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December 1, 2017

Town Board Members
Town of Orangetown
26 W. Orangeburg Rd
Orangeburg, NY 10962

Submitted via e-mail
tdiviny@orangetown.com

RE: Dr. Dimitri Laddis's Letter to the Board, Nov 27, 2017

Dear Town Board:

I have reviewed the document that Dr. Laddis provided to the Board via e-mail on November 27, 2017 and am providing a response to his criticisms of my review of the ambient air quality concentrations documented in my updated letter report provided to Mr. Thomas Diviny on November 9, 2017.

Dr. Laddis objects to the use of the data to only represent short-term exposures, and believes the data can be used as a screening tool to determine whether there are health risks to nearby residents and students from long-term exposures. Dr. Laddis believes it is fair to make a "qualified statement" such as "if the measured concentrations of toxins in the air are representative of daily concentrations, then long-term exposure would..." I don't agree with this assessment as there are only three data points taken to date. When the State or the USEPA conducts annual air monitoring, data is collected every six days for a full year. Therefore, 3 days of monitoring within in a 12 day period is insufficient data to make the assumption that the measured concentrations are representative of long term exposures. Nevertheless, a comparison has been made using the average Blauvelt concentration (average of all 24-hour data points) and comparing it against USEPA's Risk-Based Regional Screening Levels (RSL) for residential ambient air (<https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-june-2017>) which are calculated based upon a cancer risk target level of 1 in 1 million (note USEPA considers a calculated cancer risk of 1 in 1 million to 1 in 10 thousand to be acceptable) and a 24 hour/day, 350 d/year exposure period for 70 years. None of the results are indicative of a long-term health effect. Please refer to the discussion under the individual compounds for the results of the evaluation.

General Air Quality

The first three-week sampling period was conducted at four monitoring locations following the USEPA national 6 day schedule, resulting in collected samples at each location on August 8th, 14th and 20th, 2017 for a total of 12 samples. As previously discussed there were concentrations

of acrolein, benzene, carbon tetrachloride and hexachlorobutadiene that were elevated above New York State Department of Environmental Conservation short-term guideline concentrations (SGCs) and/or annual guideline concentrations (AGCs). Additionally, in my review of the ambient air data, I pointed out that these comparisons are not necessarily appropriate as they are meant for comparison to modeled one-hour and annual average concentrations emitted by a facility for permitting uses. Comparisons were made against ATSDR's Acute Minimal Risk Levels and published background concentrations found in the ATSDR's toxicity profiles for the individual compounds. Dr. Laddis took issue with the source of the background data and provided a link to a NYS DEC website (<http://www.dec.ny.gov/chemical/66478.html>) which provides site-specific VOC data from across New York encompassing the years 2008-2016 (note not all sites have a full 9 year dataset). The sampling sites include: Brookside Terrace (Tonawanda Study – Residential) – Erie County; Buffalo – Erie County; Fresh Kills West – Richmond County; IS 52 and Morrisania – Bronx County; Latourette Golf Course – Richmond County; New York Botanical Gardens – Bronx County; Niagara Falls – Niagara County; Pinnacle State Park – Steuben County; PS 274 – Kings County; Queens College – Queens County; Rochester – Monroe Count; South Albany – Albany County; and Whiteface Mountain Base – Essex County. The data provided includes the maximum of the single air samples taken over the course of the year and the average of the samples as the annual average. I have provided additional review based upon this data by running a statistical analysis comparing the Blauvelt data with the site specific VOC data provided by NYS DEC.

The data was compared using a two-tailed t-test, using USEPA's ProUCL statistical software (Version 5.1.002). The t-test tests the hypothesis whether the two sets of values are different (i.e. come from two different groups). The two-tailed t-test is used when the difference between the groups is not known (i.e, it is not known which group is smaller, larger or the same).

Two evaluations were conducted for each chemical: Blauvelt single 24-hour concentrations (12 samples) vs a compilation of the maximum site concentrations across sampling years) and Blauvelt average concentrations per sampling location (4 data points) vs a compilation of the average site concentrations across sampling years. The two-tailed t-test was used to determine whether the Blauvelt data was statistically different (either lower or greater) or not statistically different than the individual site monitoring data taken across the State. The results of the statistical evaluations are provided in the individual chemical discussions that follow.

