Measurement of Anthropogenic and Wildfire-Specific VOCs in the Las Vegas Valley during 2023 using TO-15 and TO-17 Methods

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List of Acronyms

Abbreviation	Definition
AQS	Air Quality System
BS	Boot Strapping
BS-DISP	Bootstrapping enhanced by displacement
CAA	Clean Air Act
CAS	Chemical Abstract Services
DISP	Displacement
DRI	Desert Research Institute
EPA	U.S. Environmental Protection Agency
FRM	Federal Reference Method
GC-MS	Gas Chromatograph - Mass Spectrometer
HCN	Hydrogen cyanide
HMS	Hazard Mapping System
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
inHg	inches of mercury
K^+	Potassium
LVG	Levoglucosan
LVV	Las Vegas Valley
MDA8	Maximum Daily 8-Hour Averaged Ozone
MDL	Method Detection Limit
MEK	Methyl ethyl ketone
NAAQS	National Ambient Air Quality Standards
NAM	North American Mesoscale Forecast System
NCore	National Core Network
NOAA	National Oceanic and Atmospheric Administration
PAMS	Photochemical Assessment Monitoring Stations
$PM_{2.5}$	Fine Particulate Matter (< 2.5 µm)
PMF	Positive Matrix Factorization
ppbv	parts per billion by volume
ppmv	parts per million by volume

PST	Pacific Standard Time
QC	Quality Control
RL	Reporting Limit
TD	Thermal Desorption
TIC	Tentatively Identified Compound
TO-15	Compendium Method for Toxic Organics - 15
TO-17	Compendium Method for Toxic Organics - 17
$\mu g/m^3$	micrograms per meter cubed
VAC	Volts Alternating Current
VOC	Volatile Organic Compound
VOC-TDSS	Volatile Organic Compound - Thermal Desorption Sampling System

Executive Summary

Summa Canister (EPA TO-15) and TD Tube (EPA TO-17) samples were taken in the Las Vegas Valley during the ozone season from May through September 2023 at the Jerome Mack, Sunrise Acres, Joe Neal, and Jean monitoring sites. These samples were initiated to identify the impact of wildfire smoke on the Valley using wildfire tracer VOCs. The VOCs used to identify wildfire smoke included acetonitrile, acetone, acrolein, MEK, 2,3-butanedione, 2,5-dimethylfuran, furfural, and furan. Some VOCs, such as toluene, benzene, and pentane, were included to identify anthropogenic sources and compare with established measurements such as the PAMS auto-GC. We expected that wildfire-specific VOCs would be enhanced compared with anthropogenic VOCs during a wildfire event. During the 2023 sampling season, however, only two wildfire events occurred. The York Fire (occurring at the end of July and beginning of August) and a regional smoke event originating from wildfires in northern California (occurring at the end of September). While there were too few wildfire data points to create robust statistics when analyzing individual wildfire VOCs, a large amount of background/anthropogenic data was collected and could be used to provide further information in subsequent sampling periods. Additionally, when combining all VOC data available from 2023 and running the EPA PMF tool, we find that there is a distinct wildfire factor with enhanced concentrations of wildfire-specific VOCs, such as acetonitrile and furans. While the 2023 sampling season did not provide complete wildfire versus anthropogenic/background results, expanding on this dataset through continuing TO-15 and TO-17 sampling will be critical to capture VOC trends and positively characterize wildfire smoke in the Las Vegas Valley.

1. Introduction

Over the last several decades, wildfires have been increasing in size and severity throughout North America due to changes in climate, drier fuels, and human activities (Marlon et al., 2012; Balch et al., 2017; Westerling, 2016). Intense wildfire seasons can introduce a significant amount of trace gasses and particulate matter pollution to the atmosphere (Urbanski et al., 2008). Over the last 50 years, there has been an increase in frequency and duration of large fires along with longer wildfire seasons (Westerling et al., 2006; Westerling 2016). While wildfires are a natural and important part of the ecological cycle, climate change has contributed to increasing wildfire size throughout the western U.S. (Abatzoglou and Williams, 2016; Harvey, 2016). Future projections of wildfire frequency and severity indicate a continuation of this increase, as well as substantial increases in the pollutants emitted and produced from wildfire emissions such as ozone and fine particulate matter (diameter < 2.5 µm [$PM_{2.5}$]) (McClure and Jaffe, 2018; Xie et al., 2022; Yang et al., 2022; McGinnis et al., 2023).

Wildfires emit primary pollutants such as $PM_{2.5}$ and contribute to the formation of secondary pollutants such as ozone (Akagi et al., 2011; Van Der Werk et al., 2017; Andreae, 2019). Exposure to high concentrations of these pollutants can cause detrimental acute and long-term impacts (Reid et al., 2019; Zhang et al., 2023; Williams et al., 2024). Through the Clean Air Act (CAA), the U.S. Environmental Protection Agency (EPA) sets National Ambient Air Quality Standards (NAAQS) for the protection of public health and welfare. The annual standard for $PM_{2.5}$ is a three-year running average of the annual mean, which must remain at or below 9.0 µg/m^3, while the daily standard is a three-year running average of the 98th percentile, which must remain at or below 35 µg/m^3 (EPA, 2024). The ozone standard is based on the three-year running average of the annual fourth-highest Maximum Daily 8-Hour Average (MDA8), which must remain at or below 0.070 ppmv (EPA, 2015). The CAA requires that air agencies meet the NAAQS for $PM_{2.5}$, O_3, and other pollutants. However, if an atypical or natural event, such as a wildfire, causes an exceedance that is not reasonably controllable or preventable, an "exceptional event" can be submitted to exclude that event from design value calculations (i.e., prevent NAAQS non-attainment). However, with the predictions of increasing size and severity of wildfires and stricter standards for $PM_{2.5}$ and ozone, it is likely that air agencies will experience more exceedances outside of their control and require more exceptional event demonstrations (Sarangi et al., 2020). For air agencies to remain in attainment of the NAAQS, it is increasingly important to trace impacts and determine the effects of wildfire emissions.

Proof of wildfire emissions transport can be achieved in a variety of ways. Satellite imagery of smoke plumes or National Oceanic and Atmospheric Administration (NOAA) Hazard Mapping System (HMS) smoke polygons can show the size and extent of a wildfire plume, but these products do not indicate whether the smoke was at the surface. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) forward- and/or back-trajectory modeling can also trace the path of a wildfire plume, but the results are highly dependent on the meteorological input data and cannot define the emission concentrations experienced at the surface. Surface measurements of wildfire primary and secondary pollutants such as $PM_{2.5}$, ozone, carbon monoxide, and nitrogen oxides are some of the best proof of wildfire impacts, but each wildfire has a unique emissions profile usually based on the type of vegetation burning and the plume distance traveled. Therefore, interpreting the typical ground-based pollutant measurements to determine wildfire impacts can be complicated (e.g., rapid production of ozone witnessed by Baylon et al. [2015], variable production of ozone witnessed by Jaffe and Widger [2012], and depletion of ozone downwind of a wildfire by Alvarado et al., [2010]). For this reason, wildfire tracers (i.e., compounds that have a medium-to-long atmospheric lifetime and are almost solely emitted from wildfires) are key in identifying the direct contribution of wildfire emissions, especially in urban areas where pollutant concentrations are typically enhanced.

Typical wildfire tracers include levoglucosan (LVG), potassium (K^+), hydrogen cyanide (HCN), and acetonitrile. LVG is a main product of cellulose pyrolysis in vegetation and acts as an excellent tracer, but can be decomposed by acid-catalyzed hydrolysis and, therefore, is less useful as a long-range wildfire tracer (Simoneit et al., 1999; Scaramboni et al., 2015). Potassium has been proposed and used as a wildfire tracer, but has additional sources from soil dust and fertilizers making it a less-than-ideal tracer (Andreae, 1983; Urban et al., 2012). HCN has a long atmospheric lifetime (on the order of months) and has few other source besides wildfires. However, the emission of HCN varies from fire to fire and background levels of HCN in urban areas are inconsistent (Li et al., 2000; Crounse et al., 2009). Acetonitrile has all the hallmarks of an excellent wildfire tracer with a significantly long atmospheric lifetime (5-6 months), emission sources that are predominantly from wildfires (~90-95% from wildfires and <6% from automobile emissions), and low background mixing ratios (0.1-0.3 ppbv) (De Gouw et al., 2003; Li et al., 2003; Singh et al., 2003; Akagi et al., 2011; Gilman et al., 2015). However, acetonitrile has been observed from some urban sources such as universities and labs where it is used as a solvent in liquid chromatography. Ultimately, due to its low emissions from sources other than wildfires and long atmospheric lifetime, acetonitrile is an excellent wildfire tracer. Due to the occurrence of some other local sources of acetonitrile, it is suggested that this wildfire tracer be measured concurrently with other reactive oxygenated Volatile Organic Compounds (VOCs) which are typically emitted from wildfires (e.g., acetone, furan, acrolein, methacrolein, methyl ethyl ketone (MEK), 2,3-butanedione, 2,5-dimethylfuran, and furfural) (Chandra et al., 2020). To fully characterize the sample taken, it is also best to include anthropogenic tracers such as pentane, benzene, and toluene. Overall, these tracers can help identify when and how intensely wildfire smoke is in a given area.

The Las Vegas Valley (LVV) is uniquely affected during late spring to early fall by a combination of upwind anthropogenic pollution (primarily from Los Angeles), terrain and meteorology which enhance accumulation and production of pollutants, atypical anthropogenic sources from the entertainment industry as well as typical on-road sources, and wildfire smoke. With the increasing number and intensity of wildfires in the western U.S., the need to identify and quantify the effects of wildfire smoke on the LVV is vitally important. Understanding the specific effects of wildfire smoke on primary and secondary pollutants is difficult in a pristine environment, but in an urban area the difficulty can be compounded by anthropogenic sources, urban meteorology, and terrain. In this study, we propose to use specific anthropogenic and wildfire VOC tracer species to map the VOC profile of the LVV. Thermal desorption (TD) tubes as well as Summa Canisters will be used to take VOC measurements and are an established method for measuring VOCs in anthropogenic and wildfire environments (Friedli et al., 2001; Blake et al., 2009; Ding et al., 2009; Martin et al., 2019; Chandra et al., 2022). To fully evaluate the anthropogenic and wildfire VOC profile of the LVV, we will sample acetonitrile, acetone, n-pentane, i-pentane, benzene, toluene, acrolein, MEK, 2,3-butanedione, 2,5-dimethylfuran, furfural, and furan. Before wildfire season starts, we will determine the background/anthropogenic profile of VOCs in the LVV. During the wildfire season, we will identify dates that are directly affected by wildfire smoke. On these dates, we will create a wildfire VOC profile. Based on the differences between the background/anthropogenic and wildfire VOC profiles, we will be able to positively identify dates that are affected by wildfire smoke despite complicating anthropogenic factors.

Hypothesis: The wildfire VOC profile will show enhanced wildfire-specific VOC tracer concentrations (such as Acetonitrile) and be significantly different from the background/anthropogenic VOC profile in the LVV. Enhanced ozone concentrations due to wildfire impacts will be correlated with enhanced wildfire-specific VOC tracer concentrations.

2. Methodology

To determine the background/anthropogenic and wildfire VOC profiles in the LVV, this study deployed TO-15 and TO-17 methods to collect and analyze VOCs present in the LVV during typical background/anthropogenic and wildfire periods. This study used two VOC Thermal Desorption Sampling Systems (TDSS) to collect VOCs on Thermal Desorption (TD) tubes at two established monitoring sites operated by Clark County DES. In addition to the two VOC-TDSS instruments, Summa Canisters were deployed alongside the VOC-TDSS instruments and two additional established monitoring sites in Clark County. Samples for both TD tubes and Summa Canisters were analyzed via Gas Chromatography – Mass Spectroscopy (GC-MS). The Clark County DES team and Sonoma Technology staff used Microsoft Teams to coordinate sampling (using the Calendar functionality) and keep notes concerning any sampling issues (using the Notebook functionality). All notes from the 2023 sampling season at all sites are provided in **Appendix A**.

2.1. Sampling Sites

Figure 1 shows the sampling sites for the 2023 VOC Study. The reason for site selection is provided below with a list of all collocated measurements taken at each site.

The **<u>Jerome Mack</u>** location was chosen for **TD tube** and **Summa Canister** samples for the following reasons:

- It is a valley site that was likely be smoke impacted,
- Filter-based $PM_{2.5}$ Federal Reference Method (FRM) sampler was already in place,
- $PM_{2.5}$ FRM quartz filters were used for Levoglucosan measurements,
- $PM_{2.5}$ FRM collocation was also in place,
- Site included Auto-GC VOC measurements (designated PAMS Site),
- PAMS Carbonyl measurements at site,
- Site has Trace carbon monoxide measurements,
- Routine site visits were conducted,
- Designated NCore site.

The **<u>Sunrise Acres</u>** location was chosen for **TD tube** and **Summa Canister** samples for the following reasons:

- It is a valley site that was likely be smoke impacted,
- Filter-based $PM_{2.5}$ FRM sampler was already in place,
- Served as a nearby comparison site for data correlations with Jerome Mack,
- Routine site visits were conducted,
- This site was best suited for environmental justice concerns.

The **Joe Neal** location was chosen **Summa Canister** samples for the following reasons:

- This site was a high-ozone Design Value site,
- Routine site visits are conducted.

The **Jean** location was chosen **Summa Canister** samples for the following reasons:

- This site is frequently upwind of the LVV and provides background concentrations.

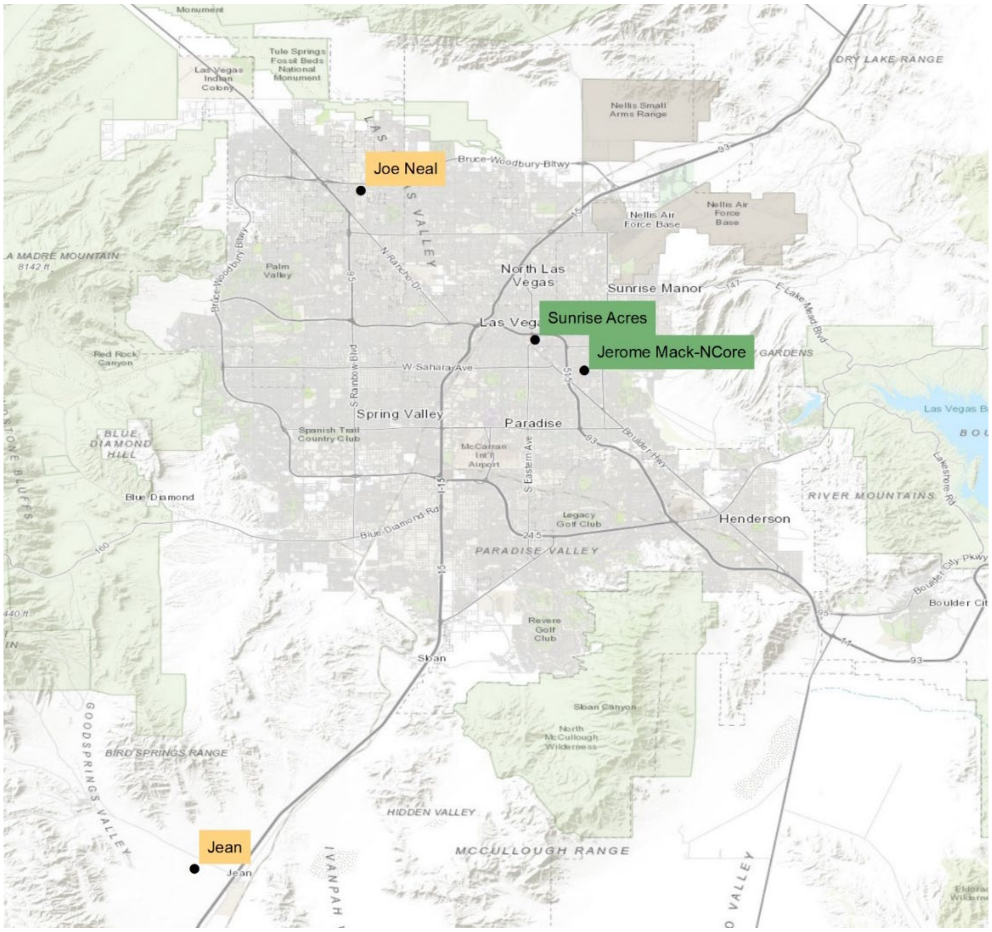

Figure 1. Map of Clark County with the TD tube + Summa canister sampling sites shown in green, and the Summa canister-only sampling sites shown in yellow.

2.2. TD Tube Sampling

TD tubes are well established as a methodology for sampling VOCs under the EPA TO-17 methodology[1]. TD tubes were supplied by Enthalpy and installed into the VOC-TDSS on a weekly basis for automated sampling. 14 tubes + 1 blank were installed to provide twice daily TD tube VOC

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[1] https://www.epa.gov/sites/default/files/2019-11/documents/to-17r.pdf

samples. TD tubes were sampled twice a day at 9 am-5 pm PST and 9 pm-5 am PST. The daytime sample was selected to encompass the ozone production window each day. The nighttime sample was selected to sample overnight emissions and any transport of pollutants into the LVV.

The TD tubes used during this sampling study were stainless steel and are packed with three sorbents: Tenax, Carboxen, and Carbotrap. These sorbents collect VOCs with 2-12 carbons. These tubes were configured for the capture of acetonitrile and other targeted VOC species. Sampling time and volume was optimized to collect the highest quantity of target compounds with the best time resolution. During this study, we collected samples at 75 mL/min for 8 hours each.

The VOC-TDSS was used to automatically collect TD tube samples and concentrate VOCs of interest, such as acetonitrile. Two VOC-TDSS instruments were built by Sonoma Technology and shipped to Clark County DES. Clark County DES installed these samplers at the Jerome Mack and Sunrise Acres monitoring sites. A short description of the VOC-TDSS instrument is provided here and also published in Chandra et al. (2020).

2.2.1. VOC-TDSS

The VOC-TDSS accommodates up to 16 TD tubes for field-sampling VOCs. The instrument is built into a hard-backed suitcase for portability and ruggedness. The VOC-TDSS can be operated at any site with a 110-120 VAC power source and (optionally) an internet connection for off-site monitoring and all external components are waterproof for operation outside. Sample integrity is maintained by two 16-port VICI Valco valves to concentrate ambient air samples one tube at a time, while keeping the other tubes sealed. Flow and sample volume are controlled with a mass flow controller, pressure sensor, and pump, along with the sampling interval set in the accompanying LabVIEW program. Flow and pressure data is monitored continually and collected at an interval set by the user. If the flow and/or pressure is too low for a set period of time, then the instrument automatically safely shuts down. The sampler temperature is kept constant using a Peltier heating/cooling system. Keeping the instrument internally warmer than the outside temperature allows for sampling ambient air without the condensation of water in the TD tubes. Keeping a constant temperature also reduces the possibility of VOC loss if the TD tubes were exposed to extreme heat. The LabVIEW program allows autonomous VOC sampling, controlling all internal components, for up to two weeks in the field. Figure 2 shows a simplified diagram of the internal structure and flow diagram.

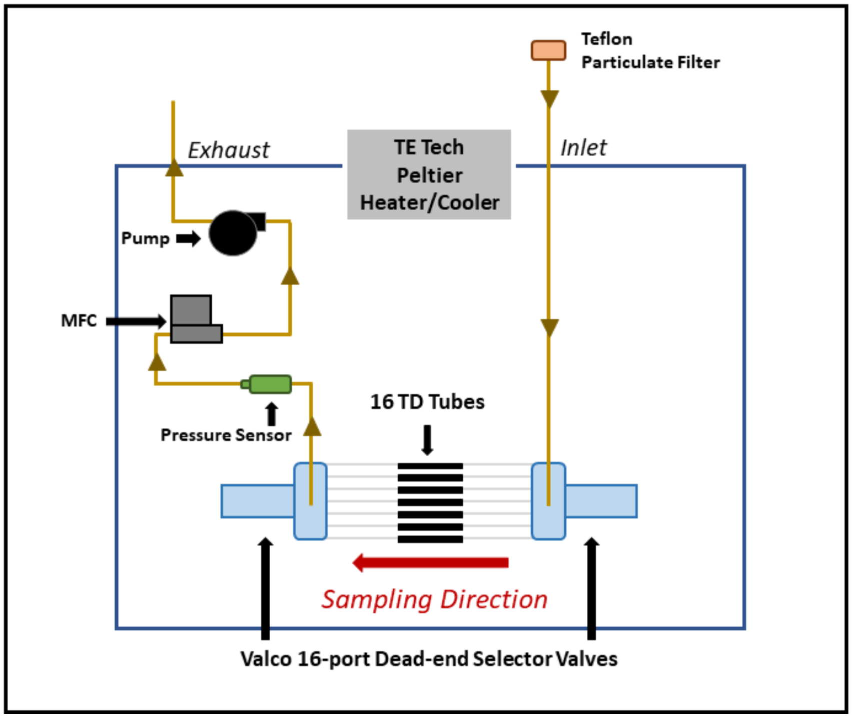

Figure 2. VOC-TDSS Simplified Flow Diagram

2.3. Summa Canister Sampling

Summa Canisters are well established as a methodology for sampling VOCs under the EPA TO-15 methodology[2]. These canisters are pre-evacuated (to approximately -30 inHg) certified passivated steel canisters that are used in combination with a flow restriction and timer to slowly collect samples over a set period of time. Summa Canisters were supplied by Enthalpy Analytical and installed at the four designated canister sites for VOC sampling. During the sampling season (May through September), Clark County DES monitoring staff triggered canister samples based on either the need to collect background/anthropogenic VOC samples or based on wildfire smoke (or ozone/$PM_{2.5}$) forecasts in the LVV area. The Clark County DES team provided smoke (or pollutant) forecasts and signaled when a canister sample should be triggered to capture wildfire VOC samples which occurred concurrently with TD tube samples.

