Developments in O3 Compliance Monitoring

OTC/MANE-VU Online Stakeholder Meeting
Friday, September 21, 2018

Mobile Sources Committee
Modeling Committee
Stationary & Area Sources Committee
Technical Support Committee

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O3 Inlet Height Gradient

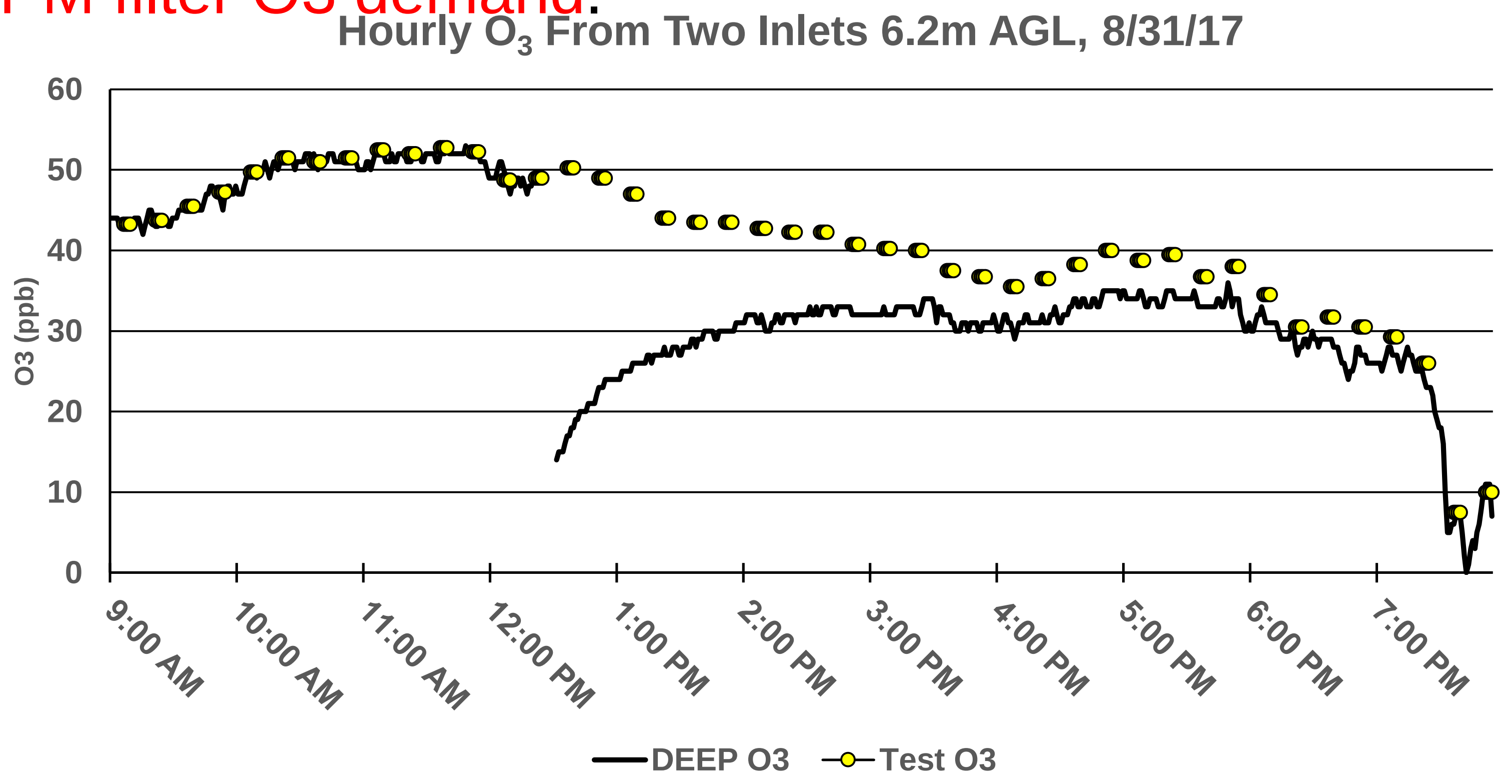
- *Lowering monitor inlet heights where feasible to 2 meters, within the allowable 2-15 meter range, better represents population outdoor exposure and improves O_3 NAAQS compliance.*

- *Substantial 2017 near-ground 10-2 meter ozone MDA8 gradients averaged about 5 ppb at Westport, CT over the 15 highest days (with an hourly value ≥ 70 ppb) and the 4^{th} highest 6.2-2 meter MDA8 gradient was 4 ppb, where conventional FEMs (T400) and conventional wisdom hold unstable daytime conditions should prevent such gradients.*

2m, 6.2m & 10m Inlet Height Array and 10m Ambient T/RH Sensors

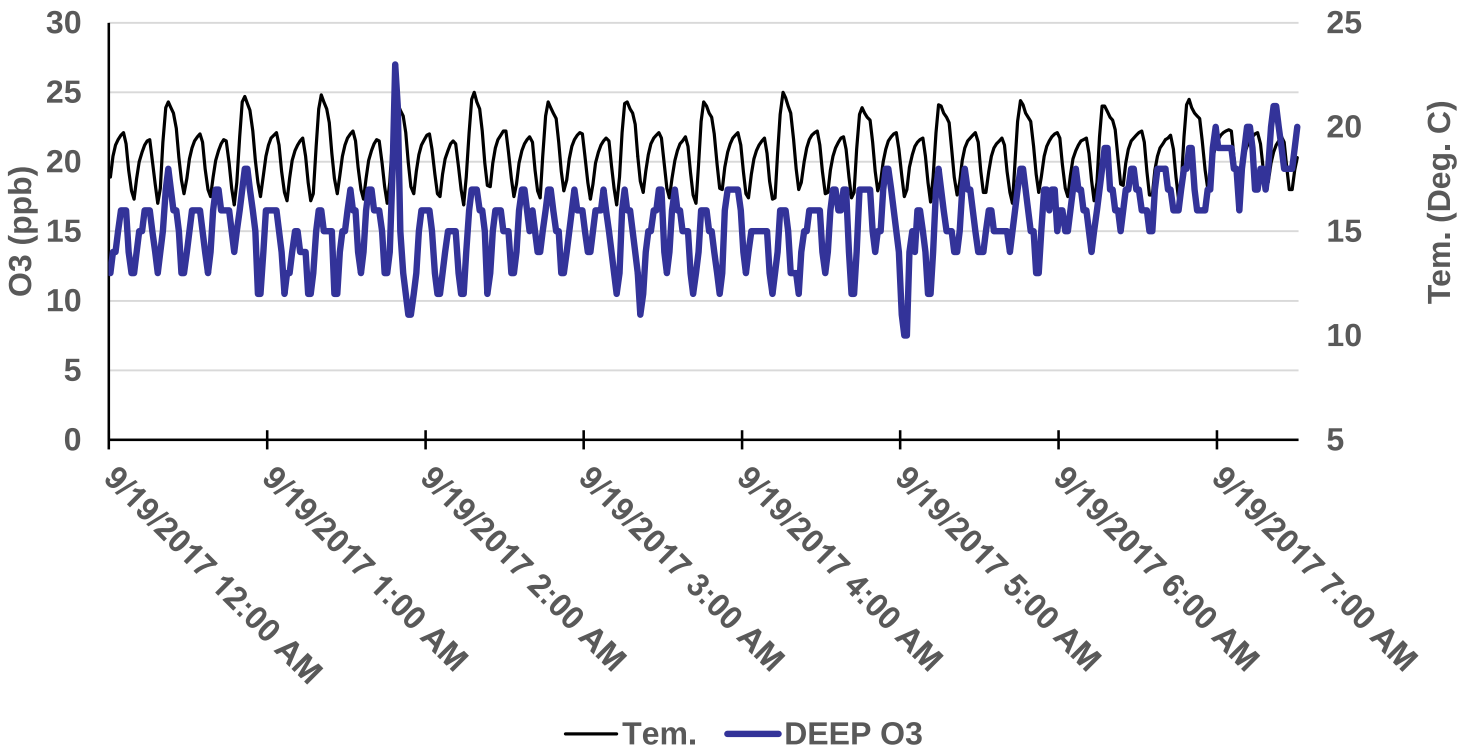
O3 Inlet Height Gradient

- A 4-5 ppb gradient may arise, absent DEEP's high O3 day SOP pausing PM filter changes, even with the 4 O&M factors found likely to reduce O3 levels: #1 New PM filter O3 demand.



