

Figure 1 shows fourth highest daily maximum 8-hour average (DM8A) O₃ concentrations measured through fourth quarter 2021. Ten western and two eastern sites exceeded the 0.070 parts per million (ppm) National Ambient Air Quality Standard for O₃. The western sites include a new 2021 site at Carlsbad Caverns National Park, NM (CAV436).

Trends

Trend analyses were performed based on filter pack pollutant concentrations measured in micrograms per cubic meter (µg/m³) of air at the 34 eastern and 16 western reference sites during fourth quarter. Trends in quarterly mean filter pack and O₃ concentrations are shown using box plots in Figures 2 through 13.

Fourth Quarter Concentrations

Fourth quarter mean NO₃⁻, total NO₃⁻, SO₂, Cl⁻, and Na⁺ concentrations decreased at eastern sites from fourth quarter 2020 to fourth quarter 2021, and HNO₃, SO₄²⁻, Ca²⁺, K⁺ and Mg²⁺ concentrations increased. Fourth quarter mean concentrations of NH₄⁺ remained unchanged between fourth quarter 2020 and 2021. Fourth quarter mean concentrations for all parameters decreased at western sites in 2021.

Quarterly O₃ concentrations were analyzed using box plots constructed by averaging all valid hourly O₃ concentrations within fourth quarter 2021 by site and then averaging those averages for all eastern and western reference sites (Figure 13). The figure shows a small increase in quarterly mean O₃ concentrations at eastern sites. Quarterly mean concentrations were higher at the western reference sites than at the eastern sites.

