058	-0.718	-0.960	-0.478	0.221
	14.642	0.983	0.901	1.065	-0.580	-0.951	-0.211	0.382
	17.784	0.915	0.830	1.001	-0.194	-0.559	0.166	0.273
	21.080	1.006	0.863	1.150	-0.500	-1.198	0.194	0.521
	24.197	1.048	0.941	1.155	-0.720	-1.282	-0.165	0.253
7	-5.875	0.706	0.647	0.765	0.307	0.093	0.521	0.509
	0.706	0.725	0.671	0.780	0.420	0.219	0.620	0.487
	5.364	0.761	0.694	0.829	0.358	0.127	0.591	0.548
	9.974	0.879	0.806	0.952	0.134	-0.113	0.378	0.448
	14.300	1.012	0.956	1.068	-0.214	-0.412	-0.016	0.269
	18.122	1.027	0.982	1.072	-0.242	-0.414	-0.073	0.223
	21.141	1.056	1.015	1.097	-0.423	-0.594	-0.254	0.200
	24.340	1.034	0.995	1.072	-0.303	-0.488	-0.120	0.030
10	-5.801	0.581	0.523	0.642	1.039	0.810	1.257	0.299
	0.680	0.674	0.611	0.735	0.821	0.590	1.052	0.260
	5.361	0.741	0.676	0.807	0.742	0.529	0.953	0.171
	10.007	0.936	0.868	1.000	0.237	0.027	0.456	0.120
	14.383	0.944	0.889	1.003	0.254	0.062	0.432	0.011
	18.025	1.000	0.938	1.061	0.039	-0.181	0.263	0.122
	21.146	1.023	0.966	1.083	-0.026	-0.262	0.197	0.098
	24.409	1.110	1.024	1.194	-0.382	-0.769	0.009	0.159

Table 5: Calibration parameter estimates and 95% confidence intervals on the square root scale for TEOM 50°C samplers (type 14) as a function of temperature.

collocated measurements, the parameter estimates developed for the same sampler type at a nearby site, or the mean parameter estimates for that sampler type, could be applied to best approximate the appropriate calibration equations.

6. TEOM sampler results

6.1. Modeling the sigmoidal temperature effect using nonlinear regression

As shown in Table 3, there were 9 TEOM samplers of three types (14 - 50°C, 16 - 30°C, and 19 - FDMS) at 8 different sites. Using the linked subsets and the temperature stratification strategy described in the path diagram of Fig. 3, calibration model parameter estimates were computed as a function of temperature. Eight temperature strata covering temperatures ranging from about -5 to 25 °C were used as described in [14]. The parameter estimates for the 50°C (type 14) TEOMs are shown in Table 5, for the 30°C (type 16) TEOMs in Table 6, and for the FDMS (type 19) TEOM in Table 7. The parameter estimates for both α and β for many of the TEOMs show a nonlinear pattern.

To describe the general relationship, nonlinear regression was used to fit a sigmoidal (logistic) model using the R `SSfp1` self-starting four-parameter logistic function with the `nls` nonlinear regression function. The four-parameter sigmoidal model is described by the following equation:

Site ID	°C	β			α			σ_i/β_i
		Estimate	Lower	Upper	Estimate	Lower	Upper	
1	-5.141	0.445	0.209	0.681	1.711	0.943	2.484	0.705
	0.731	0.772	0.653	0.893	0.712	0.308	1.110	0.261
	5.379	0.523	0.318	0.725	1.614	0.921	2.319	0.980
	10.143	0.711	0.521	0.900	1.031	0.383	1.678	0.608
	14.574	0.665	0.447	0.878	1.182	0.335	2.051	0.842
	17.908	0.568	0.324	0.806	1.639	0.698	2.602	1.057
	21.063	0.974	0.898	1.058	0.017	-0.351	0.355	0.103
	24.608	0.904	0.825	0.988	0.405	-0.074	0.862	0.236
2	-6.026	0.853	0.768	0.941	-0.114	-0.422	0.189	0.257
	0.547	0.942	0.857	1.028	-0.347	-0.653	-0.043	0.157
	5.344	0.967	0.890	1.053	-0.275	-0.566	-0.017	0.103
	10.016	1.069	0.959	1.177	-0.458	-0.808	-0.108	0.140
	14.554	1.138	1.016	1.261	-0.719	-1.143	-0.303	0.167
	17.999	1.100	0.985	1.205	-0.595	-0.989	-0.168	0.094
	21.114	0.724	0.552	0.882	0.639	-0.017	1.348	0.707
	24.333	0.924	0.838	1.011	-0.012	-0.465	0.435	0.334