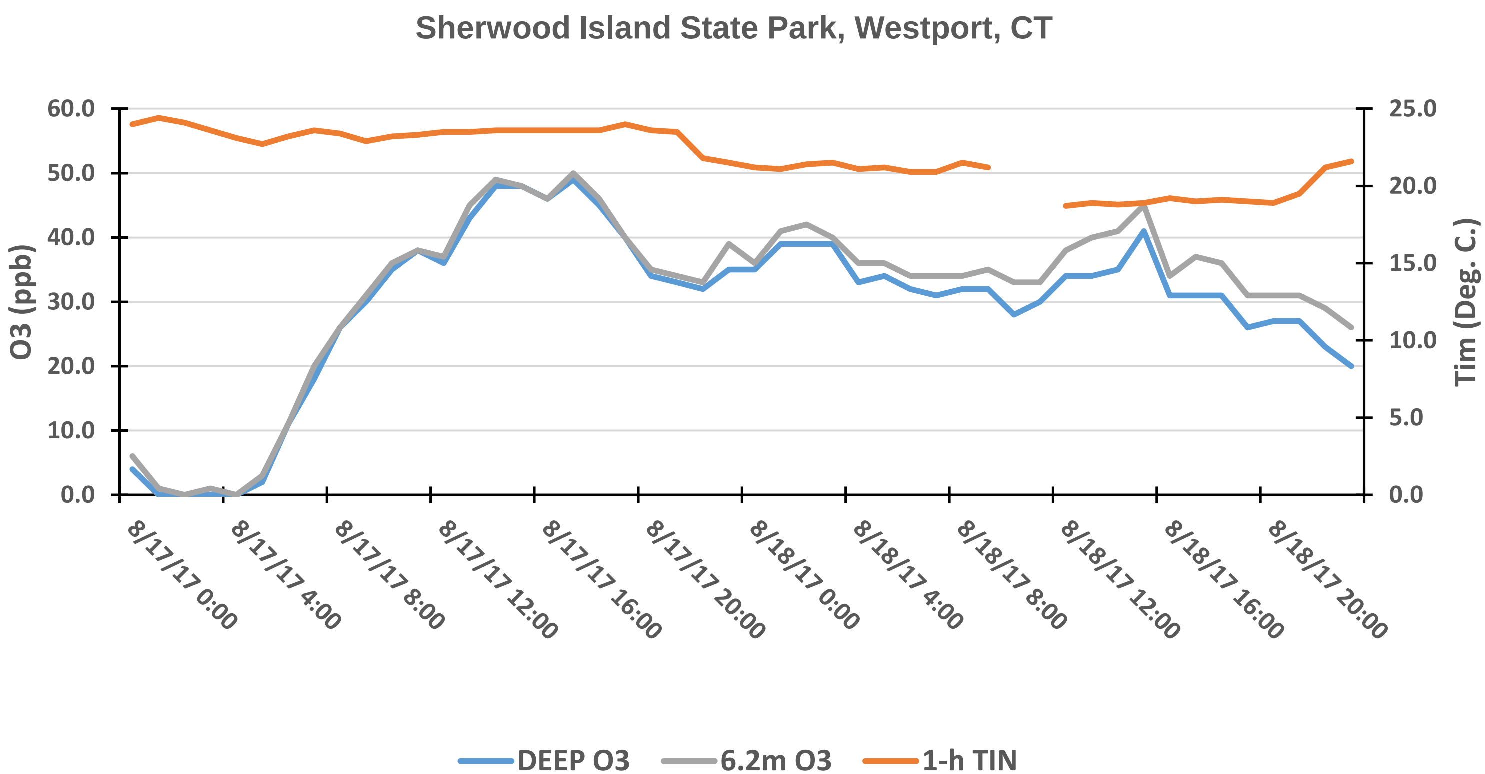
O3 Inlet Height Gradient

- A 4-5 ppb gradient may arise, even with the 4 O&M factors found likely to reduce O3 levels: #2 Shelter (1-minute) Temperature Excursions.



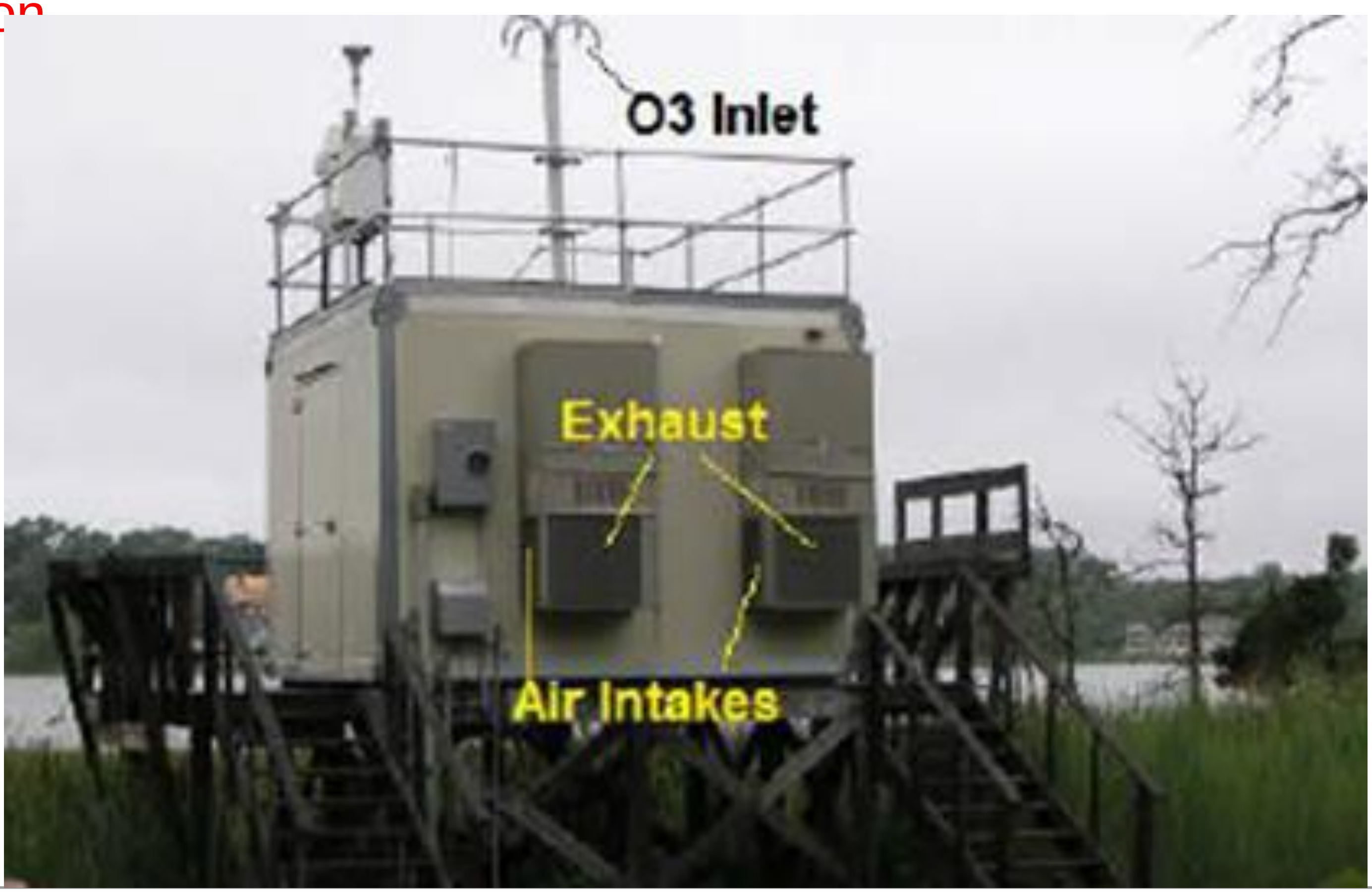
O3 Inlet Height Gradient

- A 4-5 ppb gradient may arise, even with the 4 O&M factors found likely to reduce O3 levels: #3 Shelter (1-hour) Temperature Monitor Excursion



O3 Inlet Height Gradient

- A 4-5 ppb gradient may arise, even with the 4 O&M factors found likely to reduce O3 levels: #4 HVAC Exhaust (1600 CFM) Dilution



O3 Monitoring Recommendations

- The 2017 4-5 ppb inlet height bias is especially notable given the O&M factors found likely to reduce Westport O3 levels.