Background/anthropogenic samples were triggered based on an established schedule at the beginning of the sampling season. Most of the scheduled samples collected background/anthropogenic emissions, while some regularly scheduled samples coincided with smoke events. The background/anthropogenic schedule was optimized to collect day and night samples, as well as a spread of samples across days of the week and months. Additionally, the

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[2] https://www3.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf

schedule also included measurements that coincided with carbonyl measurements to incorporate more background and wildfire smoke information.

Typical sample times were 9 am – 5 pm PST to coincide with the daytime TD tube sample. Nighttime sample times (9 pm – 5 am PST) and carbonyl-concurrent sample times (12 pm – 8 pm PST) were also included periodically. Regularly scheduled background/anthropogenic samples were scheduled with the following goals: (1) trying to evenly sample over each day of the week, (2) sample a majority of the Carbonyl days, and (3) collect a statistically significant number of overnight samples. A breakdown of the initial schedule provides detail on the samples taken:

1. Day of week breakdown:
    a. Sunday: 9 days
    b. Monday: 7 days
    c. Tuesday: 7 days
    d. Wednesday: 7 days
    e. Thursday: 9 days
    f. Friday: 9 days
    g. Saturday: 8 days
2. Monthly breakdown:
    a. May: 9 days
    b. June: 13 days
    c. July: 12 days
    d. August: 11 days
    e. September: 11 days
3. Summa Canister samples on 17 of the 31 carbonyl days (55%).
    a. Carbonyl-correlated canister samples took place from 12 pm to 8 pm PST.
4. Over the course of the season, there were 12 nighttime (9 pm – 5 am PST) sample dates planned (21%).
5. 14 planned sample dates included Joe Neal and Jean (25%).

2.4. Enthalpy Analysis

The Enthalpy Analytical labs in Mt. Pleasant, MI, and Deer Park, TX, analyzed the TO-17 and TO-15 samples, respectively. Quantitative results for the 12 selected VOCs in this study were provided by either laboratory. Reporting limits (RL) for each compound are shown in Table 1. Additional compounds, such as tetrahydrofuran, were also included in the quantitative results provided by Enthalpy if they were identified in a sample. Not all compounds were able to be quantified and were listed as "TIC" (Tentatively Identified Compound). If unable to quantify compound concentrations, compounds listed as TIC would be qualitatively identified (i.e., present or not present in the sample) without quantitative values.

Table 1. Reporting limits for selected wildfire or anthropogenic VOC that could be identified by the Enthalpy labs is shown. The Chemical Abstract Services (CAS) number is a unique identifier for each compound. The TO-17 RL is supplied by the Mt. Pleasant lab, while the TO-15 RL is supplied by the Deer Park lab. The target 12 compounds focused on in this study area highlighted in orange.

CAS	Name	TO-17 RL (ng)	TO-15 RL (ppbv)
75-05-8	Acetonitrile	10	0.2
67-64-1	Acetone	25	1
109-66-0	n-Pentane	5	0.2
78-78-4	i-Pentane	5	TIC
71-43-2	Benzene	5	0.2
108-88-3	Toluene	5	0.2
107-02-08	Acrolein	25	0.2
78-93-3	Methyl Ethyl Ketone (MEK)	10	1
431-03-08	Diacetyl/2,3-Butanedione	10	TIC
110-00-9	Furan	5	TIC
625-86-5	2,5-Dimethylfuran	5	TIC
98-01-1	2-Furaldehyde/Furfural	5	TIC
78-85-3	2-Methyl-2-propenal/Methacrolein	25	TIC
109-99-9	Tetrahydrofuran	5	0.2
534-22-5	2-Methylfuran	5	TIC
930-27-8	3-Methylfuran	5	TIC
271-89-6	2,3-Benzofuran	25	TIC
4466-24-4	2-n-Butylfuran	25	TIC
132-64-9	Dibenzofuran	50	TIC
1708-29-8	2,5-Dihydrofuran	100	TIC
3710-43-8	2,4-Dimethylfuran	25	TIC
625-86-5	2,5-Dimethylfuran	5	TIC
4265-25-2	2-Methylbenzofuran	25	TIC
3777-69-3	2-Pentylfuran	5	TIC

4229-91-8	2-Propylfuran	25	TIC

2.5. Positive Matrix Factorization (PMF)

During the analysis phase of this study, the EPA PMF version 5.0 was used to determine source factors of the VOC measurements. The EPA PMF model takes measured concentrations and uncertainties for a set of species and decomposes the data set into combinations called “source types” or “factors” (Norris et al., 2014; Paatero and Tapper, 1994). The factors function as chemical fingerprints that can then be used to determine the potential source(s) through comparison of the factors to measured profiles and consideration of additional information about the measurements (e.g., wind direction, nearby sources, etc.).

Each measured concentration has an associated uncertainty as shown in Equation 1. Uncertainty (U) for measurements above the species reporting limit (as provided by the analytical laboratory), was estimated as:

$$U = 0.1 + 0.2 \times [species] \qquad \text{(Equation 1)}$$

For measurements below the species reporting limit, the measurement uncertainty was estimated as:

$$U = \frac{5}{6} \times RL \qquad \text{(Equation 2)}$$

Measurements recorded as a concentration of 0 were set to the reporting limit for the species divided by 2 (Norris et al., 2014; Brown et al., 2015; Ryder et al., 2020). The corresponding uncertainty value was calculated using Equation 2. Additionally, any species with concentration above the RL less than fifty percent of the time was not included, with some exceptions explained below. As calculated by the EPA PMF program, species with a signal-to-noise ratio of 0 were removed and 10% extra modeling uncertainty was added to the calculation.

As is typical in PMF analysis, bootstrapping (BS), displacement (DISP) and bootstrapping enhanced by displacement (BS-DISP) were used to evaluate the validity of the results (Paatero and Trapper, 1994; Brown et al., 2015). In BS, blocks of consecutive observations from the original data set are randomly sampled to create a new input file, the re-sampled data set is re-run on PMF, and the new BS solution factors mapped to the original factors. DISP explores the rotational ambiguity of the PMF solution by perturbing each data point in the profile matrix. BS-DISP combines BS and DISP by displacing the BS resampled data. Collectively, these processes evaluate the random uncertainty and the rotational uncertainty of the PMF solution (Brown et al., 2015).

PMF was performed on TO-15 analyzed VOC samples and on TO-17 analyzed VOC samples separately. Only species with RL provided by the lab were used in the analyses. For each analysis method, data from all sites was combined, as were all day, night, and carbonyl-timed samples in an effort to improve the statistics. PMF solutions ranging from two to five factors were considered.

TO-15 details: 2-furaldehyde and tetrahydrofuran had a signal-to-noise of 0 but were set to “weak” due to its importance as a tracer for wildfire smoke. Overall, the species included in PMF for the TO-

15 samples were pentane, toluene, methylethylketone, acrolein, acetone, 2-methyl-2-propenal, acetonitrile, tetrahydrofuran, furan, 3-methylfuran, 2-methylbutane, benzene, 2-furaldehyde, and 2-methylfuran. In total, 119 samples were included using a random seed number to initiate the analysis.

TO-17 details: 2-Furaldehyde was below detection 71% of the time, but was included in the analysis as a “weak” species due to its importance as a tracer for wildfire smoke. The species included in PMF for the TO-17 samples were methylethylketone, benzene, toluene, 2-furaldehyde (set to “weak”), 2-methyl butane, and pentane. Overall, 469 samples were used as input to the PMF model using a random seed number to initiate the analysis.

3. Results

TD tube and Summa Canister samples were collected between May 10 and September 30, 2023. **Appendix B** provides the schedule for all regularly scheduled Summa Canister samples. TD tube samples were taken twice daily with tubes collected/installed on Wednesdays (as shown in Appendix B).

During the 2023 season, very few wildfires impacted the LVV. This corresponded to only two wildfire-initiated runs occurring on July 6 and August 1, 2023. While we collected very little wildfire information in 2023, we collected a wealth of background/anthropogenic VOC information which can be used to compare against wildfire data in subsequent field campaign years.

3.1. Wildfire Screening

Days during the sampling period were screened for potential wildfire influence using HMS smoke polygons and $PM_{2.5}$ concentrations. The HMS criteria evaluated if an HMS smoke polygon was present directly over the Las Vegas area, or if a 12-hour HYSPLIT back trajectory intersected a smoke polygon. HYSPLIT trajectories were run using the AirNow-Tech Navigator tool[3]. Heights were set to 500, 1,500, and 2,500 meters, and the North American Mesoscale (NAM) 12-km meteorological data was used. Back trajectories were set to run for -12 hours from 12:00 PST with a starting location set to the Las Vegas city center. The $PM_{2.5}$ concentration screening evaluated if at least one site in Clark County had daily $PM_{2.5}$ greater than the 3-year (2021-2023) monthly 90th percentile at each site. Daily mean $PM_{2.5}$ from for 2021-2023 were downloaded from the EPA Air Quality System (AQS). A 90th percentile threshold was calculated for each monitoring site and month from the three years of data. If both the HMS and $PM_{2.5}$ concentration conditions were met, the ground-level air quality was classified as a fire day. Due to high $PM_{2.5}$ concentrations associated with the 4th of July holiday; July 4-6 were excluded from analysis.

An example fire screening from September 21, 2023 of an HMS smoke polygon analysis with overlaid HYSPLIT trajectory is shown in **Figure 3**, and the corresponding $PM_{2.5}$ time series in **Figure 4**.

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[3] https://www.airnowtech.org/

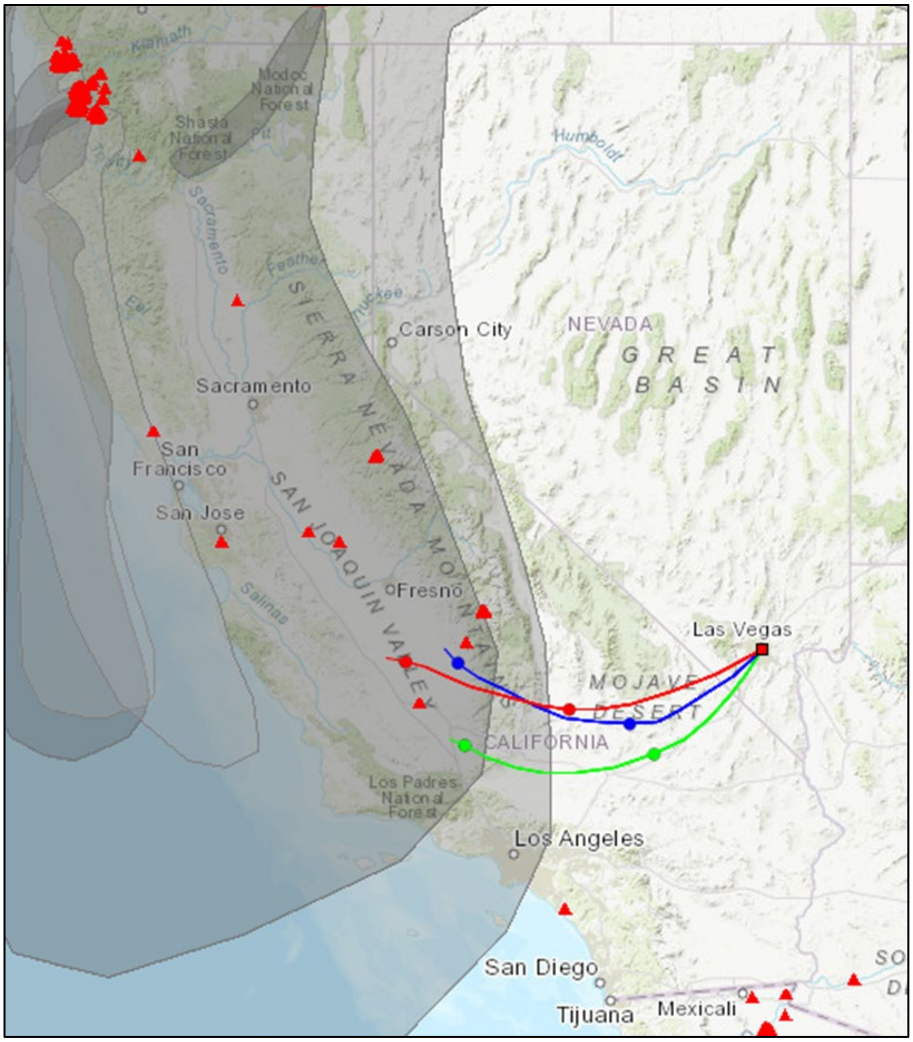

Figure 3. HMS smoke polygon and HYSPLIT 12-hour back trajectory for September 21, 2023. Red triangles are HMS fire detections and gray polygons are HMS smoke detections, with thicker smoke shown in darker gray. HYSPLIT trajectories are shown at 500 m (green), 1,500 m (blue), and 2,500 m (red). Figure generated using the AirNow-Tech Navigator tool.

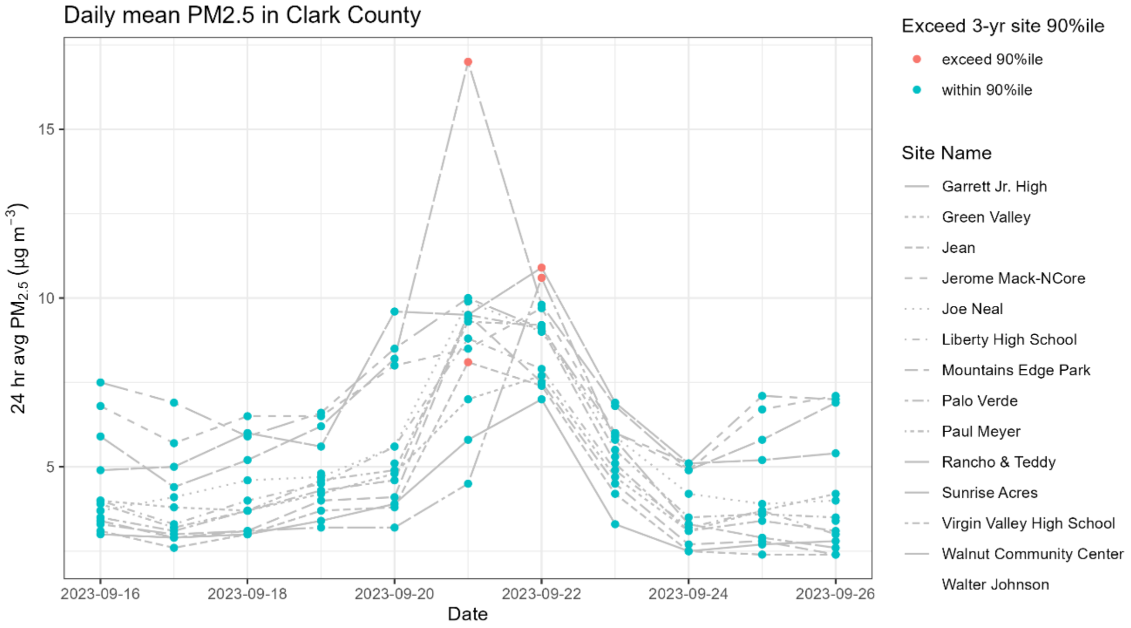

Figure 4. Daily mean $PM_{2.5}$ concentrations (µg/m^3) at sites in Clark County. Data points are colored by if the measurement exceeds the 3-year (2021-2023) monthly 90th percentile for that specific site.

The results of the screening identified seven fire days during the 2023 sampling period, summarized in Table 2. Due to the relatively low number of wildfires in 2023, this was a lower number of days compared to recent years for the location, and sample size is a limiting factor on the statistical significance of the analysis.

The smoke source region was estimated from the HMS data, and plume type and transport range were inferred. The event identified in the screening from July 28 to July 31 was determined to be due to the local York Fire,[4] which occurred near Clark County in the Mojave National Preserve with a likely chaparral fuel source. The other days were classified as regional smoke undergoing long-range transport. For example, the smoke influence identified in the screening on September 21 likely originates from wildfires located in Northern California with a likely conifer forest fuel source, as shown in the HMS smoke image in Figure 3.

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[4] https://www.nps.gov/moja/learn/news/york-fire-incident.htm

Table 2. Fire screening results and resultant categorization of smoke and non-smoke days.

Screening result	Date (y-m-d)	Estimated plume type	24-hour $PM_{2.5}$ description
Fire	2023-07-17	Regional smoke, long-range transport	Lower $PM_{2.5}$, < 15 µg/m^3
Fire	2023-07-23	Regional smoke, long-range transport	Lower $PM_{2.5}$, < 15 µg/m^3
Fire	2023-07-28 through 2023-07-31	Local fire, short transport	Higher $PM_{2.5}$, 25 µg/m^3 max)
Fire	2023-09-21 and 2023-09-22	Regional smoke, long-range transport	Lower $PM_{2.5}$, < 15 µg/m^3
Exclude Days	2023-07-04 through 2023-07-06	--	--

3.2. Data Completeness

Quality Control (QC) analysis of samples was evaluated using field and laboratory notes, as well as evaluation of blanks in the TO-17 analysis. TO-15 had 89% valid data and TO-17 had 94% valid data. Samples that were not considered valid were classified as either "suspect" due to high blank values (available for TO-17 only), or "invalid" due to field sampling errors or occurring during the July 4th holiday exclusion days (see Table 3). Only data classified as valid were included in further analysis. Of the valid data, 7% of TO-15 and 6% of TO-17 data were classified as fire days data (see Table 4). Time series of all data showing their QC assignments are available in Appendix C.

Table 3. Sample validity summary.

Data Quality	TO-15 (cannisters)	TO-17 (sorbent tubes)
Valid	89%	94%
Suspect	0%	5%
Invalid	11%	1%

Table 4. Number and percent of valid observations of unique chemical species by sample type.

Sample type	TO-15 (cannisters)	TO-17 (sorbent tubes)
Blank	--	451 (7%)
Fire	85 (7%)	408 (6%)
No fire	1205 (93%)	5672 (87%)

3.3. Time Series During Wildfire Events

VOC concentrations measured using method TO-15 (cannisters) showed a weak trend that varied by estimated plume type and species oxidation, as shown in the time series in **Figure 5**. More highly oxidized species, such as diacetyl with two carbonyl bonds, showed enhancements during a regional smoke event, with concentrations at the Jerome Mack site increasing by a factor of 2. During the local fire event, enhancements of oxidized species were not observed but rather a smaller enhancement of less oxidized species, such as acetonitrile, may be present. This trend appears to confirm that the VOCs observed during the event in September were due to smoke undergoing long range transport with sufficient time for secondary product formation from atmospheric oxidation reactions, while the VOCs observed during the local fire event are more likely to be primary emissions from the fire.

The limited amount of fire data during this sampling period limits the insights available from this analysis, and some trends observed in the comparison of these periods do not currently have a clear explanation. It is noted that enhancements of two likely primary fire VOC emissions, toluene and pentane, appeared to be strongly enhanced immediately before the local fire event. The reason for this is not clear, but may suggest a different source was contributing more strongly immediately before the known fire ignition date. Secondly, the strong oxidized species enhancements during the regional smoke event were observed at the Jerome Mack site, but not strongly observed at the Sunrise Acres site. The reason for the discrepancy is not clear: the sites are both located at elementary schools roughly 3 miles apart and located in the central Las Vegas valley east of the original downtown. This may suggest that VOCs on this day were not strongly impacted by the regional smoke, which would be in agreement with the HMS smoke polygons not being observed directly over the sampling area (Figure 3), and that the fire day screening should have a higher threshold.

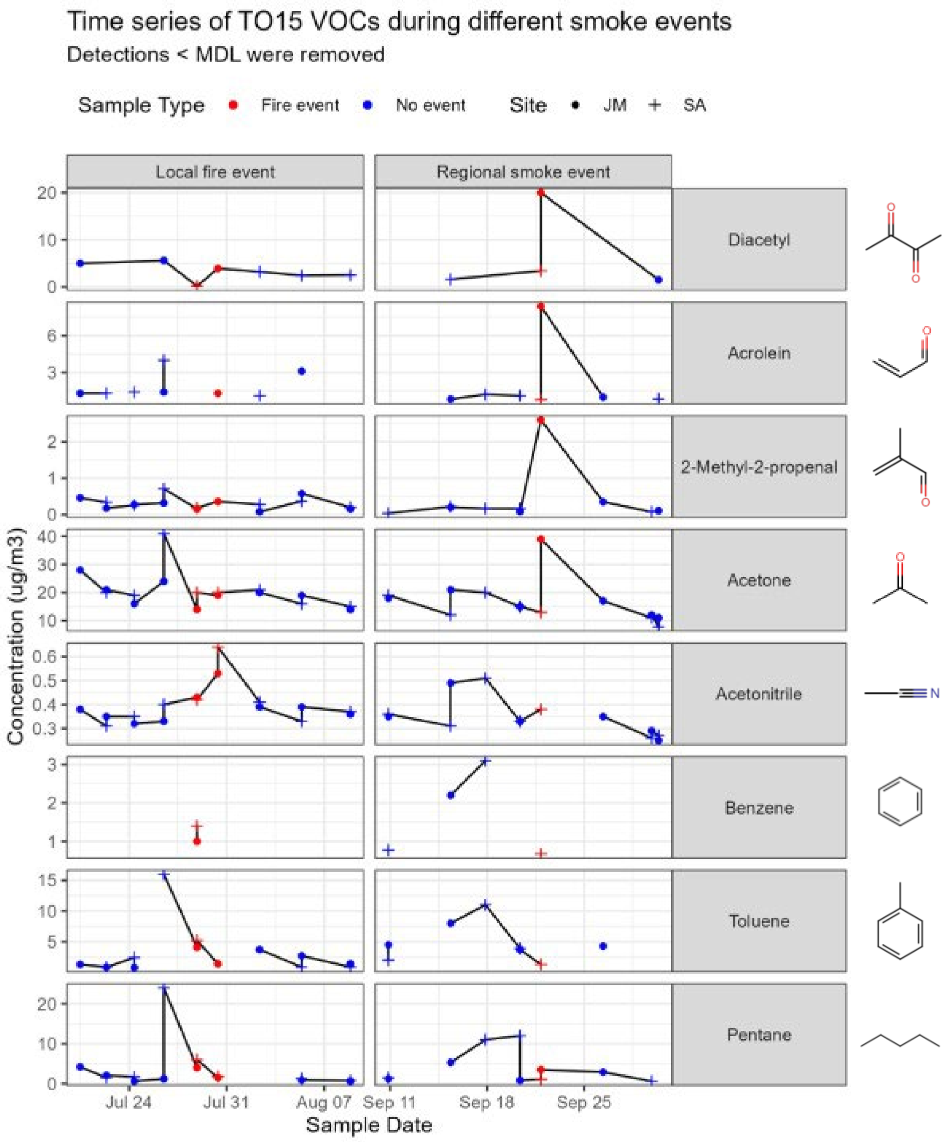

Figure 5. Time series of TO-15 VOCs during a local fire event (left) and a regional smoke event (right). Time series species are roughly arranged by descending level of oxidation.