Figure 2. Trends in Fourth Quarter Mean HNO₃ Concentrations

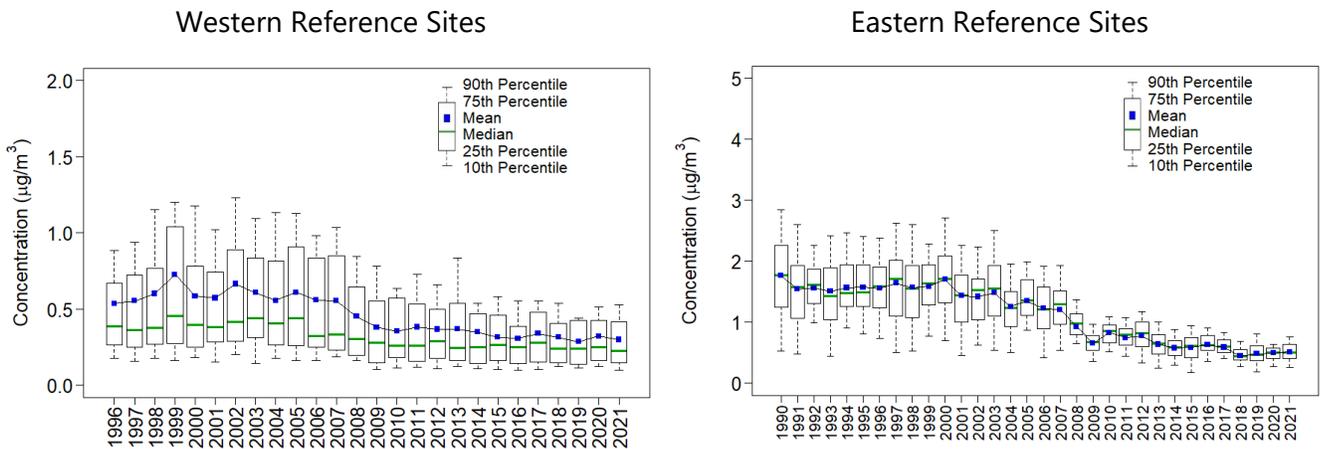


Figure 3. Trends in Fourth Quarter Mean NO₃ Concentrations

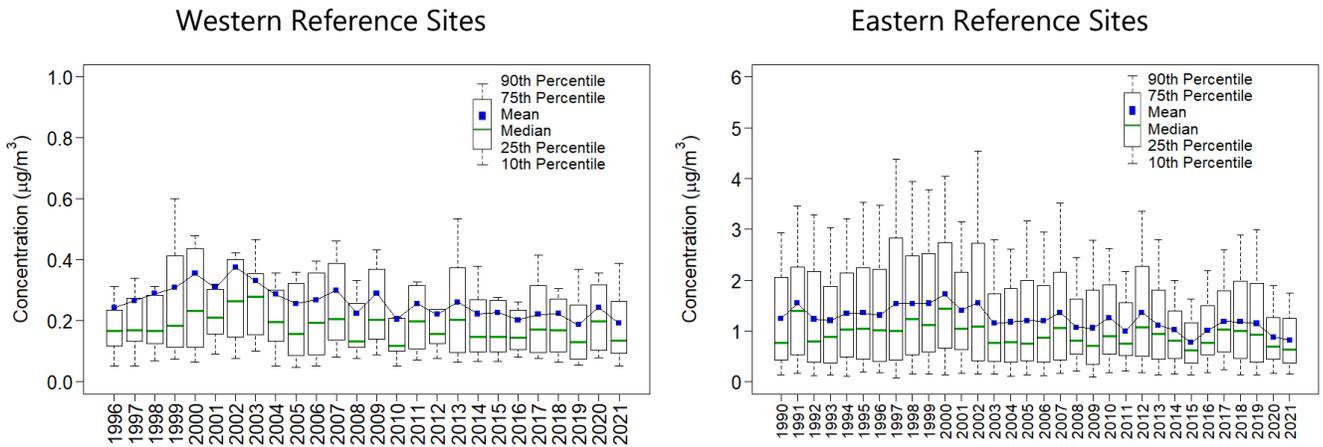


Figure 4. Trends in Fourth Quarter Mean NH₄⁺ Concentrations

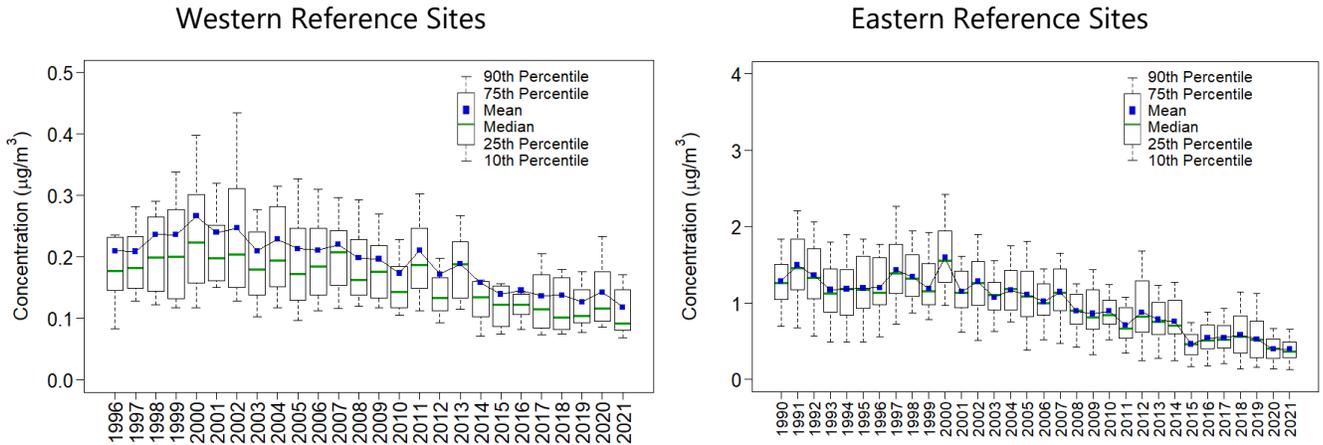


Figure 5. Trends in Fourth Quarter Mean Total NO₃ Concentrations

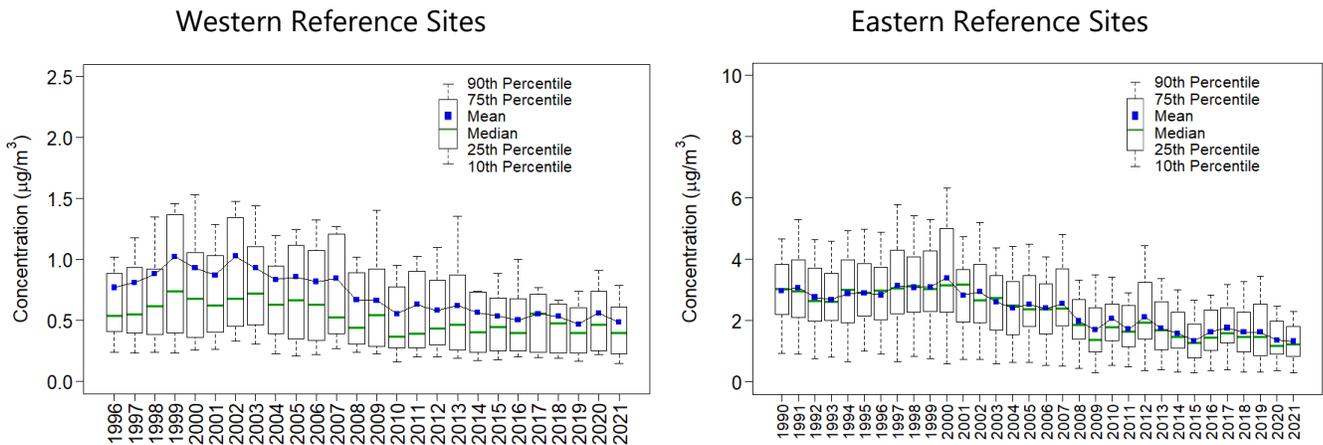


Figure 6. Trends in Fourth Quarter Mean SO₂ Concentrations

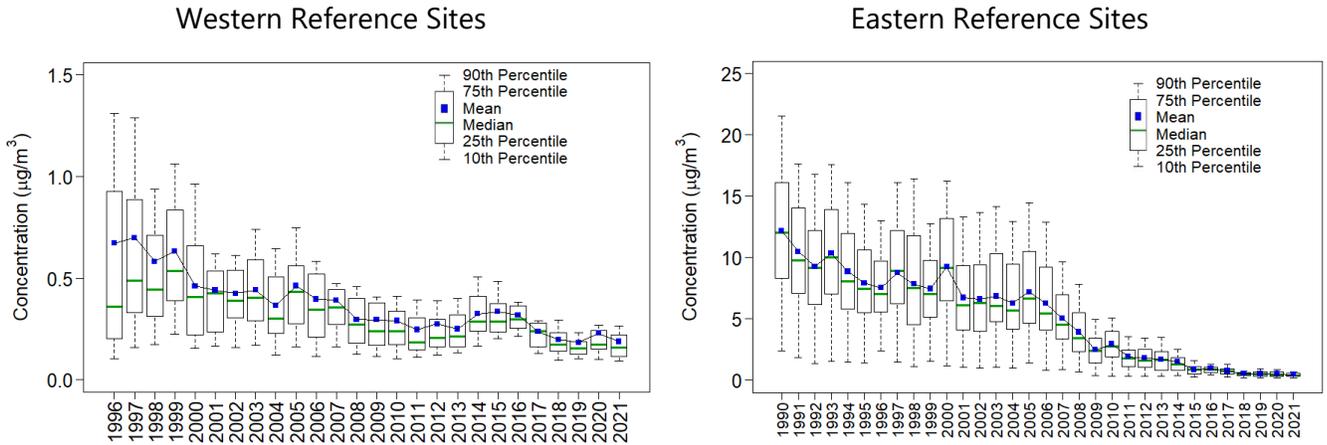


Figure 7. Trends in Fourth Quarter Mean SO₄²⁻ Concentrations

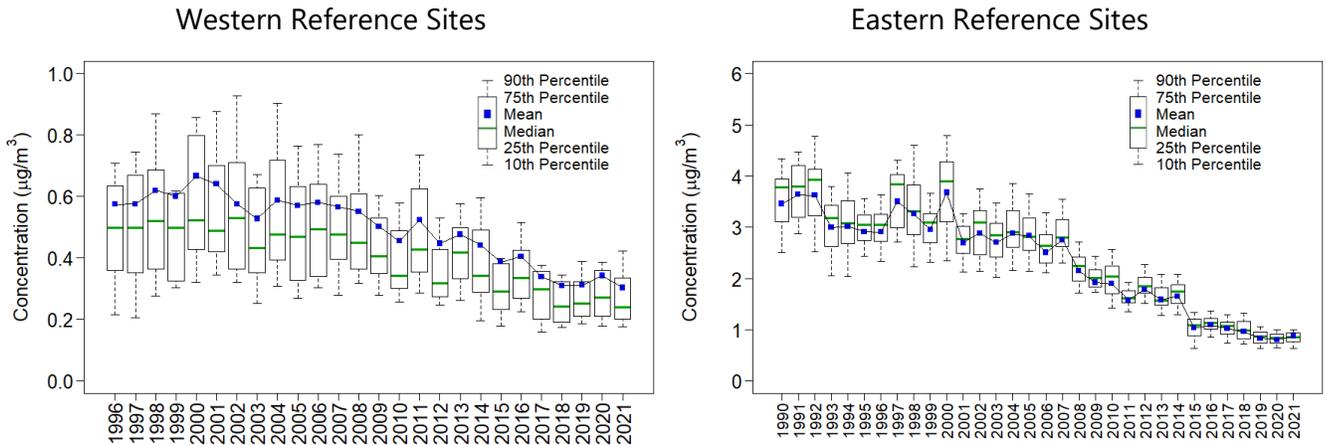


Figure 8. Trends in Fourth Quarter Mean Cl⁻ Concentrations

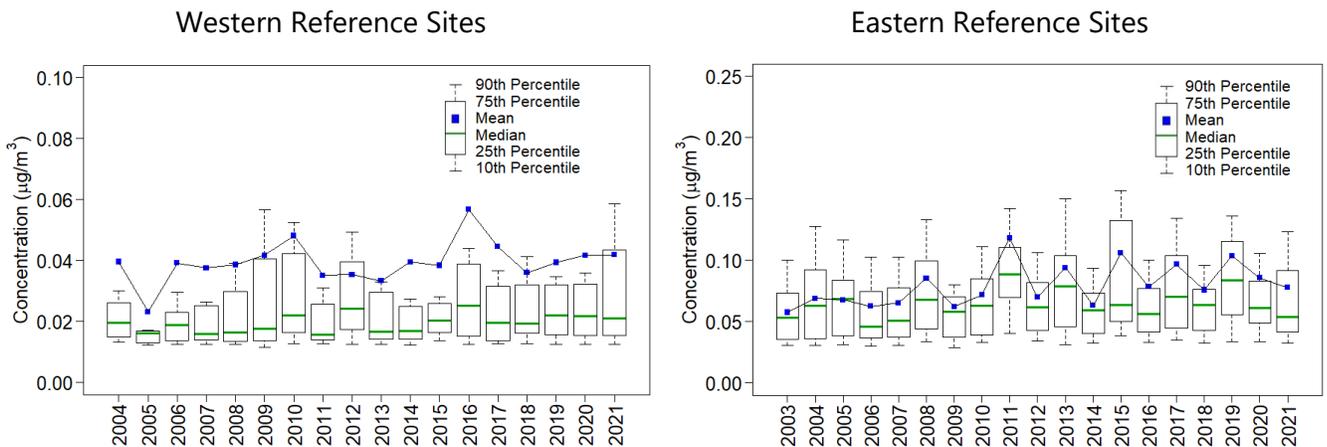


Figure 9. Trends in Fourth Quarter Mean Ca²⁺ Concentrations

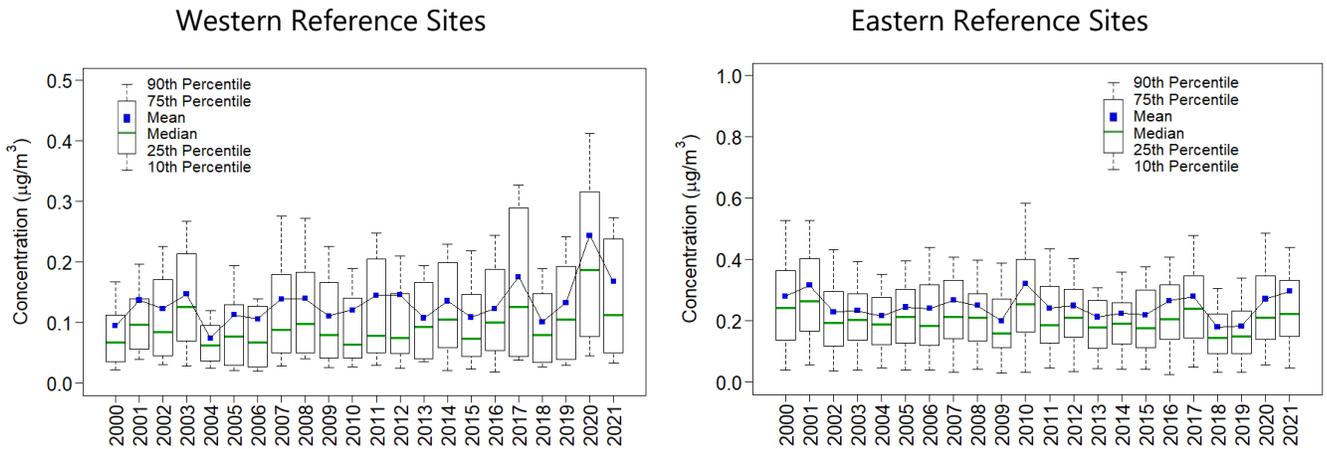


Figure 10. Trends in Fourth Quarter Mean K⁺ Concentrations

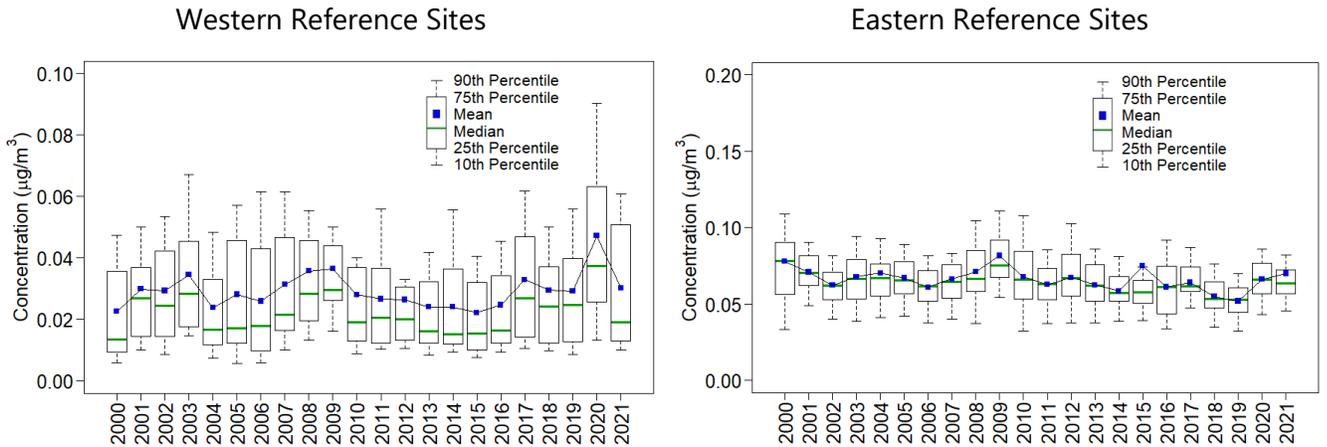


Figure 11. Trends in Fourth Quarter Mean Mg²⁺ Concentrations

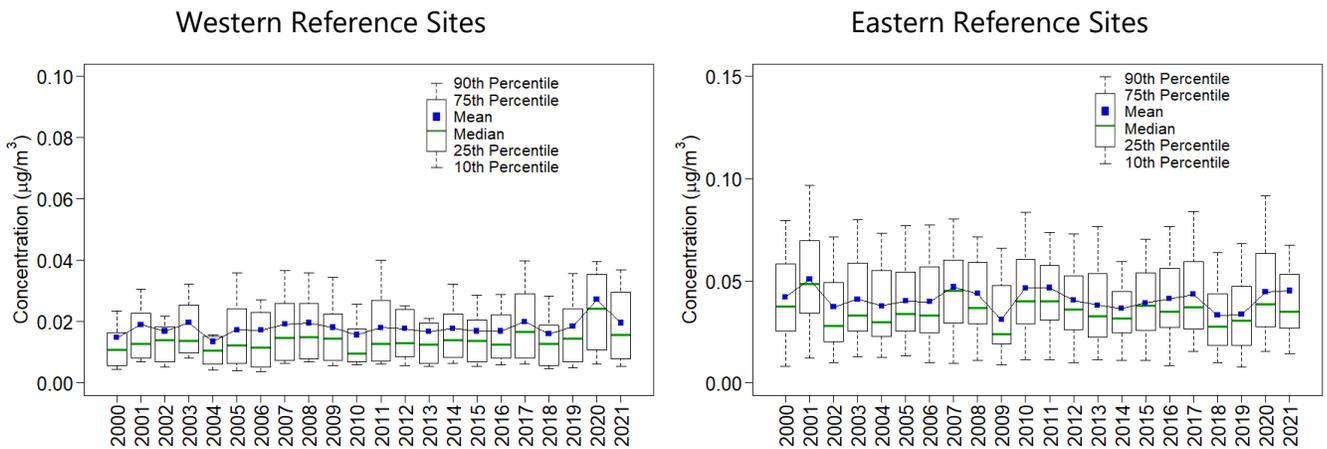


Figure 12. Trends in Fourth Quarter Mean Na⁺ Concentrations

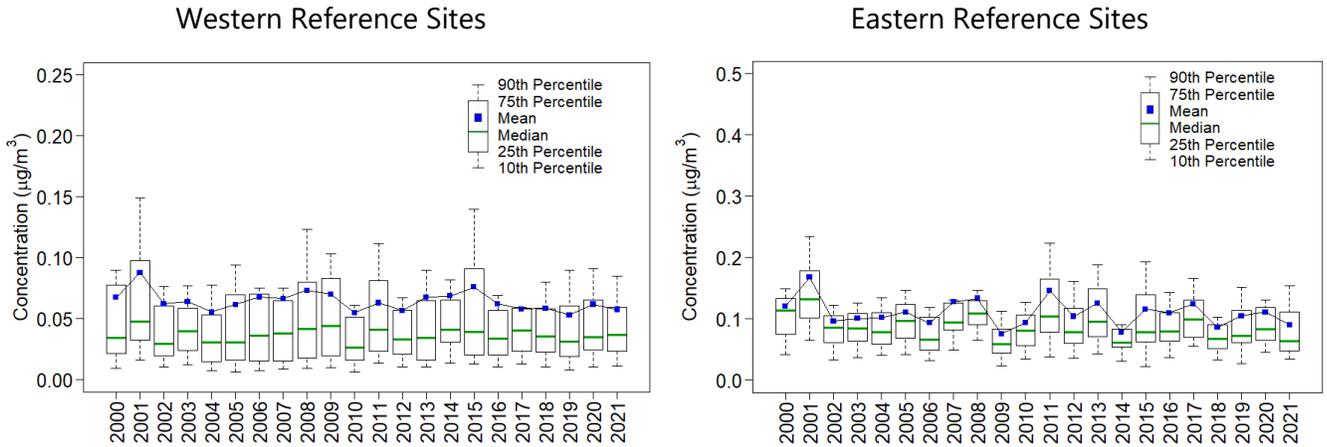
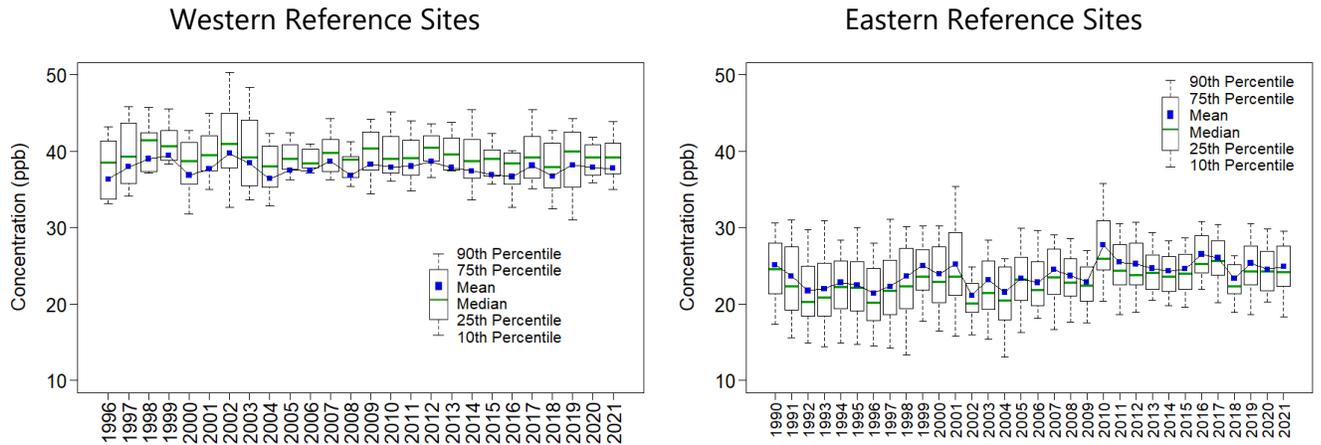


Figure 13. Trends in Fourth Quarter Mean O₃ Concentrations



Changes in 3-year Average Fourth Quarter Concentrations

Three-year averages of quarterly mean concentrations of total NO₃⁻, NH₄⁺, SO₂, and SO₄²⁻ were reduced over the period 1990–1992 through 2019–2021 for eastern reference sites and 1996–1998 through 2019–2021 for western reference sites. O₃ concentrations increased at eastern sites and showed no change at western sites. Tables 1 and 2 summarize changes in 3-year average fourth quarter concentrations.

