Clean Air Status and Trends Network (CASTNET) Quarterly Data Summary for Fourth Quarter 2019 (October through December)

Prepared for: U.S. Environmental Protection Agency (EPA), Clean Air Markets Division
EPA Contract No.: EP-W-16-015, CASTNET Base Program (3003), EPA Task Order 68HERH19F0243
Prepared by: Wood Environment & Infrastructure Solutions, Inc. (Wood), Gainesville, Florida
Wood Project No.: 6064193003
Submitted: March 27, 2020

Introduction

This quarterly report summarizes the Clean Air Status and Trends Network (CASTNET) data collected during fourth quarter 2019. Trends in pollutants measured at eastern and western reference sites are shown. Results from the quality assurance/quality control (QA/QC) program are presented for fourth quarter data and include completeness and precision of filter concentrations and hourly O₃ concentrations. This report also analyzes data for continuous, trace-level NO_y concentrations from eight sites and continuous SO₂ concentrations from three sites. Other QC statistics are given in the CASTNET Fourth Quarter 2019 Quality Assurance Report with 2019 Annual Summary (Wood, 2020).





Figure 1 shows fourth highest daily maximum 8-hour average (DM8A) O_3 concentrations measured through fourth quarter 2019. Three sites exceeded the 0.070 parts per million (ppm) National Ambient Air Quality Standard for O_3 .

Trends

Trend analyses were performed based on filter pack pollutant concentrations measured in micrograms per cubic meter (μ g/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

Quarterly mean NO₃, NH₄⁺, SO₄²⁻, and K⁺ concentrations decreased at eastern sites in 2019; HNO₃, Cl⁻, and Na⁺ concentrations increased; and total NO₃⁻, SO₂, Ca²⁺, and Mg²⁺ levels showed almost no change. Quarterly mean HNO₃, NO₃⁻, NH₄⁺, total NO₃⁻, SO₂, K⁺, and Na⁺ concentrations decreased at western sites in 2019 while SO₄²⁻, Cl⁻, Ca²⁺, and Mg²⁺ concentrations increased.

Quarterly O_3 concentrations were analyzed using box plots constructed by averaging all valid hourly O_3 concentrations within fourth quarter 2019 by site and then averaging those averages for all eastern and western reference sites (Figure 13). The figure shows little change in quarterly mean O_3 concentrations at eastern and western sites over their respective measurement periods. Mean O_3 concentrations at both sets of sites increased in fourth quarter 2019. Quarterly mean concentrations were higher at the western reference sites than at the eastern sites.

Figure 2. Trends in Fourth Quarter Mean HNO₃ Concentrations Western Reference Sites

Eastern Reference Sites



Figure 3. Trends in Fourth Quarter Mean NO⁻₃ Concentrations Western Reference Sites





Eastern Reference Sites



Figure 5. Trends in Fourth Quarter Mean Total NO³ Concentrations Western Reference Sites Ea

Eastern Reference Sites



Eastern Reference Sites

Figure 6. Trends in Fourth Quarter Mean SO₂ Concentrations Western Reference Sites





Eastern Reference Sites





Eastern Reference Sites



Eastern Reference Sites

Eastern Reference Sites

Figure 9. Trends in Fourth Quarter Mean Ca²⁺ Concentrations Western Reference Sites









Eastern Reference Sites







Eastern Reference Sites







Changes in 3-year Average Fourth Quarter Concentrations

Three-year averages of quarterly mean concentrations of total NO₃, NH⁺₄, SO₂, and SO²⁻₄ were reduced over the period 1990–1992 through 2017–2019 for eastern reference sites and 1996–1998 through 2017–2019 for western reference sites. O₃ concentrations increased by 6 percent at eastern sites and showed no change at western sites.

| Tahlo 1 | Fastern Reference | Sites: 3-Vear | Mean Nitrogen | Sulfur and O | Pollutant | Concentrations |
|----------|-------------------|-----------------|-----------------|----------------|-----------|----------------|
| Table T. | Lastern Reference | Siles. S-fear i | viean Mitrogen, | Sullui, and O | Fonutant | Concentrations |

| | Total NO₃ (µg/m³) | NH₄ (µg/m³) | SO₂ (µg/m³) | SO ²⁻ (μg/m ³) | O ₃ (ppb) |
|----------------|----------------------|----------------|----------------|--|-------------------------|
| 1990–1992 | 2.9 | 1.4 | 10.6 | 3.6 | 24 |
| 2017–2019 | 1.7 | 0.6 | 0.6 | 0.9 | 25 |
| Percent Change | -43 | -60 | -95 | -74 | 6 |