Acrolein

Dr. Laddis expressed concern about the detected concentrations of acrolein. In reviewing the NYS DEC data, I do agree that the acrolein concentrations detected during the sampling conducted by TRC are significantly higher than what has been detected in New York State as part of the air monitoring network. As a result of discussions with Mr. Ron McCullen of MayFly Environmental (personal communication) regarding the detections of acrolein as a result of sampling with Summa canisters, he indicated to me that this is not an acceptable methodology as there have been documented issues using the canisters. Upon further research, I found two EPA documents (provided in Appendix A) discussing this issue. The first document entitled "*Data Quality Evaluation Guidelines for Ambient Air Acrolein Measurements*", dated December 17, 2010, discusses that as a result of studies completed by the Office of Air Quality Planning & Standards (OAQPS), Acrolein monitoring results could be affected by factors that include how the canisters are cleaned in preparation for sample collection and the gas standards used to calibrate the equipment. Specifically, it was determined that acrolein can be elevated even in canisters that are considered clean, resulting in ambient measurements that are biased high. The study also demonstrated that the acrolein standards used by various laboratories to calibrate the analytical systems was quite variable, thus resulting in additional biases that increased the

uncertainties surrounding the acrolein growth issue. EPA provided Sampling and Analysis Guidelines for canister cleaning (heating to 90° C) and testing; calibration standards and timeliness of sampling.

The second document (*How Well Are We Able to Measure Acrolein, Formaldehyde and other HAP Carbonyls*), dated January 31, 2011, documents the results of a small study that evaluated variable factors such as canister design, preparation, and lab analysis and calibration gas standards. The result of the testing showed that blank Summa canisters that were not heat treated showed significant increased acrolein concentrations (~3 – 5 times higher) over canisters treated with heat. Therefore, canisters that are to be used for acrolein sampling must be specifically heat treated and periodically tested to determine whether there is acrolein contamination in the canisters which would bias high the collected ambient air samples.

As background on the inclusion of acrolein as part of the sampling program, it was not originally included in the VOC analyte list and was only added after the lab was contracted based upon discussions with NYS DEC. TRC wasn't aware that acrolein was a contaminant of interest until sampling had already started. NYSDEC (George Sweikert) informed the residents of acrolein's odor description, saying it matched descriptions of their complaints, and asked if TRC was analyzing for it as part of our monitoring program. TRC subsequently asked the lab if they could report it as part of the TO-15 method. The standard passed their quality control so they informed us they would be able to report it. I queried ConTest Analytical Laboratory as to their canister preparation methods and provided them with the EPA Data Quality Evaluation Guidelines document and was told that the cleaning method was not something that is done at the lab (see Appendix B, e-mail communication between K. Vetrano – TRC and M. Kelly – ConTest). Additionally, I contacted Mr. Tom Gentile of NYS DEC (see Appendix B, e-mail communication between K. Vetrano – TRC and T. Gentile – NYS DEC) as to the state's sampling methodologies. He replied that he had significant concerns regarding the acrolein results obtained by TRC and that NYS DEC has spent considerable time working with USEPA on this issue. During the next round of sampling, NYS DEC is planning on co-locating samplers with the TRC samplers. Additionally, TRC will determine if there is a commercial laboratory that follows EPA guidelines for the cleaning of the sampling canisters for acrolein.

Based on this information, I believe that the acrolein concentrations are potentially biased high based upon the lack of proper canister preparation by the analytical laboratory. Therefore, a statistical comparison of the Blauvelt acrolein data and the New York State monitoring data was not conducted and any judgments regarding the ambient air concentrations of acrolein in the community must be reserved until the second phase of sampling is completed by TRC and NYS DEC.

Benzene

A statistical comparison of the Blauvelt 24-hour sample benzene dataset and a dataset comprised of the maximum detected concentrations over the course of the sampled years (2008-2016) for each individual community, was conducted using a two-tailed t-test. The results of the statistical testing showed that the benzene concentrations measured in Blauvelt were statistically less than the maximum measured concentrations across New York, including rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the data sets were compared. This indicates that the Blauvelt benzene concentrations are statistically less than the measured background concentrations across the state. The data and statistical test results (Blauvelt vs. Pinnacle State Park and Whiteface Mountain) are provided in Appendix C.