Similar analysis was applied to the TO-17 (sorbent tubes) data, however, despite the increase in sampling frequency, trends were less clear with this analysis technique (Figure 6). In general, this technique showed consistent concentrations before, during, and after the fire events. The only notable exceptions are single point enhancements of methylethylketone, furan, and acetonitrile during the regional fire event at the Sunrise Acres site. This may again suggest that the impact on local VOCs during the limited smoke events in 2023 was likely weak, and/or that the TO-15 technique was better able to identify trends during this period than the TO-17 technique.

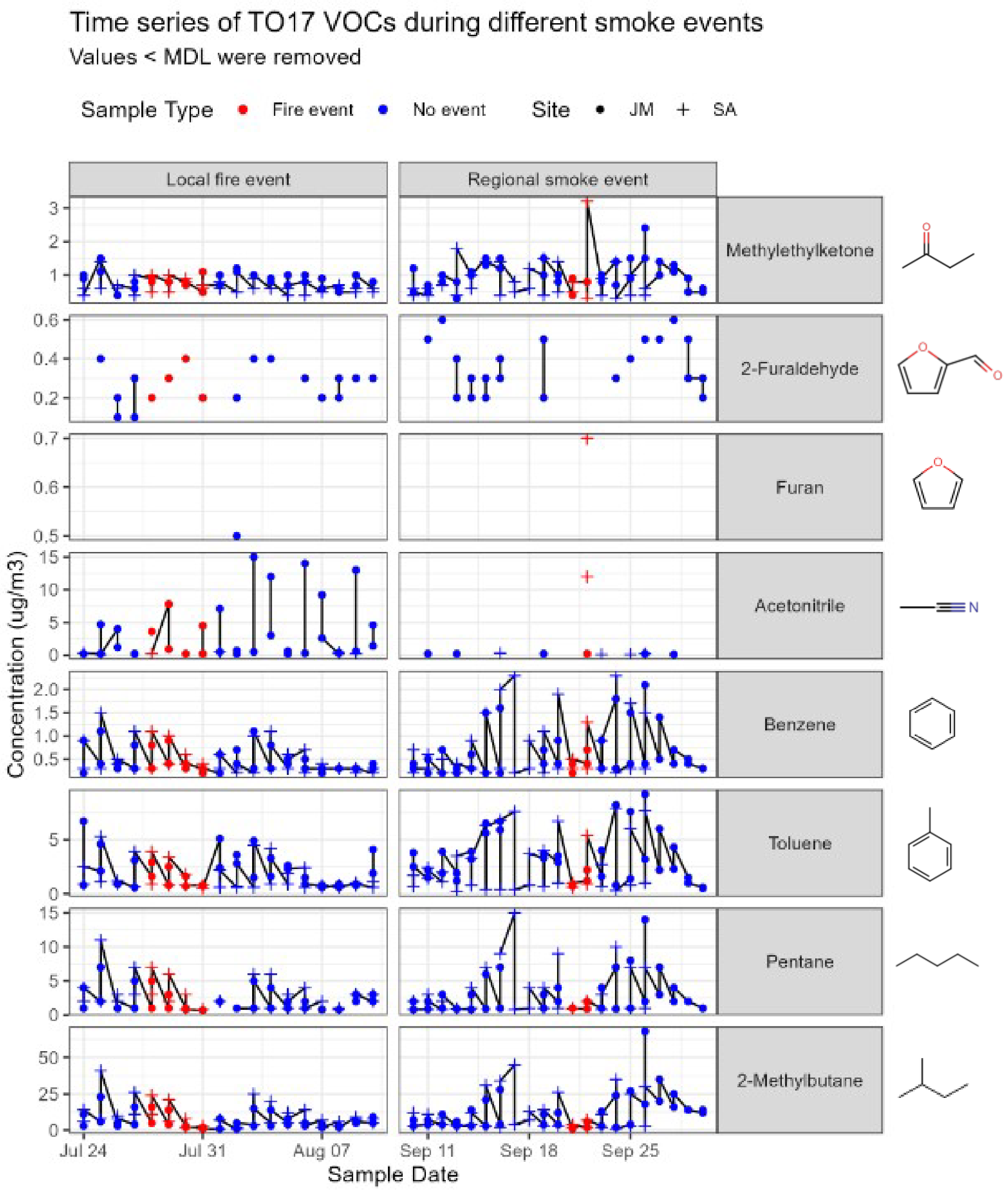

Figure 6. Time series of TO-17 VOCs during a local fire event (left) and a regional smoke event (right). Time series species are roughly arranged by descending level of oxidation.

3.4. Background vs Wildfire Concentrations

Figure 7 shows the TO-15 concentration results when comparing background ("No Fire") to dates screened according to Section 3.1 ("Fire"). Compounds with a dot included on the right-hand side shows a statistically significant difference between the "Fire" and "No Fire" regime with a p-value <

0.05 using a Wilcoxen test for non-parametric data. This includes toluene, pentane, acetonitrile, the benzene/toluene ratio, benzene, tetrahydrofuran.

Figure 8 shows the same “Fire” versus “No Fire” results but for TO-17 data. For these data, methylethylketone, acrolein, 2,5-dimethylfuran, the benzene/toluene ratio, and furan show a statistical difference between the “Fire” and “No Fire” regime. Acetonitrile TO-17 data showed significant artifacts in the “No Fire” regime that caused the two regimes to not be statistically different (see Jerome Mack TO-17 acetonitrile data in Appendix C).

Overall, there were too few “Fire” data points to provide significant results during 2023 despite some regimes being statistically different.

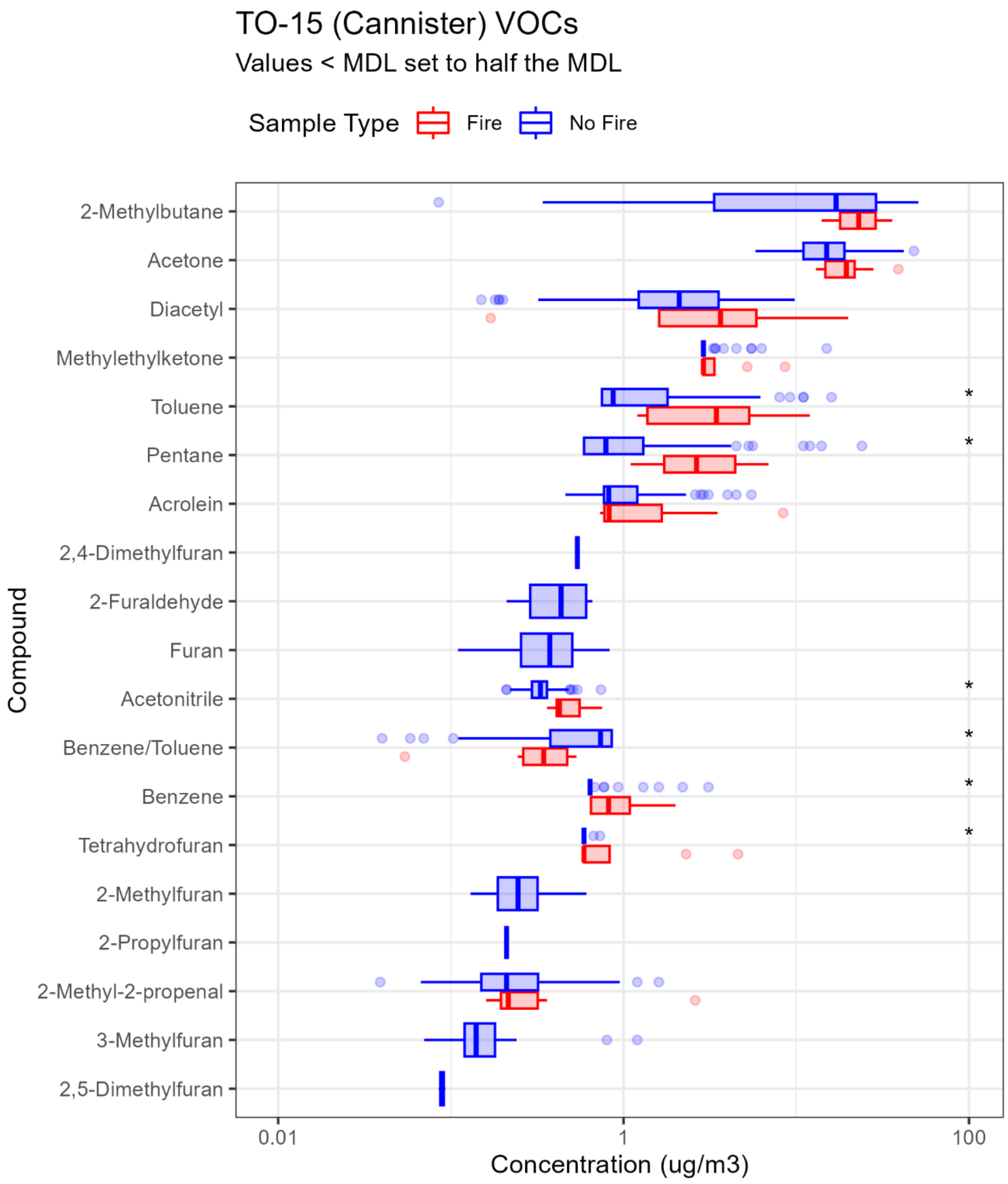

Figure 7. TO-15 data with compounds ordered from highest concentration (top) to lowest concentration (bottom) with "No Fire" data shown in blue and "Fire" data shown in red.

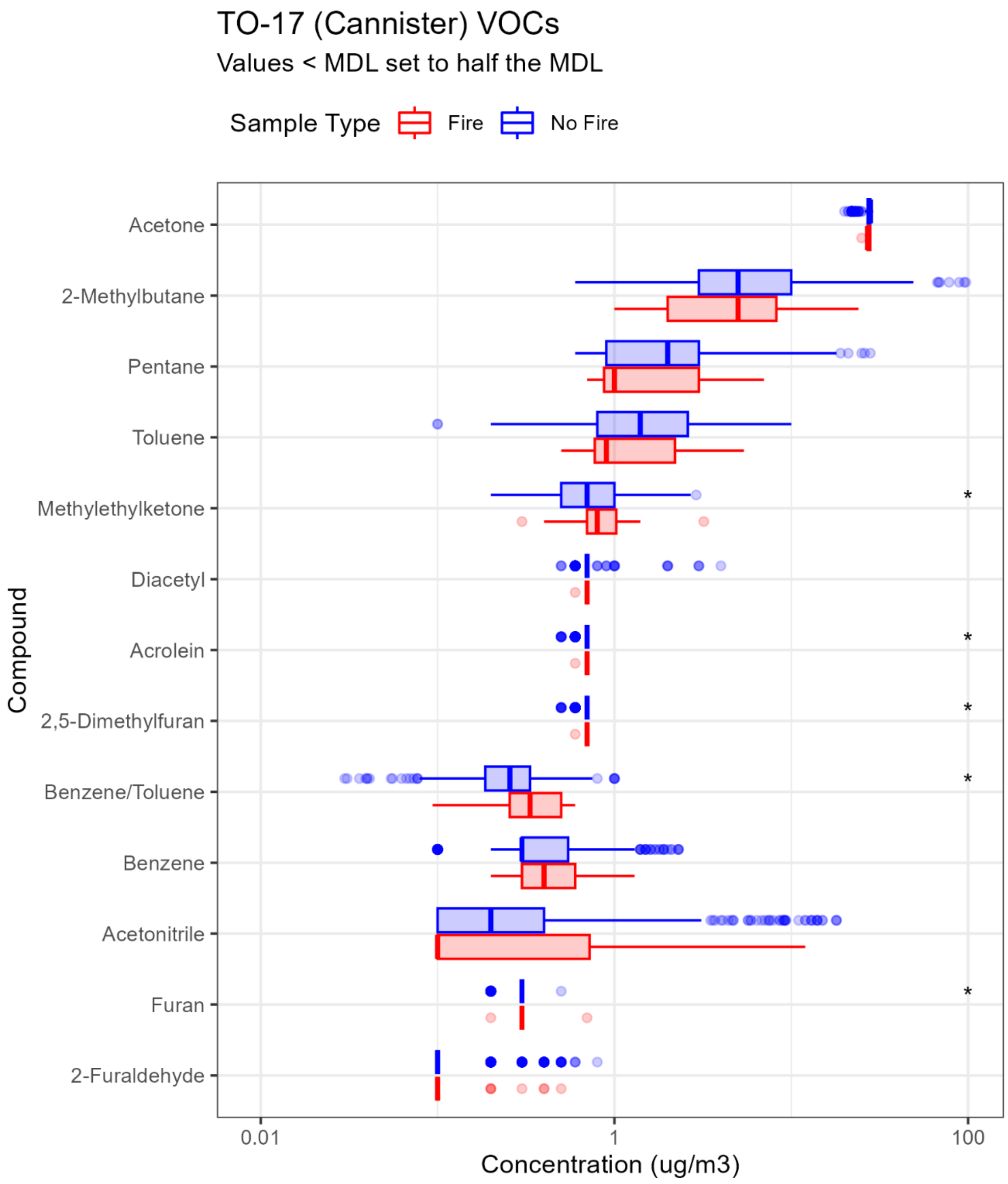

Figure 8. TO-17 data with compounds ordered from highest concentration (top) to lowest concentration (bottom) with “No Fire” data shown in blue and “Fire” data shown in red.

3.5. Short-range vs Long-range Transport

Based on the analysis in Section 3.1, two fire events were observed in 2023. The fire event at the end of July, associated with the York Fire, included short range transport (due to its proximity just to the south of Clark County) and mostly grass and chaparral vegetation burning. The other fire event during September 2023 was a regional event that included longer range transport of smoke from fires in northern California which were likely burning conifer forest. We have separated the two smoke events because they would have likely included a very different set of VOCs from the two fuel sources and reaction pathways would be different between short- and long-range transport.

Figure 9 shows the TO-15 data with this separation in fire regimes. For toluene and pentane, both the short- and long-range fire regimes are above the “No Fire” regime but nearly the same concentration between fire regimes. Toluene shows a slightly higher concentration in the short-range fire compared to the long range. For acetone, the long-range fire shows concentrations higher than the short-range fire. For acetonitrile, the short-range fire concentration is significantly higher than the long-range fire and “No Fire” regime.

Figure 10 shows the same data but for TO-17. In this case, toluene and pentane are lower for both fire regimes compared to the “No Fire” regime (contrary to the TO-15 data). Methylethylketone shows higher concentrations for the fire regime versus “No Fire” regime with the long-range fire regime showing the highest concentrations. The benzene/toluene ratio also shows high values in the fire regime compared to the “No Fire” regime. Benzene concentrations on their own are also higher in the fire versus no fire regime, as expected.

While some data shown are plausible given the difference in fuels, the toluene and pentane data are opposite when comparing TO-15 and TO-17 data. Overall, again, we find that there were too few “Fire” data points to provide significant results during 2023 despite some separation in regimes being statistically different.

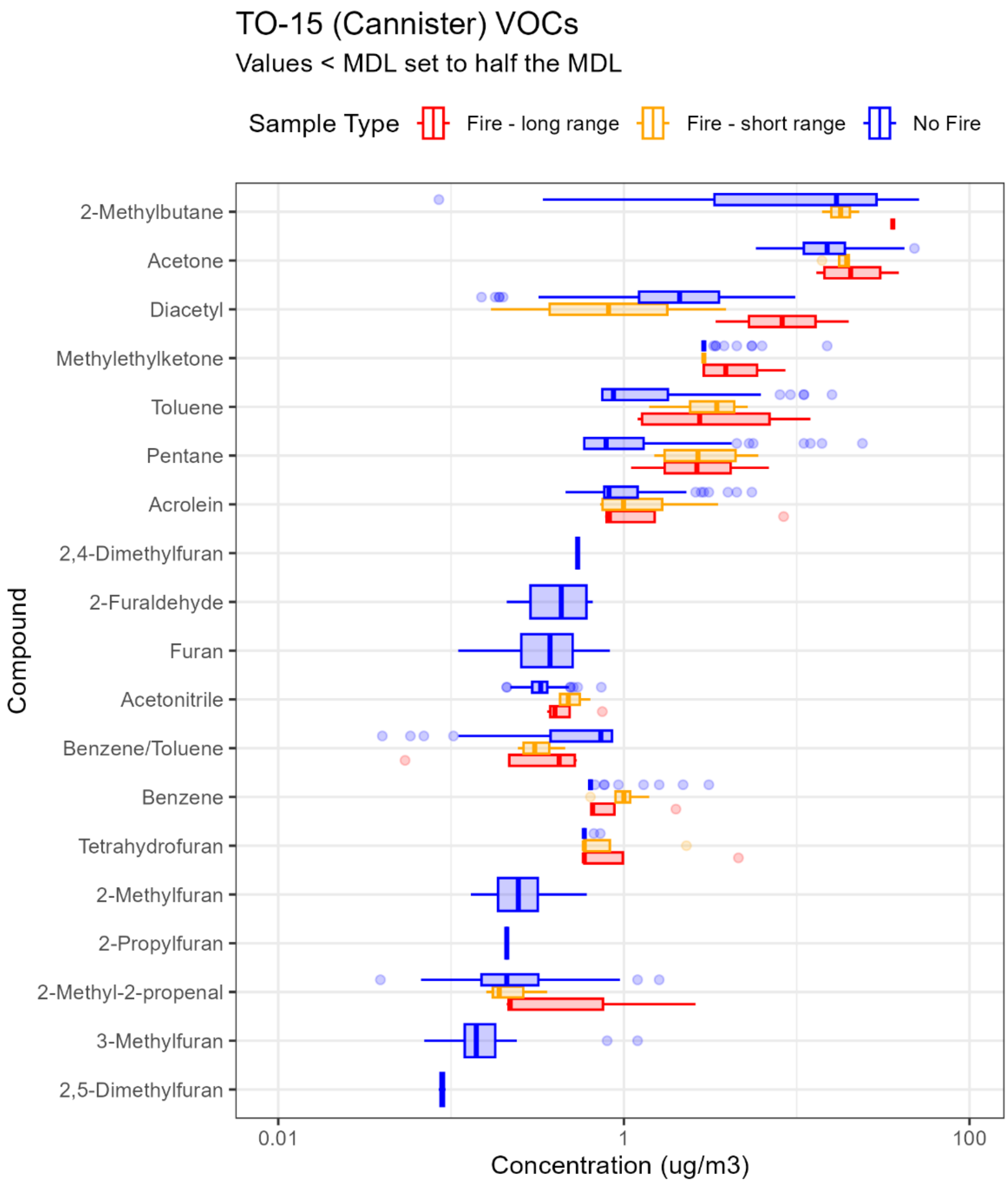

Figure 9. TO-15 data compounds ordered from highest concentration (top) to lowest concentration (bottom) separated by "No Fire" data shown in blue, "Fire – short range" data shown in yellow, and "Fire – long range" data shown in red.

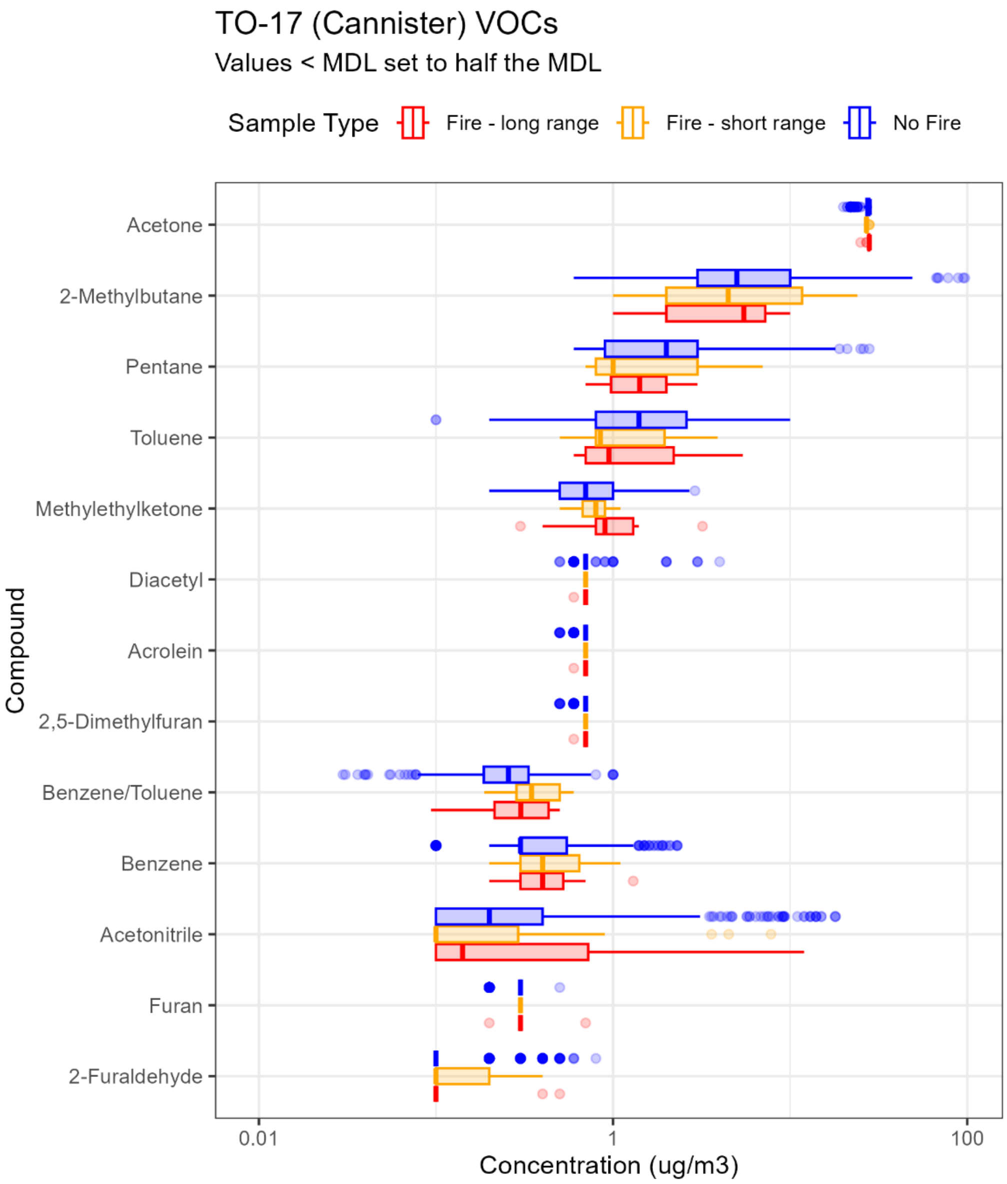

Figure 10. TO-17 data compounds ordered from highest concentration (top) to lowest concentration (bottom) separated by "No Fire" data shown in blue, "Fire – short range" data shown in yellow, and "Fire – long range" data shown in red.