1. Passivation of new PM filter O3 demand should become a routine installation task (e.g., a 10-minute 900 ppb O3 filter treatment with appropriate O3 outlet scrubbing).

2. Photometer cell and shelter temperatures (1-minute) should be periodically logged & checked for O3 impacts.

3. Photometer internal shelter inlet line heating/insulation continuity should be ensured.

4. Photometer inlets should be positioned to avoid

A Technique for Measuring Near-Ground Ozone Gradients

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Summary and Recommendations

Noteworthy differences in O3 values were found at inlets sampling 2 m, 6.2 m (DEEP monitor and Test monitor) and 10 m above ground level (AGL) during our 94-day 2017 Westport, CT study.

- Maximum daily average 8-hour (MDA8) O3 values at the DEEP 6.2 m inlet were substantially higher than those at the 2 m test inlet on 30% of all study days and that percentage increased to 66% on the 15 highest O3 days (i.e., any day with hourly O3 value $\geq$ 70 ppb).
- The 4th highest MDA8 value at the DEEP inlet (the "design value" for the study) was 4 ppb higher than at the 2 m test inlet.
- The DEEP 6.2 m to 2 m MDA8 O3 gradient averaged 0.54 ppb/m for the study period and averaged 0.9 ppb/m for the 15 highest O3 days.
- On the 15 highest O3 days the MDA8 10 m/2 m gradient averaged 0.62 ppb/m somewhat lower than the 2.13 ppb/m and 1.13 ppb/m differentials reported by earlier researchers (1,2) although those studies were performed at much higher O3 concentrations.

Finally, caution is advised when locating air sampling inlets near shelter HVAC units which exhaust large volumes of warm, buoyant O3-depleted air along shelter walls near rooflines.

Methodology

The study at Westport (41.11822, -73.33661) employed two T400 O3 monitors, a regulatory unit (CT Dept. of Energy & Environmental Protection – DEEP) sampling continuously from a 6.2 m AGL inlet midway on the eastern edge of the shelter roof and a second T400 3-inlet array, sampling 5-minute sequential intervals at 2 m, 6.2 m, and 10 m. Equal test array 12.7 m length Teflon, 3.175 mm ID inlet lines were exteriorly shielded by PVC pipe and within the shelter by foam insulation. The DEEP inlet tip was located 2 m above and 0.3 m inboard of the roof edge. Test array inlets were stacked vertically, 1.5 m off the SW corner of the shelter's west wall, a location sampling the southerly winds which historically result in the site's highest O3 values. The DEEP monitor used the T400 internal filter holder while the array inlet line tips used Savillex Teflon filter holders (to prevent fouling of the longer than usual sample lines) and 47 mm 4-5 µm filters. Our study also collected 10 m wind speed/direction, 2 m & 10 m air temperatures, 7 m solar radiation, and barometric pressure data. Daily zero/span checks were performed on both monitors as were every 6th day precision checks. All span/precision checks were well within EPA QA performance specifications. The test monitor experienced minor zero drift (1-2 ppb) during the first 2 weeks of the study. Comparative calibrations (Fig. 5) were performed at the beginning and end of the study to ascertain the integrity of the lines, fittings, and filters in the sampling array. During these checks the inlet tips of all four sampling lines were brought to within 1.5 m horizontally and 0.5 m vertically of each other on the shelter roof. Both instruments sampled ambient air for at least 50 minutes in this configuration.

Results

Based on "comparative" calibration data we believe that a difference of 3 ppb or greater between any two inlets is important and likely real. On 30% of study days the DEEP MDA8 level exceeded the coincident 2 m level by 3 ppb or more; on the 15 days with the highest O3 the DEEP MDA8 inlet level exceeded the coincident 2 m level by 3 ppb or more 10 times (66%).

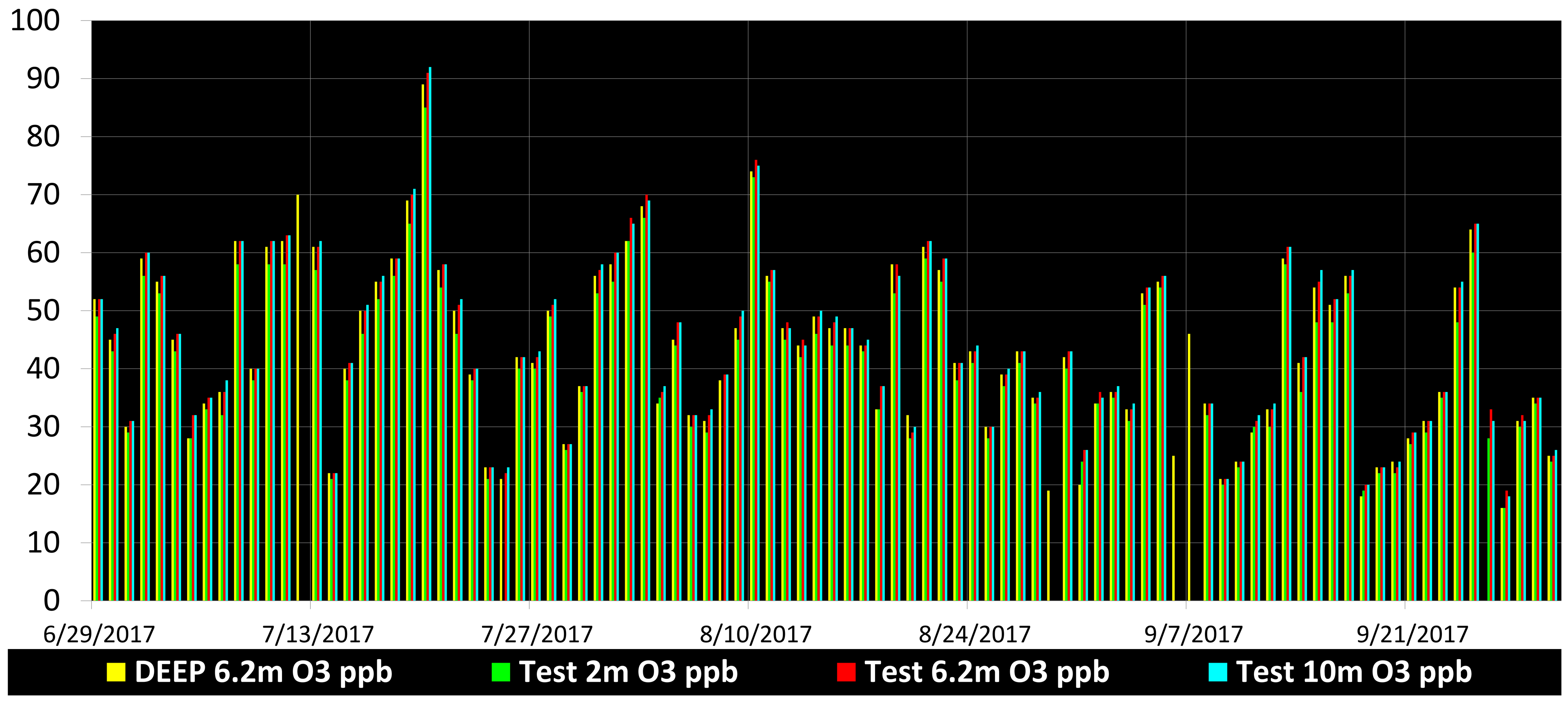


Figure 1. MDA8 O3 values for 2, 6.2, & 10m Test Inlets and 6.2 DEEP monitor.