A statistical comparison of the average 24-hour benzene concentrations at each Blauvelt sampling location and a dataset comprised of the average detected concentrations over the course of the sampled years (2008-2016) for each individual community, was conducted using a two-tailed t-test. The results of the statistical testing showed that the average benzene concentrations measured in Blauvelt were statistically less than the average measured concentrations across New York, with the exception of the rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the data sets were compared. This indicates that the Blauvelt benzene concentrations are for the most part are statistically less than the measured background concentrations as compared to the monitored towns and cities. The data and statistical test results (Blauvelt vs. Pinnacle State Park, Whiteface Mountain and Buffalo, NY) are provided in Appendix C.

The average benzene concentration in the Blauvelt sampling area (assuming consistent concentrations over the twelve day sampling period) was 0.446 ug/m^3 which is only slightly higher than USEPA's RSL for residential ambient air of 0.37 ug/m^3 . Assuming a lifetime exposure at this concentration, the calculated cancer risk is 1.2 in 1 million which is considered acceptable. Note, the ATSDR citation that Dr. Laddis provided regarding the exposure of 0.4 ppb would result in a cancer risk of 1 in 100,000 cancer risk is incorrect. At an exposure of 0.4 ppb (1.276 ug/m^3), the expected cancer risk would be 3.5 in a million. See Appendix D for cancer risk and non-cancer risk calculations using USEPA's RSL calculator.

Carbon Tetrachloride

A statistical comparison of the Blauvelt 24-hour sample carbon tetrachloride dataset and a dataset comprised of the maximum detected concentrations over the course of the sampled years (2008-2016) for each individual community was conducted using a two-tailed t-test. The results of the statistical testing showed that the carbon tetrachloride concentrations measured in Blauvelt were statistically less than the maximum measured concentrations across New York including rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the datasets were compared. This indicates that the Blauvelt carbon tetrachloride concentrations are statistically less than the measured background concentrations measured across the state. The data and statistical test results (Blauvelt vs. Pinnacle State Park and Whiteface Mountain) are provided in Appendix C.

A statistical comparison of the average 24-hour carbon tetrachloride concentrations at each Blauvelt sampling location and a dataset comprised of the average detected concentrations over the course of the sampled years (2008-2016) for each individual community, was conducted using a two-tailed t-test. The results of the statistical testing showed that the average carbon tetrachloride concentrations measured in Blauvelt were statistically less than the average measured concentrations across New York, including the rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the data sets were compared. This indicates that the Blauvelt carbon tetrachloride concentrations are statistically less than the measured background concentrations measured across the state. The data and statistical test results (Blauvelt vs. Pinnacle State Park and Whiteface Mountain) are provided in Appendix C.

The average carbon tetrachloride concentration in the Blauvelt sampling area (assuming consistent concentrations over the twelve day sampling period) was 0.436 ug/m^3 which is less than USEPA's RSL for residential ambient air of 0.47 ug/m^3 . Assuming a lifetime exposure at this concentration, the calculated cancer risk is 9.3 in 10 million which is considered acceptable. See Appendix D for cancer risk and non-cancer risk calculations using USEPA's RSL calculator.

Hexachlorobutadiene

Hexachlorobutadiene was detected in only one of 12 samples collected in the Blauvelt area during the 12 day sampling period, and in none of the 1-hour samples taken during odor events (10 samples). Although Dr. Laddis states that the detected concentration of 0.044 ppb is “the highest reported DEC measurement in NYS”, he is incorrect. There have been higher maximum measurements in Buffalo, NY (0.1 ppb in 2013) and in Niagara Falls (0.046 ppb in 2007) and it is only greater than the highest recorded ambient air samples measured in rural areas such as Pinnacle State Park and Whiteface Mountain by about 2 fold (0.024 and 0.019 ppb, respectively). Additionally, using this one sample as representative of the air quality in Blauvelt, especially with 11 other 24-hour samples being non-detect (two of which were obtained from the same location) is not a scientifically valid assumption.