Table 1. Eastern Reference Sites: 3-Year Mean Nitrogen, Sulfur, and O₃ Pollutant Concentrations

| | Total NO ₃ ⁻ (µg/m ³) | NH ₄ ⁺ (µg/m ³) | SO ₂ (µg/m ³) | SO ₄ ²⁻ (µg/m ³) | O ₃ (ppb) |
|----------------|--|--|---|---|-------------------------|
| 1990–1992 | 2.9 | 1.4 | 10.6 | 3.6 | 24 |
| 2019–2021 | 1.4 | 0.4 | 0.5 | 0.8 | 25 |
| Percent Change | -51 | -68 | -95 | -77 | 6 |

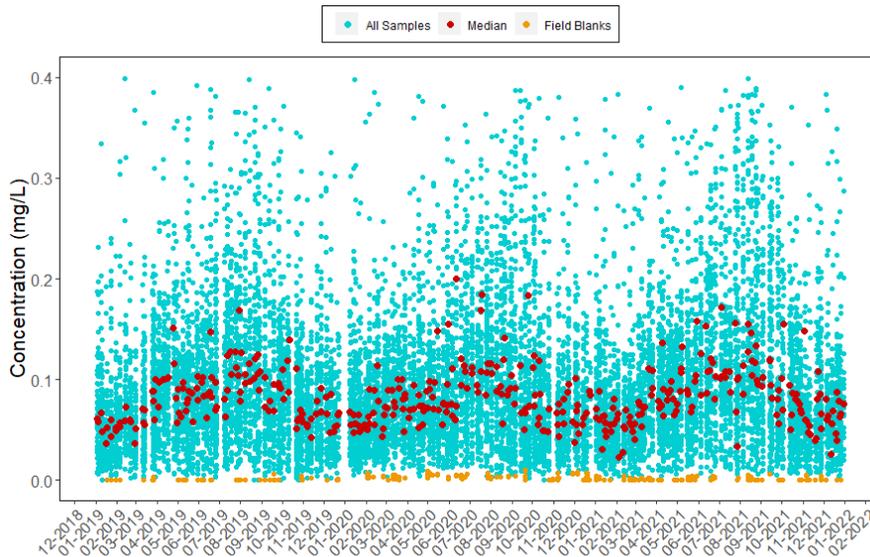
Table 2. Western Reference Sites: 3-Year Mean Nitrogen, Sulfur, and O₃ Pollutant Concentrations

| | Total NO ₃ ⁻ (µg/m ³) | NH ₄ ⁺ (µg/m ³) | SO ₂ (µg/m ³) | SO ₄ ²⁻ (µg/m ³) | O ₃ (ppb) |
|----------------|--|--|---|---|-------------------------|
| 1996–1998 | 0.8 | 0.2 | 0.7 | 0.6 | 38 |
| 2019–2021 | 0.5 | 0.1 | 0.2 | 0.3 | 38 |
| Percent Change | -39 | -41 | -69 | -46 | 0 |

Time Series of Laboratory Analysis Parameters for All Sites

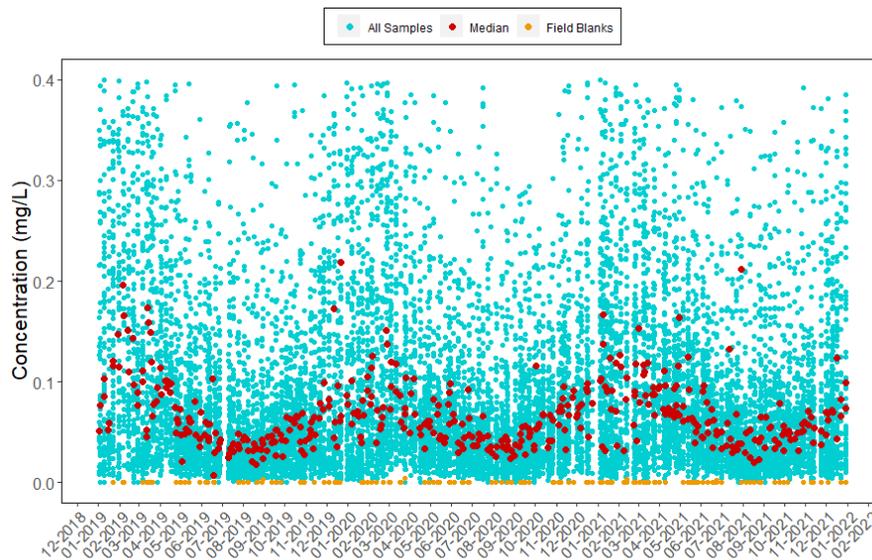
Figures 14 through 24 give time series of laboratory-analyzed concentrations of field samples and field blanks in milligrams per liter (mg/L) of 11 parameters from first quarter 2019 through fourth quarter 2021. These figures provide indications of potential issues with concentration measurements relative to detection and reporting limits.

Figure 14. Concentrations of NO₃⁻ (as N) from Nylon Filters



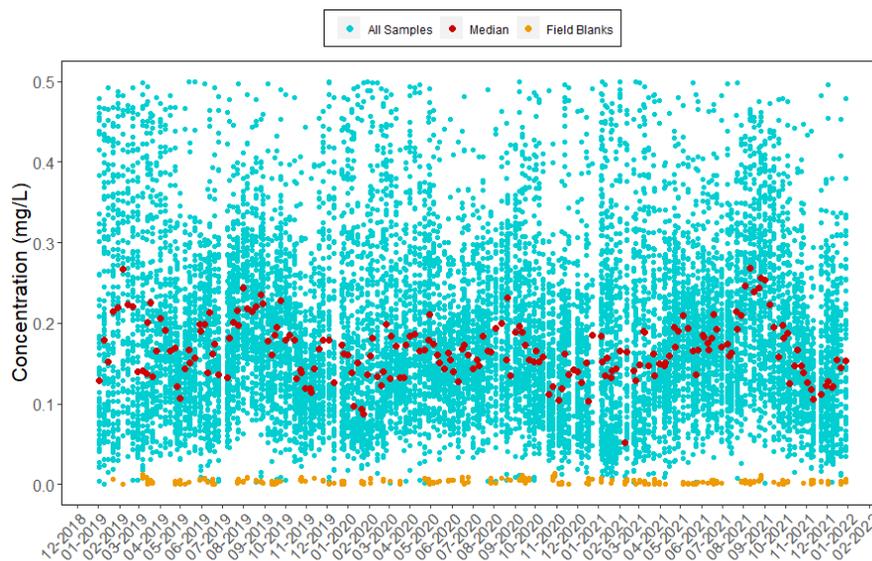
Note: Nominal reporting limit is 0.008 mg/L.

Figure 15. Concentrations of NO_3^- (as N) from Teflon Filters



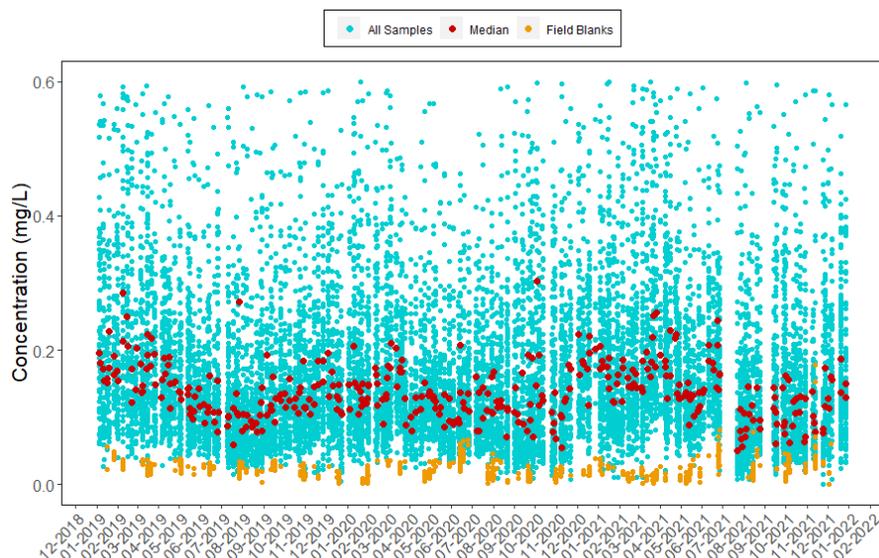
Note: Nominal reporting limit is 0.008 mg/L.