3.6. Positive Matrix Factorization

While the comparison of individual compounds did not provide significant evidence of a fire regime due to too few fire events in 2023, we decided to run the EPA PMF model on the data to possibly identify regimes based on multiple compounds. The EPA PMF model reduces a large number of variables in complex measurement data sets into combinations of species called source factors, which function as fingerprints and can be combined with other information to assign potential sources. In the PMF analysis for TO-17 too few species had concentrations above the RL to be able to confidently assign identities to the output factors. For the TO-15 data, solutions ranging from 2 to 5 factors were considered. A 4-factor solution provided the most interpretable and reproducible solution. The factors were fire-dominant (Factor 1), anthropogenic (Factor 2), saturated hydrocarbon (Factor 3), and toluene-dominant (Factor 4) factors.

The resultant PMF factors are shown in **Figure 11**. The amount of each individual gas species in a given factor is shown in bars (left axis), while the percentage of each total species that contributes to each factor is shown by markers (right axis). For a given species, summing the percentage values over all four factors equals 100%.

Factor 1 (Fire Factor) is dominated by acetonitrile, benzene, tetrahydrofuran, 2-methyl furan, 3-methyl furan, and 2-furaldehyde. Of these, acetonitrile, tetrahydrofuran, 2-methylfuran, furan, 3-methylfuran, and 2-furaldehyde are oxygenated reactive VOCs indicative wildfire smoke (Akagi et al., 2011; Chandra et al., 2022). 88.7% of acetonitrile, 90.1% of tetrahydrofuran, 79.5% of 2-methylfuran, 53.7% of 3-methylfuran, and 77.3% of the total 2-Furaldehyde concentration reside in this Factor. Additionally, furan, also suggestive of wildfire smoke, is elevated (41.3%) in this Factor. Though benzene and acetone are also present in high proportions and are usually attributable to anthropogenic and other sources, these compounds can be enhanced during wildfire episodes. Benzene to toluene ratios can also provide an indication of wildfire smoke because the ratio of the two from anthropogenic sources is different than during a wildfire episode.

Factor 2 (Anthropogenic Factor) is characterized by anthropogenic sources, dominated by acrolein and 2-methyl-2-propenal (methacrolein), where 76.6% of acrolein and 54.5% of 2-methyl-2-propenal are contained in this factor. Acrolein and 2-methyl-2-propenal are produced during combustion of petroleum-based fuels and oils.[5] It is likely the source of this factor is vehicle exhaust-derived.

Factor 3 (Saturated Hydrocarbon Factor) is a saturated hydrocarbon factor dominated by pentane, and 2-methylbutane. Pentane is the most volatile liquid hydrocarbon and is found in petroleum (Grabato et al., 2024). While 2-methylbutane is a chemical component of gasoline, it has also been measured in combustion of pine wood (Galvin et al., 1999). It is possible that, similar to Factor 2, this factor is related to vehicle exhaust, however this could also be a factor influenced by both fire and anthropogenic sources. When a 3-factor solution was evaluated, this factor was dominated by pentane and 2-methylbutane was also present, suggesting that this factor is robust, despite the precise source being unclear.

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[5] https://www.epa.gov/sites/default/files/2016-08/documents/acrolein.pdf

Factor 4 (Toluene Factor) is dominated by toluene, and 76.6% of the toluene concentration resides in this factor. While toluene is present in wildfire smoke, it is unlikely that this factor is related to toluene from wildfire since no other VOC species are present in the factor.

Overall, PMF isolated a Fire Factor from the TO-15 data, despite the lower-than-average wildfire smoke concentrations influencing the sampling region in 2023. In future iterations of this work the same approach should be applied to both TO-15 and TO-17 data when available.

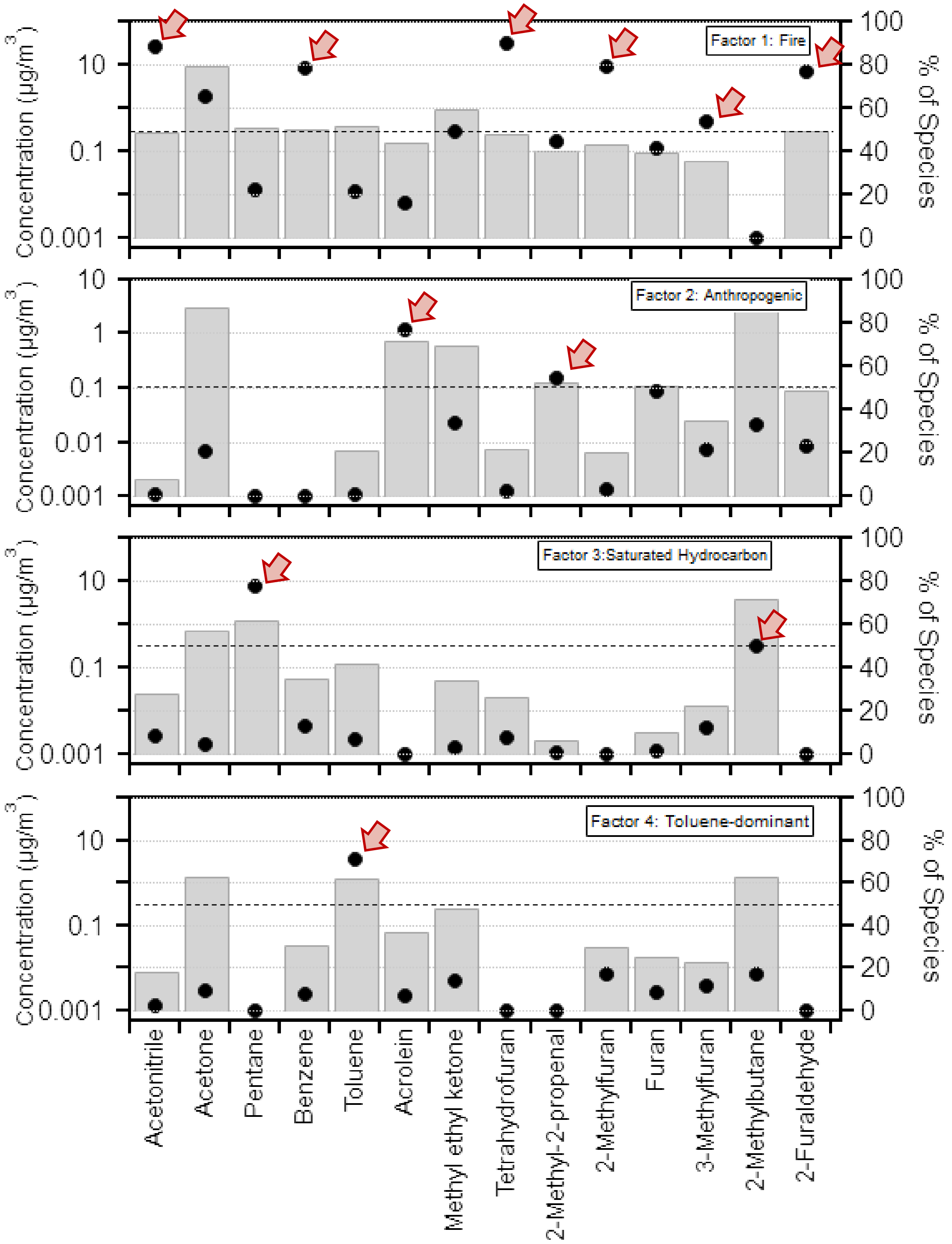

Figure 11. PMF profiles for the 5-factor TO-15 solution where bars (left axis) correspond to the concentration of each species, and the markers (right axis) represent the percentage of the species. Red arrows highlight the dominant species in each factor and black dashed lines are guides to show the 50 percent mark.

3.7. Other Datasets

3.7.1. Carbonyl Comparison

Carbonyl data were also collected during the sampling period on the 1-in-3-day schedule for PAMS (June – August). A comparison of fire versus non-fire regimes for the carbonyls collected is shown in Figure 12, similar to the VOC time series shown in Section 3.5. Since the PAMS collection period is only during June through August, the long-range fire was not sampled (fire occurred during September 2023). From Figure 12 we see that almost all of the carbonyls were enhanced during the near fire, but none were statically different between regimes. This, again, is a consequence of very few fires sampled during the 2023 field campaign. Comparison between the VOCs collected via the TO-15 or TO-17 method and Carbonyl time periods were too few to create statistics as well.

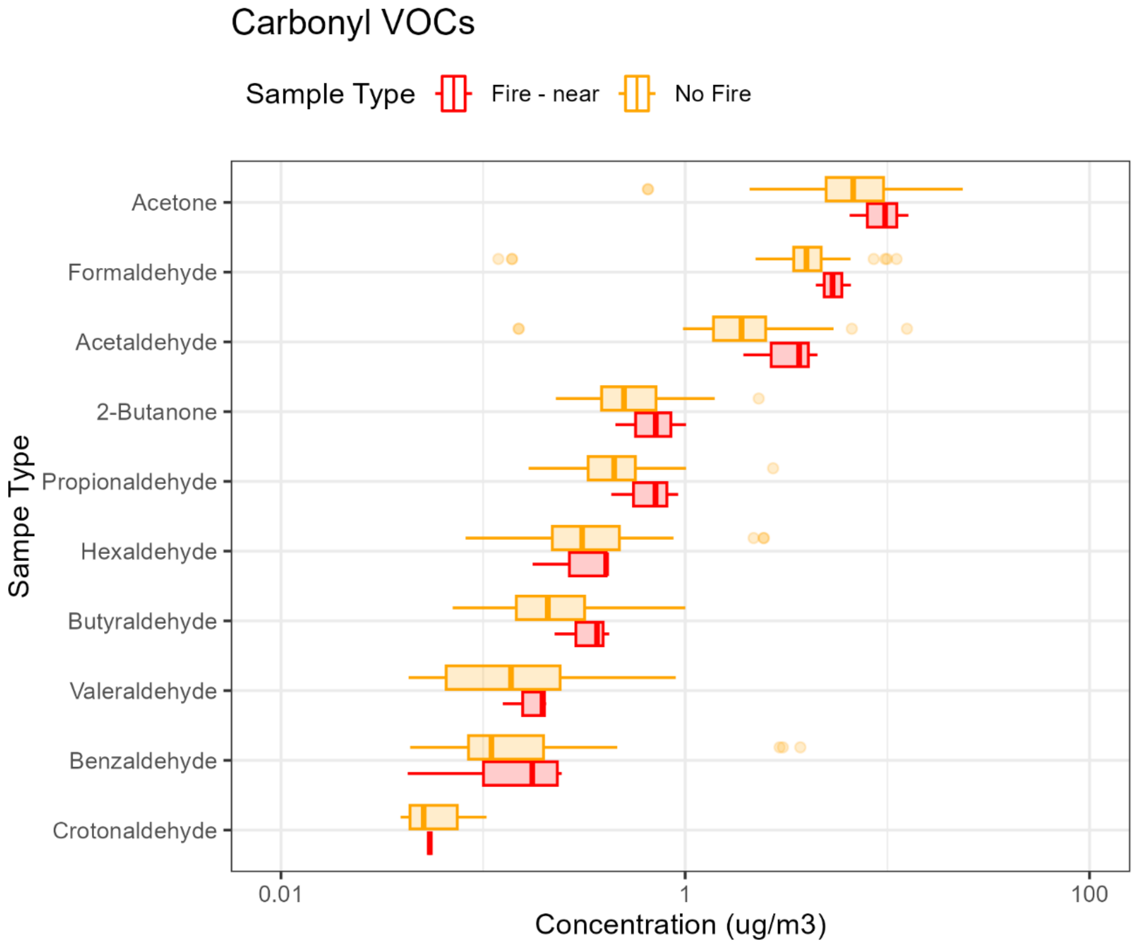

Figure 12. Carbonyl data compounds ordered from highest concentration (top) to lowest concentration (bottom) separated by "No Fire" data shown in yellow, "Fire – near" data shown in red.

3.7.2. DRI Data Comparison

Desert Research Institute (DRI) analyzed filter samples taken year-round in Clark County in 2023. We also examined this data and did not find a significant correlation between the two fire events in 2023 with any metals data. Another wildfire tracer, LVG, was also analyzed by DRI from the filter samples shown in Figure 13. All of the filter samples showed very low or 0 µg/m^3 concentrations of LVG during the summer sampling period.

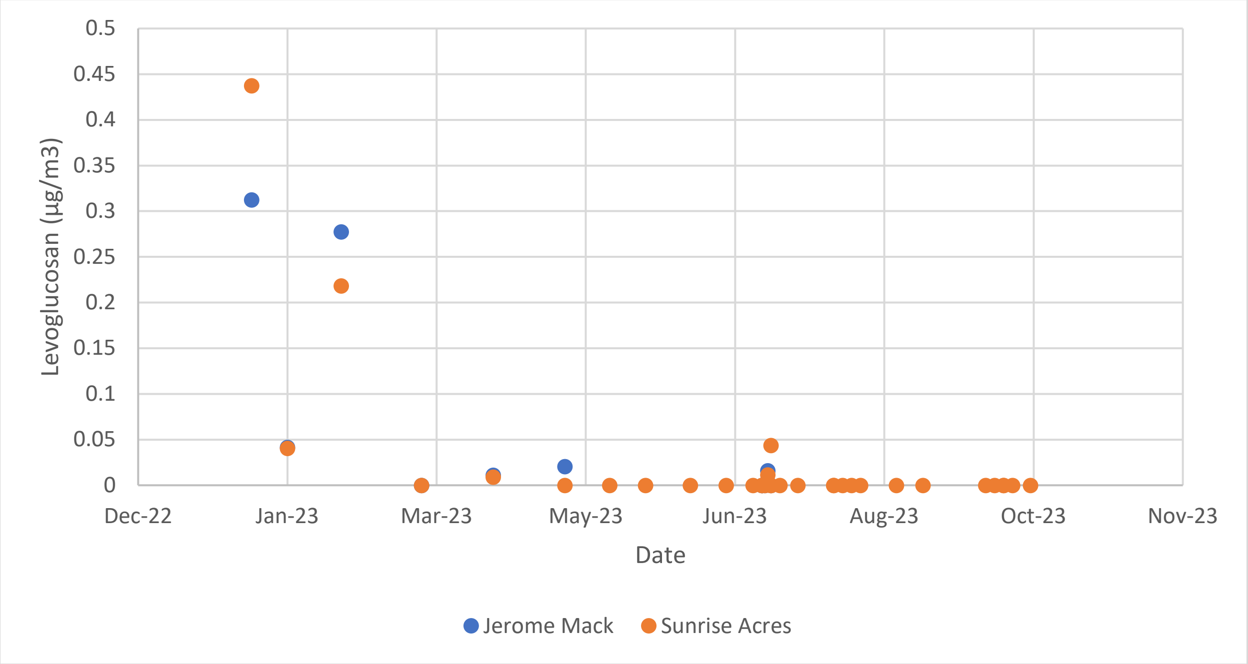

Figure 13. Levoglucosan concentrations from filter measurements analyzed by DRI during 2023. Data from Jerome Mack are shown in blue and data from Sunrise Acres are shown in orange.

3.8. TO-15 v TO-17

We also compared the TO-15 and TO-17 methods for high concentration and wildfire-specific compounds (i.e., Benzene, Toluene, and Acetonitrile). Correlation information shown in **Figure 14 through Figure 16** compare data only when the canister was sample concurrently with TD tubes and both had data for the respective compound above the RL. For benzene, we see that the correlation is consistent except for one outlier and TO-15 is consistently higher than TO-17 (despite the few data points). For toluene, the correlation is much more robust because there were many more data points above the RL. We see that TO-15 concentrations are consistently higher than TO-17 with high confidence (r^2 = 0.88). For acetonitrile, the correlation is poor due to fewer data points and three outliers. However, the rest of the data is clustered around the 1:1 line. We evaluated the TO-17 outliers that we classified as suspect data points, but could find no reason to invalidate them.

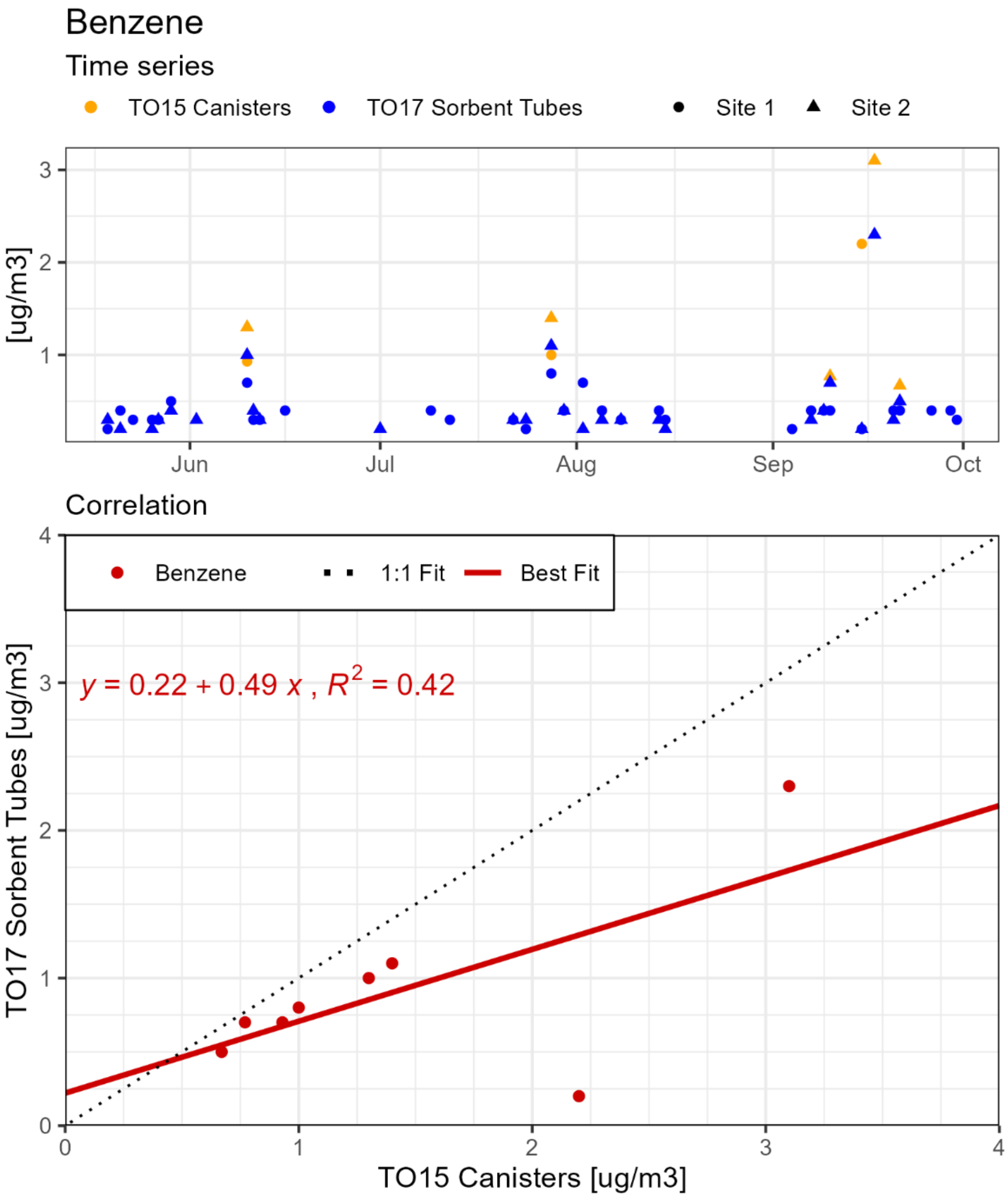

Figure 14. (Top) Time series of Benzene data from TO-15 Canisters (yellow) and TO-17 Sorbent tubes (blue) at Jerome Mack (Site 1 – circles) and Sunrise Acres (Site 2 – triangles). (Bottom) Correlation plot between TO-15 and TO-17 Benzene data with the red line showing the regression and dashed black line showing the 1:1 comparison.