A statistical comparison of the Blauvelt 24-hour sample hexachlorobutadiene dataset and a dataset comprised of the maximum detected concentrations over the course of the sampled years (2008-2016) for each individual community using a two-tailed t-test. The results of the statistical testing showed that the hexachlorobutadiene concentrations measured in Blauvelt were statistically less than the maximum measured concentrations across New York including rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the datasets were compared. This indicates that the Blauvelt hexachlorobutadiene concentrations are statistically less than the measured background concentrations measured across the state. Note, the New York DEC presented non-detect concentrations as zero, therefore, non-detect concentrations in the TRC dataset were also treated as zero in order to run the statistical comparisons. The data and statistical test results (Blauvelt vs. Pinnacle State Park and Whiteface Mountain) are provided in Appendix C.

A statistical comparison of the average 24-hour hexachlorobutadiene concentrations at each Blauvelt sampling location and a dataset comprised of the average detected concentrations over the course of the sampled years (2008-2016) for each individual community, was conducted using a two-tailed t-test. The results of the statistical testing showed that the average hexachlorobutadiene concentrations measured in Blauvelt were statistically less than the average measured concentrations across New York, including the rural areas such as Pinnacle State Park and Whiteface Mountain, when the means of the data sets were compared. This indicates that the Blauvelt hexachlorobutadiene concentrations are statistically less than the measured background concentrations measured across the state. Note, the New York DEC presented non-detect concentrations as zero, therefore, non-detect concentrations in the TRC dataset were also treated as zero in order to run the statistical comparisons. The data and statistical test results (Blauvelt vs. Pinnacle State Park and Whiteface Mountain) are provided in Appendix C.

In order to be conservative (i.e., health protective) the average hexachlorobutadiene concentration in the Blauvelt sampling area (assuming consistent concentrations over the twelve day sampling period) was calculated to be 0.38 ug/m^3 using $\frac{1}{2}$ the detection limit for the non-detect concentrations (rather than zero). The USEPA's RSL for Hexachlorobutadiene in residential ambient air is 0.128 ug/m^3 . Assuming a lifetime exposure at this concentration, the calculated cancer risk is 2.98 in 1 million which is considered acceptable. See Appendix D for cancer risk and non-cancer risk calculations using USEPA's RSL calculator.

Conclusions

As previously discussed in my November 9th letter to the board and as shown by the risk evaluation conducted in this report, the concentrations of benzene, carbon tetrachloride and hexachlorobutadiene measured in August 2017, do not represent a health risk to the community of Blauvelt, both on a short-term and on a long-term basis. Additionally, as shown by the results of the statistical analysis, the measured concentrations in Blauvelt are statistically less than those concentrations measured in monitored towns and cities across New York State, even as measured in rural areas such as Pinnacle State Park and Whiteface Mountain.

As Dr. Laddis requested, these short-term measurements were evaluated for long-term exposure. The long-term health risk was evaluated by using USEPA's RSL calculator. The calculator uses EPA exposure assumptions (24-hour per day, 350 d/year, 70 year exposure period) and cancer-based toxicity criteria to calculate a predicted cancer risk from long-term exposure. Using the average of the detected concentrations as the representative exposure concentration, the calculated cancer risks ranged from 9.3 in 10 million (carbon tetrachloride) to 2.98 in 1 million (hexachlorobutadiene) which are all within USEPA's acceptable risk range of 1 in 1 million to 1 in ten thousand.

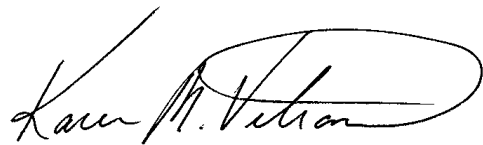
TRC and NYS DEC believe there were issues with the acrolein sampling data due to use of Summa canisters that were not specifically cleaned for acrolein analysis. NYS DEC is planning on conducting side-by-side testing during the second phase of the ambient air testing. This side-by-side testing will also provide additional data for the determination of actual hexachlorobutadiene concentrations in the community.