Table 6: Calibration parameter estimates and 95% confidence intervals on the square root scale for TEOM 30°C samplers (type 16) as a function of temperature

$$y(T) = A + \frac{B - A}{1 + e^{\frac{T_{mid} - T}{S}}} + \epsilon \quad (4)$$

where $y(T)$ denotes a particular bias parameter (either α or β) and T denotes the temperature in °C. This model was fitted to the eight observed temperature stratum means and the corresponding values for α and for β , respectively. A denotes the fixed effect asymptote as $T \rightarrow -\infty$, B denotes the fixed effect asymptote as $T \rightarrow +\infty$, T_{mid} is a fixed effect measure of location (the temperature for the single inflection point of the logistic curve), and S is a fixed effect measure of spread (the distance between T_{mid} and the temperature at which y reaches about 3/4 of the distance between B and A). (When y increases as T increases, $B - A$ is positive, and when y decreases

°C	β			α			σ_i/β_i
	Estimate	Lower	Upper	Estimate	Lower	Upper	
-5.732	0.975	0.880	1.070	-0.189	-0.517	0.140	0.323
0.766	0.983	0.902	1.062	-0.076	-0.358	0.209	0.314
5.299	1.030	0.947	1.113	-0.101	-0.376	0.176	0.265
10.022	0.896	0.797	0.996	0.327	0.004	0.652	0.361
14.302	0.851	0.761	0.942	0.476	0.172	0.779	0.308
18.082	0.884	0.815	0.955	0.393	0.129	0.653	0.255
21.164	0.883	0.825	0.942	0.434	0.183	0.682	0.177
24.435	0.908	0.868	0.949	0.423	0.223	0.622	0.160

Table 7: Calibration parameter estimates and 95% confidence intervals on the square root scale for the single FDMS TEOM sampler (type 19) as a function of temperature at Site ID 11.

Site ID	Sampler ID	$\beta(T)$				$\alpha(T)$			
		<i>A</i>	<i>B</i>	<i>T_{mid}</i>	<i>S</i>	<i>A</i>	<i>B</i>	<i>T_{mid}</i>	<i>S</i>
1	16	0.609	0.959	19.607	<i>1.000</i>	1.320	0.162	19.687	<i>1.000</i>
2	16	0.956	0.001			-0.336	0.009		
	14	0.582	0.863	5.202	1.699	0.990	0.454	5.084	<i>1.000</i>
4	14	0.796	1.082	16.542	4.578	0.333	-0.152	18.524	0.951
5	14	0.697	1.050	10.572	3.934	0.488	-0.261	14.292	3.085
6	14	0.961	0.002			-0.813	-0.488	11.718	1.313
7	14	0.713	1.045	9.807	2.337	0.372	-0.336	11.378	1.965
10	14	0.464	1.139	6.586	7.635	0.876	-0.030	9.102	<i>1.000</i>
11	19	0.996	0.880	8.616	<i>1.000</i>	-0.132	0.432	8.395	1.080

Table 8: Sigmoidal model parameter estimates for $\beta(T)$ and $\alpha(T)$ for TEOM's using non-linear regression models. Here *A* denotes the left asymptote and *B* denotes the right asymptote. *T_{mid}* denotes the location parameter and *s* denotes the spread or scale parameter on the temperature (°C) axis. Values shown in *italics* are fixed, not estimated. Rows with only estimates for *A* and *B* for either/or both α and β were estimated by ordinary regression with *A* denoting the intercept and *B* denoting the slope.

as T increases, $B - A$ is negative.)