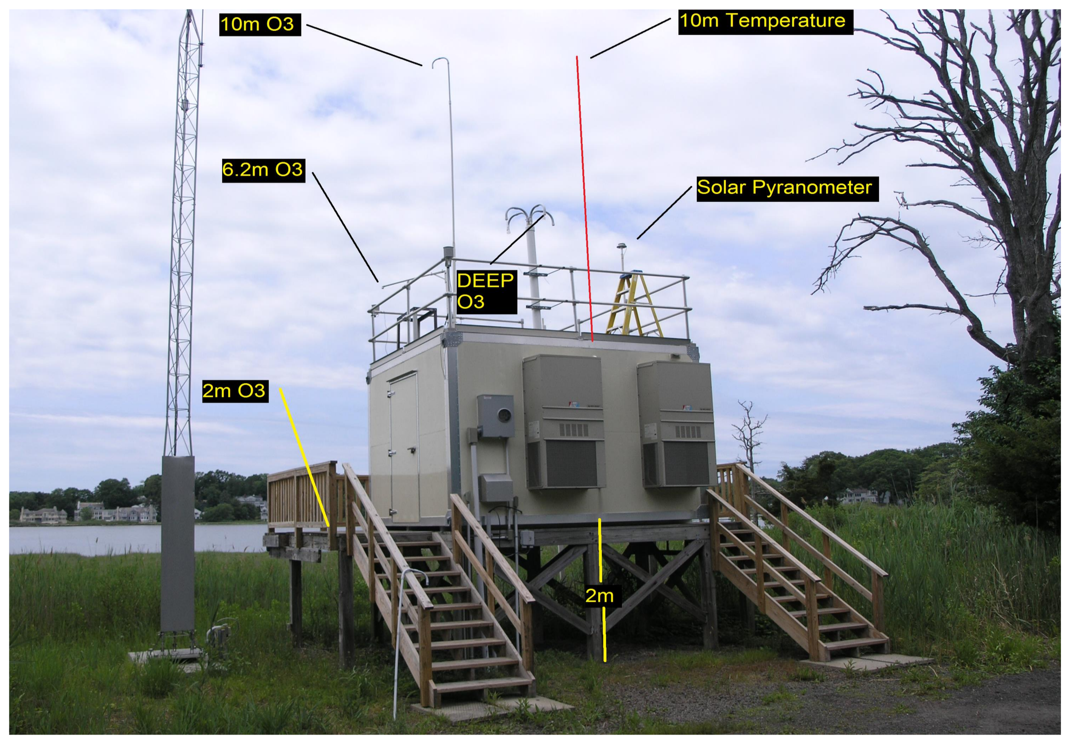


Figure 2. Westport shelter with sensor/inlet locations.

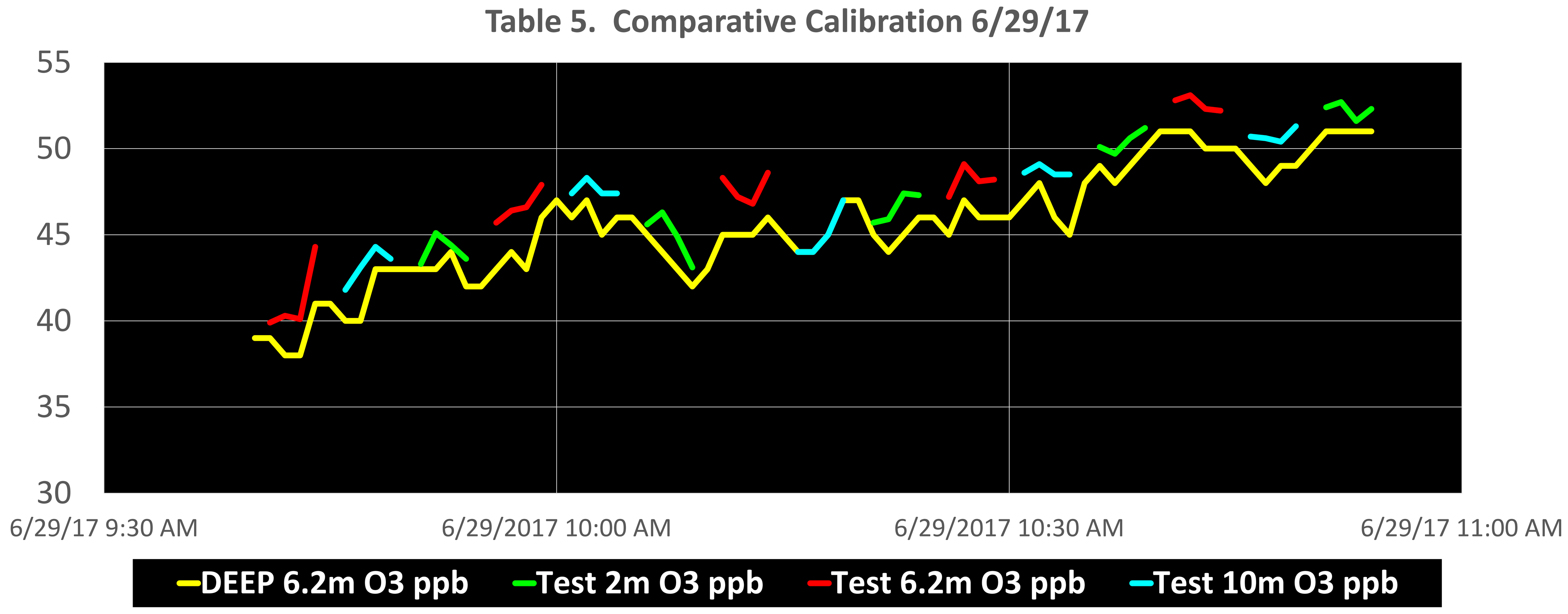
Figure 4. Three O3 test array inlets from ground level.

Figure 3. 2m O3 inlet and temperature probe.

Table 1. Westport MDA8s and Gradients

	DEEP 6.2m O3 ppb	Test 2m O3 ppb	Test 6.2m O3 ppb	Test 10m O3 ppb	DEEP 6.2m-2m ppb/m	Test 10m-2m ppb/m
94 Study Days	43.3	42.2	44.7	45.2	0.54	0.45
15 High Days	67.6	63.8	68.5	68.8	0.9	0.62

Table 5. Comparative Calibration 6/29/17



MDA8 values determine ozone DVs since an area's O3 DV is the annual 4th highest MDA8 averaged over three consecutive years. The 4th highest MDA8 recorded during our 94-day 2017 study at the test inlet 2 m AGL was 4 ppb lower than the coincident MDA8 value recorded at the DEEP 6.2 m inlet. A study limitation is its late June deployment, missing several May/June 2017 O3 exceedances; however, we believe the captured exceedances are representative of the O3 season at Westport. MDA8 values at the DEEP 6.2 m inlet almost always exceeded those at the 2 m inlet. The average *gradient* between those two inlets for the study was 0.54 ppb/m but nearly doubled to 0.90 ppb/m on high O3 days. Higher gradients were found between 2 m and 10 m with 10 m values always equal to or larger than 2 m values. Gradients averaged 0.45 ppb/m for the study and 0.62 ppb/m for the 15 highest O3 days. Johnson et al (1997) found a 10 m/2 m gradient of 1.13 ppb/m but with 10 m O3 values 8% higher than in this study. Wisbith et al (1996) found a 10 m/2 m gradient of 2.13 ppb/m when 10 m O3 levels were 42% higher than those in our study. Higher gradients are expected when O3 levels are higher since near-ground gradients are nonlinear, especially within a few meters of the surface (3).

Future Work

Inlet Height Uncertainty - Compliance network inlet heights are limited to a 2-15 m range AGL but inlets are only required to be 1 m distant from shelter supporting structures such as a monitor shelter roof. Some network operators interpret EPA guidance as requiring inlets 2 m above the shelter roof but others adhere to a 1 m roof clearance height. To the extent (4,5) that shelter roof vortices mix elevated O3 down to a reactive roof surface (e.g., reactive from deposition and accumulation of debris), a 1 m spacing may be more like a 1 m inlet above a shelter roof "ground".