Finally, appropriate background samples should be taken to document ambient air quality away from the facility. Background locations should take into account equivalent traffic and potentially other sources. For example, it should be noted that there are many potential sources of acrolein such as fires, exhaust from cars, trucks, wood heating and industrial boilers. Acrolein is also found in cigarette smoke and smoke from cooking animal fats. Based on this information, there is a BBQ restaurant located near the affected residential area which smokes meat over wood fires. It is recommended that this location also be selected as a background sampling location to determine whether there are alternative sources for acrolein (if actually detected in the second phase of sampling).

Should you need further information, please do not hesitate to contact me at (860) 298-6351. Thank you.

Very Truly Yours,

TRC

A handwritten signature in black ink, appearing to read "Karen M. Vetrano". The signature is fluid and cursive, with a large loop at the end.

Karen M. Vetrano, Ph.D.
Manager of Risk Assessment and Toxicology

APPENDIX A
USEPA DOCUMENTS

Data Quality Evaluation Guidelines for Ambient Air Acrolein Measurements

December 17, 2010

Overview

In 2010, OAQPS completed a study that determined acrolein monitoring results could be affected by factors that include how canisters are cleaned in preparation for sample collection and the gas standards used to calibrate analytical equipment. Due to the resulting data quality concerns, EPA worked with the NACAA Monitoring Steering Committee to develop an AQS reporting framework for acrolein measurements that bins data as either “acrolein - *unverified*” or “acrolein - *verified*”. This document is intended to support state, local, and tribal air pollution control agencies who must decide whether to leave their data in the re-named “unverified” parameter code or move the data to a new “verified” parameter code, both of which are described below.

Background

Historically, the default method for measuring ambient air acrolein concentrations was by collection on a DNPH-coated silica gel cartridge followed by HPLC analysis (e.g., EPA Method TO-11A). However, the “Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air — Second Edition” (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/toxcompd.pdf>) was amended in October 2000 to remove acrolein from the list of applicable target analytes due to significant data quality concerns.

In 2002, OAQPS released the first National Air Toxics Assessment based upon 1996 air toxics emissions; acrolein was the dominant non-cancer risk driver. Given the significant risk from acrolein, OAQPS began to investigate alternative means of measuring ambient air acrolein concentrations. Air samples collected in canisters and analyzed by GC/MS (i.e., EPA Method TO-15) emerged as the most feasible option. The National Contract Laboratory (Eastern Research Group) was tasked with evaluating this approach, the results from which supported the viability of ambient acrolein measurements via EPA Method TO-15. These results are documented in a report and are available at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/finacrolein.pdf>.

As this approach was implemented over the course of several years, questions arose regarding the potential for growth of acrolein in canisters, a problem that could result in a high bias. In 2010, OAQPS worked with several state and local air quality agencies to conduct a study to determine whether monitoring results were affected by the process used to clean canisters in preparation for sample collection. The study showed that acrolein can be elevated even in canisters that are considered clean, resulting in ambient measurements that were biased high.

Additionally, the study demonstrated that the accuracy of acrolein gas standards used to calibrate analytical systems was quite variable between different laboratories, resulting in significant biases that worsened the uncertainties arising from the growth issue.

While there are continuing OAQPS/ORD efforts to improve acrolein monitoring methods for the future, there are several key factors that can be considered now to significantly improve the accuracy of acrolein sampling and analysis by EPA Method TO-15. EPA recommends that agencies monitoring ambient air acrolein concentrations (via TO-15 or comparable) consider adopting the practices described below.

Sampling and Analysis Guidelines

Canister Cleaning Practices

An important factor in preparing canisters for acrolein sampling is the addition of heat to the cleaning process (i.e., heat the canisters to a temperature on the order of 90°C). Following cleaning, initially and periodically (e.g., annually) test each canister for acrolein growth over a two to three week period. This is done by adding humidified air or nitrogen to each canister (to 5-10 psig) and testing each canister for cleanliness by GC/MS using an ambient air pre-concentrator. Test each canister immediately after cleaning and then once a week for two to three weeks to help determine whether acrolein is likely to “grow” in the canister. Plot the data from each test to assess whether or not (and if so, the degree to which) there is growth of acrolein over time. If there is evidence of acrolein growth in a particular canister, it may be prudent to repeat the cleaning and testing until negligible growth is evident. Some canisters may not pass the acrolein growth test even after repeated cleaning; such cans may not be suitable for measuring ambient air acrolein.