Figure 16. Concentrations of NH_4^+ (as N) from Teflon Filters



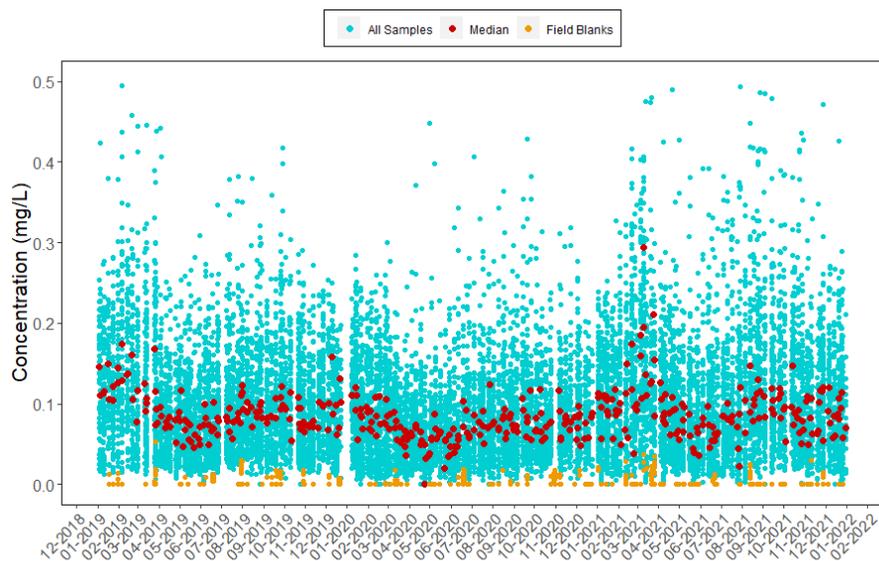
Note: Nominal reporting limit is 0.020 mg/L.

Figure 17. Concentrations of SO₂ from K₂CO₃-impregnated Cellulose Filters



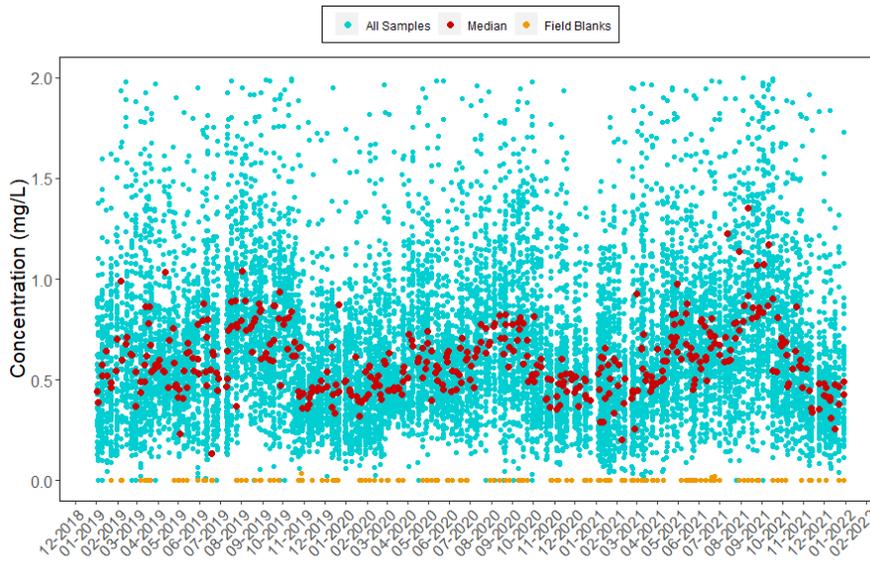
Note: Nominal reporting limit is 0.040 mg/L.

Figure 18. Concentrations of SO₄²⁻ from Nylon Filters



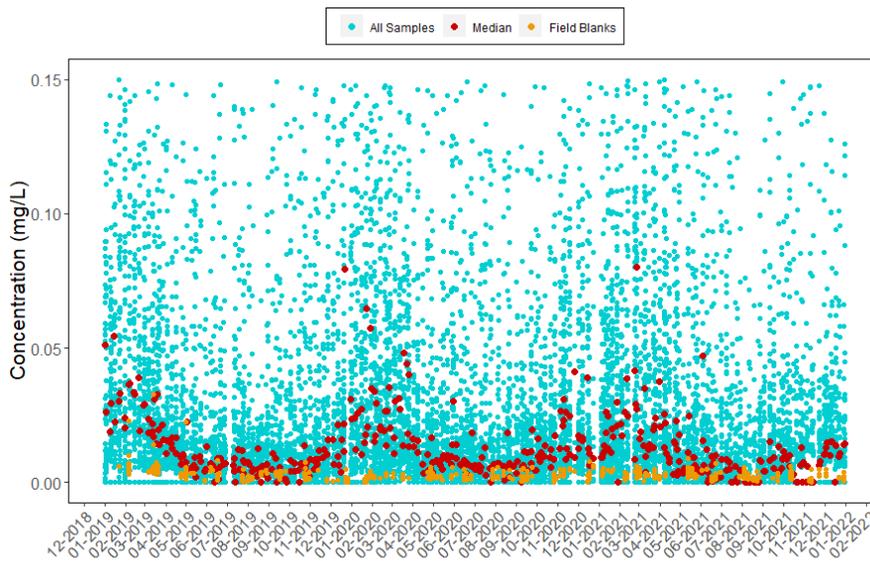
Note: Nominal reporting limit is 0.040 mg/L.

Figure 19. Concentrations of SO_4^{2-} from Teflon Filters



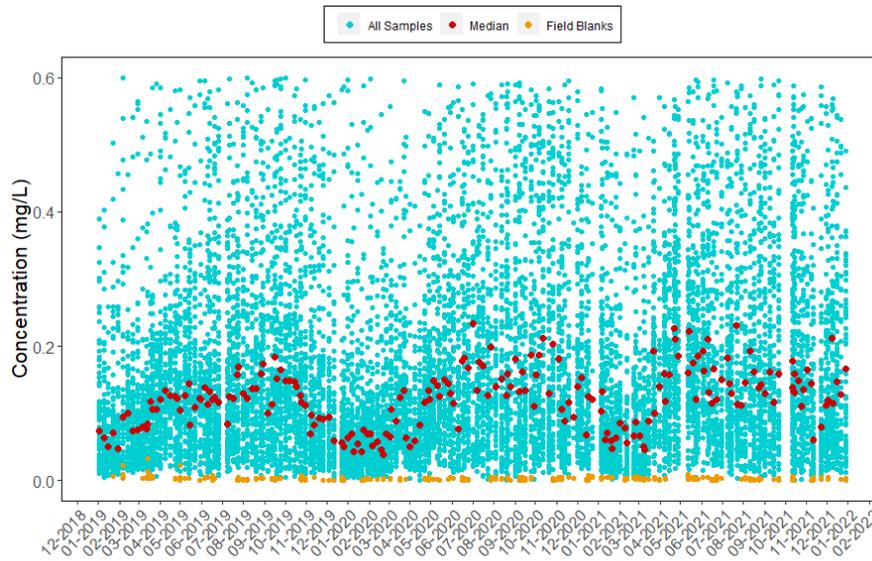
Note: Nominal reporting limit is 0.040 mg/L.

Figure 20. Concentrations of Cl^- from Teflon Filters



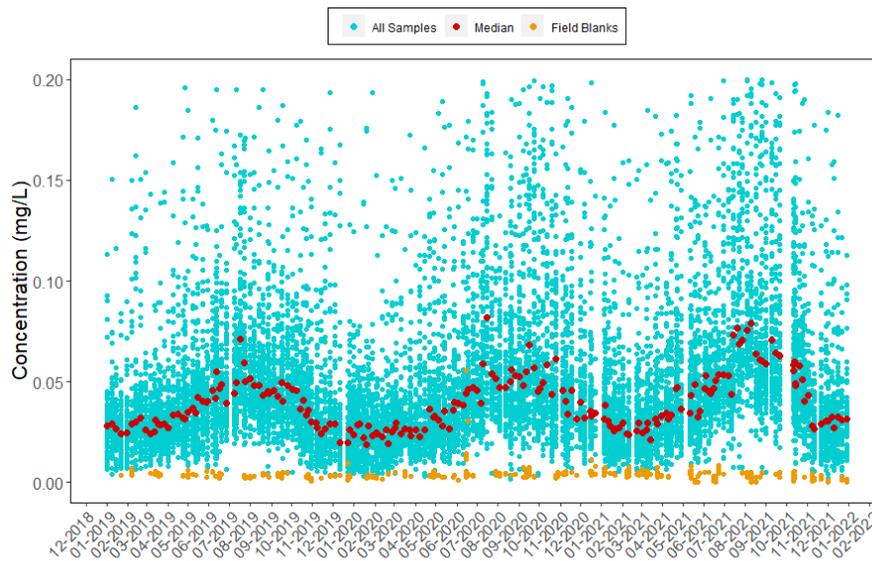
Note: Nominal reporting limit is 0.020 mg/L.

Figure 21. Concentrations of Ca²⁺ from Teflon Filters



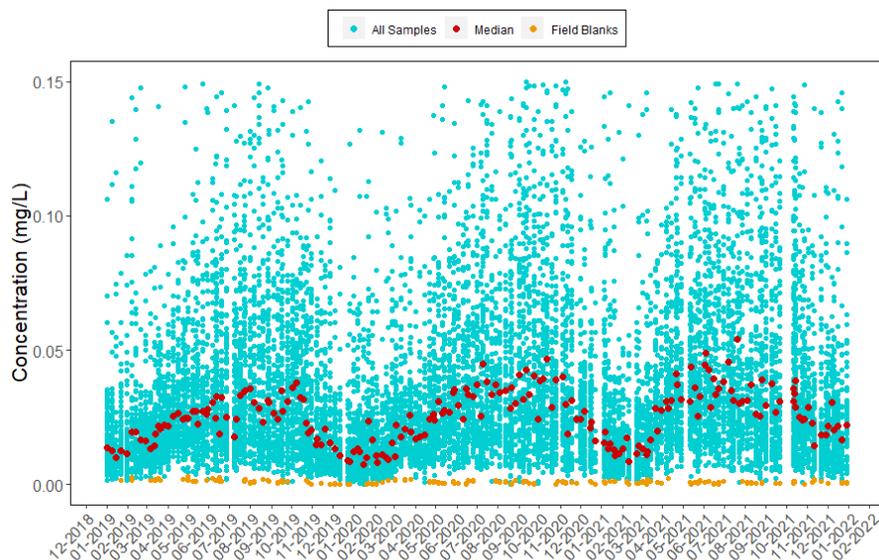
Note: Nominal reporting limit is 0.006 mg/L.