| | Total NO₃ (µg/m³) | NH₄ (µg/m³) | SO₂ (µg/m³) | SO ₄ ²⁻ (μg/m ³) | O₃ (ppb) |
|----------------|----------------------|----------------|----------------|---|-------------|
| 1996–1998 | 1.4 | 0.4 | 0.6 | 1.2 | 38 |
| 2017–2019 | 0.9 | 0.3 | 0.3 | 0.7 | 38 |
| Percent Change | -33 | -30 | -49 | -42 | 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 2017 through fourth quarter 2019. These figures provide indications of potential issues with concentration measurements relative to detection and reporting limits.

Previous review of filter pack analysis control charts indicated possible potassium contamination (Figure 22). Corrective actions were implemented and subsequent testing indicated these actions have been effective. Consider the recent 18-month data record in Figure 22.





Note: Nominal reporting limit is 0.008 mg/L.



Figure 15. Concentrations of NO₃ (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 19. Concentrations of SO_4^{2-} 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 23. Concentrations of Mg²⁺ 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 colocated sites. View Table 4 for data completeness percentage and explanation for 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 2019. The MARPD values met the 20 percent criterion except for NO_3^- at ROM406/206. An approximate 75 percent difference in concentrations was measured during the weeks beginning 10/22/19 and 11/19/19. This discrepancy was produced by 34-hour differences in off times at the two sites.

| | | | | | | | | | | | Total |
|-------------------------------------|-------------|-----------------|----------|------------------|------------------|------|---------|------|---------|-----------------|-----------------|
| | SO_4^{2-} | NO ₃ | NH_4^+ | Ca ²⁺ | Mg ²⁺ | Na⁺ | K^{+} | Cl | HNO_3 | SO ₂ | NO ₃ |
| MCK131/231 | ., KY | | | | | | | | | | |
| \overline{X} (µg/m ³) | 0.99 | 1.13 | 0.60 | 0.17 | 0.03 | 0.07 | 0.05 | 0.04 | 0.83 | 0.61 | 1.81 |
| $\overline{Y}(\mu g/m^3)$ | 0.94 | 1.11 | 0.58 | 0.17 | 0.02 | 0.06 | 0.05 | 0.04 | 0.80 | 0.59 | 1.90 |
| MAD | 0.05 | 0.03 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.05 | 0.02 | 0.06 |
| MARPD | 4.89 | 4.21 | 4.42 | 5.18 | 6.57 | 7.11 | 8.84 | 2.96 | 6.20 | 3.43 | 3.51 |
| ROM406/206 | 5, CO | | | | | | | | | | |
| $\overline{X}(\mu g/m^3)$ | 0.27 | 0.09 | 0.12 | 0.05 | 0.01 | 0.02 | 0.01 | 0.02 | 0.29 | 0.15 | 0.38 |
| $\overline{Y}(\mu g/m^3)$ | 0.27 | 0.11 | 0.12 | 0.05 | 0.01 | 0.02 | 0.01 | 0.02 | 0.28 | 0.15 | 0.38 |
| MAD | 0.01 | 0.03 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.01 | 0.04 |
| MARPD | 3.44 | 27.91 | 8.96 | 11.23 | 9.91 | 9.54 | 12.32 | 7.25 | 10.08 | 9.44 | 11.01 |

Table 3. Precision (MARPD) for Co-located Filter Pack Data during Fourth Quarter 2019

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.

| | | | | Teflon | | | | | |
|------------|-------------------------------|------------------------------|----------|---------|--------|-------|-------------------------------|-----------------|--|
| | Teflon | Teflon | Teflon | Minor | Teflon | Nylon | Nylon | Cellulose | |
| Site ID | SO ₄ ²⁻ | NO ⁻ ₃ | NH_4^+ | Cations | Cl | HNO₃ | SO ₄ ²⁻ | SO ₂ | Comment |
| ABT147, CT | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | The mass flow controller malfunctioned. Flow data were invalidated from 10/1/19 to 10/21/19, when it was replaced. |
| BWR139, MD | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | 76.9 | Three different samples were installed for two-week run periods during the quarter. |
| CAN407, UT | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | One week was affected by a flow pump failure. A filter pack that was installed 12/17/19 sampled for three weeks. |
| CAT175, NY | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | Power failures affected two samples. |
| FOR605, WY | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | Site was offline for repairs during first two weeks of the quarter. Last sample of the quarter was affected by a polling issue. |
| JOT403, CA | 69.2 | 69.2 | 69.2 | 69.2 | 69.2 | 69.2 | 69.2 | 69.2 | A flow system leak affected the first three samples of the quarter. The last sample was installed for two weeks and was affected by a flow issue during sampling. |
| LAV410, CA | 61.5 | 61.5 | 61.5 | 61.5 | 61.5 | 61.5 | 61.5 | 61.5 | Power failures affected four samples. |
| МСК231, КҮ | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | The mass flow controller malfunctioned, affecting two samples. |
| VOY413, MN | 69.2 | 69.2 | 69.2 | 69.2 | 69.2 | 76.9 | 76.9 | 76.9 | Flow data were invalid from 12/3/19 to 12/17/19 due to a flow system leak. The Teflon fraction of one sample was invalidated due to a laboratory error. |
| WST109, NH | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | 84.6 | The mass flow controller malfunctioned affecting two samples. |