Calibration Standards

The other factor that can play a large role in the acrolein sampling results is the calibration gas standards that laboratories use to calibrate their GC/MS analytical systems. Performance tests for the National Air Toxics Trends Station (NATTS) Network over the past five years have yielded acrolein results that are quite variable. As part of the 2010 study, several laboratories analyzed samples containing known values of acrolein. The study results indicated that labs using higher concentration acrolein standards (*diluted to target range concentrations*) to calibrate their equipment provided more consistent analytical results. The higher concentration standards are more stable; however, it is important to have the TO-15 standard re-certified by the manufacturer at their suggested frequency or at least every year to ensure the best acrolein stability possible.

Timeliness

In the interest of sample stability and integrity, EPA recommends analyzing samples (particularly whole air samples) as soon as reasonably possible after collection.

Quality Assurance (QA) Guidelines

Acrolein data can also be assessed using the conventional Data Quality Indicators (DQIs) of precision and bias that allow for an understanding of data certainty.

Method precision is determined by calculating the coefficient of variation (CV) between collocated or duplicate sample analyses. Analytical precision is determined by calculating the CV between replicate (split sample) analyses. For the NATTS Network, a CV within 15% is considered acceptable.

Bias is the systematic or persistent distortion of a measurement process that causes the expected sample measurement value to trend either higher or lower from the sample’s true value. For the NATTS program, bias is determined by creating and distributing single blind proficiency test (PT) samples to all participating laboratories, the analysis results from which are compared with the

known concentration values. For the NATTS Network, a Relative Percent Difference (RPD) within 25% is considered acceptable.

Further information on the NATTS Network Quality Assurance Program is available at <http://www.epa.gov/ttn/amtic/airtoxqa.html>.

Summary of Reporting Guidelines: Acceptable Parameter and Method Codes

Because of the uncertain accuracy of acrolein measurements, OAQPS has changed the name of the existing acrolein parameter code in AQS (43505) to “Acrolein - Unverified” to indicate the current level of uncertainty that exists with the data already reported to AQS. Correspondingly, a new parameter code (43509) has been created in AQS for “Acrolein - Verified.” Whether or not all or a subset of existing data remain in the unverified parameter code, or are re-categorized as verified and moved / reported to this new parameter code, is a choice over which each owning agency has complete discretion. Until such time as agencies evaluate their acrolein monitoring procedures and the quality of reported data, we recommend that already-reported data remain in the unverified method code.

At the time during which this document was written, there were 29 method codes for acrolein in AQS. Data arising from methods which collect samples via canister and analyze those samples via GC/MS are acceptable for consideration as either unverified or verified acrolein data in AQS. These method codes are listed below in Table 1.

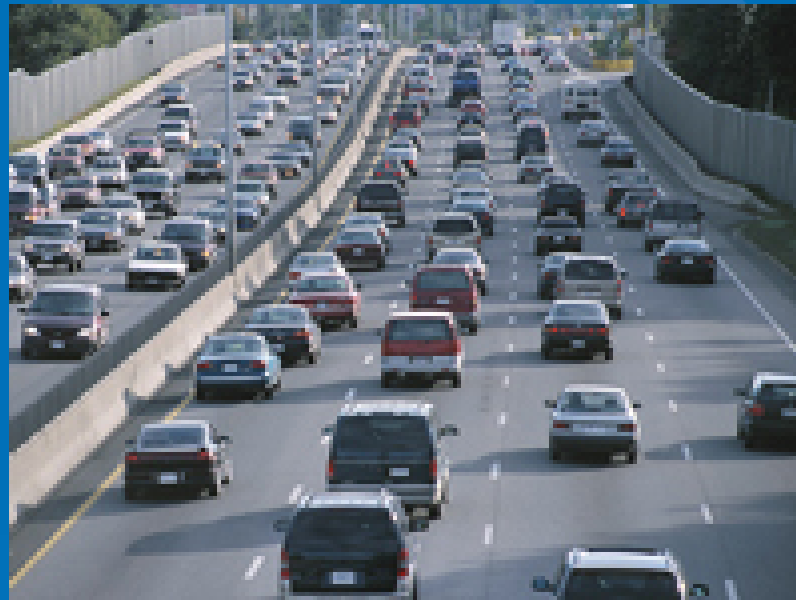
Table 1: Available AQS Method Codes for Parameter Code 43509, Acrolein - Verified

