

A Field Evaluation to Compare the Performance of Personal Exposure Multi-Pollutant Samplers vs. Federal Method Monitors at a Central Ambient Air Monitoring Station in Steubenville, Ohio

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Abstract

One of the National Research Council (NRC) research priorities for PM_{2.5} is to investigate the relationship between measurements conducted at a central outdoor ambient air monitoring station and personal exposure measurements. The research described addresses a key aspect in the relationship by examining the performance of the different sampling equipment and methods used to measure fine particulate and gaseous pollutants at an outdoor ambient air station and in the breathing space of studied individuals.

The performance of a federal reference method PM_{2.5} sampler and federal equivalent gaseous pollutant analyzers for SO₂, NO₂, and O₃ were compared to the performance of the Harvard School of Public Health's multi-pollutant sampler, which was used to measure personal exposure of PM_{2.5}, sulfate (SO₄²⁻), SO₂, NO₂, and O₃. Instrumental and method issues, such as bias, precision, and detection limits, were quantified. The results will help establish a foundation for quantifying the relationship between personal exposure and a central ambient air monitoring station.

Introduction

The U.S. EPA promulgated new ambient air standards for PM_{2.5} based on several epidemiological studies showing an association between PM_{2.5} concentration and adverse health effects. However, before the standards are finalized, the National Research Council has recommended that scientific uncertainties regarding the relationship between PM_{2.5} and health effects be clarified. Two questions raised by the NRC were, "Do measurements conducted at a central outdoor ambient air monitoring station accurately reflect personal exposure?" and "Is the total PM_{2.5} mass, a component(s) of PM_{2.5}, a co-pollutant, or a combination responsible for the observed association with adverse health effects?"

CONSOL Energy Inc. is conducting a research program, the Steubenville Comprehensive Air Monitoring Program (SCAMP), to help address these and other fundamental uncertainties regarding PM_{2.5}. A research team comprised of the Harvard School of Public Health, Franciscan University of Steubenville, Ohio University, St. Vincent

College, and Wheeling Jesuit University are participating in the study. Funding was provided by the United States Department of Energy National Energy Technology Laboratory, Ohio Coal Development Office, Electric Power Research Institute, American Petroleum Institute, American Iron and Steel Institute, National Mining Association, Edison Electric Institute, National Institute of Environmental Health Sciences, United States Environmental Protection Agency, and CONSOL Energy Inc. The sampling and the majority of the analytical work are complete. The data analysis and reporting phases remain.

The sampling program for SCAMP was comprised of two overlapping and interdependent programs focused on measuring fine particulate and gaseous pollutants in the outdoor ambient air, inside the home, and in the breathing space of individuals. The outdoor ambient air program utilized a central ambient air monitoring station equipped with both federal reference method integrated particulate samplers and federal equivalent method continuous gaseous pollutant analyzers. The indoor and personal sampling program utilized an integrated, filter-based, multi-pollutant sampler, developed by the Harvard School of Public Health. The multi-pollutant sampler is a modular sampling system that collects both particulate and gaseous pollutants simultaneously. The multi-pollutant sampler can be used to collect a variety of different pollutant combinations and can be deployed to sample in different sampling environments (i.e., on a person, inside a home, and outdoors). In SCAMP the multi-pollutant sampler was utilized to sample all of the mentioned environments.

Twenty weeks of SCAMP collocated field sampling data collected during the summer and fall of 2000 were used to compare the multi-pollutant sampler versus the federal method monitors.

Experimental

The central ambient air monitoring station, which was located on the campus of Franciscan University of Steubenville, was comprised of a sampling trailer and an adjacent courtyard. The trailer was equipped with federal equivalent continuous gaseous pollutant analyzers. The analyzers were rack-mounted and integrated into a turnkey sampling platform, including real-time data logging, mass-flow calibration, zero air generation, and automatic calibration capabilities. The courtyard contained the integrated, filter-based, sampling equipment, including the federal reference method particulate samplers. In addition, the courtyard served as one of the outdoor sampling sites for the multi-pollutant samplers, therefore providing collocated samples and the focus of this paper. The multi-pollutant samplers were affixed on top of a sampling tripod, guarded against weather, and positioned at approximately the same sampling height as the federal reference method PM_{2.5} sampler.