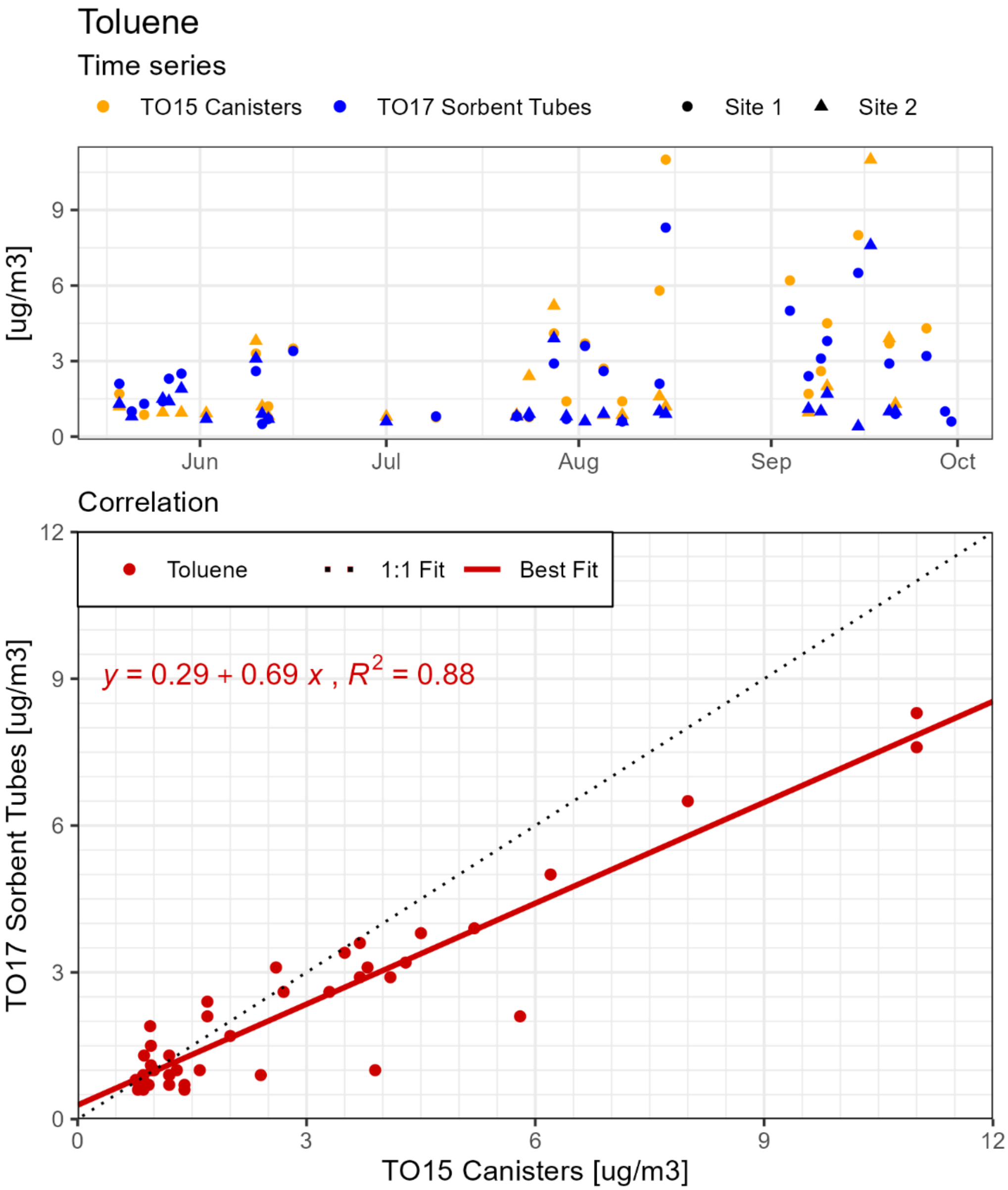

Figure 15. (Top) Time series of Toluene data from TO-15 Canisters (yellow) and TO-17 Sorbent tubes (blue) at Jerome Mack (Site 1 – circles) and Sunrise Acres (Site 2 – triangles). (Bottom) Correlation plot between TO-15 and TO-17 Toluene data with the red line showing the regression and dashed black line showing the 1:1 comparison.

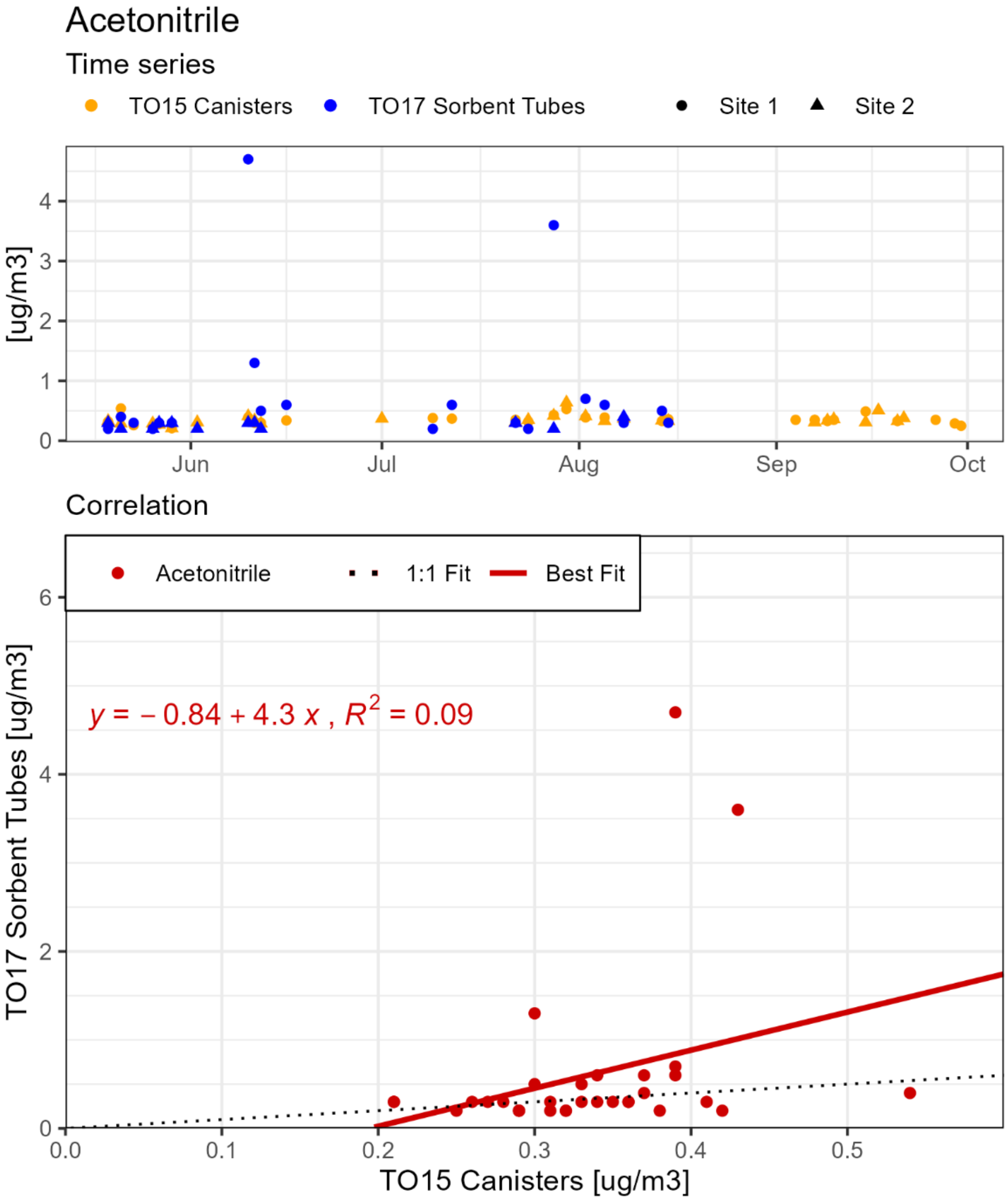

Figure 16. (Top) Time series of Acetonitrile data from TO-15 Canisters (yellow) and TO-17 Sorbent tubes (blue) at Jerome Mack (Site 1 – circles) and Sunrise Acres (Site 2 – triangles). (Bottom) Correlation plot between TO-15 and TO-17 Acetonitrile data with the red line showing the regression and dashed black line showing the 1:1 comparison.

4. Discussion

During this study period, only two wildfires were identified. The York Fire was the most impactful fire to affect Clark County during the 2023 study period due to its close proximity. Study data between July 28 and July 31 were identified as associated with this fire. Regional wildfire smoke from northern California fires affected Clark County during late September. Samples during September 21 and 22 were identified as being associated with this regional smoke event. Due to the small sample size of fires impacting Clark County in 2023, robust conclusions are not able to be drawn from this study. However, we summarize what we were able to find given the small sample size below.

We performed comparisons of individual wildfire and anthropogenic-tracer VOCs between the "Fire" and "No Fire" regimes. We found that for TO-15 data we saw expected wildfire tracers such as acetonitrile, benzene, and tetrahydrofuran were statistically enhanced. For the TO-17 data, we did not find the same enhancements, instead we found that wildfire compounds such as 2,5-dimethylfuran, the benzene/toluene ratio, and furan were enhanced instead, as expected. The lack of wildfire data in 2023 could cause the different method results between the individual compound "Fire" versus "No Fire" regimes.

For the comparison of short- and long-range transport to the non-fire regime, we again found conflicting results between the methods. For toluene and pentane, there was a positive enhancement from the short- and long-range fire regimes compared to the "No Fire" regime for TO-15, but the opposite enhancement for TO-17. For acetonitrile, the short-range fire concentration was significantly higher than the long-range fire and "No Fire" regime for TO-15, but TO-17 did not show an enhancement. However, for the TO-17, we saw an enhancement of the benzene/toluene ratio in the fire regime compared to the "No Fire" regime and benzene concentrations on their own are also higher in the fire versus no fire regime, as expected. Again, while some data shown are plausible given the difference in fuels, the toluene and pentane data are opposite when comparing TO-15 and TO-17 data. This suggests that there were too few "Fire" data points to provide significant results during 2023 despite some separation in regimes being statistically different.

However, when using the PMF analysis, we were able to go beyond the individual compound comparisons and pool more data together, which was critical when using a small dataset such as this one. The PMF analysis resulted in a 4-factor solution that provided the most interpretable and reproducible solution. The factors were fire-dominant (Factor 1), anthropogenic (Factor 2), saturated hydrocarbon (Factor 3), and toluene-dominant (Factor 4) factors. Within the Fire Factor the dominant species were acetonitrile, benzene, tetrahydrofuran, 2-methyl furan, 3-methyl furan, and 2-furaldehyde. Of these compounds, acetonitrile, tetrahydrofuran, 2-methylfuran, furan, 3-methylfuran, and 2-furaldehyde, which are oxygenated reactive VOCs indicative of wildfire smoke. 88.7% of acetonitrile, 90.1% of tetrahydrofuran, 79.5% of 2-methylfuran, 53.7% of 3-methylfuran, and 77.3% of the total 2-Furaldehyde concentration reside in the Fire Factor. Additionally, furan, also suggestive of wildfire smoke, is enhanced (41.3%) in the Fire Factor. All of these compounds are indicative of wildfire and this factor can be used to help identify wildfire smoke influenced days in future studies.

Since the 2023 wildfire sample size was small, we suggest running the PMF again with more wildfire events to confirm this result.

5. Conclusions

Overall, we find that due to the small sample size of wildfires (two wildfires: one nearby and one regional), robust conclusions are not able to be drawn based on the data from the 2023 sampling season. Although individual comparisons of wildfire and anthropogenic VOCs were not able to be significantly distinguished, PMF analysis did offer some insight into a wildfire-specific factor that can be used on future data to determine wildfire impacts. We suggest that this analysis be repeated with a larger dataset (i.e., a multi-year dataset, with significantly more fire information) to confirm the Fire Factor results. Additionally, continuing collection of TO-15 and TO-17 data in the LVV is critical for building a robust wildfire dataset. During the 2023 sampling season, we were able to collect enough background data to create statistics for each method and priority VOC compound. However, without additional wildfire data, this dataset cannot be completed. VOC concentrations from Summa Canister and TD tube studies need longer time periods of sampling (> 6-12 months) to identify trends. With more years of sampling and (likely) more wildfire data collected, we will be able to identify background/anthropogenic versus wildfire incidents with confidence.

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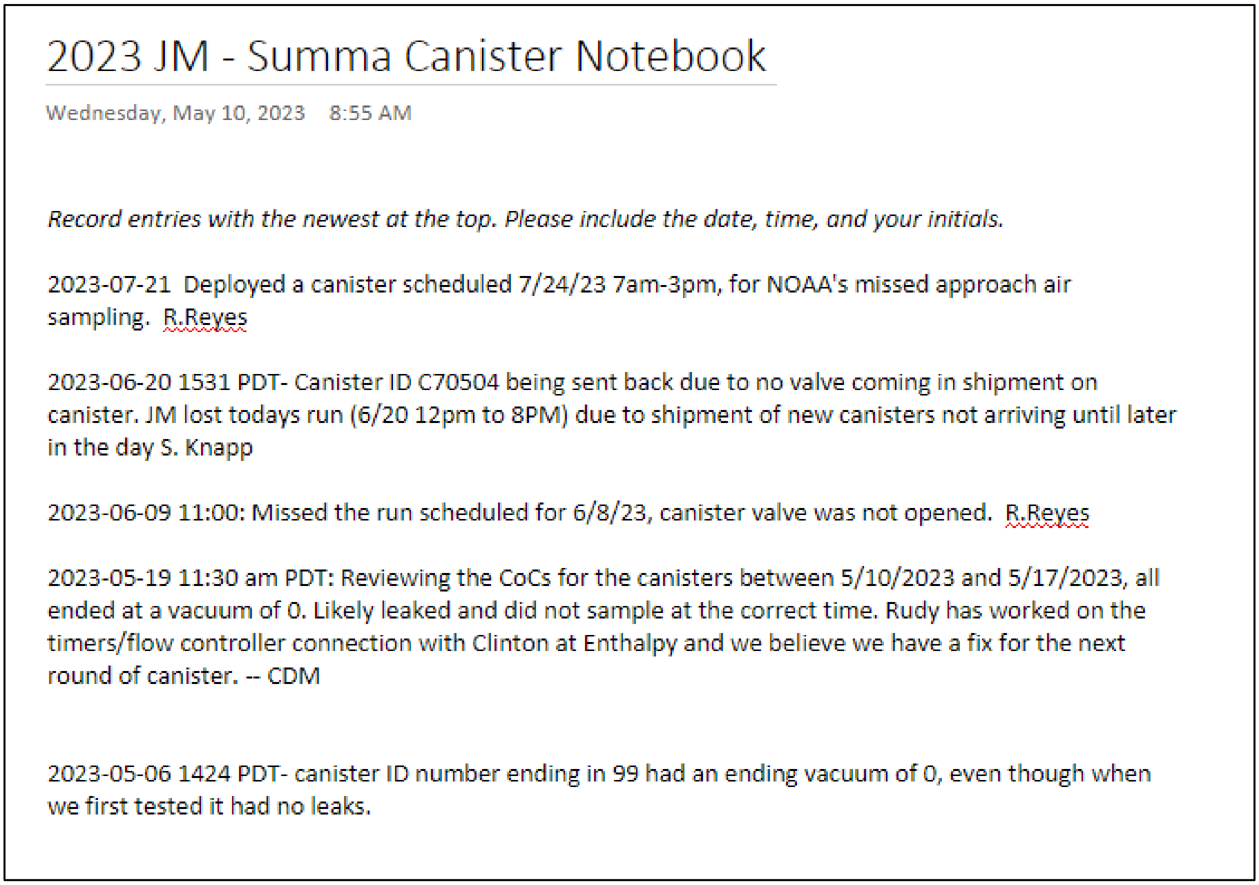
Appendix A – 2023 Field Notebooks

Jerome Mack Summa Canister Field Notebook:



2023 JM - Summa Canister Notebook

Wednesday, May 10, 2023 8:55 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

2023-07-21 Deployed a canister scheduled 7/24/23 7am-3pm, for NOAA's missed approach air sampling. R.Reyes

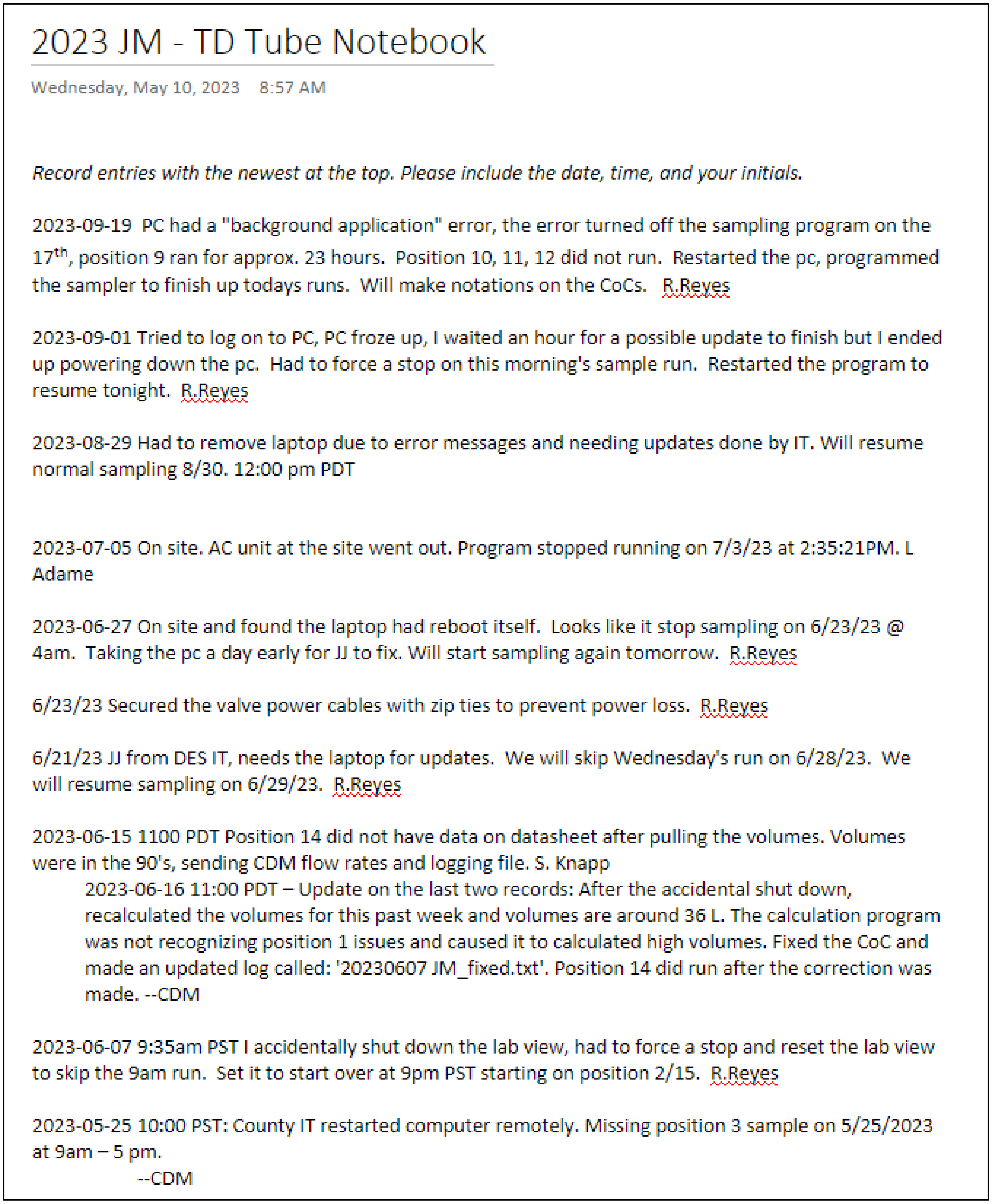
2023-06-20 1531 PDT- Canister ID C70504 being sent back due to no valve coming in shipment on canister. JM lost todays run (6/20 12pm to 8PM) due to shipment of new canisters not arriving until later in the day S. Knapp

2023-06-09 11:00: Missed the run scheduled for 6/8/23, canister valve was not opened. R.Reyes

2023-05-19 11:30 am PDT: Reviewing the CoCs for the canisters between 5/10/2023 and 5/17/2023, all ended at a vacuum of 0. Likely leaked and did not sample at the correct time. Rudy has worked on the timers/flow controller connection with Clinton at Enthalpy and we believe we have a fix for the next round of canister. -- CDM

2023-05-06 1424 PDT- canister ID number ending in 99 had an ending vacuum of 0, even though when we first tested it had no leaks.