| Table 4. | Sites with less | than 90 Percent | Data Completenes | ss for Filter Concent | trations for Fourth (| Quarter 2019 |
|----------|-----------------|-----------------|------------------|-----------------------|-----------------------|--------------|
|----------|-----------------|-----------------|------------------|-----------------------|-----------------------|--------------|

Precision of Ozone Concentrations

Time series of co-located hourly O_3 concentration differences for fourth quarter 2019 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 28. Time Series of the Differences in Co-located O₃ Concentrations for ROM406/206, CO



Table 5 gives MARPD data for O_3 data measured at the two co-located sites.

| Site Pair | Quarter | Start Date MARPD | | Records | | | | |
|----------------|---------|------------------|-----|---------|--|--|--|--|
| MCK131/231, KY | | | | | | | | |
| | 1 | 1/1/19 | 2.0 | 1873 | | | | |
| | 2 | 4/1/19 | 1.5 | 2064 | | | | |
| | 3 | 7/1/19 | 0.8 | 2085 | | | | |
| | 4 | 10/1/19 | 1.1 | 2003 | | | | |
| ROM406/206, 0 | 0 | | | | | | | |
| | 1 | 1/1/19 | 1.5 | 1983 | | | | |
| | 2 | 4/1/19 | 1.3 | 1949 | | | | |
| | 3 | 7/1/19 | 1.4 | 2030 | | | | |
| | 4 | 10/1/19 | 1.1 | 1989 | | | | |

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

Completeness for O₃ Concentrations

Calculation of an annual O_3 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 O_3 concentrations. Comments are provided for these sites.

| Table 6. | Sites with less than 90 Percent Data Completeness for DM8A Concentrations during |
|----------|--|
| | Fourth Quarter 2019 |

| | Percent | |
|------------|--------------|--|
| Site ID | Completeness | Comments |
| LAV410, CA | 77.2 | Intermittent power failures reduced data completeness. |
| GRC474, AZ | 89.1 | Ozone data were invalid from 11/2/19 to 11/8/19 because the pump was not operating. Data were also affected by a power failure from 11/29/19 to 11/30/19. |
| HOX148, MI | 89.1 | Ozone concentrations were not measured for 10 days over the course of the quarter due to a variety of issues, including a power failure, a calibration event, and the instrument being left in check mode. |
| HWF187, NY | 89.1 | Ozone concentrations were not measured for 10 days over the course of the quarter primarily due to power failures and a calibration event. |

Table 7 shows CASTNET sites with less than 90 percent completeness for hourly O_3 concentrations. Comments are provided for these sites. The annual average for each of these sites is included for reference.

| Site ID | Q4 2019 | Q1 2019– Q4 2019 | Comments |
|------------|---------|---------------------|--|
| LAV410, CA | 85.4 | 91.2 | Intermittent power failures reduced data completeness. |

| Table 7. | Sites with le | ss than 90 |) Percent D | ata Comp | leteness fo | or O_{2} | Concentrations |
|----------|---------------|------------|-------------|----------|-------------|-------------|----------------|
| | Sites with it | 55 than 5t | | utu comp | 1010103510 | $n \circ 3$ | concentrations |

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 3.92 at PNF126 to 8.85 at HWF187.

| Site ID | Elevation | Total NO ₃ (ppb) | NO _y (ppb) | Ratio |
|------------|-----------|-----------------------------|-----------------------|-------|
| DUK008, NC | 164 | 0.60 | 3.37 | 6.41 |
| BVL130, IL | 213 | 1.12 | 4.95 | 5.27 |
| MAC426, KY | 243 | 0.71 | 3.11 | 4.44 |
| HWF187, NY | 497 | 0.17 | 1.13 | 8.85 |
| GRS420, TN | 793 | 0.37 | 1.89 | 5.46 |
| PNF126, NC | 1216 | 0.25 | 0.94 | 3.92 |
| PND165, WY | 2386 | 0.10 | 0.60 | 6.26 |
| ROM206, CO | 2742 | 0.12 | 0.83 | 7.09 |