Figure 22. Concentrations of K⁺ from Teflon Filters



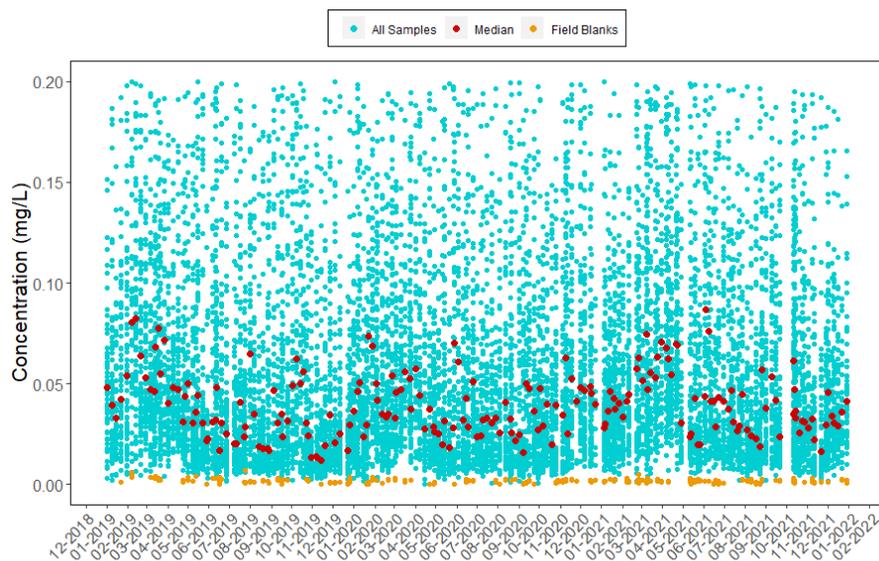
Note: Nominal reporting limit is 0.006 mg/L.

Figure 23. Concentrations of Mg^{2+} from Teflon Filters



Note: Nominal reporting limit is 0.003 mg/L.

Figure 24. Concentrations of Na^{+} from Teflon Filters



Note: Nominal reporting limit is 0.005 mg/L.

Time Series of Concentration Differences from Co-located Sites

Figures 25 and 26 show times series of concentration differences between the two sets of co-located sites. The differences shown in Figure 25 were caused by flow issues at MCK231 during mid- to late November. See also Table 3.

Figure 25. Time Series of Filter Concentration Differences between MCK131 and MCK231, KY

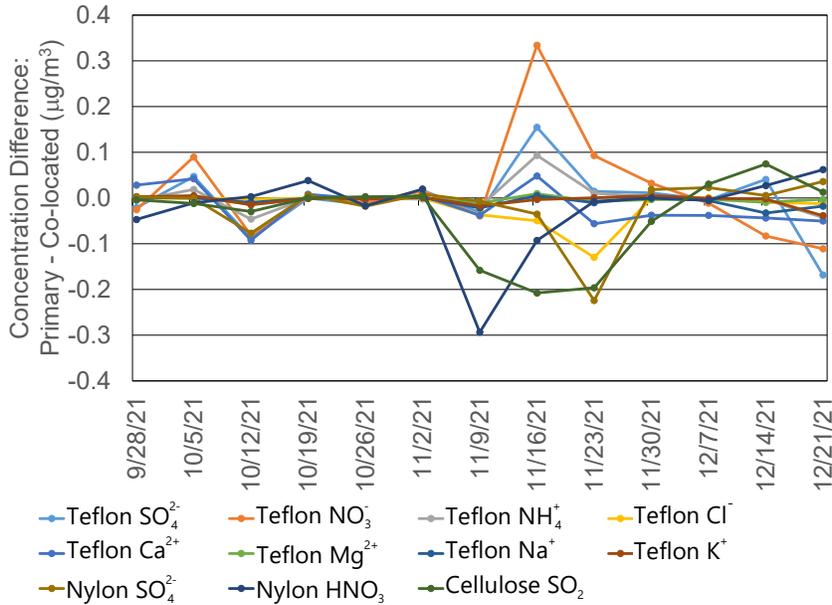
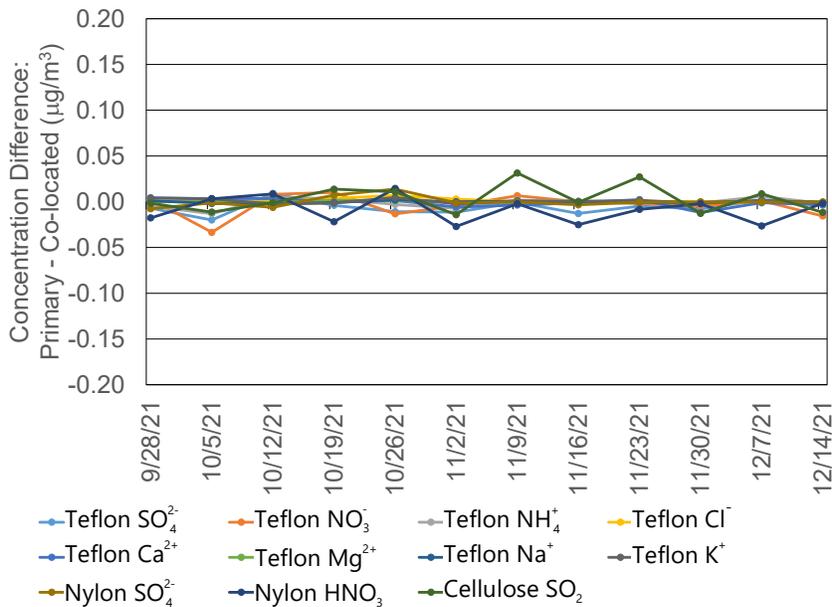


Figure 26. Time Series of Filter Concentration Differences between ROM406 and ROM206, CO



Precision of Filter Pack Concentrations

Table 3 shows mean absolute relative percent differences (MARPD) for concentrations measured at MCK131/231 and ROM406/206 during fourth quarter 2021. The MARPD values met the 20 percent criterion.

Table 3. Precision (MARPD) for Co-located Filter Pack Data during Fourth Quarter 2021

| | SO ₄ ²⁻ | NO ₃ ⁻ | NH ₄ ⁺ | Ca ²⁺ | Mg ²⁺ | Na ⁺ | K ⁺ | Cl ⁻ | HNO ₃ | SO ₂ | Total NO ₃ ⁻ |
|--------------------------------|-------------------------------|------------------------------|------------------------------|------------------|------------------|-----------------|----------------|-----------------|------------------|-----------------|---------------------------------------|
| MCK131/231, KY | | | | | | | | | | | |
| \bar{X} (μg/m ³) | 0.96 | 0.65 | 0.38 | 0.34 | 0.04 | 0.08 | 0.07 | 0.06 | 0.76 | 0.50 | 1.39 |
| \bar{Y} (μg/m ³) | 0.96 | 0.64 | 0.38 | 0.36 | 0.04 | 0.08 | 0.08 | 0.07 | 0.79 | 0.53 | 1.42 |
| MAD | 0.05 | 0.07 | 0.02 | 0.04 | 0.00 | 0.01 | 0.01 | 0.01 | 0.05 | 0.06 | 0.09 |
| MARPD | 5.03 | 11.08 | 4.85 | 10.90 | 12.19 | 10.09 | 9.77 | 15.21 | 7.03 | 11.41 | 6.94 |
| ROM406/206, CO | | | | | | | | | | | |
| \bar{X} (μg/m ³) | 0.24 | 0.10 | 0.11 | 0.07 | 0.01 | 0.02 | 0.02 | 0.02 | 0.24 | 0.14 | 0.33 |
| \bar{Y} (μg/m ³) | 0.25 | 0.10 | 0.11 | 0.07 | 0.01 | 0.02 | 0.02 | 0.02 | 0.25 | 0.14 | 0.33 |
| MAD | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | 0.02 |
| MARPD | 3.94 | 12.89 | 4.81 | 7.57 | 11.58 | 8.54 | 16.43 | 10.17 | 7.53 | 13.96 | 7.30 |

Completeness for Filter Pack Concentrations

Table 4 shows CASTNET sites with less than 90 percent completeness for weekly filter pack concentrations. Comments are included to provide information on why these sites experienced low data completeness.

Table 4. Sites with less than 90 Percent Data Completeness for Filter Concentrations for Fourth Quarter 2021 (1 of 2)

| Site ID | Teflon SO ₄ ²⁻ | Teflon NO ₃ ⁻ | Teflon NH ₄ ⁺ | Teflon Minor Cations | Teflon Cl ⁻ | Nylon HNO ₃ | Nylon SO ₄ ²⁻ | Cellulose SO ₂ | Comment |
|------------|---|--|--|----------------------------|---------------------------|---------------------------|--|------------------------------|---|
| EGB181, ON | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | The dry deposition monitoring system was turned off while the shelter is being refurbished. |
| THR422, ND | 23 | 23 | 23 | 23 | 23 | 23 | 23 | 23 | An EEMS audit on 10/19/21 identified a leak in the flow system. It was repaired 11/16/21. |
| WNC429, SD | 54 | 54 | 54 | 54 | 54 | 54 | 54 | 54 | A flow system leak was identified 8/3/21 and was repaired 11/9/21. |
| GRS420, TN | 69 | 69 | 69 | 69 | 69 | 69 | 69 | 69 | Flow issues affected two samples. December samples were analyzed but are not yet finalized in the database. |
| KIC003, KS | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | Intermittent power failures affected three filter packs. |
| LAV410, CA | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | A power failure affected all December filter packs. |
| SEK430, CA | 77 | 77 | 77 | 77 | 77 | 77 | 77 | 77 | Wildfire in the park resulted in its extended closure. Power to the site was turned off. The filter pack installed 9/7/21 remained on the tower until 10/14/21. |
| ALC188, TX | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | Two December samples were analyzed but are not yet finalized in the database. |
| BEL116, MD | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | The quarter included one 2-week sample. Another was received late and was not processed in time for this report. |
| BWR139, MD | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | The quarter included two 2-week samples. |

Table 4. Sites with less than 90 Percent Data Completeness for Filter Concentrations for Fourth Quarter 2021 (2 of 2)

| Site ID | Teflon SO ₄ ²⁻ | Teflon NO ₃ ⁻ | Teflon NH ₄ ⁺ | Teflon Minor Cations | Teflon Cl ⁻ | Nylon HNO ₃ | Nylon SO ₄ ²⁻ | Cellulose SO ₂ | Comment |
|------------|---|--|--|----------------------------|---------------------------|---------------------------|--|------------------------------|--|
| CNT169, WY | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | One filter pack was lost in shipping. Another was received late and was not processed in time for this report. |
| FOR605, WY | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | Flow issues affected two samples. |
| PAL190, TX | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | Flow issues affected two samples. |
| YOS404, CA | 85 | 85 | 85 | 85 | 85 | 85 | 85 | 85 | Two December samples were analyzed but are not yet finalized in the database. |

Precision of Ozone Concentrations

Time series of co-located hourly O₃ concentration differences for fourth quarter 2021 are provided in Figures 27 and 28 for MCK131/231 and ROM406/206, respectively. The figures indicate no consistent bias between the co-located analyzers at these site locations.