Method Code	Sample Collection Description	Sample Analysis Description
101	CANISTER SUBAMBIENT PRESSURE	MULTI DETECTOR GC
109	SS-CANISTER-SUBAMBIENT-PRESURE	GAS CHROMATOGRAPH MASS SELECTIV DET
110	SS-CANISTER-PRESSURIZED	GAS CHROMATOGRAPH MASS SPECTRO
113	SS-Canister Pressurized	Capillary GC ITD Mass Spectro
127	6L SUBAMBIENT SS-CANISTER	INCOS 50XL GC/MS
129	6L SUBAMBIENT SS-CANISTER	VARIAN SATURN-2 GC/MS
136	6L Pressurized Canister	Entech Precon w/ Agilent GC/MS/FID
145	6 L SS Canister Subamb press, passive coll	GC/Mass Spectro
147	6L PRESSURIZED CANISTER	ENTECH PRECON - SATURN II GC/FID
148	6L PRESSURIZED CANISTER	ENTECH PRECON - HP GC/FTIR/MS
149	6L SUBATM CANISTER	Entech Precon- GC/FID/MSD
150	SS 6L- PRESSURIZED CANISTER	CRYOGENIC PRECON: GC/MS
153	Pressurized Canister	GC with Multiple Detectors
171	6L Pressurized Canister	Precon Saturn GC/MS
172	6L Pressurized Canister	Precon HP GC/MS
175	Passivated Canister	Cryogenic Preconcentration GC/MS
176	6L SUBATM SS CANISTER	ENTECH PRECONCENTRATOR GC/MS
210	SS 6L Pressurized Canister	Cryogenic Precon GC/MS
211	SS Canister Subambient Pressure	Gas Chromatograph Mass Spectro

For more information on acrolein reporting procedures, please contact Mike Jones of OAQPS at jones.mike@epa.gov or 919-541-0528.

How Well Are We Able to Measure Acrolein, Formaldehyde, and other HAP Carbonyls?

*Jason Herrington, David Shelow, Donald
Whitaker*



National Ambient Air Toxics Trends Stations (NATTS) are to monitor formaldehyde, acetaldehyde, and acrolein once every 6 days, for a 24-hour duration.



EPA Compendium Method TO-11A

- Inarguably the most frequently utilized method to date.
- “Gold Standard”
- Utilizes a cartridge packed with acidified 2,4-dinitrophenylhydrazine (DNPH)-coated Silica-Gel.



EPA Compendium Method TO-15

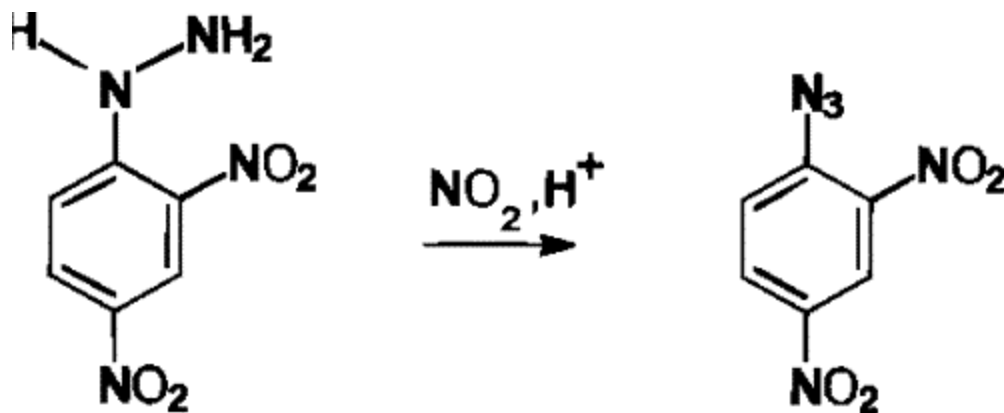
- Sampling with 6 L silonite coated passivated canisters.
- Recently, utilized for the sampling and analysis of acrolein.