Fig. 4 plots the estimated parameters for each temperature stratum with the corresponding sigmoidal model (or other appropriate model) superimposed. For β , a clear sigmoidal pattern was observed for all samplers with the exception of the 30°C TEOM sampler (type 16) at site 2 and the 50°C TEOM sampler (type 14) at site 6. Otherwise, the pattern was

358 the same - β was below 1 for colder temperatures and approached 1 as the
 359 temperature increased - except for the FDMS TEOM (type 19) at site 11
 360 which showed the opposite pattern (β was near 1 for colder temperatures
 361 and quickly dropped below 1 as the temperature increased). This opposite
 362 behavior might be expected, as the FDMS TEOM is specifically designed to
 363 avoid the loss of semi-volatile material that affects the 50°C TEOM at low
 364 temperatures. Several other studies [28, 29] have observed FDMS TEOM
 365 samplers to be biased high relative to collocated FRM samplers and have
 366 attributed this bias to partial loss of semivolatile species (e.g., ammonium
 367 nitrate and semivolatile organic material) from the FRM measurement. The
 368 single FDMS TEOM sampler used in PARIES did not exhibit this behavior;
 369 rather it was statistically equivalent to the FRM sampler at low tempera-
 370 tures and was biased low relative to the FRM at higher temperatures (roughly
 371 10°C and above). The cause of the discrepancy between our study and these
 372 previous studies is unknown; we suspect it could result from differences in
 373 PM_{2.5} chemical composition among the studies and, in particular, from dif-
 374 ferences in the measurement of particle-bound water, which has been shown
 375 to contribute substantially to the mass of PM_{2.5} determined using the FRM
 376 in the Pittsburgh region during summer [13].

377 For α , all samplers except for the type 16 sampler at site 2 showed a
 378 sigmoidal pattern. Not surprisingly, the FDMS TEOM (type 19) at site 11
 379 showed a pattern that was opposite of the general pattern. For the cases
 380 indicated above in which sigmoidal patterns were not observed, simple linear

381 regression models were fitted instead.

382 Table 8 shows the estimated calibration model parameters for all nine
 383 TEOMs. For example, the calibration between the 50°C TEOM and the
 384 FRM sampler at site 4 is given by:

$$E[TEOM(T)] = \left(\alpha(T) + \beta(T) \sqrt{E[FRM]} \right)^2 \quad (5)$$

$$E[FRM(T)] = \left(-\frac{\alpha(T)}{\beta(T)} + \frac{1}{\beta(T)} \sqrt{E[TEOM]} \right)^2 \quad (6)$$

385 where

$$\alpha(T) = 0.333 + \frac{-0.152 - 0.333}{1 + e^{\frac{18.524 - T}{0.951}}} \quad (7)$$

386 and

$$\beta(T) = 0.796 + \frac{1.082 - 0.796}{1 + e^{\frac{16.542 - T}{4.578}}} \quad (8)$$

Figure 4: Regression model fits for each TEOM. For β at Site 6 (Type 14) and Site 2 (Type 16), and for α at Site 2 (Type 16), linear regression was used. Otherwise, a nonlinear sigmoidal regression was used.

Figure 5: Nonlinear mixed effects model sigmoidal fits to TEOM 50°C (Type 14) calibrations parameters (β and α) as a function of temperature for sites 4, 5, 7, and 10. Fixed effect (typical) fit is denoted by the grey curve. Random effect (site-specific) fit is denoted by the black curve. The dashed horizontal line for β denotes the lack of a scale bias. The dashed horizontal line for α denotes the lack of a constant bias when there is no scale bias. The vertical dashed line for both β and α denotes the temperature (17.65 °C) at which the scale bias vanishes as estimated in [14].