The methodologies outlined in *Federal Reference Method 40 CFR Parts 50, 58* and the guidelines in the *USEPA Quality Assurance Guidance Document 2.12* were used for measuring PM_{2.5} from both the federal reference method PM_{2.5} sampler and the multi-pollutant samplers. These guidance documents provided the recommended procedures for collecting, handling, weighing, sampling, and validating PM_{2.5} mass data.

The measurements conducted with the gas analyzers were made in accordance with the instrument manufacturers' recommendations, the *USEPA Quality Assurance Handbook for Air Pollution Measurement Systems*, and the schedule outlined in *40 CFR, Part 58, Appendix B, Quality Assurance Requirements for Prevention of Significant Deterioration*.

The multi-pollutant sampler uses a filter for measuring all of the pollutants, which include gases and particulate. The multi-pollutant sampler is comprised of a number of different sampling modules or mini-samplers integrated into one sampling platform. The multi-pollutant sampler employs a battery-powered, personal sampling pump that pulls air through an elutriator, which serves as a manifold for all of the sampling modules and mini-samplers. Particulate and particulate components, including PM_{2.5}, SO₄²⁻, and carbon are collected within impaction-based personal exposure modules (PEMs). The gases, SO₂, NO₂ and O₃, are collected with Ogawa passive samplers. Whereas the PEMs actively sample the air at a constant controlled flow from the elutriator, the Ogawa samplers passively collect the gases. Air diffuses from the active stream passing through the elutriator, across a chemically coated filter, initiating a reaction with the gaseous pollutant (SO₂, NO₂ or O₃) and an active chemical on the filter. These passive sampling methodologies were developed over numerous field campaigns conducted by the Harvard School of Public Health and Ogawa & Company. To ensure high capture efficiency and to minimize contamination, strict handling procedures were followed in SCAMP, from coating the filters to sampler assembly, through sampling, sampler break-down, and filter storage. The filters were stored in a refrigerator, in sealed plastic bottles, until they were ready to be extracted and analyzed on an ion chromatograph to complete the measurement.

Included in Table 1, is a summary of all the methods used in the field comparison.

Table 1. Summary of Sampling and Analytical Methods.

Pollutant	Central Station	Multi-Pollutant Sampler
PM_{2.5}	PM _{2.5} was collected on a Teflon filter in a FRM PM _{2.5} sampler. The mass of the PM _{2.5} was determined gravimetrically.	PM _{2.5} was collected with a PEM (personal exposure module) loaded with Teflon filter. The mass of the PM _{2.5} was determined gravimetrically.
SO₂	SO ₂ was measured with an Automated Federal Equivalent Method UV Fluorescence analyzer.	An Ogawa type badge, loaded with a cellulose filter, coated with a triethanolamine solution, collected SO ₂ and NO ₂ simultaneously. Prior to analysis, the filter was treated with H ₂ O ₂ , oxidizing the SO ₂ to SO ₄ ²⁻ . The filter was then extracted into an aqueous solution. An extract was analyzed by ion chromatography.
NO₂	NO ₂ was measured with an Automated Federal Reference Method chemiluminescence analyzer.	An Ogawa type badge, loaded with a cellulose filter, coated with a triethanolamine solution, collected SO ₂ and NO ₂ simultaneously. Prior to analysis, the filter was treated with H ₂ O ₂ , oxidizing the SO ₂ to SO ₄ ²⁻ . The filter was then extracted into an aqueous solution. An extract was analyzed by ion chromatography.

Pollutant	Central Station	Multi-Pollutant Sampler
O ₃	O ₃ was measured with an Automated Federal Equivalent Method UV analyzer.	An Ogawa type badge loaded with a glass fiber filter coated with a sodium nitrite/potassium carbonate solution collected O ₃ . The filter was then extracted into an aqueous solution. The extract was analyzed by ion chromatography.
SO ₄ ²⁻	Following weighing, the same Teflon filter used to collect PM _{2.5} , was wetted and extracted into an aqueous solution. The extract was analyzed by ion chromatography.	SO ₄ ²⁻ was collected with a mini-PEM loaded with a fluoropore type filter. The filter was then wetted and extracted into an aqueous solution. The extract was analyzed by ion chromatography.