Figure 27. Time Series of the Differences in Co-located O₃ Concentrations for MCK131/231, KY

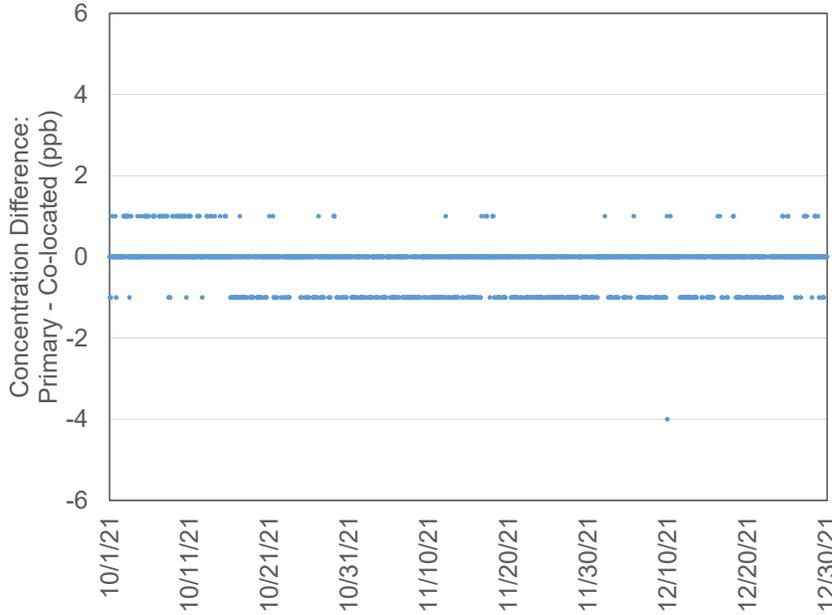


Figure 28. Time Series of the Differences in Co-located O₃ Concentrations for ROM406/206, CO

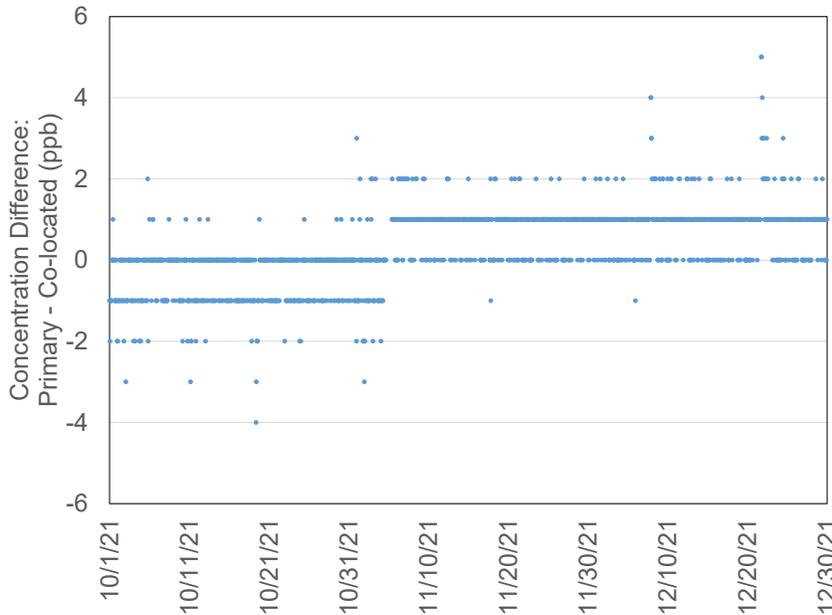


Table 5 gives MARPD data for O₃ data measured at the two co-located sites.

Table 5. Quarterly Precision (MARPD) for Co-located O₃ Concentrations

| Site Pair | Quarter | Start Date | MARPD | Records |
|----------------|---------|------------|-------|---------|
| MCK131/231, KY | | | | |
| | 1 | 1/1/21 | 1.0 | 2046 |
| | 2 | 4/1/21 | 0.6 | 2075 |
| | 3 | 7/1/21 | 0.8 | 2082 |
| | 4 | 10/1/21 | 1.0 | 2086 |
| ROM406/206, CO | | | | |
| | 1 | 1/1/21 | 4.5 | 2015 |
| | 2 | 4/1/21 | 1.9 | 2013 |
| | 3 | 7/1/21 | 1.4 | 2078 |
| | 4 | 10/1/21 | 1.7 | 2075 |

Completeness for O₃ Concentrations

Calculation of an annual O₃ value requires 75 percent completeness. However, calculation of the 3-year design value used for regulatory purposes requires 90 percent completeness. Table 6 shows CASTNET sites with less than 90 percent completeness for DM8A O₃ concentrations. Comments are provided for these sites.

Table 6. Sites with less than 90 Percent Data Completeness for DM8A Concentrations during Fourth Quarter 2021

| Site ID | Percent Completeness | Comments |
|------------|----------------------|---|
| CAD150, AR | 71.7 | The analyzer solenoid malfunctioned, and the analyzer was replaced 11/30/21. |
| LAV410, CA | 81.5 | The ozone sample pump failed 11/11/21 and was replaced 11/17/21. In addition, intermittent power failures occurred in December. |
| BBE401, TX | 82.6 | The ozone sample pump failed on 12/10/21 and was replaced 12/21/21. |
| ASH135, ME | 87.0 | The ozone sample pump failed on 11/3/21 and was replaced 11/12/21. |
| PND165, WY | 88.0 | The ozone sample pump failed on 11/21/21 and was replaced 11/30/21. |
| JOT403, CA | 88.0 | The ozone sample pump failed on 12/13/21 and was replaced 12/22/21. |
| SEK430, CA | 89.1 | Power to the monitoring site was shut off on 9/14/21 due to wildfires near the site. Power to the site was restored on 10/8/21. |

Table 7 shows CASTNET sites with less than 90 percent completeness for hourly O₃ concentrations. Comments are provided for these sites. The annual average for each of these sites is included for reference.

Table 7. Sites with less than 90 Percent Data Completeness for O₃ Concentrations

| Site ID | Q4 2021 | Q1 2021– Q4 2021 | Comments |
|------------|---------|---------------------|---|
| CAD150, AR | 72.3 | 92.5 | The analyzer solenoid malfunctioned, and the analyzer was replaced 11/30/21. |
| BBE401, TX | 84.3 | 92.9 | The ozone sample pump failed on 12/10/21 and was replaced 12/21/21. |
| LAV410, CA | 85.5 | 94.9 | The ozone sample pump failed 11/11/21 and was replaced 11/17/21. In addition, intermittent power failures occurred in December. |
| JOT403, CA | 88.4 | 95.9 | The ozone sample pump failed on 12/13/21 and was replaced 12/22/21. |
| PND165, WY | 89.1 | 95.0 | The ozone sample pump failed on 11/21/21 and was replaced 11/30/21. |
| ASH135, ME | 89.3 | 97.1 | The ozone sample pump failed on 11/3/21 and was replaced 11/12/21. |

Filter Pack Total Nitrate and Continuous Trace-level NO_y Concentrations at Eight CASTNET Sites

Figures 29 through 36 show a comparison of weekly average continuous NO_y measurements with weekly filter pack total NO₃⁻ concentrations collected at the eight sites with NO_y measurements. The NO_y concentrations were consistently higher than the total NO₃⁻ levels at all sites. The average weekly NO_y levels, the weekly total NO₃⁻ concentrations, and their ratios for the eight sites with available data are shown in Table 8. Ratios of NO_y to total NO₃⁻ varied from 3.44 at PNF126 to 8.22 at HWF187.

Table 8. Summary of Total NO₃⁻ and NO_y Measurements for Fourth Quarter 2021

| Site ID | Elevation | Total NO ₃ ⁻ (ppb) | NO _y (ppb) | Ratio |
|------------|-----------|--|-----------------------|-------|
| DUK008, NC | 164* | 0.49 | 2.80 | 5.88 |
| BVL130, IL | 213 | 0.78 | 4.04 | 5.14 |
| MAC426, KY | 243 | 0.54 | 2.29 | 4.31 |
| HWF187, NY | 497 | 0.17 | 1.22 | 8.22 |
| GRS420, TN | 793 | 0.40 | 1.63 | 4.19 |
| PNF126, NC | 1216 | 0.28 | 0.94 | 3.44 |
| PND165, WY | 2386 | 0.09 | 0.38 | 4.38 |
| ROM206, CO | 2742 | 0.10 | 0.55 | 5.48 |

Note: *Enhanced NO_y monitor is located at the top of the 30-meter tower.