HVAC Exhaust - The Westport shelter is equipped with twin HVAC heat pumps for shelter heating/cooling. Exhaust flow is rated by the manufacturer at 1600 CFM. The late September exhaust temperature was found to exceed ambient temperature by up to 10-15ºC, reaching 40ºC at times. A summer day's exhaust temperatures would likely be considerably higher. The HVAC exhaust stream passes over a large air debris-laden heat exchange surface (power washed quarterly) that will likely denude a portion of its reactive O3 content, resulting in a large volume of warm, O3-depleted air exiting the HVAC unit in the vicinity of one of the shelter roof/wall junctures. Persons tasked with siting air monitoring shelters and associated instrument inlets should address potential HVAC exhaust inlet impacts on their site design checklists.

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A Technique for Measuring Near-Ground Ozone Gradients (and some cautionary notes)

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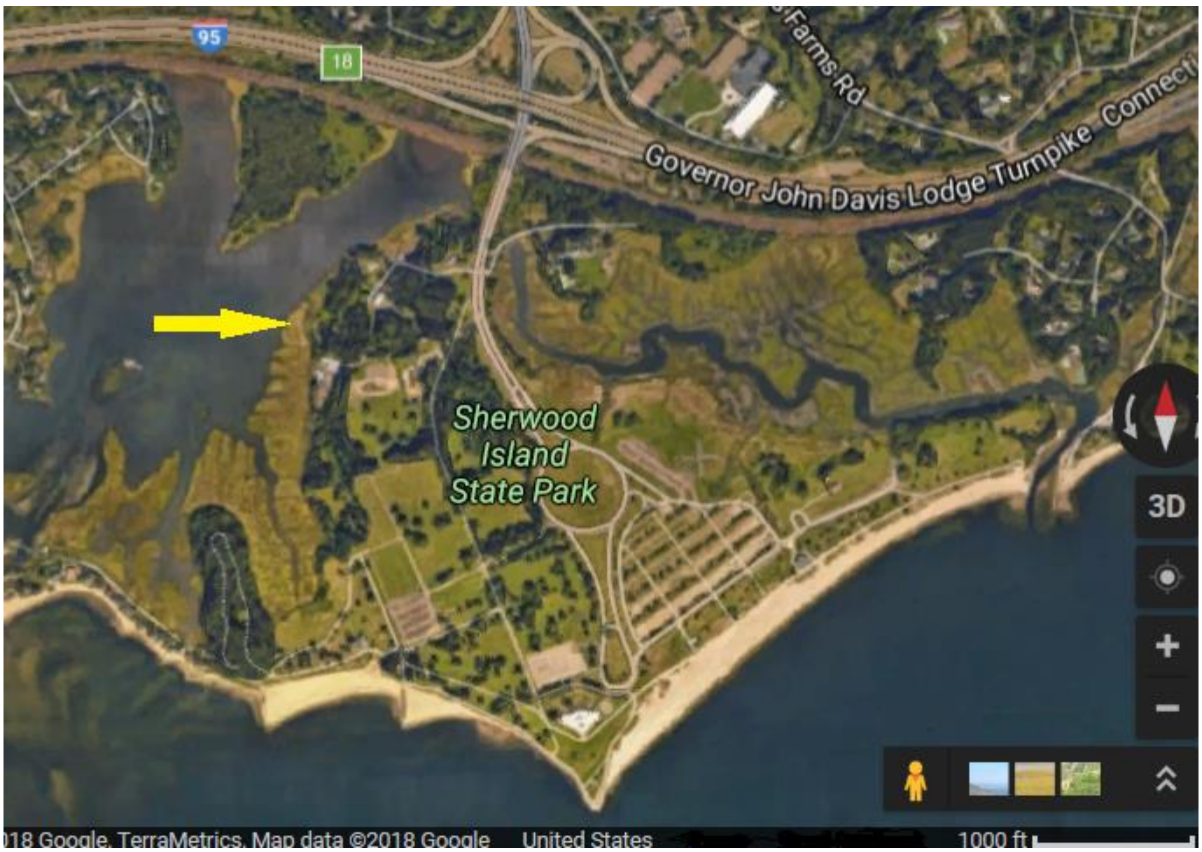
INTRODUCTION

Understanding the concept that near-ground ozone (O_3) concentrations may vary with small changes in elevation is an essential step in improving O_3 data-use programs including health effects studies, photochemical modeling and regulatory compliance programs. Measuring the O_3 differential at varying elevations can improve health effects studies by providing data more relevant to the human breathing zone, better characterize base atmospheric layers in O_3 models and more accurately report regulatory data such as design values. A study was performed during the summer of 2017 in southwestern Connecticut to investigate the near-ground O_3 differentials at a design value site for the Northern New Jersey, New York Metropolitan, and South Western Connecticut "Tri-State" area. In order to minimize relative monitor drift associated with multi-monitor O_3 measurements at multiple elevations a Teledyne API Model T400 photometric O_3 monitor was attached to a vertical sampling array equipped through a pair of Teflon solenoid valves which alternately switched the sample flow between three inlets located at 2 meters (m), 6.2m and 10m above ground level (AGL). A second T400 monitor, operated by the Connecticut Dept. of Energy and Environmental Protection (DEEP) sampled continuously from a separate inlet at 6.2m AGL. Noteworthy O_3 differentials (i.e., $\geq$3ppb) between inlet pairs at both 6.2m/ 2m and 10m/2m AGL were noted throughout the study and were more prevalent on days with high O_3 and reached a level possibly impacting the site's design value. Great care is required in the measurement of ambient O_3 due to its highly reactive nature since O_3 may react with new non-passivated particulate matter (PM) filters, be lost in condensed water within sampling lines, or diluted by heating, ventilation, air conditioning (HVAC) exhausts or shelter surface deposition from shelter flow turbulence near the sampling instrument inlet. The United States Environmental Protection Agency (EPA) has recognized some of these issues and has published guidance regarding best practices for avoiding O_3 loss during measurement.[1] Our empirical data suggests continuing reported O_3 bias from newly installed PM filter demand, shelter temperature excursions within EPA specifications or by O_3 dilution from shelter HVAC and flow turbulence.

EXPERIMENTAL PROCEDURE

The study at the Sherwood Island State Park monitoring site (Figure 1) is centered on two T400 O_3 monitors, the DEEP monitor sampling continuously from an inlet 6.2m AGL at the eastern edge of the instrument shelter roof and a second T400 three-inlet test array sequentially sampling at 5-minute intervals at 2.0m, 6.2m and 10.0m AGL. Our test array inlet at 6.2m mirrored the DEEPs regulatory-oriented inlet; the 10m inlet was representative of EPA's rural Clean Air Status and Trends Network (CASTNet) which measures O_3 at 10m AGL. Test array inlet lines (Teflon, 3.175 mm ID) were of equal length (12.7m), shielded on the exterior by PVC pipe and insulated within the shelter with foam insulation. The DEEP 4.5m inlet line was similarly shielded. The DEEP inlet tip was located about 2 meters above the shelter roof and 0.3m inboard of the eastern edge of the shelter roof. The test array inlets were stacked vertically at a point about 1.5m off the southwest corner of the shelter's west wall, a location sampling south-to-southwesterly winds historically accompanying the highest O_3 concentrations at the site. The DEEP monitor employed the standard T400 internal filter holder while the test array sample lines were equipped with Savillex Teflon filter holders at their inlet tips to prevent contamination of the longer than usual sample lines. All particle filters were Teflon, 47 mm diameter Savillex, 4-5-micron pore size. The study ran from 6/29/17 through 9/30/17 and collected wind speed/direction (10m AGL), air temperature (2m, 7m, 10m AGL), solar radiation (7m AGL), nitrogen dioxide and barometric pressure data.

Figure 1. Monitoring site at Sherwood Island State Park (Lat. 41.118228°, Long. -73.336753°) in Westport, CT.