Jerome Mack TD Tube Field Notebook:



2023 JM - TD Tube Notebook

Wednesday, May 10, 2023 8:57 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

2023-09-19 PC had a "background application" error, the error turned off the sampling program on the 17th, position 9 ran for approx. 23 hours. Position 10, 11, 12 did not run. Restarted the pc, programmed the sampler to finish up todays runs. Will make notations on the CoCs. R.Reyes

2023-09-01 Tried to log on to PC, PC froze up, I waited an hour for a possible update to finish but I ended up powering down the pc. Had to force a stop on this morning's sample run. Restarted the program to resume tonight. R.Reyes

2023-08-29 Had to remove laptop due to error messages and needing updates done by IT. Will resume normal sampling 8/30. 12:00 pm PDT

2023-07-05 On site. AC unit at the site went out. Program stopped running on 7/3/23 at 2:35:21PM. L Adame

2023-06-27 On site and found the laptop had reboot itself. Looks like it stop sampling on 6/23/23 @ 4am. Taking the pc a day early for JJ to fix. Will start sampling again tomorrow. R.Reyes

6/23/23 Secured the valve power cables with zip ties to prevent power loss. R.Reyes

6/21/23 JJ from DES IT, needs the laptop for updates. We will skip Wednesday's run on 6/28/23. We will resume sampling on 6/29/23. R.Reyes

2023-06-15 1100 PDT Position 14 did not have data on datasheet after pulling the volumes. Volumes were in the 90's, sending CDM flow rates and logging file. S. Knapp

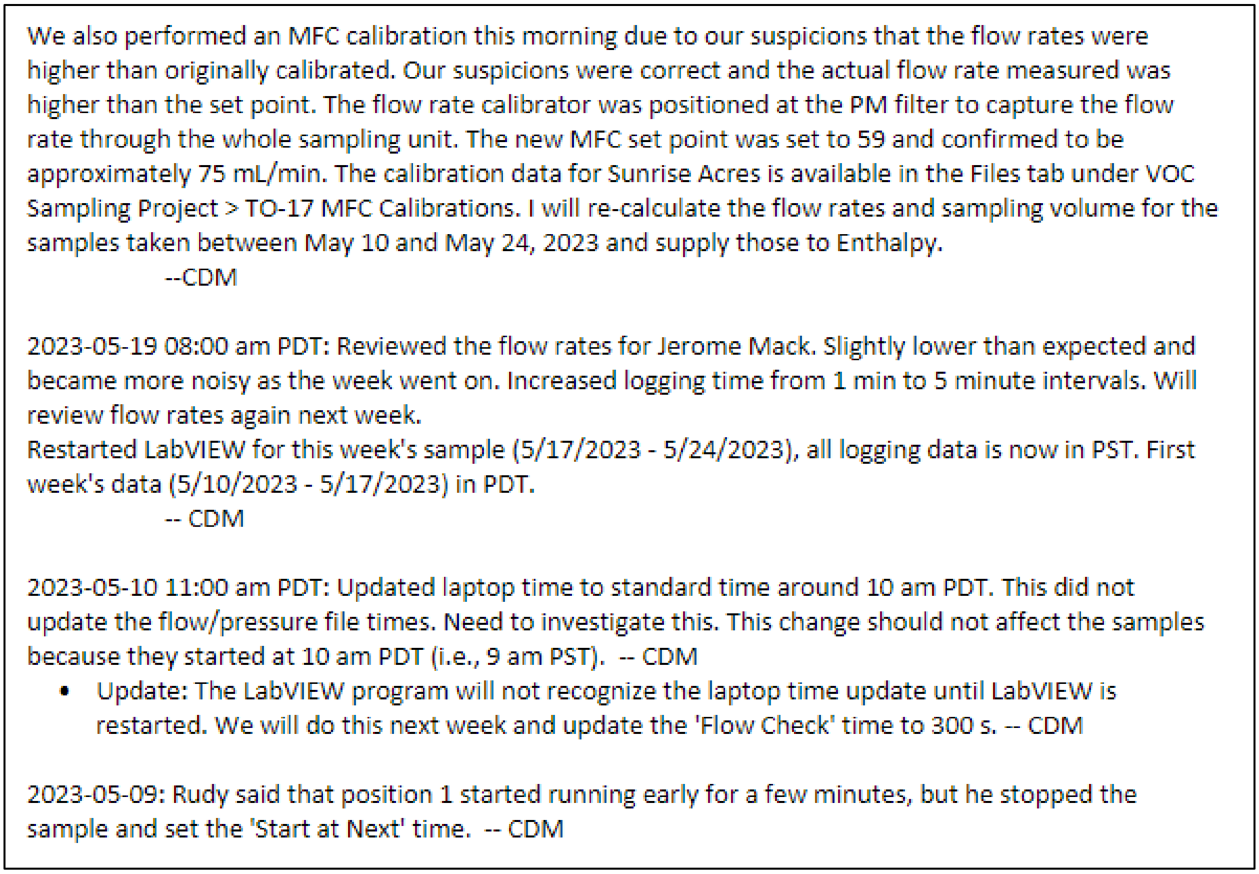
> 2023-06-16 11:00 PDT – Update on the last two records: After the accidental shut down, recalculated the volumes for this past week and volumes are around 36 L. The calculation program was not recognizing position 1 issues and caused it to calculated high volumes. Fixed the CoC and made an updated log called: '20230607 JM_fixed.txt'. Position 14 did run after the correction was made. --CDM

2023-06-07 9:35am PST I accidentally shut down the lab view, had to force a stop and reset the lab view to skip the 9am run. Set it to start over at 9pm PST starting on position 2/15. R.Reyes

2023-05-25 10:00 PST: County IT restarted computer remotely. Missing position 3 sample on 5/25/2023 at 9am – 5 pm.

--CDM

2023-05-24 9:00 PST: Sampling seemed to go smoothly for the week of 5/17 through 5/24, but there was some black/brown dust present on tube position #10 upon arrival to replace the tubes today. Pictures below show the dust on the fittings. Noted this with Enthalpy and we will add more quartz wool packing if this occurs again. Will note this in CoC. Rudy checked all the tubes and none were empty, likely that we lost a small amount of packing and that sample should be discarded.



We also performed an MFC calibration this morning due to our suspicions that the flow rates were higher than originally calibrated. Our suspicions were correct and the actual flow rate measured was higher than the set point. The flow rate calibrator was positioned at the PM filter to capture the flow rate through the whole sampling unit. The new MFC set point was set to 59 and confirmed to be approximately 75 mL/min. The calibration data for Sunrise Acres is available in the Files tab under VOC Sampling Project > TO-17 MFC Calibrations. I will re-calculate the flow rates and sampling volume for the samples taken between May 10 and May 24, 2023 and supply those to Enthalpy.

--CDM

2023-05-19 08:00 am PDT: Reviewed the flow rates for Jerome Mack. Slightly lower than expected and became more noisy as the week went on. Increased logging time from 1 min to 5 minute intervals. Will review flow rates again next week.
Restarted LabVIEW for this week's sample (5/17/2023 - 5/24/2023), all logging data is now in PST. First week's data (5/10/2023 - 5/17/2023) in PDT.

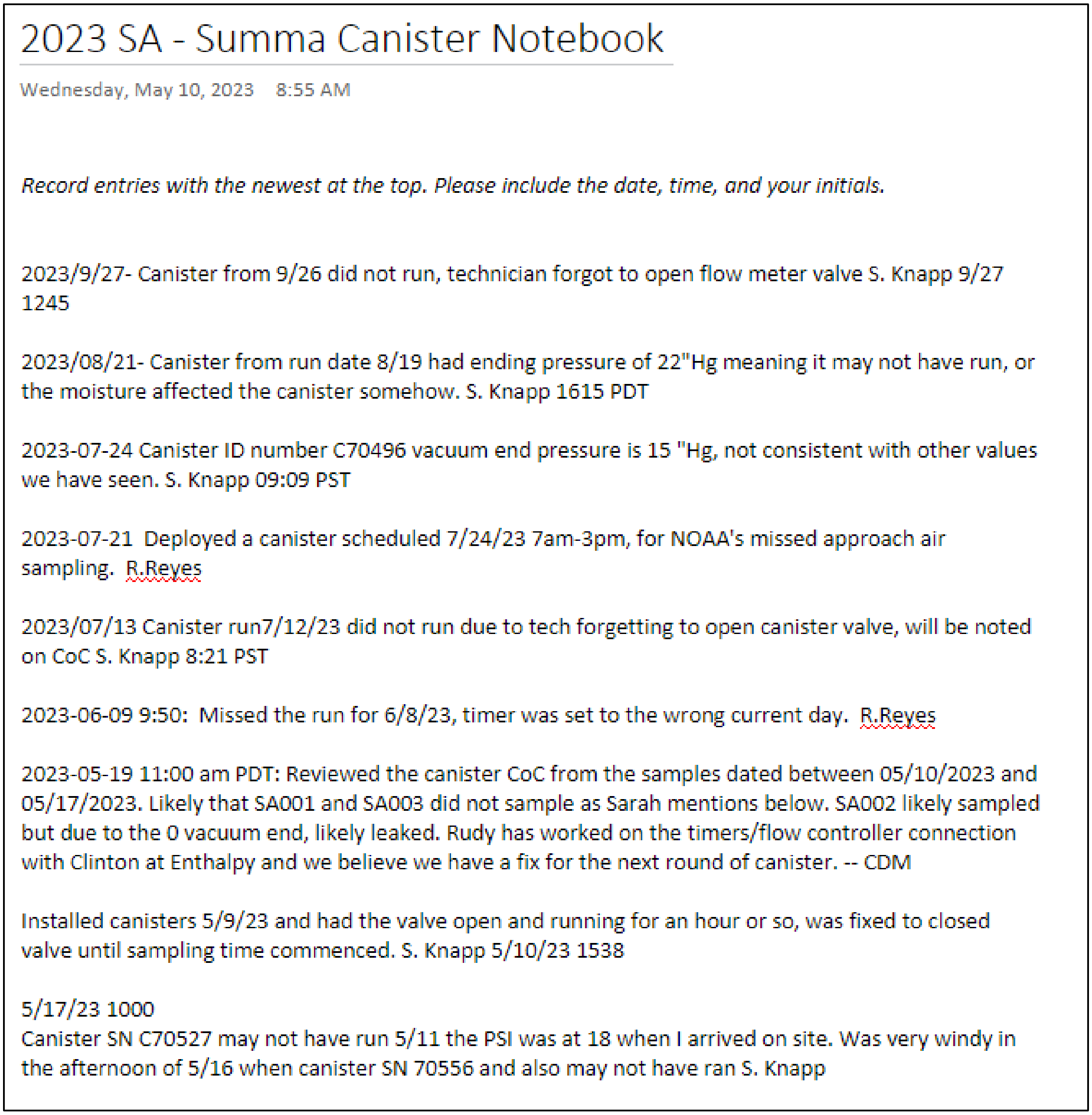
-- CDM

2023-05-10 11:00 am PDT: Updated laptop time to standard time around 10 am PDT. This did not update the flow/pressure file times. Need to investigate this. This change should not affect the samples because they started at 10 am PDT (i.e., 9 am PST). -- CDM

- Update: The LabVIEW program will not recognize the laptop time update until LabVIEW is restarted. We will do this next week and update the 'Flow Check' time to 300 s. -- CDM

2023-05-09: Rudy said that position 1 started running early for a few minutes, but he stopped the sample and set the 'Start at Next' time. -- CDM

Sunrise Acres Summa Canister Field Notebook:



2023 SA - Summa Canister Notebook

Wednesday, May 10, 2023 8:55 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

2023/9/27- Canister from 9/26 did not run, technician forgot to open flow meter valve S. Knapp 9/27 1245

2023/08/21- Canister from run date 8/19 had ending pressure of 22"Hg meaning it may not have run, or the moisture affected the canister somehow. S. Knapp 1615 PDT

2023-07-24 Canister ID number C70496 vacuum end pressure is 15 "Hg, not consistent with other values we have seen. S. Knapp 09:09 PST

2023-07-21 Deployed a canister scheduled 7/24/23 7am-3pm, for NOAA's missed approach air sampling. R.Reyes

2023/07/13 Canister run7/12/23 did not run due to tech forgetting to open canister valve, will be noted on CoC S. Knapp 8:21 PST

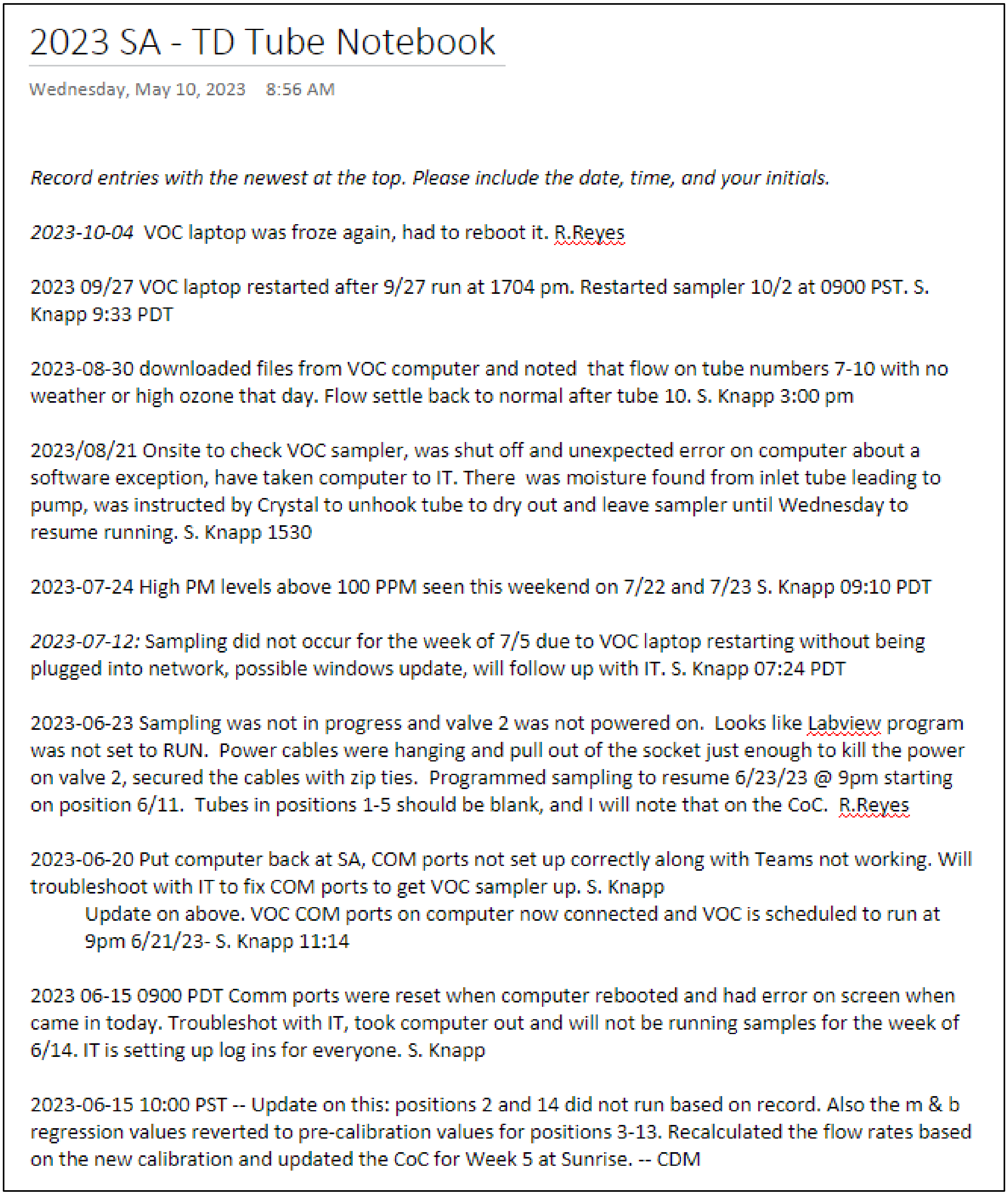
2023-06-09 9:50: Missed the run for 6/8/23, timer was set to the wrong current day. R.Reyes

2023-05-19 11:00 am PDT: Reviewed the canister CoC from the samples dated between 05/10/2023 and 05/17/2023. Likely that SA001 and SA003 did not sample as Sarah mentions below. SA002 likely sampled but due to the 0 vacuum end, likely leaked. Rudy has worked on the timers/flow controller connection with Clinton at Enthalpy and we believe we have a fix for the next round of canister. -- CDM

Installed canisters 5/9/23 and had the valve open and running for an hour or so, was fixed to closed valve until sampling time commenced. S. Knapp 5/10/23 1538

5/17/23 1000
Canister SN C70527 may not have run 5/11 the PSI was at 18 when I arrived on site. Was very windy in the afternoon of 5/16 when canister SN 70556 and also may not have ran S. Knapp

Sunrise Acres TD Tube Field Notebook:



2023 SA - TD Tube Notebook

Wednesday, May 10, 2023 8:56 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

2023-10-04 VOC laptop was froze again, had to reboot it. R.Reyes

2023 09/27 VOC laptop restarted after 9/27 run at 1704 pm. Restarted sampler 10/2 at 0900 PST. S. Knapp 9:33 PDT

2023-08-30 downloaded files from VOC computer and noted that flow on tube numbers 7-10 with no weather or high ozone that day. Flow settle back to normal after tube 10. S. Knapp 3:00 pm

2023/08/21 Onsite to check VOC sampler, was shut off and unexpected error on computer about a software exception, have taken computer to IT. There was moisture found from inlet tube leading to pump, was instructed by Crystal to unhook tube to dry out and leave sampler until Wednesday to resume running. S. Knapp 1530

2023-07-24 High PM levels above 100 PPM seen this weekend on 7/22 and 7/23 S. Knapp 09:10 PDT

2023-07-12: Sampling did not occur for the week of 7/5 due to VOC laptop restarting without being plugged into network, possible windows update, will follow up with IT. S. Knapp 07:24 PDT

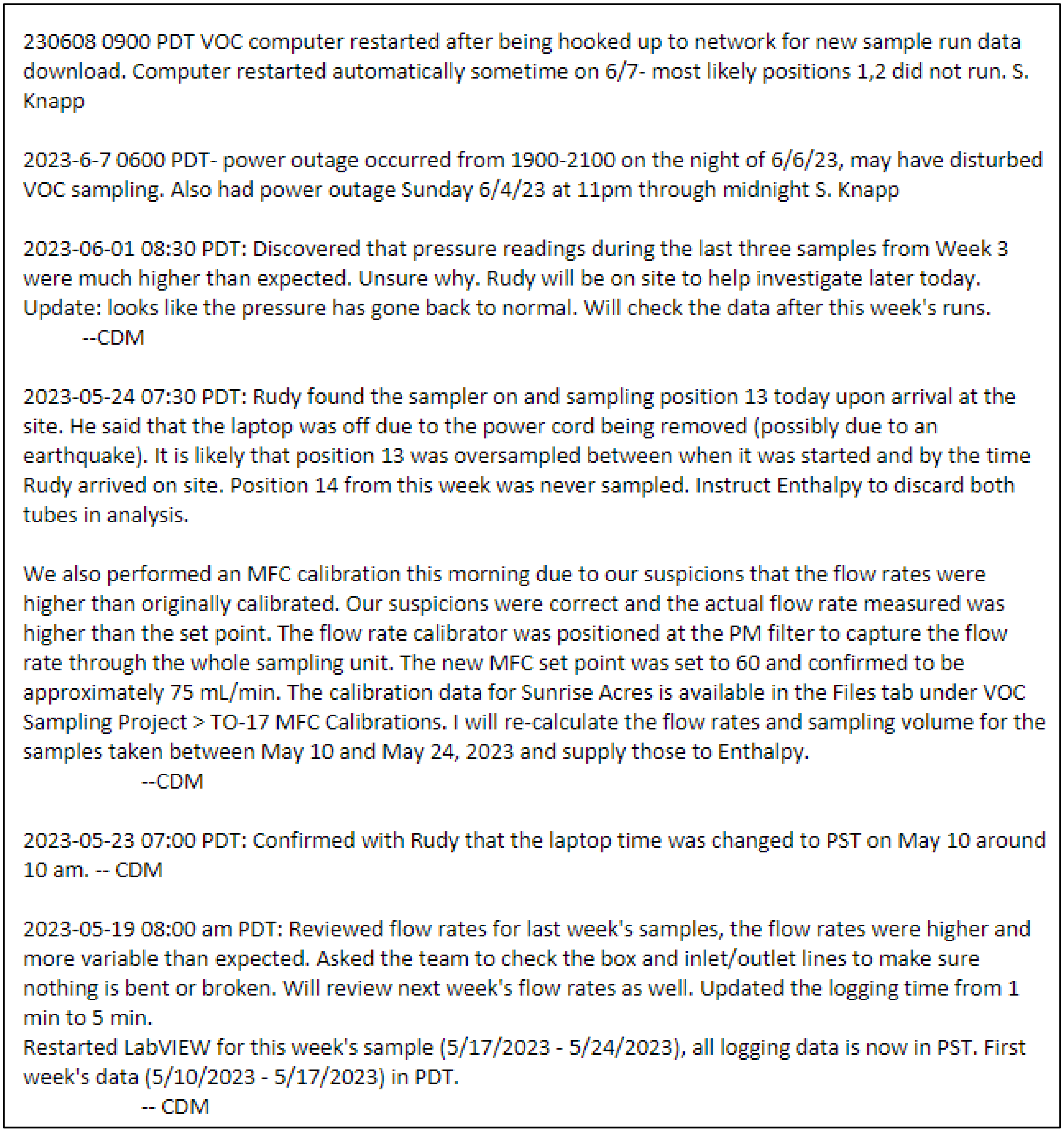
2023-06-23 Sampling was not in progress and valve 2 was not powered on. Looks like Labview program was not set to RUN. Power cables were hanging and pull out of the socket just enough to kill the power on valve 2, secured the cables with zip ties. Programmed sampling to resume 6/23/23 @ 9pm starting on position 6/11. Tubes in positions 1-5 should be blank, and I will note that on the CoC. R.Reyes

2023-06-20 Put computer back at SA, COM ports not set up correctly along with Teams not working. Will troubleshoot with IT to fix COM ports to get VOC sampler up. S. Knapp

> Update on above. VOC COM ports on computer now connected and VOC is scheduled to run at 9pm 6/21/23- S. Knapp 11:14

2023 06-15 0900 PDT Comm ports were reset when computer rebooted and had error on screen when came in today. Troubleshot with IT, took computer out and will not be running samples for the week of 6/14. IT is setting up log ins for everyone. S. Knapp

2023-06-15 10:00 PST -- Update on this: positions 2 and 14 did not run based on record. Also the m & b regression values reverted to pre-calibration values for positions 3-13. Recalculated the flow rates based on the new calibration and updated the CoC for Week 5 at Sunrise. -- CDM



230608 0900 PDT VOC computer restarted after being hooked up to network for new sample run data download. Computer restarted automatically sometime on 6/7- most likely positions 1,2 did not run. S. Knapp

2023-6-7 0600 PDT- power outage occurred from 1900-2100 on the night of 6/6/23, may have disturbed VOC sampling. Also had power outage Sunday 6/4/23 at 11pm through midnight S. Knapp

2023-06-01 08:30 PDT: Discovered that pressure readings during the last three samples from Week 3 were much higher than expected. Unsure why. Rudy will be on site to help investigate later today. Update: looks like the pressure has gone back to normal. Will check the data after this week's runs.
--CDM