Table 8. Summary of Total NO₃ and NO_y Measurements for Fourth Quarter 2019



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







Figure 31. Comparison of MAC426 Weekly Mean NO_y and Total NO₃⁻ Concentrations







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







Figure 35. Comparison of PND165 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 generally lower than filter pack concentrations at BVL130 and GRS420 and were comparable at MAC426.











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 2019. The annual hourly average for each of the sites is included for reference.

| | | | Q1 2019 – | |
|------------|------------|---------|-----------|--|
| Site ID | Parameter* | Q4 2019 | Q4 2019 | Comments |
| BVL130, IL | CO | 0 | 7 | The analyzer continued to malfunction after its reinstallation in late July 2019. Readings would not stabilize. Wood continued to work with the manufacturer to resolve this issue. |
| | NO | 96 | 85 | |
| | NOY | 96 | 89 | |
| | NOYDIF | 96 | 85 | |
| | SO2_GA | 92 | 89 | |
| CHC432, NM | NO | 97 | 95 | |
| | NOX | 97 | 95 | |
| | NOXDIF | 97 | 95 | |
| DUK008, NC | HNO3 | 56 | 60 | The analyzer had problems with recurring drift. |
| | NH3 | 64 | 63 | The instrument was recalibrated twice during |
| | NO | 68 | 77 | October 2019. In addition, data completeness |
| | NO2_TRUE | 68 | 77 | was affected by a broken NOY_Minus denuder |
| | NOX_TRUE | 68 | 77 | and system leak during October. Colder |
| | NOY | 64 | 63 | temperatures (< 5C) affected measurements |
| | NOY_MINUS | 56 | 72 | during December. The cause is under |
| | NOYDIF | 64 | 63 | investigation. |
| | TNX | 68 | 76 | |
| GRS420, TN | CO | 82 | 87 | Data were invalidated due to station |
| | NO | 86 | 81 | Data were invalidated due to numerous |
| | NOY | 86 | 81 | calibration events and maintenance. |
| | NOYDIF | 89 | 84 | |
| | SO2_GA | 83 | 90 | Data were invalidated due to station |
| | | | | temperatures exceeding criteria. |
| HWF187, NY | NO | 73 | 83 | Failures were caused by a malfunctioning |
| | NOY | 50 | 77 | solenoid. It was replaced 12/11/19. |
| | NOYDIF | 50 | 77 | |
| MAC426, KY | CO | 84 | 88 | The CO analyzer locked up following a power failure on 10/8/19 due to a failed power supply. A new power supply was installed on 10/16/19. |
| | NO | 94 | 90 | |
| | NOY | 71 | 84 | Data were invalid from 10/14/19 to 11/5/19 due |
| | NOYDIF | 71 | 84 | to a failed external board on the convertor. |
| | SO2_GA | 94 | 91 | |
| PND165, WY | NO | 86 | 88 | Due to analyzer drift in late October. The |
| | NOY | 86 | 88 | analyzer was recalibrated in early November |
| | NOYDIF | 86 | 88 | 2019. |

Table 9 Percent Data Completeness for Continuous Trace-level Gas Measurements (1 of 2)

| | | | Q1 2019 – | |
|------------|------------|---------|-----------|--|
| Site ID | Parameter* | Q4 2019 | Q4 2019 | Comments |
| PNF126, NC | NO | 89 | 93 | Data were invalidated as suspect during late |
| | NOY | 89 | 93 | December 2019 when NO > NOY. |
| | NOYDIF | 89 | 93 | |
| ROM206, CO | NO | 96 | 93 | |
| | NOY | 96 | 93 | |
| | NOYDIF | 96 | 93 | |

Table 9 Percent Data Completeness for Continuous Trace-level Gas Measurements (2 of 2)

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.

| Parameter Name | How Obtained | Description of Process |
|----------------|--------------|--|
| СО | 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 |

Table 10. CASTNET Trace-level Gas Measurements

References

Wood Environment & Infrastructure Solutions, Inc. 2020. *Clean Air Status and Trends Network* (CASTNET) Fourth Quarter 2019 Quality Assurance Report with 2019 Annual Summary. https://java.epa.gov/castnet/documents.do