DISCUSSION

Ozone Differential Results

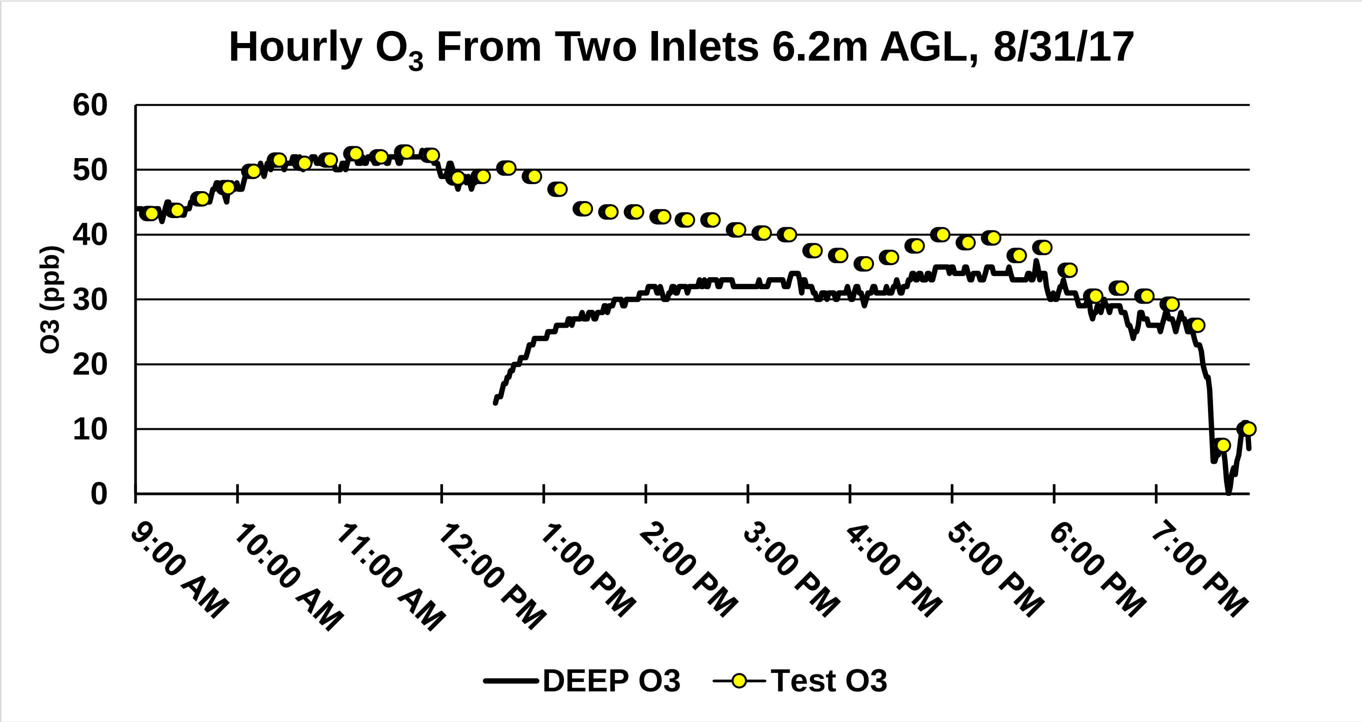
In discussing O_3 concentration results we will refer to the test array inlets by their heights (i.e., 2m, 6.2m and 10m) and the DEEP inlet as "DEEP". Since in general O_3 tends to peak during daylight hours, study analyses focused on maximum daily one-hour (MDA1) and maximum daily eight-hour (MDA8) averages. Based on "comparative" calibrations performed at the beginning and end of the study we believe that a difference of 3ppb or greater between any two inlets was important and likely real. Comparative calibrations were performed by locating the tips of all four O_3 inlet lines at the same elevation on the shelter roof within 2m horizontally of each other and allowing the instruments to sample ambient air for at least one hour. Results of these two comparisons showed maximum inter-inlet differences of less than 2ppb. There were 89 study days for which both MDA1 and MDA8 data were available for the DEEP and the 2m inlets. On 26 of those days (29%) the DEEP MDA1 O_3 concentration exceeded the coincident 2m concentration by 3ppb or more; on the 15 study days with the highest O_3 levels, days when at least one hour reached or exceeded 70ppb at the DEEP inlet, the DEEP inlet exceeded the 2m inlet by 3ppb or more 10 times (66%). On 27 study days (30%) the DEEP MDA8 level exceeded the coincident 2m level by 3ppb or more; on the 15 days with the highest O_3 the DEEP MDA8 inlet level exceeded the coincident 2m level by 3 ppb or more 10 times (66%). MDA8 values determine ozone DVs since an area's O_3 DV is the annual 4th highest MDA8 averaged over three consecutive years. The fourth highest MDA8 recorded during our 89-day 2017 study at the test inlet 2m AGL was 4 ppb lower than the coincident MDA8 value recorded at the DEEP inlet. A similar fourth high MDA8 differential (4ppb) between the DEEP and 2m inlet was found in a near-ground O_3 study performed at Westport in 2015.[2]

As expected, higher differentials were found between the 2m and 10m inlets. The 10m values always equaled or exceeded those at 2m with differentials ranging 0 to 9ppb and averaging 3.2ppb; for the 15 highest O_3 days the differential averaged 4.7ppb. Other researchers investigating urban 10m/2m O_3 differentials[3,4] and near road ways in suburban areas have found higher values. Johnson et al (1995) found a 10m/2m differential of 9ppb but with 10m O_3 concentrations 8% higher than this study. Wisbith et al (1996) found a 10m/2m differential of 17ppb when 10m O_3 levels were 42% higher than those in our study. Higher differentials are expected when O_3 levels are higher since NGOGs are nonlinear especially within a few meters of the surface.[5]

New Filter Ozone Demand

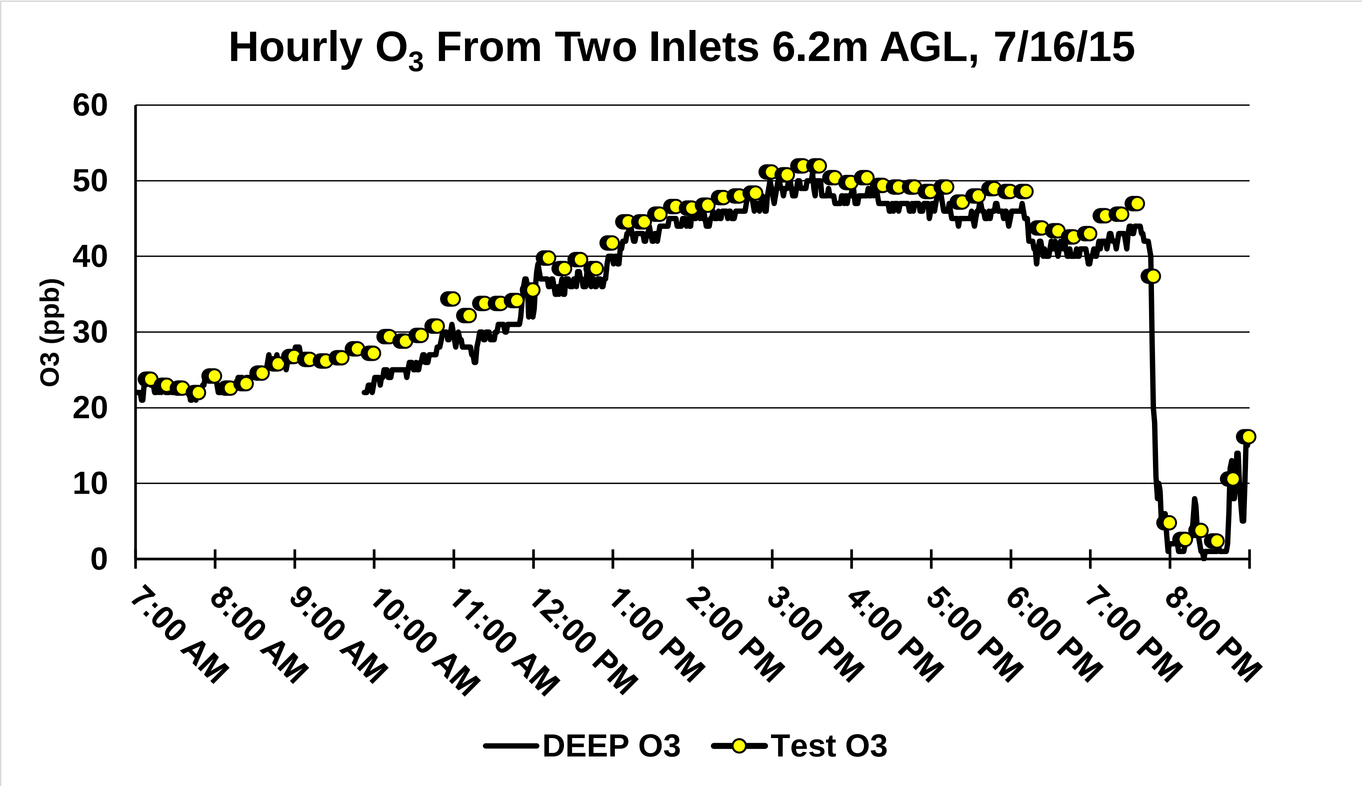
Graphs of O_3 data from the two inlets at 6.2m AGL occasionally showed significant step changes ranging up to 35 ppb (as in Figure 2 at around 12:30 PM). Those differences correlated with (approximately) biweekly particulate filter changes on the DEEP O_3 monitor. In contrast, test array filters were housed in filter holders at the tips of inlet lines and were changed monthly due to their less demanding sampling regime (i.e., 20 minutes/hour versus the DEEP's continuous sampling). Test array filters were handled with stainless steel tweezers and after installation they were exposed to a 10-minute 900 ppb O_3 concentration to passivate any new filter O_3 demand. The test array filters showed no sign of new filter O_3