Figure 29. Comparison of DUK008 Weekly Mean NO_y and Total NO₃⁻ Concentrations

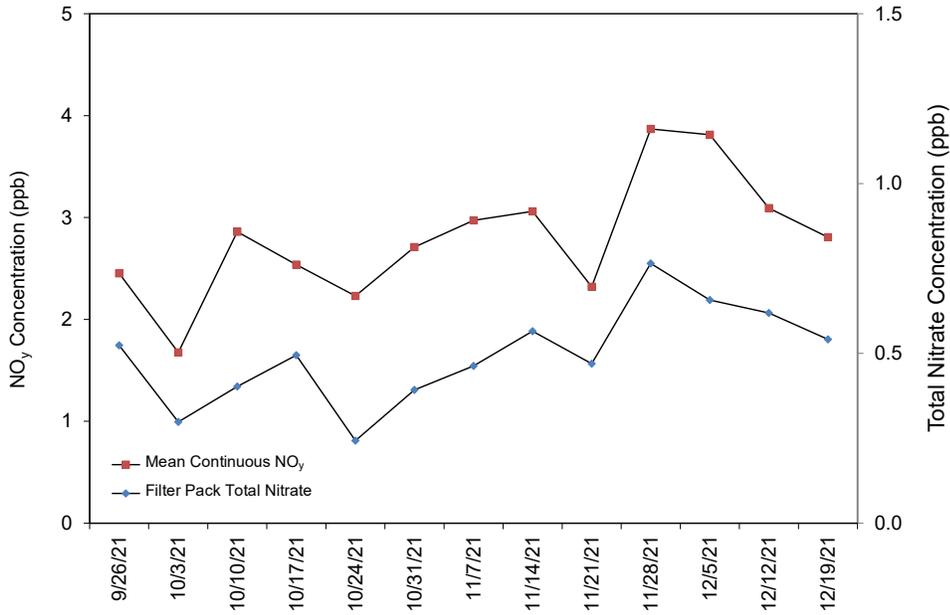


Figure 30. Comparison of BVL130 Weekly Mean NO_y and Total NO₃⁻ Concentrations

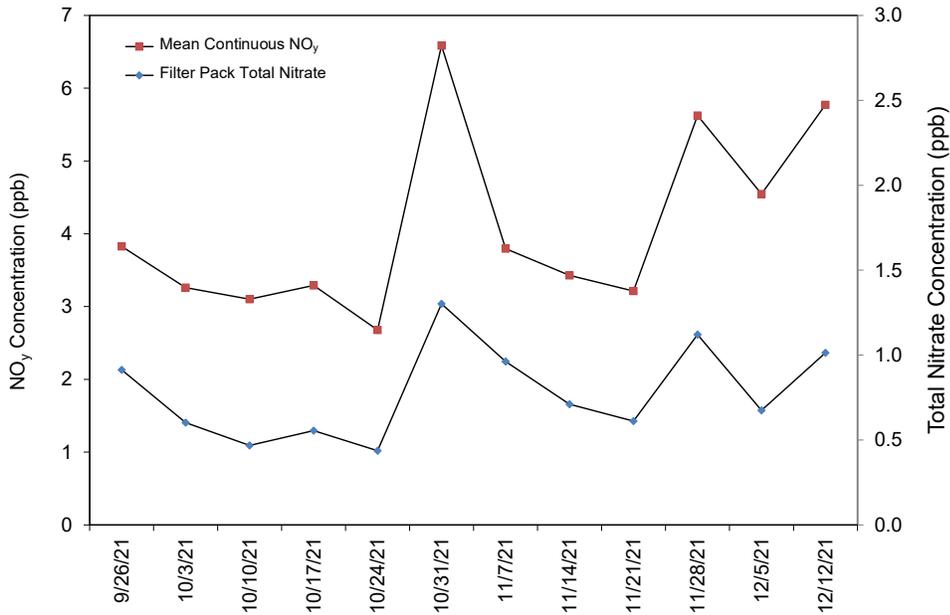


Figure 31. Comparison of MAC426 Weekly Mean NO_y and Total NO_3^- Concentrations

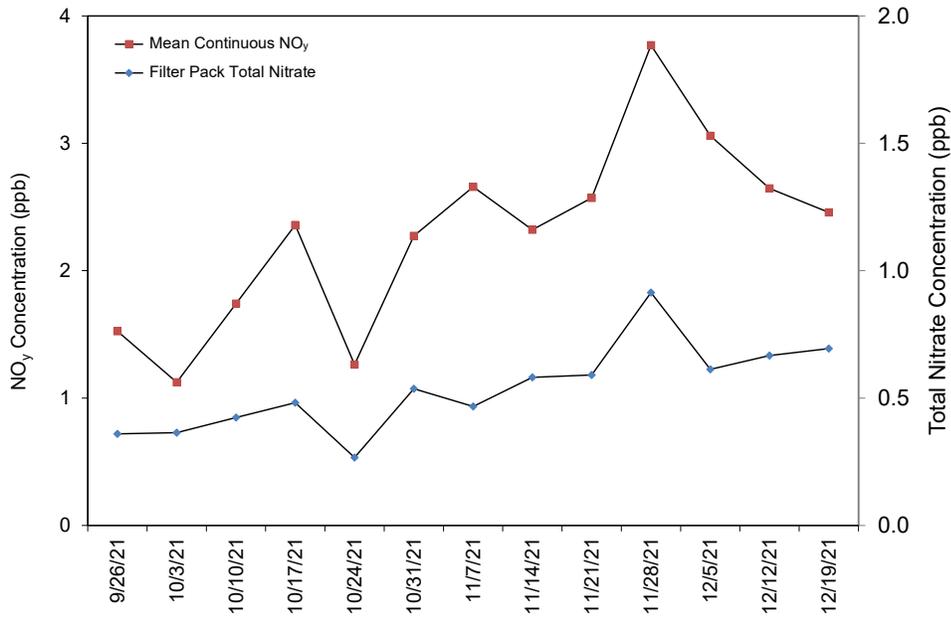


Figure 32. Comparison of HWF187 Weekly Mean NO_y and Total NO_3^- Concentrations

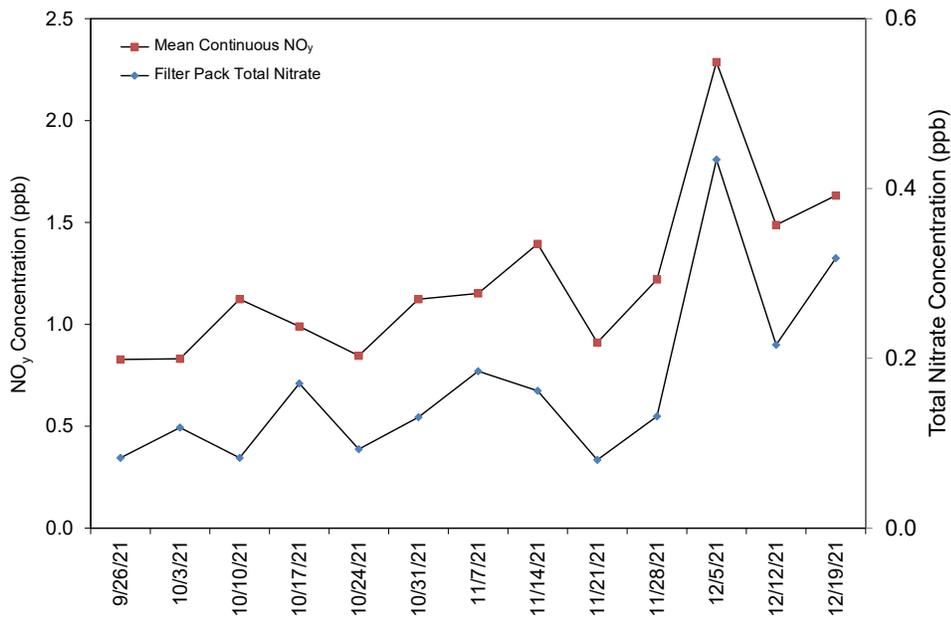


Figure 33. Comparison of GRS420 Weekly Mean NO_y and Total NO₃ Concentrations

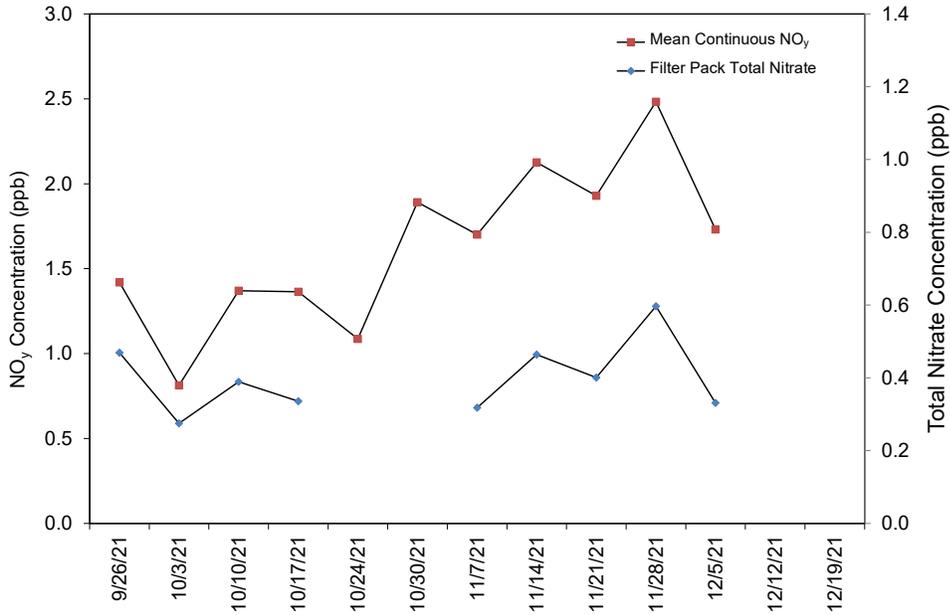


Figure 34. Comparison of PNF126 Weekly Mean NO_y and Total NO₃ Concentrations

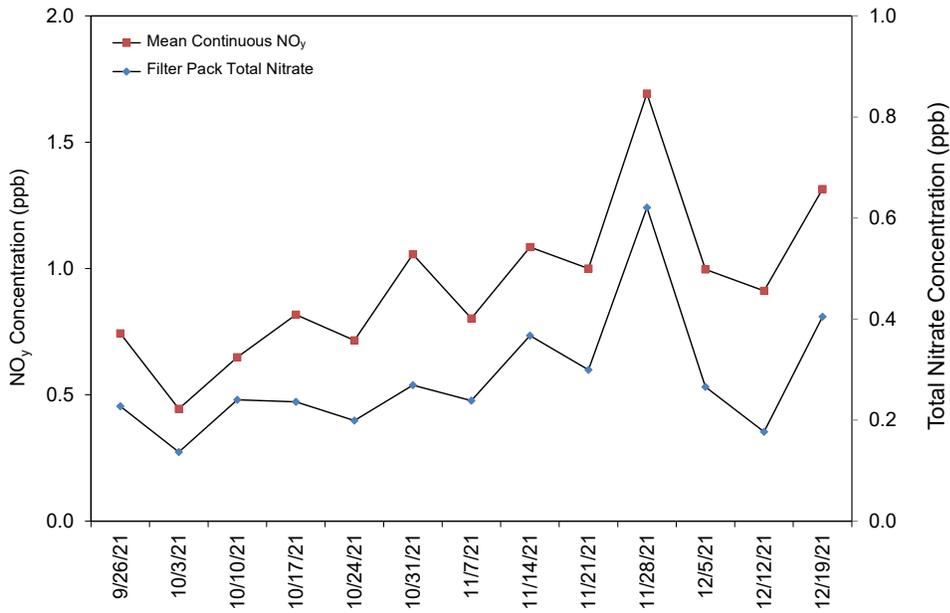


Figure 35. Comparison of PND165 Weekly Mean NO_y and Total NO₃⁻ Concentrations

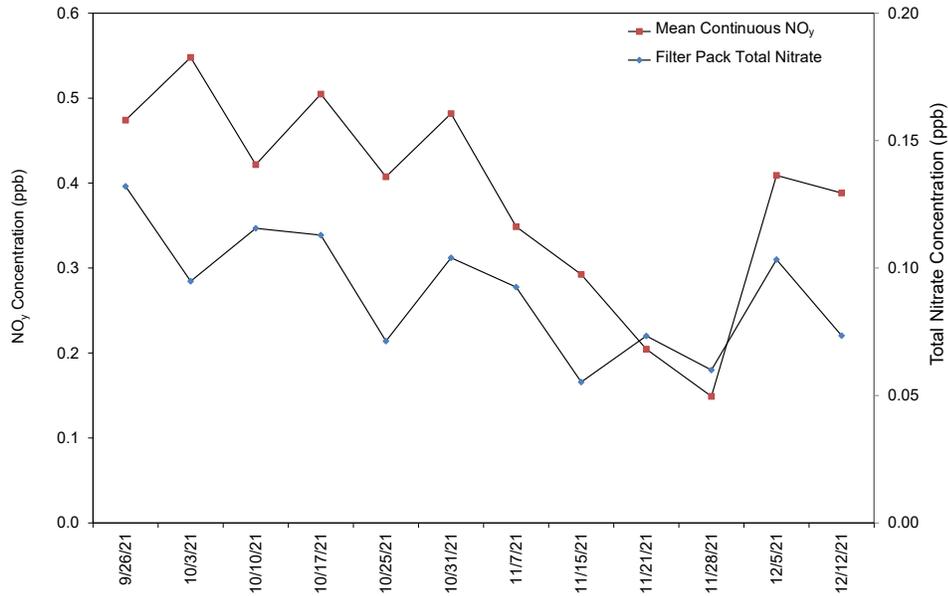
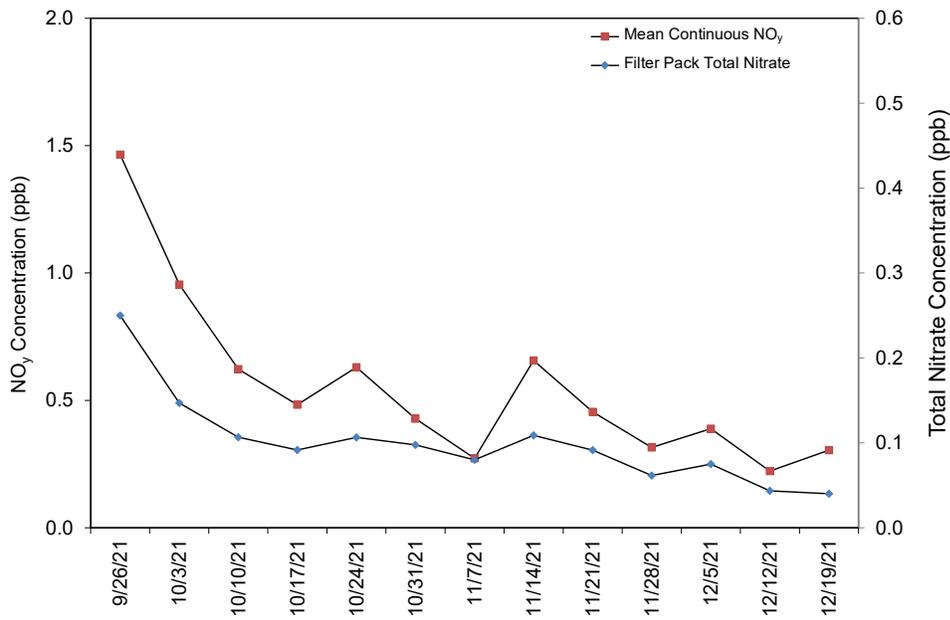