387 *6.2. Nonlinear mixed effects model accounting for temperature*

388 Four of the 50°C (type 14) TEOMs had similar, well-defined sigmoidal
 389 patterns for α and for β . For these samplers at sites 4, 5, 7, and 10, a
 390 nonlinear mixed effects model was fitted using the `nlme` and `SSfp1` functions
 391 from the `nlme` R package. The nonlinear sigmoidal mixed effects model is
 392 similar to the model shown by equation 4 and is described as follows:

$$y(T) = (A + a) + \frac{(B + b) - (A + a)}{1 + e^{\frac{(T_{mid} + t) - T}{S + s}}} + \epsilon \quad (9)$$

393 where a , b , t , and s are the corresponding random effects (site-specific ef-
 394 fects), assumed to be normally distributed with means of zero and standard
 395 deviations σ_a , σ_b , σ_t , and σ_s , respectively. When fitting these models for α
 396 and β , the reciprocal of the confidence interval width was used as the weight
 397 for each calibration parameter estimate so that less precise estimates were
 398 given less weight. Also, a variance function was used to allow each site to
 399 have its own variance for ϵ using site 4 as the (arbitrary) reference. Random
 400 effects for α were included for A (a) and for T (t). For β , random effects
 401 were included for A (a) and S (s).

402 Tables 9 and 10 show the estimated parameters for the two logistic non-
 403 linear mixed effects calibration models. In general, the confidence intervals
 404 for A and B for both α and β are reasonably narrow. The remaining param-
 405 eters tend to have fairly wide confidence intervals. The fixed effects parameters

(A, B, T_{mid} , and S) describe the *typical* temperature effect. Although all of
 the 50°C (type 14) TEOMs can be directly calibrated to the FRM sampler
 in this study, this relationship could be used to calibrate a 50°C TEOM
 located in the same region that had no available collocated FRM sampler.
 Notably, the estimated A and B for β are statistically significantly different
 from 1, with A being substantially less and B being slightly greater than 1.
 Analogously, the estimated A and B for α are statistically significantly dif-
 ferent from zero with A being substantially greater and B being substantially
 less than zero. The random effect standard deviation $\sigma_t = 3.2799$ °C for α
 when compared with the fixed effect $T_{mid} = 15.7733$ °C indicates that there
 is substantial variation in the location of the sigmoidal curves across sites.
 Similarly, the random effect standard deviation $\sigma_s = 1.5321$ °C for β when
 compared with the fixed effect $S = 3.9384$ °C indicates that there is sub-
 stantial variation in the scale or spread of the sigmoidal curves across sites.
 The standard deviations for the other random effects are relatively small. For
 α , the random error standard deviation for site 4 is estimated as 0.0385 (on
 the square root transformed scale). All of the variance structure estimates
 for sites 5, 7 and 10 are above 1 indicating that the random error standard
 deviations for these sites may be larger than for site 4. Only the standard
 deviation for site 10 is substantially greater than 1 and at minimum is likely
 to be at least twice the standard deviation for site 4. Analogously, for β , the
 random error standard deviation for site 10 is at least 25% higher than for
 site 4. The β for sites 5 and 7 may have lower random error than the β for

429 site 4, but the confidence intervals for the variance factors include 1, so this is
 430 not conclusive. Finally, Table 11 shows the site-specific sigmoidal model pa-
 431 rameter estimates for α and for β . Fig. 5 shows the typical sigmoidal model
 432 based on the fixed effects (grey curves), which is the same across all sites,
 433 and the site-specific models based on the random effects (added to the fixed
 434 effects) that vary across sites (black curves). In a mixed effects model, sites
 435 with more variable observations (in this case, parameter estimates), tend
 436 to *borrow* information from the other sites. For illustration, the calibration
 437 equations for site 4 are given by equations 5 and 6 where

$$\alpha(T) = 0.3755 + \frac{-0.3118 - 0.3755}{1 + e^{\frac{(19.5379+t)-T}{2.5413}}} \quad (10)$$

$$\beta(T) = 0.7240 + \frac{1.0474 - 0.7240}{1 + e^{\frac{(9.9925+t)-T}{6.0362}}} \quad (11)$$