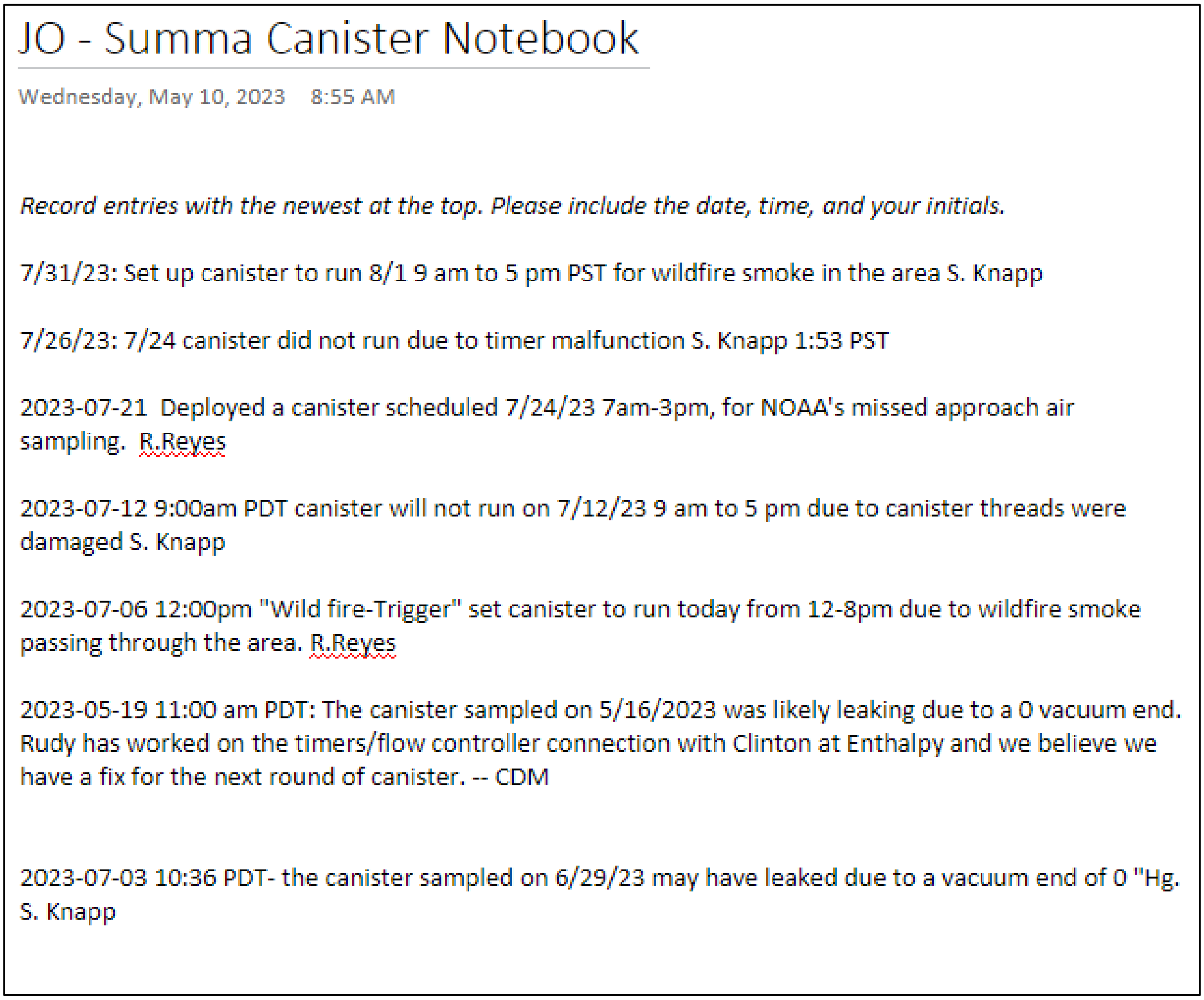
2023-05-24 07:30 PDT: Rudy found the sampler on and sampling position 13 today upon arrival at the site. He said that the laptop was off due to the power cord being removed (possibly due to an earthquake). It is likely that position 13 was oversampled between when it was started and by the time Rudy arrived on site. Position 14 from this week was never sampled. Instruct Enthalpy to discard both tubes in analysis.

We also performed an MFC calibration this morning due to our suspicions that the flow rates were higher than originally calibrated. Our suspicions were correct and the actual flow rate measured was higher than the set point. The flow rate calibrator was positioned at the PM filter to capture the flow rate through the whole sampling unit. The new MFC set point was set to 60 and confirmed to be approximately 75 mL/min. The calibration data for Sunrise Acres is available in the Files tab under VOC Sampling Project > TO-17 MFC Calibrations. I will re-calculate the flow rates and sampling volume for the samples taken between May 10 and May 24, 2023 and supply those to Enthalpy.
--CDM

2023-05-23 07:00 PDT: Confirmed with Rudy that the laptop time was changed to PST on May 10 around 10 am. -- CDM

2023-05-19 08:00 am PDT: Reviewed flow rates for last week's samples, the flow rates were higher and more variable than expected. Asked the team to check the box and inlet/outlet lines to make sure nothing is bent or broken. Will review next week's flow rates as well. Updated the logging time from 1 min to 5 min.
Restarted LabVIEW for this week's sample (5/17/2023 - 5/24/2023), all logging data is now in PST. First week's data (5/10/2023 - 5/17/2023) in PDT.
-- CDM

Joe Neal Summa Canister Field Notebook:



JO - Summa Canister Notebook

Wednesday, May 10, 2023 8:55 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

7/31/23: Set up canister to run 8/1 9 am to 5 pm PST for wildfire smoke in the area S. Knapp

7/26/23: 7/24 canister did not run due to timer malfunction S. Knapp 1:53 PST

2023-07-21 Deployed a canister scheduled 7/24/23 7am-3pm, for NOAA's missed approach air sampling. R.Reyes

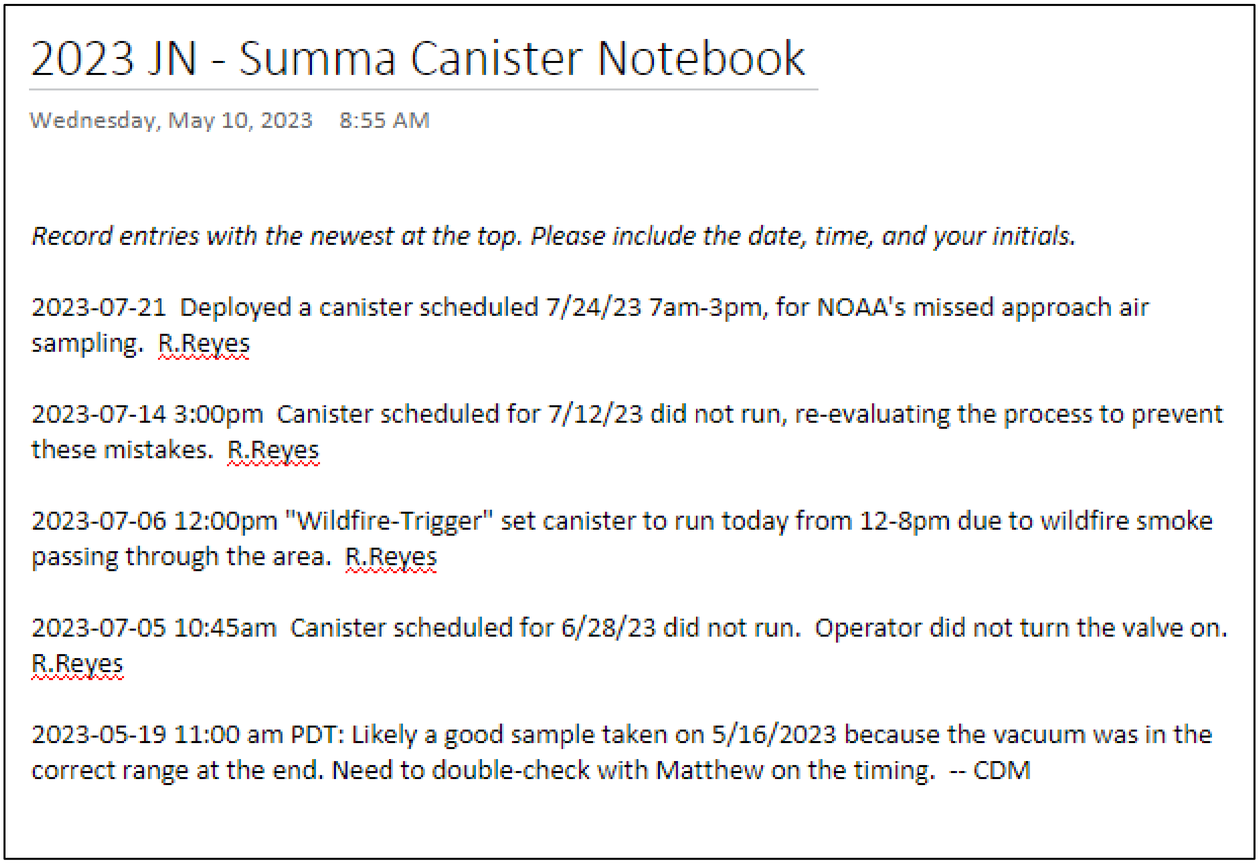
2023-07-12 9:00am PDT canister will not run on 7/12/23 9 am to 5 pm due to canister threads were damaged S. Knapp

2023-07-06 12:00pm "Wild fire-Trigger" set canister to run today from 12-8pm due to wildfire smoke passing through the area. R.Reyes

2023-05-19 11:00 am PDT: The canister sampled on 5/16/2023 was likely leaking due to a 0 vacuum end. Rudy has worked on the timers/flow controller connection with Clinton at Enthalpy and we believe we have a fix for the next round of canister. -- CDM

2023-07-03 10:36 PDT- the canister sampled on 6/29/23 may have leaked due to a vacuum end of 0 "Hg. S. Knapp

Jean Summa Canister Field Notebook:



2023 JN - Summa Canister Notebook

Wednesday, May 10, 2023 8:55 AM

Record entries with the newest at the top. Please include the date, time, and your initials.

2023-07-21 Deployed a canister scheduled 7/24/23 7am-3pm, for NOAA's missed approach air sampling. R.Reyes

2023-07-14 3:00pm Canister scheduled for 7/12/23 did not run, re-evaluating the process to prevent these mistakes. R.Reyes

2023-07-06 12:00pm "Wildfire-Trigger" set canister to run today from 12-8pm due to wildfire smoke passing through the area. R.Reyes

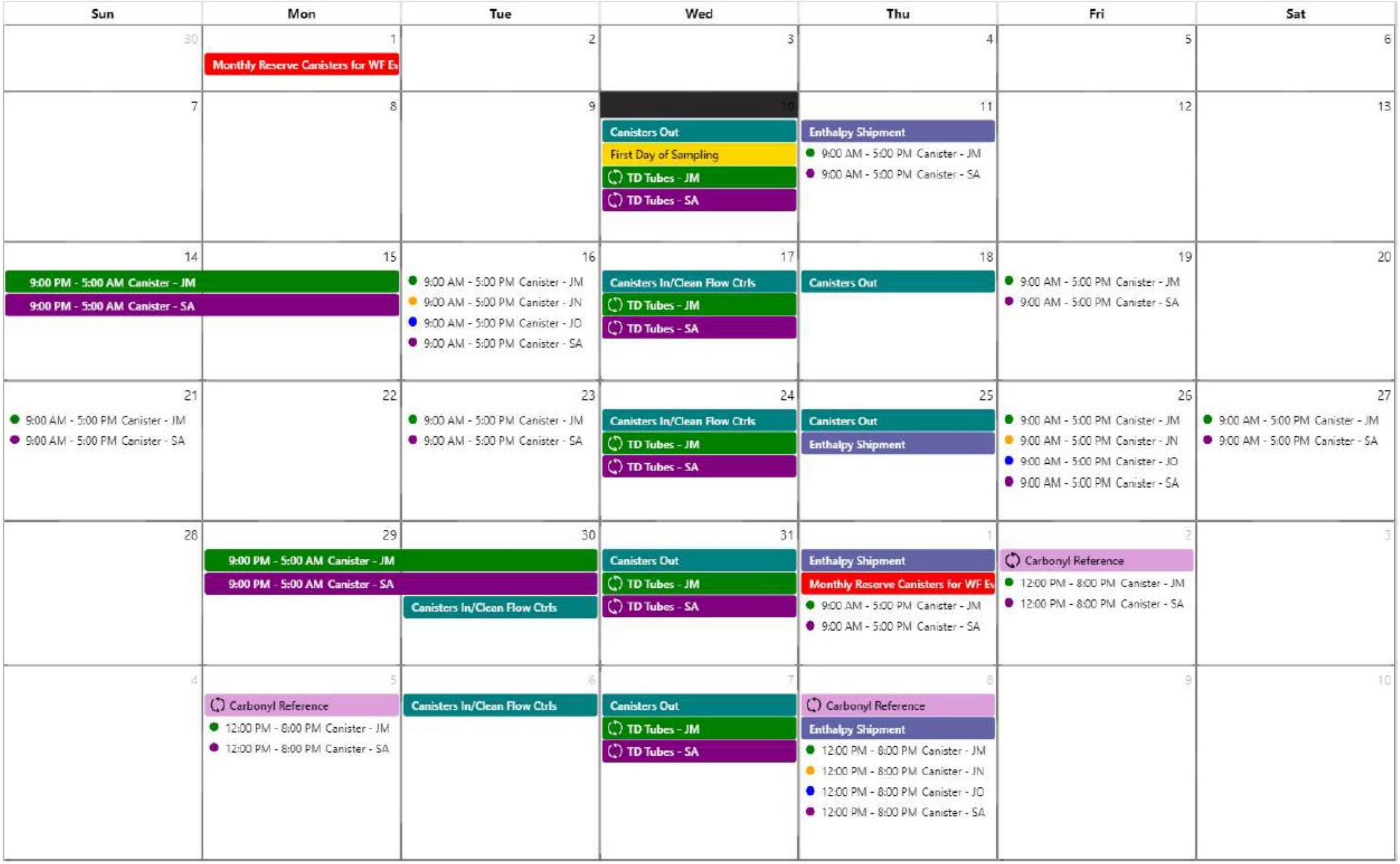
2023-07-05 10:45am Canister scheduled for 6/28/23 did not run. Operator did not turn the valve on. R.Reyes

2023-05-19 11:00 am PDT: Likely a good sample taken on 5/16/2023 because the vacuum was in the correct range at the end. Need to double-check with Matthew on the timing. -- CDM

Appendix B – 2023 Sampling Schedule

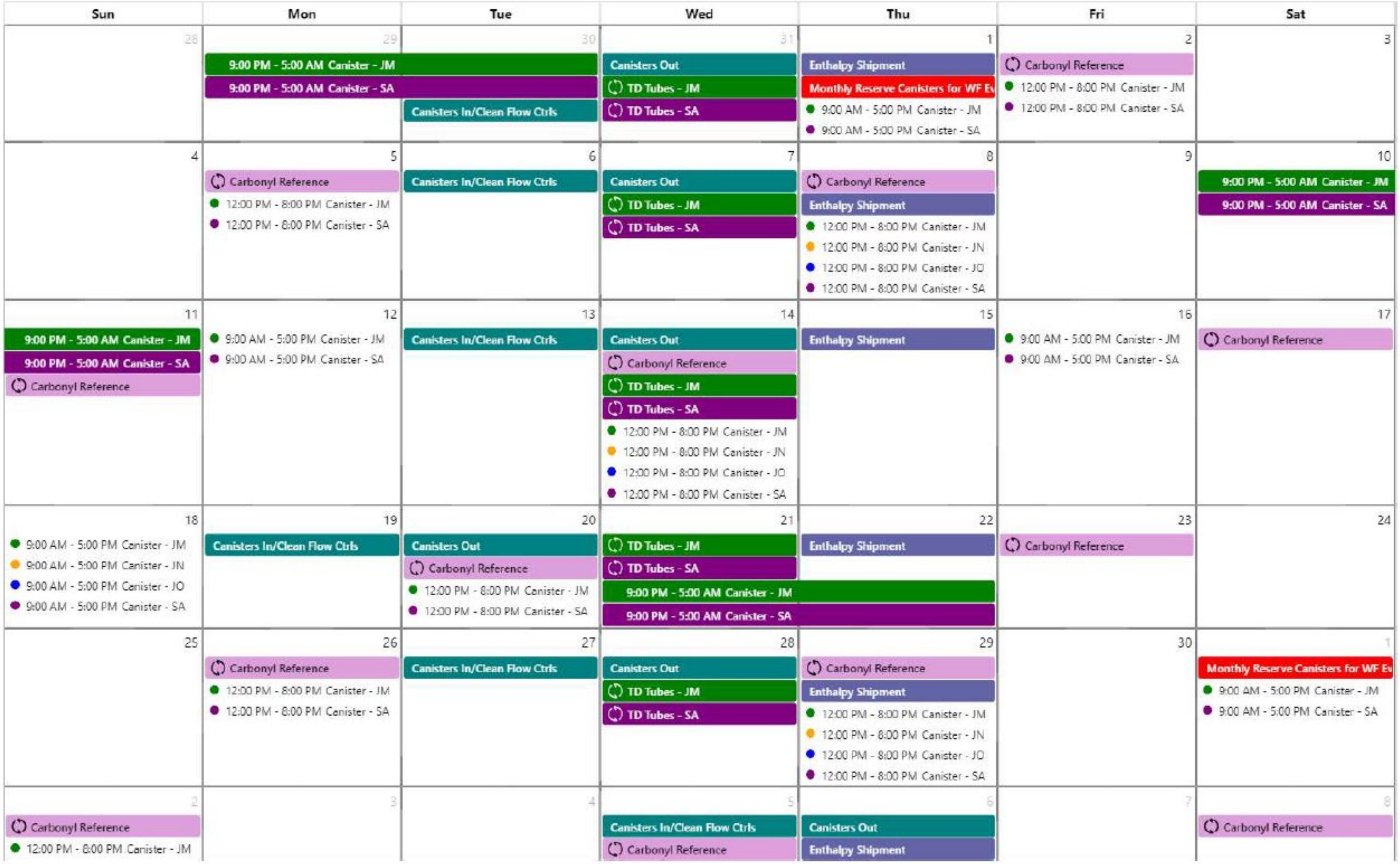
Regularly scheduled Summa Canister samples are shown for May – September 2023 in this Appendix. TD tube samples were collected twice daily with samples collected on a weekly basis as shown in the calendars.

Calendar Pro - May 2023



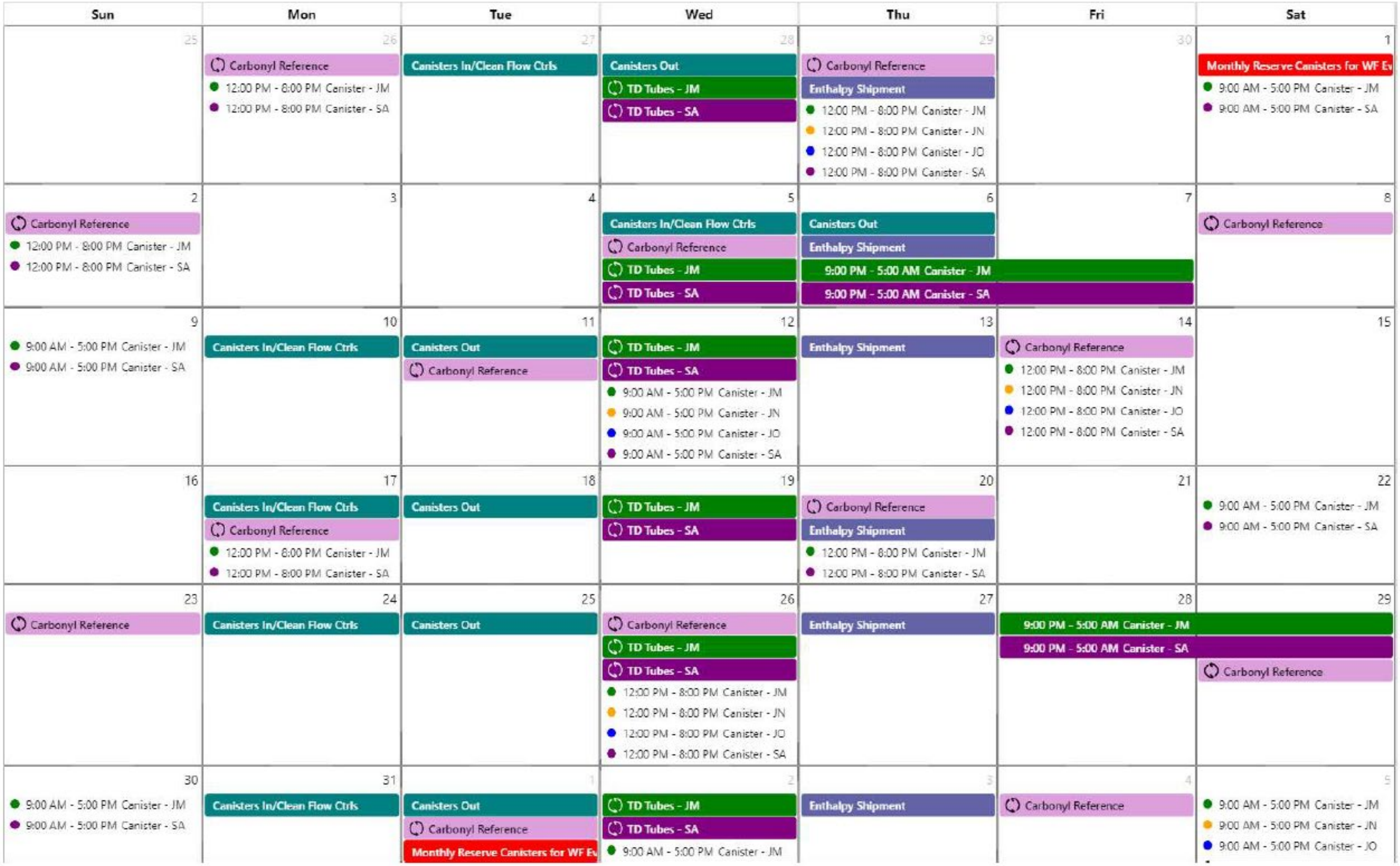
Sun	Mon	Tue	Wed	Thu	Fri	Sat
30	1 Monthly Reserve Canisters for WF Ev	2	3	4	5	6
7	8	9	10 Canisters Out First Day of Sampling TD Tubes - JM TD Tubes - SA	11 Enthalpy Shipment ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	12	13
14 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	15	16 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	17 Canisters In/Clean Flow Ctrls TD Tubes - JM TD Tubes - SA	18 Canisters Out	19 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	20
21 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	22	23 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	24 Canisters In/Clean Flow Ctrls TD Tubes - JM TD Tubes - SA	25 Canisters Out Enthalpy Shipment	26 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	27 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA
28	29 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	30 Canisters In/Clean Flow Ctrls	31 Canisters Out TD Tubes - JM TD Tubes - SA	1 Enthalpy Shipment Monthly Reserve Canisters for WF Ev ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	2 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	3
4	5 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	6 Canisters In/Clean Flow Ctrls	7 Canisters Out TD Tubes - JM TD Tubes - SA	8 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	9	10