Figure 36. Comparison of ROM206 Weekly Mean NO_y and Total NO₃⁻ Concentrations



Filter Pack and Continuous Trace-level Gas Sulfur Dioxide Concentrations

Figures 37 through 39 provide diagrams that compare weekly filter pack SO₂ concentrations with continuous trace-level gas data measured at BVL130, MAC426, and GRS420. The continuously measured trace-level concentrations were higher than filter pack concentrations at BVL130 and were comparable at MAC426 and GRS420.

Figure 37. Comparison of BVL130 Weekly Mean SO₂ Concentrations

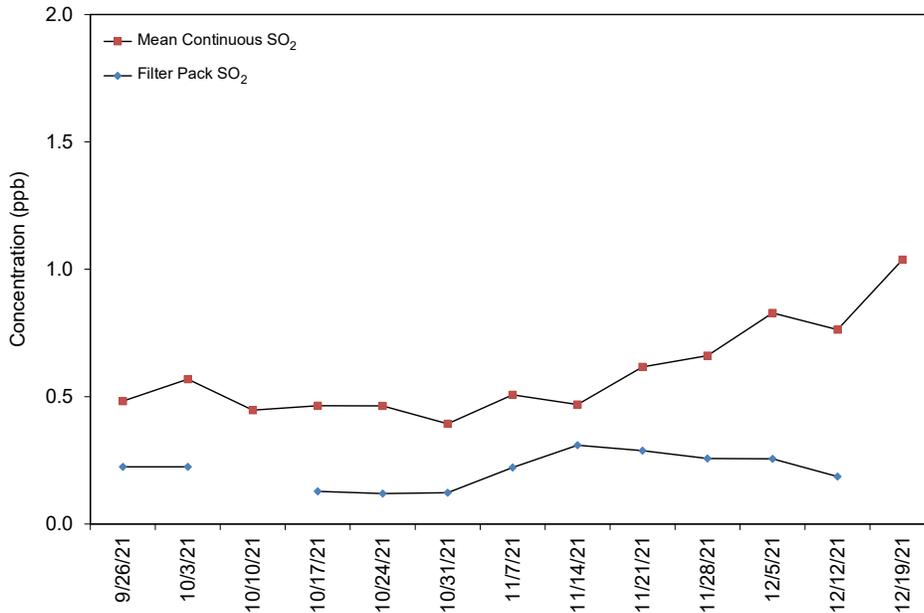


Figure 38. Comparison of MAC426 Weekly Mean SO₂ Concentrations

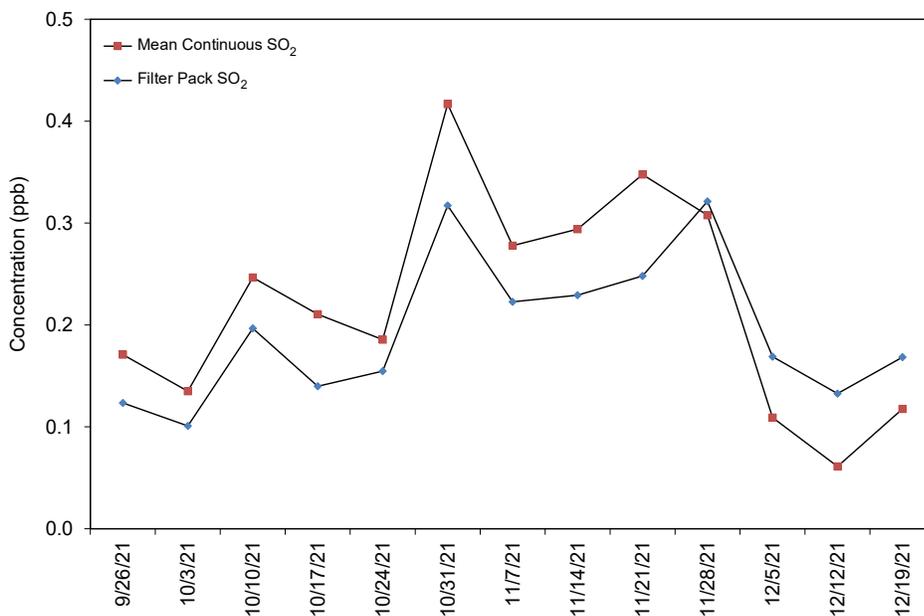
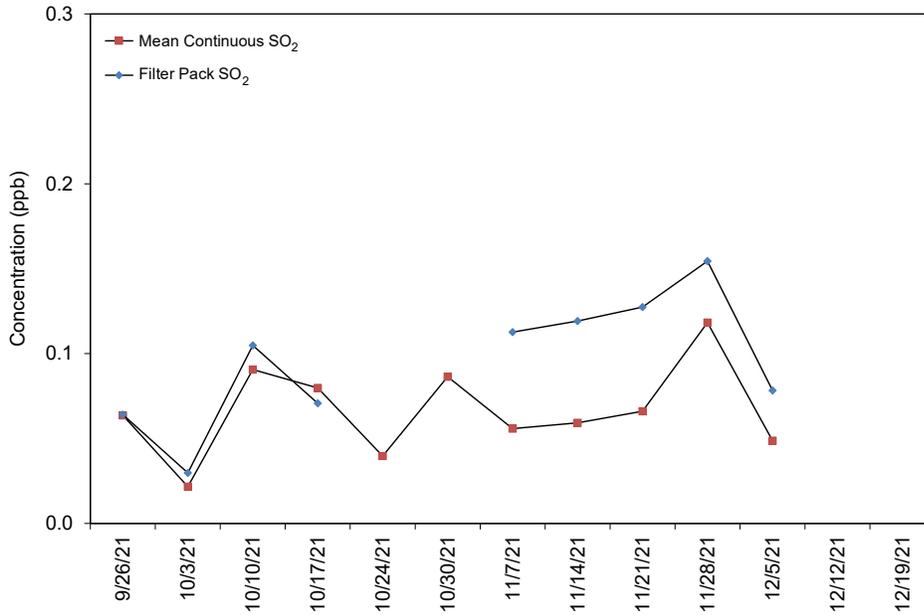


Figure 39. Comparison of GRS420 Weekly Mean SO₂ Concentrations



Completeness for Continuous Trace-level Gas Measurements

Table 9 shows the percent completeness for CASTNET trace-level gas measurements. Comments are provided for sites with less than 90 percent completeness for hourly trace-level gas concentrations during fourth quarter 2021. The average for first quarter 2021 through fourth quarter 2021 for each of the sites is included for reference.

Table 9. Percent Data Completeness for Continuous Trace-level Gas Measurements

| Site ID | Parameter* | Q4 2021 | Q1 2021 – Q4 2021 | Comments |
|------------|------------|---------|-------------------|--|
| BVL130, IL | CO | 29 | 42 | The CO analyzer malfunctioned and was replaced in December 2021. |
| | NO | 95 | 94 | |
| | NOY | 95 | 94 | |
| | NOYDIF | 95 | 94 | |
| | SO2_GA | 92 | 87 | |
| CHC432, NM | NO | 97 | 97 | |
| | NOX | 97 | 97 | |
| | NOXDIF | 97 | 97 | |
| DUK008, NC | HNO3 | 90 | | Monitoring restarted in August 2021, but QC functions were not fully operational until December 2021. Since no valid data are available until December 2021, the average for Q1 2021 through Q4 2021 was not calculated. |
| | NH3 | 91 | | |
| | NO | 91 | | |
| | NO2_TRUE | 91 | | |
| | NOX_TRUE | 91 | | |
| | NOY | 91 | | |
| | NOY_MINUS | 91 | | |
| | NOYDIF | 91 | | |
| GRS420, TN | CO | 90 | 91 | |
| | NO | 92 | 93 | |
| | NOY | 92 | 93 | |
| | NOYDIF | 92 | 94 | |
| | SO2_GA | 92 | 95 | |
| HWF187, NY | NO | 90 | 93 | |
| | NOY | 90 | 93 | |
| | NOYDIF | 90 | 93 | |
| MAC426, KY | CO | 95 | 86 | |
| | NO | 97 | 96 | |
| | NOY | 97 | 96 | |
| | NOYDIF | 97 | 96 | |
| | SO2_GA | 97 | 97 | |
| PND165, WY | NO | 95 | 88 | |
| | NOY | 95 | 87 | |
| | NOYDIF | 95 | 87 | |
| PNF126, NC | NO | 89 | 80 | The bypass box was off from 10/7/21 to 10/12/21. |
| | NOY | 89 | 81 | |
| | NOYDIF | 89 | 79 | |
| ROM206, CO | NO | 95 | 91 | |
| | NOY | 95 | 94 | |
| | NOYDIF | 95 | 91 | |

Note: * See Table 10

The parameters listed in Table 9 are both calculated and measured. Table 10 provides information on how the parameters listed in Table 9 are obtained.

Table 10. CASTNET Trace-level Gas Measurements

| Parameter Name | How Obtained | Description of Process |
|----------------|--------------|---|
| CO | Measured | Gas filter correlation |
| HNO3 | Calculated | NOY minus NOY_MINUS |
| NH3 | Calculated | TNX minus NOY |
| NO | Measured | Chemiluminescence reaction/no converter used |
| NO2_TRUE | Calculated | NOX_TRUE minus NO |
| NOX_TRUE | Measured | Photolytic converter |
| NOY | Measured | Molybdenum converter at 315° Celsius |
| NOYDIF | Calculated | NOY minus NO |
| NOY_MINUS | Measured | Sodium carbonate denuder followed by molybdenum converter at 315° Celsius |
| NOX | Measured | Molybdenum converter at 325° Celsius |
| NOXDIF | Calculated | NOX minus NO |
| SO2_GA | Measured | Ultraviolet fluorescence |
| TNX | Measured | Platinum/stainless steel converter at 825° Celsius followed by molybdenum converter at 315° Celsius |

References

Wood Environment & Infrastructure Solutions, Inc. 2022. *Clean Air Status and Trends Network (CASTNET) Fourth Quarter 2021 Quality Assurance Report with 2021 Annual Summary*. <https://java.epa.gov/castnet/documents.do>