438 Equations 10 and 11 should be compared to equations 7 and 8 that were
 439 derived for the same samplers using nonlinear regression and to the equations
 440 for the fixed effect model (which are not shown). We pooled together the
 441 TEOMs for sites 4, 5, 7, and 10 because they appeared to operate in a similar
 442 manner. By using the nonlinear mixed effects model, we *borrow* information
 443 from all of these sites in order to temper each site-specific prediction. The

Fixed Effects			Random Effects				Variance Factor				Site 4
<i>A</i>	<i>B</i>	<i>T_{mid}</i>	<i>S</i>	σ_a	σ_b	σ_t	σ_s	Site 5	Site 7	Site 10	σ_ϵ
Lower	0.3411	-0.4029	11.9733	1.4008	0.0054	1.5197		0.3974	0.4312	2.2597	0.0202
Estimate	0.4099	-0.3118	15.7733	2.5413	0.0400	3.2799		1.0625	1.0792	5.3374	0.0385
Upper	0.4787	-0.2208	19.5733	3.6819	0.2940	7.0790		2.8408	2.7009	12.6067	0.0734

Table 9: 95% Confidence intervals for sigmoidal mixed effects model for TEOM calibration $\alpha(T)$. The variance factor is used as a multiplier $\times$ the random error standard deviation σ_ϵ for site 4.

Fixed Effects			Random Effects				Variance Factor				Site 4
<i>A</i>	<i>B</i>	<i>T_{mid}</i>	<i>S</i>	σ_a	σ_b	σ_t	σ_s	Site 5	Site 7	Site 10	σ_ϵ
Lower	0.6799	1.0334	9.4662	2.0685	0.0028		0.4973	0.2501	0.1830	1.2669	0.0037
Estimate	0.7058	1.0474	9.9925	3.9384	0.0178		1.5321	0.5943	0.4504	3.0032	0.0071
Upper	0.7317	1.0614	10.5188	5.8083	0.1124		4.7204	1.4126	1.1088	7.1191	0.0139

Table 10: 95% Confidence intervals for sigmoidal mixed effects model for TEOM calibration $\beta(T)$. The variance factor is used as a multiplier $\times$ the random error standard deviation σ_ϵ for site 4.

Site ID	Asymptote $t \rightarrow -\infty$ $A + a$	Asymptote $t \rightarrow \infty$ $B + b$	Location °C $T_{mid} + t$	Scale °C $S + s$
Sigmoidal Model for $\alpha(T)$				
4	0.3755	-0.3118	19.5379	2.5413
5	0.4378	-0.3118	15.5430	2.5413
7	0.3955	-0.3118	11.2089	2.5413
10	0.4309	-0.3118	16.8033	2.5413
Sigmoidal Model for $\beta(T)$				
4	0.7240	1.0474	9.9925	6.0362
5	0.6916	1.0474	9.9925	4.0302
7	0.7136	1.0474	9.9925	2.4034
10	0.6939	1.0474	9.9925	3.2836

Table 11: Predicted site-specific parameters for the nonlinear sigmoidal models fitted to the estimated calibration parameters for the eight temperature strata. The model predictions (pink curves) are plotted in Figure 5.

444 site-specific curve is *pulled* toward the *typical* curve, the curve determined by
445 data from all sites. The *pull* will be stronger for sites with few observations
446 and/or more variable observations. However, as shown in Figure 5, the choice
447 in which sites to group together as a sample from a specific population only
448 makes much of a difference for the bias parameter α for site 10 given the
449 greater variability in the observations for this parameter at this site.