In previous sampling campaigns, the multi-pollutant sampler was integrated with two PEMs for collecting particulate matter. One PEM module collected PM_{2.5} and the other collected PM₁₀. An objective of SCAMP was to quantify various elements in the total and in the water-soluble portion of the particulate. This would allow for assessing elements and elemental compounds that have potential to be soluble in lung tissue and determining the amounts of the elements in the total particulate, which are also needed to do a mass balance of the particulate. Determining water soluble and total elements requires two different extractions, a water-soluble leach and an acid digestion. Therefore, it was necessary to configure the multi-pollutant sampler with two PM_{2.5} PEM modules to generate two duplicate PM_{2.5} filters to satisfy the two extractions. The concentrations of PM_{2.5} from each of the duplicate filters were averaged to produce one PM_{2.5} result per multi-pollutant sampler to be compared versus the federal method PM_{2.5} sampler concentration.

PM_{2.5} data collected from both the federal method and multi-pollutant sampler were not blank corrected with the field blank concentration. Blank correction is not permitted per data treatment procedures outlined in the federal reference method for PM_{2.5}. However, for the gaseous measurements, federal equivalent gaseous pollutant analyzer data were zero and drift corrected. Gaseous data determined with the multi-pollutant samplers were blank corrected with the concentration of the field blanks.

Because the sampling comparison was made in the field and not in a controlled laboratory setting, it was impossible to introduce a “standard reference” mixture of air, certified for all of the pollutants, to assess bias and precision. Instead, the actual daily pollutant concentrations from the collocated sampling equipment were used. Therefore, statistical techniques outlined by Jaech¹ were selected to estimate bias and precision. Each observed concentration Y was assumed to be a linear function of the true concentration μ :

$$Y_{ik} = \alpha_i + \beta_i \mu_k + \varepsilon_{ik}$$

where

Y_{ik} is the observed concentration for the k^{th} of n parcels of air and the i^{th} of N samplers

α, β characterize the relative bias of the i^{th} sampler

μ_k is the true concentration of k^{th} air parcel

ε_{ik} is the random error from a Normal distribution with variance σ_i^2 for the i^{th} sampler

Maximum likelihood estimates were computed for determining the samplers' imprecision variances (σ_s), along with corresponding estimates for determining the relative bias (α_s and β_s) between samplers. A likelihood ratio test was then used to determine if the relative bias was constant or changing with concentration (i.e., a function of the true concentration).

Detection limits were determined as three times the standard deviation of the blank. Two detection limits were determined for NO₂ and O₃ for the multi-pollutant sampler, one for the summer and one for the fall. Because the reactions associated with the chemically coated filters proceed much faster in warmer temperatures, different field blank concentrations were likely for different seasons. The summer limit of detection is listed first in Table 2. Detection limits for the federal equivalent gas analyzers were determined as three times the standard deviation of zero air blank measurements. The gas analyzers experienced a high number of failures, repairs, and re-calibrations. As a result, the zero air blank measurements varied significantly, approximately plus or minus 50%, over extended periods of time. Therefore, it was deemed that the most appropriate limit of detection to report for a specific gas analyzer would be an average of individual detection limits calculated at various intervals during the twenty-week comparison.

Results and Discussion

A summary of the bias and precision estimates and the calculated limits of detection are included in Table 2. Point estimates of bias and precision were reported for ease of comparison. Note that the precision and bias results reported in Table 2 represent an average of two multi-pollutant samplers, since they were operated in duplicate. Furthermore, each multi-pollutant sampler represents an average, since each multi-pollutant sampler contains duplicate PM_{2.5} filters.

The multi-pollutant sampler was determined to be as precise as the federal reference method PM_{2.5} sampler and the federal automated equivalent gas analyzers. All estimates of precision detailed in Table 2 were on the order of a few $\mu\text{g}/\text{m}^3$ for the particulate measurements and a few ppbv for the gas measurements.