Figure 2. Impact of particle filter change on ozone concentration Westport, CT. 2017.



demand. New filter O_3 demand was also noted during a similar O_3 gradient study at Westport during the summer of 2015[2] (Figure 3.).

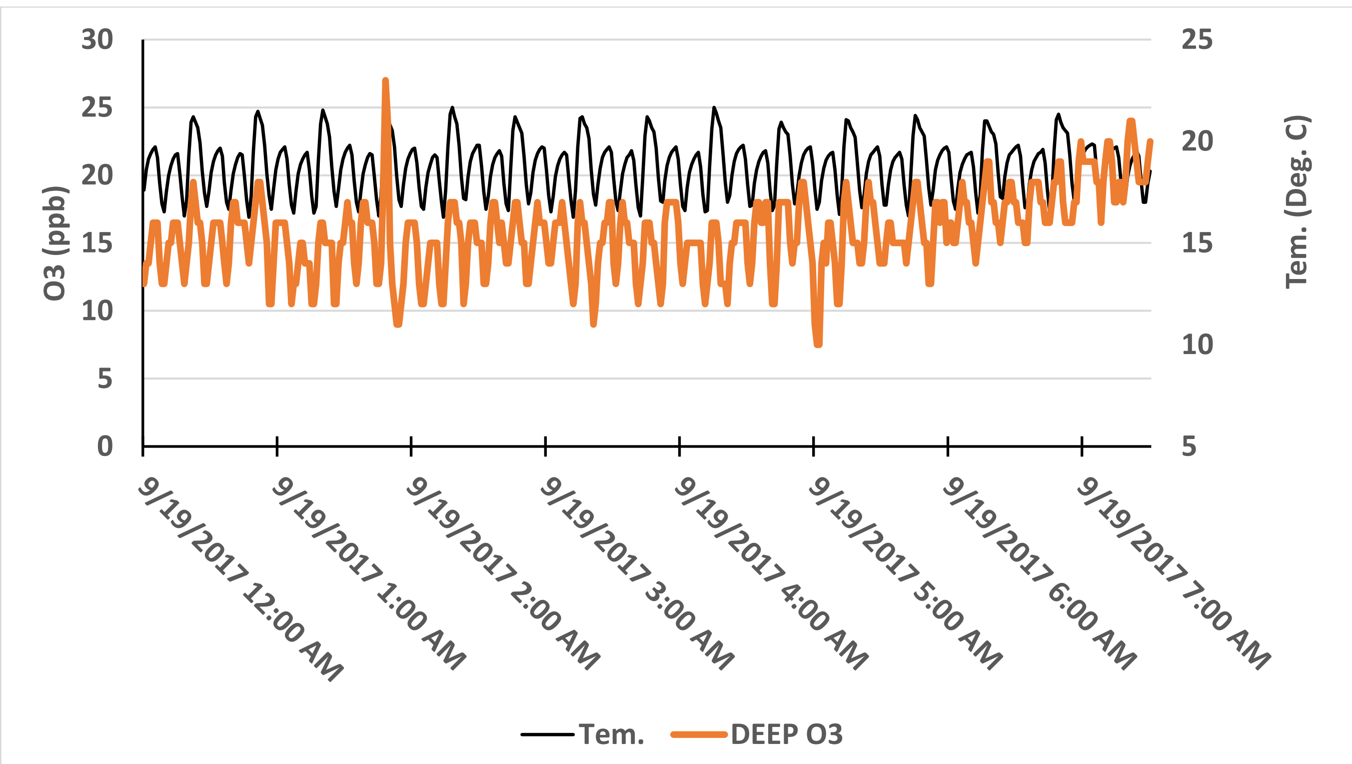
Figure 3. Impact of particle filter change on ozone concentration Westport, CT. 2015.



Shelter Temperature Excursions

EPA O_3 monitoring guidance calls for insulating interior sample lines or elevating shelter interior temperatures to avoid loss of O_3 via contact with condensed water in sample lines. On the morning of 9/19/17 the DEEP performed an in-house audit on their monitor which coincided with our calibration of the test array. Prior to the audit the DEEP monitor displayed an oscillation that was coupled to the site temperature as shown in Figure 4. The DEEP normally seeks to maintain shelter in the 26-28 Deg. C range during the ozone season. However Figure 3 shows the shelter temperature repeatedly exceeded both minimum and maximum values and that the O_3 monitor's performance was degraded. During the audit the DEEP monitor's response oscillated by ±2-3ppb in rhythm with the shelter temperature. However, the output concentration from the audit calibrator/zero-air system (Environics, Model 6301/Teledyne API, Model 701) also seemed to vary with shelter temperature – an observation confirmed by the auditor. This could not have been due to moisture in the O_3 sampling system because the audit air supply uses silica gel to remove moisture before generating O_3. On-site temperature and relative humidity measurements at the time of the audit show ambient air dew points in the range of 18-20°C and as Figure 4 shows the shelter interior was well within the dew point range. It's clear that monitor inlet lines, filter, and/or filter holder had water build-up in the hours prior to the audit but it is not clear why the audit calibrator would demonstrate instability when operating under these conditions.

Figure 4 – DEEP O_3 monitor response vs. shelter temperature prior to audit on 9/19/17.