450 6.3. TEOM imprecision

451 Although the primary focus of this study is calibration of the various
452 samplers with the FRM sampler, it is useful to examine the imprecision
453 of the samplers after adjusting the imprecision standard deviations (σ_i) for
454 scale changes (σ_i/β_i). There were 9 TEOM samplers with six of these being

455 50°C TEOMs. In general, the 50°C TEOM imprecision standard deviation
 456 was higher than that of the FRM samplers. For most of the 50°C TEOMs,
 457 the imprecision decreased with increasing temperature. The change in σ_i^2/β_i^2
 458 with temperature was roughly linear as previously described in [14]. For the
 459 two 30°C TEOMs and one FDMS TEOM, there is less clear evidence of a
 460 relationship with temperature.

461 7. Discussion and conclusions

462 The analysis presented here represents a complex, but necessary, step in
 463 incorporating data from a number of disparate measurement devices into a
 464 common epidemiology study. The PM_{2.5} measurements made by the seven air
 465 monitoring programs in the 35-county area were independent efforts without
 466 an overall goal for integration or eventual use in a comprehensive health ef-
 467 fects study. Making comparisons temporally and spatially (i.e., for purposes
 468 of characterizing variations in human exposure to ambient PM_{2.5} throughout
 469 the region) requires measurements made effectively on the same scale. For-
 470 tunately, in the case of PARIES, enough multiple collocated measurements
 471 from different types of samplers were available so that all non-FRM samplers
 472 could be calibrated to the FRM sampler. We used the calibration equations
 473 reported above to convert all measurements made by non-FRM samplers to
 474 their FRM-equivalent values, and then used the resulting FRM-equivalent
 475 values in geostatistical modeling to develop daily ZIP-code-specific estimates
 476 of PM_{2.5} exposure in the three-county study area. (Results of this expo-

sure modeling will be presented in a future paper). This same approach is recommended for other retrospective epidemiology studies in order to take advantage of all available data without introducing exposure misclassification as a result of the relative biases between measurement devices. The general calibration methodology presented here could also be applied by air monitoring networks to develop robust calibration equations for the monitors in their operating region without requiring full collocated monitoring at every site. (As established above, at least three collocated monitors are required to conduct a properly designed calibration study at a single monitoring site).

It is noteworthy that the conclusions developed here for a number of $\text{PM}_{2.5}$ monitors and monitoring sites in the Pittsburgh region are generally consistent with those developed in [14] for a single site (42-3-8, site 5 in Table 2). Specifically, (1) the 50°C TEOM samplers tended to show a large downward bias relative to the FRM sampler at low temperatures, and the magnitude of this bias decreased according to a nonlinear (sigmoidal) pattern with increasing temperature, (2) the other types of integrated samplers (i.e., speciation and dichotomous samplers) generally showed smaller biases relative to the FRM sampler that were not temperature-dependent, and (3) the FRM samplers tended to be more precise than the non-FRM samplers. (The noteworthy exception was the IMPROVE sampler, which had approximately the same imprecision as the FRM sampler). This consistency lends credence to our methodology.

Finally, it should be mentioned that the approach used here to model

the temperature dependence of the TEOM was not ideal but was a necessary approximation to avoid substantially further complicating the analysis. Ideally, the effect of temperature would be directly incorporated into the structural equation model. However, incorporating nonlinear components into a structural equation model is complicated, whereas the stratification of measurements into eight temperature classes provided a workable alternative for our purposes. Also, because the temperatures that were used as the independent variable in the nonlinear regression and nonlinear mixed effects modeling were necessarily measured with some random error, the parameter estimates from these models (describing the temperature dependence of the relationship between TEOM and FRM) will have some bias. (As with ordinary regression, these models assume that the independent variable is a highly precise measurement having little or no random error). This bias should be relatively small, though, when the observations are close to the estimated site-specific curve.

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