Not included in Table 2 is a determination of intra-filter precision within one multi-pollutant sampler (each sampler contained two filters for PM_{2.5}). However, the results were in agreement with the average precision reported for the multi-pollutant sampler, at approximately 1 to 2 $\mu\text{g}/\text{m}^3$. The results suggest there was no significant difference between separate filters within a multi-pollutant sampler.

For all of the pollutants except NO₂, bias was determined to increase with pollutant concentration (i.e., non-constant). For NO₂, bias remained constant over the concentration range of the comparison and was approximately 20% or 2 ppbv at the mean concentration of 10ppbv. The bias was determined to be constant at approximately 2 ppbv even with increasing concentration. For PM_{2.5}, SO₄²⁻, and O₃, bias ranged from 5 to 10% at the mean ambient concentration, and increased to 20% at higher pollutant concentrations. For SO₂, bias was 80% at the mean ambient concentration of the

comparison. The double-bordered cell in Table 2 identifies the bias at the mean ambient pollutant concentration for the 20-week comparison.

The limits of detection for the sampling equipment indicated that they were adequate for measuring most of the pollutants. However, the detection limits calculated for the multi-pollutant sampler for SO₂ and O₃ were greater than most of the indoor and personal concentrations measured during SCAMP. Consequently, the interpretation of such data will be primarily limited to averages and trends and not to single day or individual SO₂ and O₃ measurements.

Table 2. Results

Precision of Sampling Equipment					
	PM_{2.5} ($\mu\text{g}/\text{m}^3$)	SO₄²⁻ ($\mu\text{g}/\text{m}^3$)	SO₂ (ppbv)	O₃ (ppbv)	NO₂ (ppbv)
FRM PM _{2.5} Sampler	2.6	0.9	-----	-----	-----
Federal Automated Equivalent Gas Analyzer	-----		4.5	4.1	3.9
Multi-Pollutant Samplers	1.9	0.6	2.5	5.7	7.0
Bias of the Multi-Pollutant Samplers Compared to the FRM PM_{2.5} Sampler for PM_{2.5}					
Ambient Concentration of PM _{2.5}	5.0	10.0	20.0	30.0	50.0
Bias	-0.8	0.2	2.0	4.5	8.7
Bias of the Multi-Pollutant Samplers Compared to the FRM PM_{2.5} Sampler for SO₄²⁻					
Ambient Concentration of SO ₄ ²⁻	2.0	4.0	6.0	8.0	10.0
Bias	-0.7	-0.4	0.0	0.3	0.6
Bias of the Multi-Pollutant Samplers Compared to the Federal Automated Equivalent Gas Analyzers					
Ambient Concentration of Gas	5.0	10.0	25.0	45.0	70.0
Bias for O ₃	-0.4	0.2	2.2	4.8	9.4
Bias for NO ₂	2.0	2.0	2.0	-----	-----
Bias for SO ₂	6.0	7.9	13.4	20.7	-----
Limits of Detection of Sampling Equipment					
	PM_{2.5} ($\mu\text{g}/\text{m}^3$)	SO₄²⁻ ($\mu\text{g}/\text{m}^3$)	SO₂ (ppbv)	O₃ (ppbv)	NO₂ (ppbv)
FRM PM _{2.5} Sampler	1.2	0.1	-----	-----	-----
Federal Automated Gas Analyzers	-----	-----	2.4	2.1	1.2
Multi-Pollutant Samplers	6	0.2	6.4	12.7, 10.7	10.8, 6.1

Conclusions

The performance of the personal exposure multi-pollutant sampler was comparable to the federal method sampling equipment at the central ambient air station. Results were comparable for all measured pollutants, except for SO₂, and agreed to within 10 to 20% at typical ambient concentrations. This suggests that the multi-pollutant sampler is generally acceptable for use in sampling campaigns such as SCAMP.

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References

1. Jaech, John L. *Statistical Analysis of Measurement Errors*; John Wiley & Sons, New York, 1985.