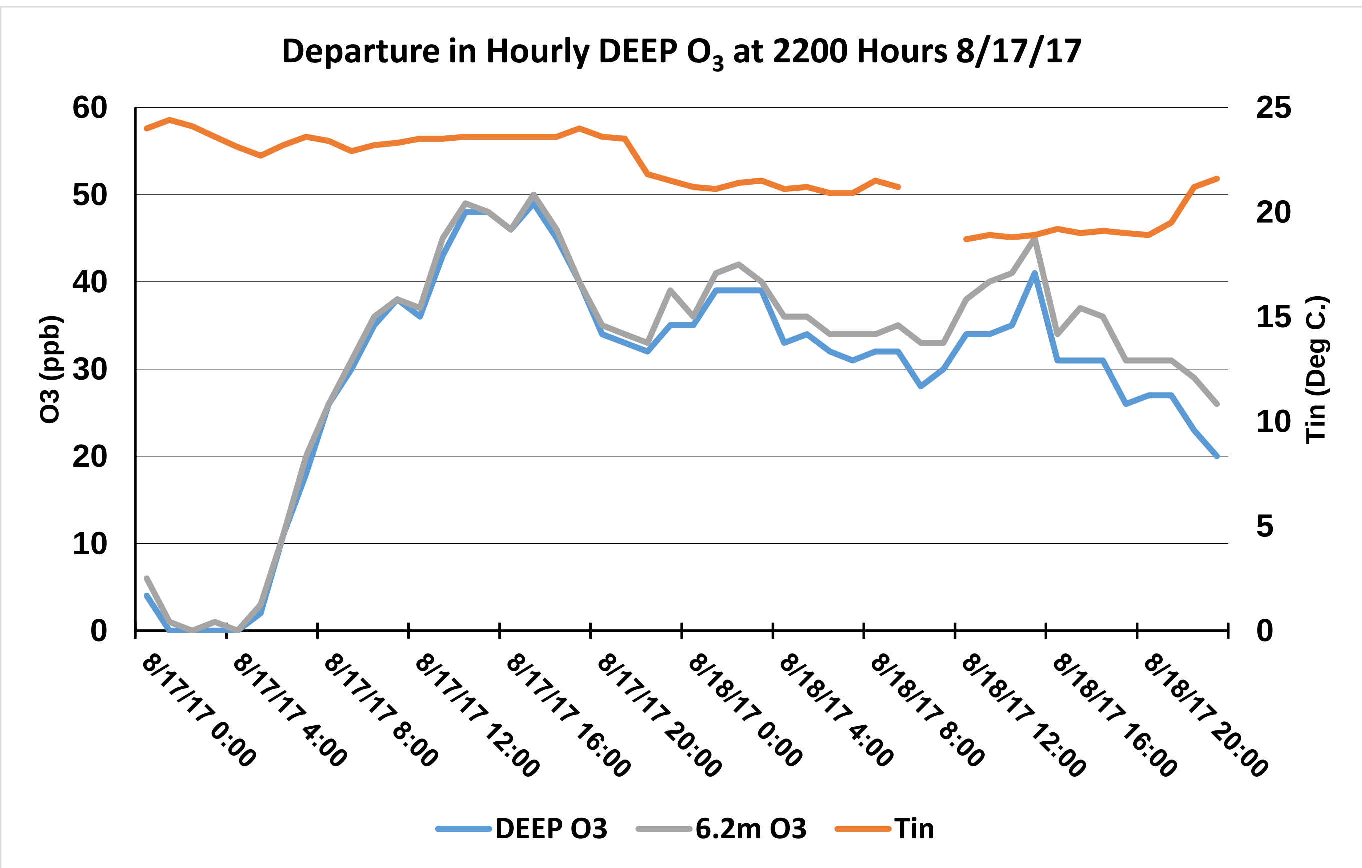
The Teledyne T400 O_3 monitor has received EPA approval as a Federal Equivalent Method FEM over an ambient operating range of 5-40 Deg. C and the DEEP's Westport shelter was within that range. However, the problem with detecting short cycle issues such as that shown in Figure 4 is that data analysts would need to look at one-minute or five-minute average data in order to identify them and that is impractical with large networks. Note that the oscillation in Figure 4 is not evident in hourly averaged data.

Selective Temperature Impact on Monitors

The study design placed a test array inlet at the same elevation (6.2m AGL) as the DEEP inlet to replicate “compliance” O_3 measurements. The inlets were separated horizontally by 2m with both inlets about 2m above the instrument shelter roof and no obstruction between them. However, out of the more than 2200 study hours there were over 150 hours when the DEEP concentrations fell below the test array 6.2m values by more than 2ppb whereas only 22 hours when the DEEP inlet exceeded the 6.2m inlet by more than 2ppb, indicating a bias.

A temperature-related issue was noted after sorting [DEEP-6.2m] concentration differences least to greatest showed that the August 17-18 period showed a decline in DEEP concentrations (Figure 5) following a 3° C. shelter temperature (Tin) drop. The Figure 5 pattern appeared multiple times when the shelter temperature dropped below about 24° C. for extended periods (i.e., an hour or more). Because this phenomenon was not recognized before the study had ended it can only be surmised there were cold spots in some portion of the DEEP sampling line which allowed a water layer build-up when the shelter thermostat deviated from its normal standard 25-30°C range. The test array sample line appeared relatively more insulated and did not experience the temperature related bias seen in the DEEP monitor.

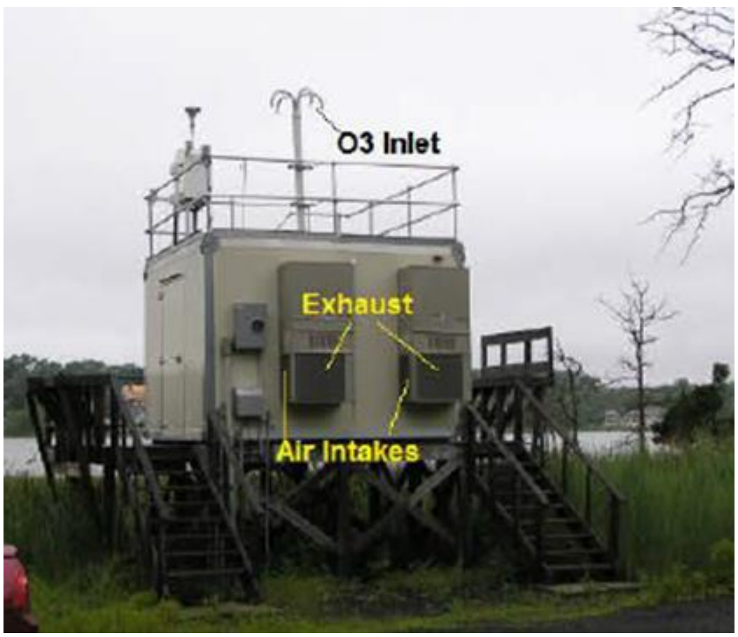
Figure 5 – DEEP 6.2m O_3 shelter temperature dependence.



Possible Dilution from HVAC System?

While investigating the periodic differences between the two 6.2m inlet concentrations we noticed possible exhaust dilution from the two dual air phase heat pumps (Bard Model H24A1-A05) which supply heating, ventilation and air conditioning (HVAC) to the Westport instrument shelter. The units are mounted on the east wall of the shelter (Figure 6) and typically operate on alternate weeks. In the AC-mode the units draw O_3 laden air through their intake grills and pass it over extensive metallic heat exchanger surfaces to extract heat from the working fluid. The heated exhaust air, now likely stripped of some O_3 after extensive contact with heat exchanger surfaces, is vented at up to 1,600 cubic feet per minute about 4.5 meters below the DEEP's O_3 inlet which is set back approximately 0.3m from the eastern shelter wall surface. Releasing this quantity of likely O_3-depleted air near an O_3 sample inlet seems problematic especially when it is warmer than the surrounding ambient air and more buoyant. Wind induced turbulence at the shelter wall-roof edge[6,7] immediately above the HVAC units may also induce mixing of exhausted air with ambient air near the rooftop inlet.

Figure 6 – Westport CT Instrument shelter HVAC configuration.



SUMMARY

Noteworthy differences in O_3 concentrations were found at 2m, 6.2m and 10m AGL during the summer of 2017 at Westport, CT. Assuming our three-month study, which missed several earlier 2017 O_3 NAAQS exceedances, is characteristic of the entire monitoring season at Westport, the 4th highest DEEP MDA8 O_3 concentration measurement at 6.2m AGL would be 4 ppb higher than if measured at 2m AGL. On the 15 highest O_3 days the average MDA8 differential between 10m and 2m was 4.7ppb, nearly 5ppb higher than if measured at 2m AGL.

These positive inlet height DV biases are especially notable given coincidental operational and maintenance factors found likely to lower O_3 DVs at this site.

1. Passivation of new particle filter O_3 demand should be included in routine O&M tasks.
2. Internal shelter and photometer absorption cell temperatures should be logged and compared for evidence of shelter temperature impacts on photometer operation.
3. Photometer inlet line insulation continuity should be ensured to avoid moisture cold spots.
4. Photometer inlets should be positioned to avoid possible impacts from HVAC exhaust plumes.

ACKNOWLEDGEMENTS

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