Calendar Pro - June 2023



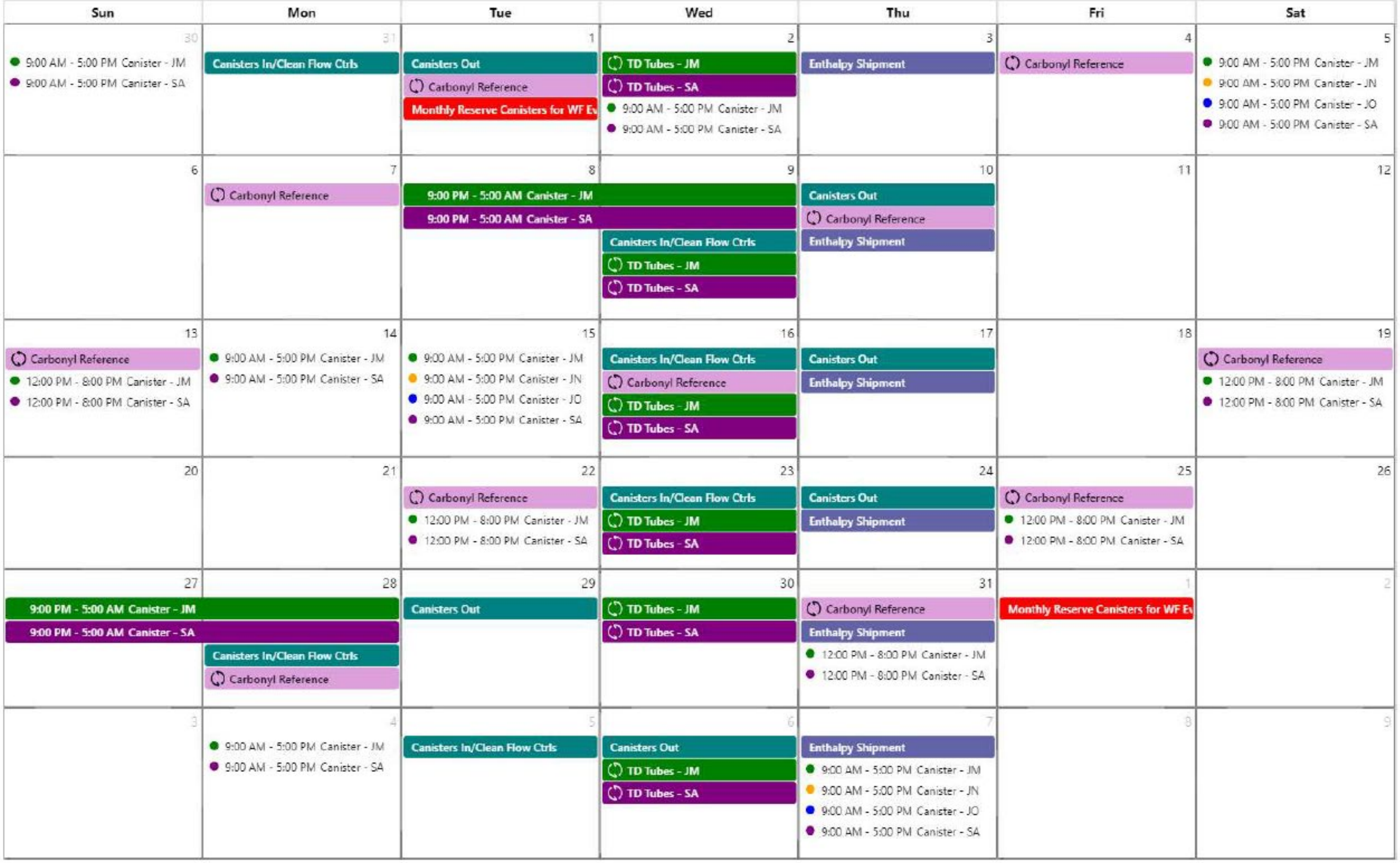
Sun	Mon	Tue	Wed	Thu	Fri	Sat
28	29 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	30 Canisters In/Clean Flow Ctrls	31 Canisters Out TD Tubes - JM TD Tubes - SA	1 Enthalpy Shipment Monthly Reserve Canisters for WF E ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	2 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	3
4	5 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	6 Canisters In/Clean Flow Ctrls	7 Canisters Out TD Tubes - JM TD Tubes - SA	8 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	9	10 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA
11 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA Carbonyl Reference	12 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	13 Canisters In/Clean Flow Ctrls	14 Canisters Out Carbonyl Reference TD Tubes - JM TD Tubes - SA ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	15 Enthalpy Shipment	16 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	17 Carbonyl Reference
18 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	19 Canisters In/Clean Flow Ctrls	20 Canisters Out Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	21 TD Tubes - JM TD Tubes - SA 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	22 Enthalpy Shipment	23 Carbonyl Reference	24
25	26 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	27 Canisters In/Clean Flow Ctrls	28 Canisters Out TD Tubes - JM TD Tubes - SA	29 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	30	1 Monthly Reserve Canisters for WF E ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA
2 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM	3	4	5 Canisters In/Clean Flow Ctrls Carbonyl Reference	6 Canisters Out Enthalpy Shipment	7	8 Carbonyl Reference

Calendar Pro - July 2023



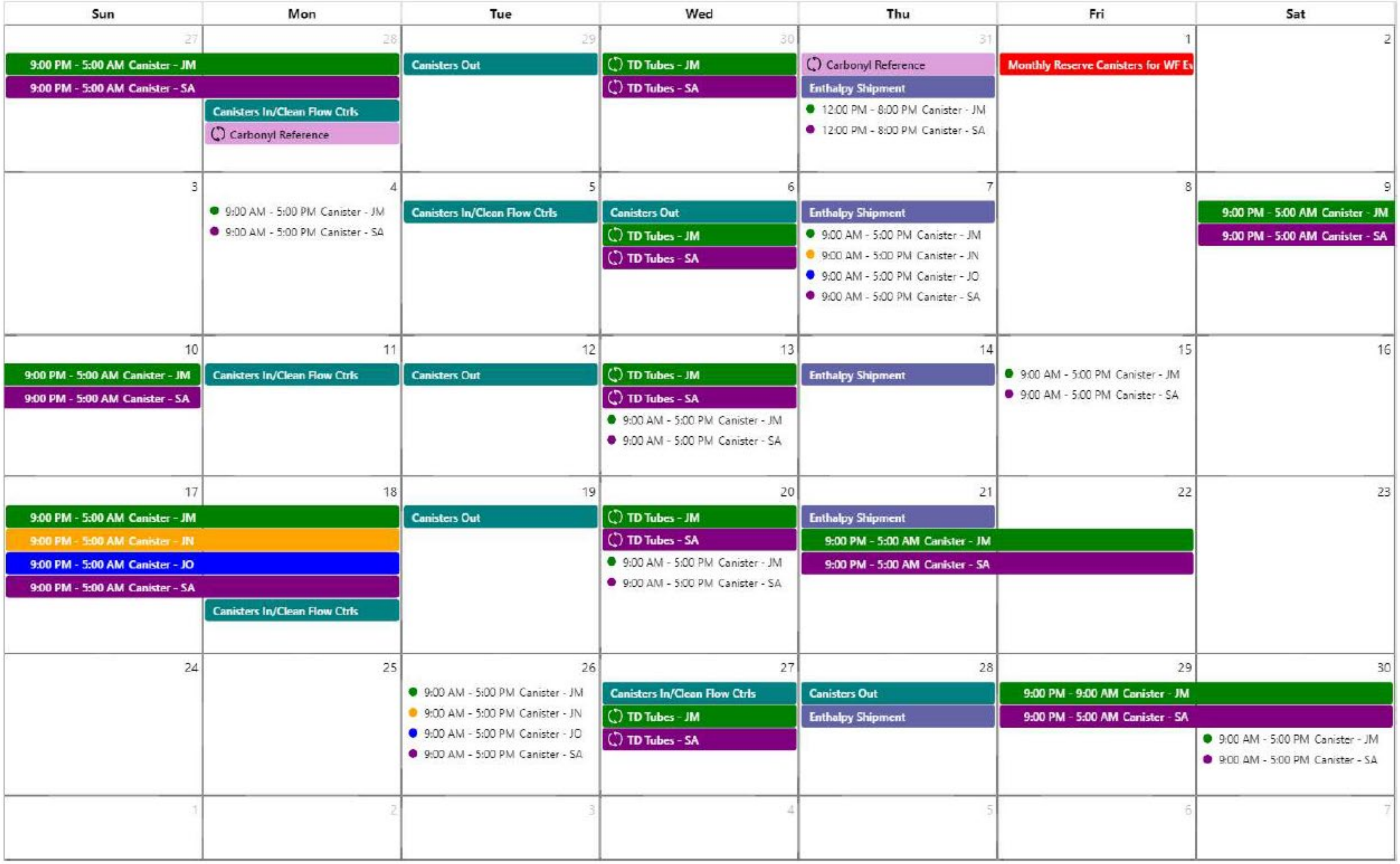
Sun	Mon	Tue	Wed	Thu	Fri	Sat
25	26 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	27 Canisters In/Clean Flow Ctrls	28 Canisters Out TD Tubes - JM TD Tubes - SA	29 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	30	1 Monthly Reserve Canisters for WF Ev ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA
2 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	3	4	5 Canisters In/Clean Flow Ctrls Carbonyl Reference TD Tubes - JM TD Tubes - SA	6 Canisters Out Enthalpy Shipment 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	7	8 Carbonyl Reference
9 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	10 Canisters In/Clean Flow Ctrls	11 Canisters Out Carbonyl Reference	12 TD Tubes - JM TD Tubes - SA ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	13 Enthalpy Shipment	14 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	15
16	17 Canisters In/Clean Flow Ctrls Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	18 Canisters Out	19 TD Tubes - JM TD Tubes - SA	20 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	21	22 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA
23 Carbonyl Reference	24 Canisters In/Clean Flow Ctrls	25 Canisters Out	26 Carbonyl Reference TD Tubes - JM TD Tubes - SA ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - JN ● 12:00 PM - 8:00 PM Canister - JO ● 12:00 PM - 8:00 PM Canister - SA	27 Enthalpy Shipment	28 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	29 Carbonyl Reference
30 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	31 Canisters In/Clean Flow Ctrls	1 Canisters Out Carbonyl Reference Monthly Reserve Canisters for WF Ev	2 TD Tubes - JM TD Tubes - SA ● 9:00 AM - 5:00 PM Canister - JM	3 Enthalpy Shipment	4 Carbonyl Reference	5 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO

Calendar Pro - August 2023



Sun	Mon	Tue	Wed	Thu	Fri	Sat
30 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	31 Canisters In/Clean Flow Ctrls	1 Canisters Out Carbonyl Reference Monthly Reserve Canisters for WF Ev	2 TD Tubes - JM TD Tubes - SA ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	3 Enthalpy Shipment	4 Carbonyl Reference	5 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA
6	7 Carbonyl Reference	8 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	9 Canisters In/Clean Flow Ctrls TD Tubes - JM TD Tubes - SA	10 Canisters Out Carbonyl Reference Enthalpy Shipment	11	12
13 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	14 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	15 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	16 Canisters In/Clean Flow Ctrls Carbonyl Reference TD Tubes - JM TD Tubes - SA	17 Canisters Out Enthalpy Shipment	18	19 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA
20	21	22 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	23 Canisters In/Clean Flow Ctrls TD Tubes - JM TD Tubes - SA	24 Canisters Out Enthalpy Shipment	25 Carbonyl Reference ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	26
27 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	28 Canisters In/Clean Flow Ctrls Carbonyl Reference	29 Canisters Out	30 TD Tubes - JM TD Tubes - SA	31 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	1 Monthly Reserve Canisters for WF Ev	2
3	4 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	5 Canisters In/Clean Flow Ctrls	6 Canisters Out TD Tubes - JM TD Tubes - SA	7 Enthalpy Shipment ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	8	9

Calendar Pro - September 2023



Sun	Mon	Tue	Wed	Thu	Fri	Sat
27 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	28 Canisters In/Clean Flow Ctrls Carbonyl Reference	29 Canisters Out	30 TD Tubes - JM TD Tubes - SA	31 Carbonyl Reference Enthalpy Shipment ● 12:00 PM - 8:00 PM Canister - JM ● 12:00 PM - 8:00 PM Canister - SA	1 Monthly Reserve Canisters for WF E	2
3	4 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	5 Canisters In/Clean Flow Ctrls	6 Canisters Out TD Tubes - JM TD Tubes - SA	7 Enthalpy Shipment ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	8	9 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA
10 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	11 Canisters In/Clean Flow Ctrls	12 Canisters Out	13 TD Tubes - JM TD Tubes - SA ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	14 Enthalpy Shipment	15 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	16
17 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - JN 9:00 PM - 5:00 AM Canister - JO 9:00 PM - 5:00 AM Canister - SA	18 Canisters In/Clean Flow Ctrls	19 Canisters Out	20 TD Tubes - JM TD Tubes - SA ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA	21 Enthalpy Shipment 9:00 PM - 5:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	22	23
24	25	26 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - JN ● 9:00 AM - 5:00 PM Canister - JO ● 9:00 AM - 5:00 PM Canister - SA	27 Canisters In/Clean Flow Ctrls TD Tubes - JM TD Tubes - SA	28 Canisters Out Enthalpy Shipment	29 9:00 PM - 9:00 AM Canister - JM 9:00 PM - 5:00 AM Canister - SA	30 ● 9:00 AM - 5:00 PM Canister - JM ● 9:00 AM - 5:00 PM Canister - SA
1	2	3	4	5	6	7

Appendix C – QC Data Assignments

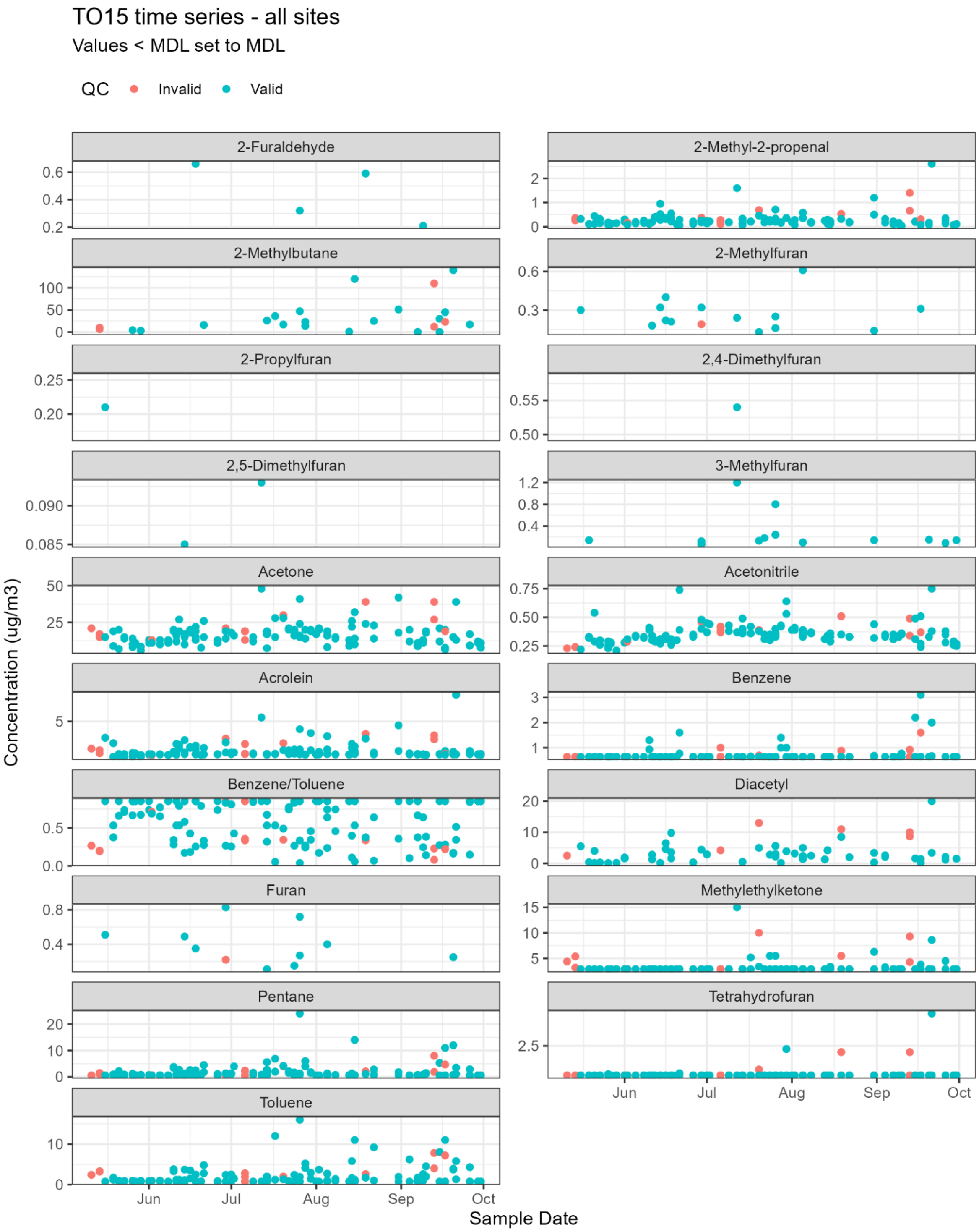


Figure 17. Time series of all TO-15 species. Concentrations reported as "< MDL" were set to the MDL. Color indicates the quality code assigned to the data. Invalid data were not included in the statistical analysis.

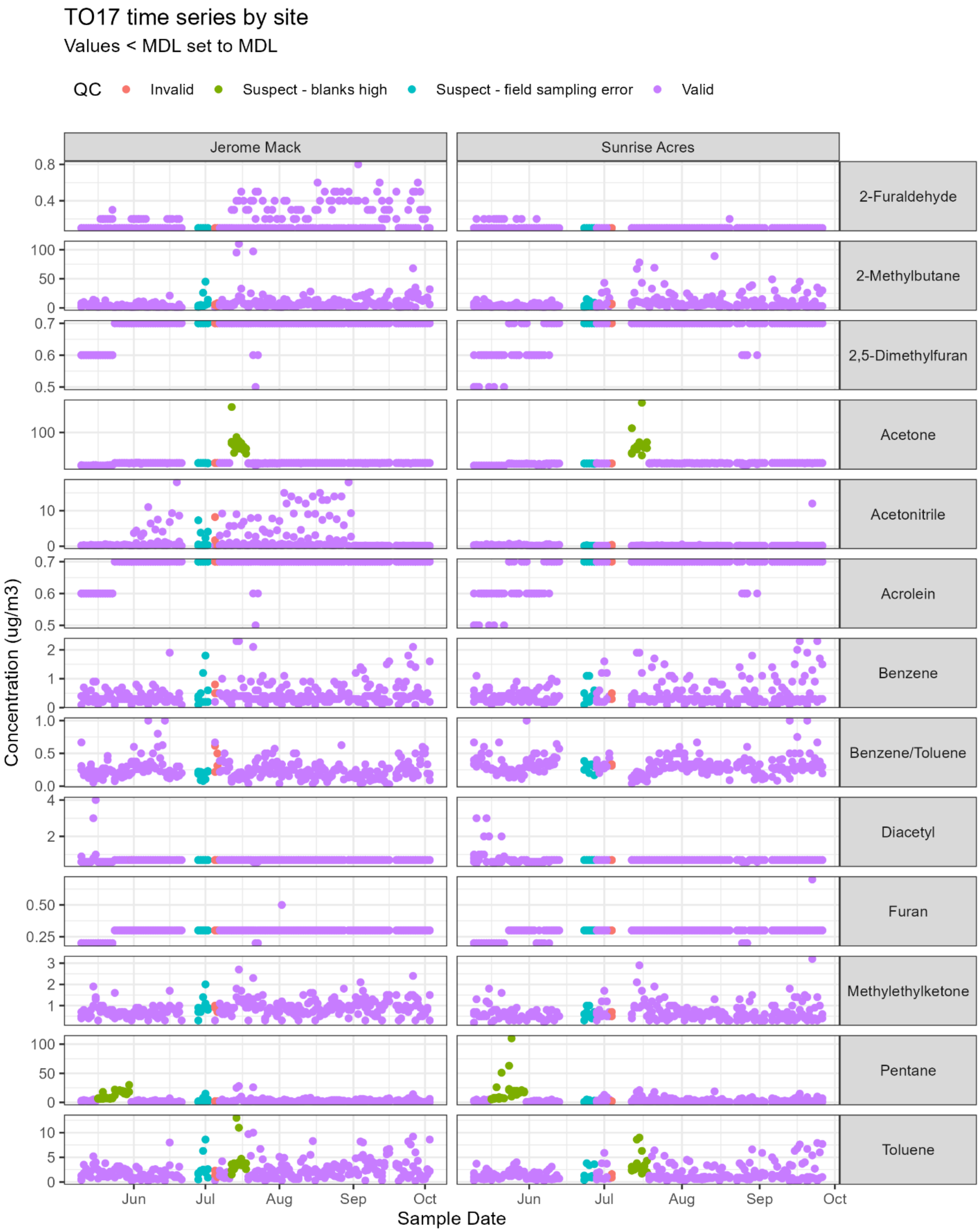


Figure 18. Time series of all TO-17 species by site. Concentrations reported as "< MDL" were set to the MDL. Color indicates the quality code assigned to the data. Suspect and invalid data were not included in the statistical analysis.