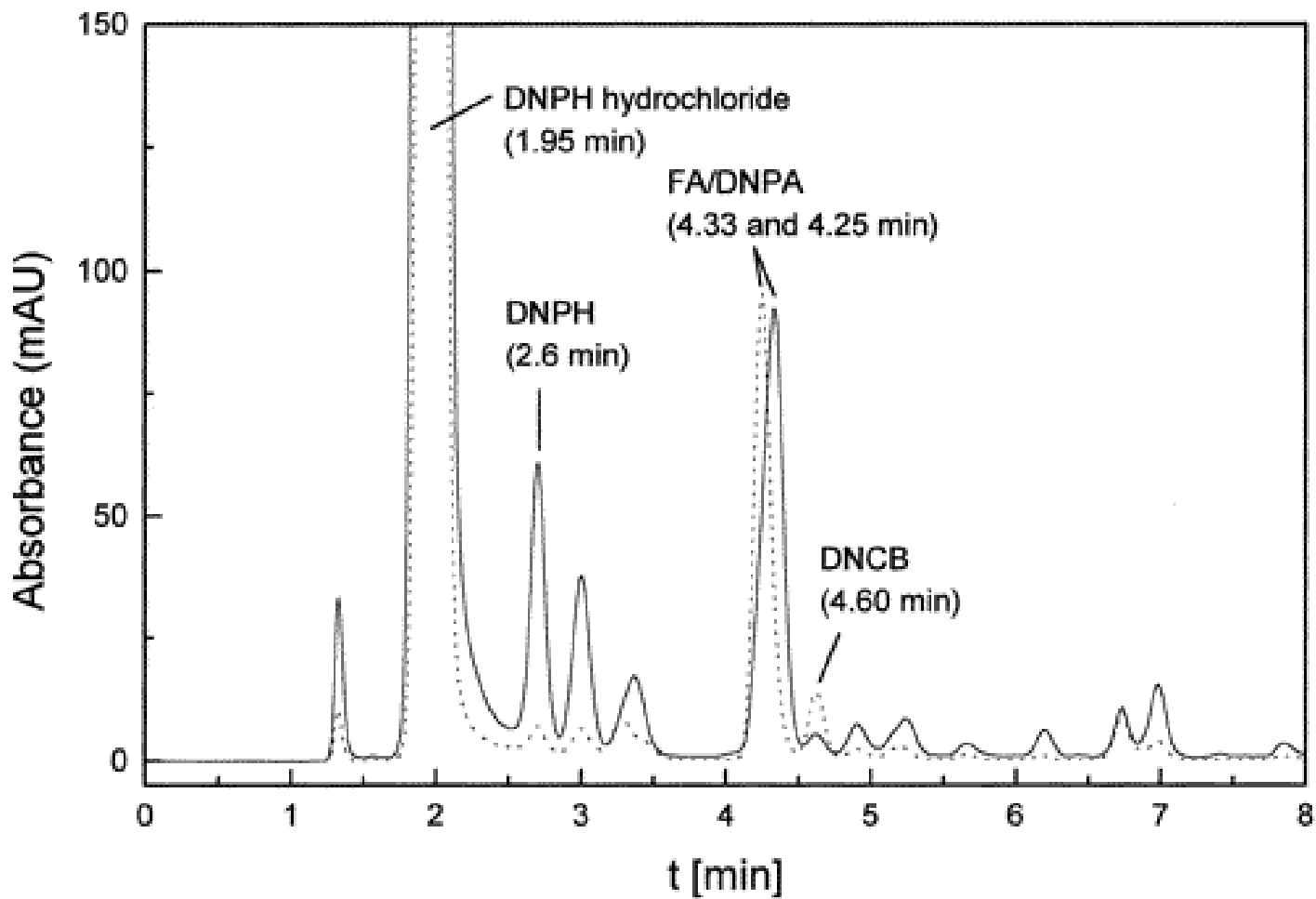
Formaldehyde

DNPH reacts with NO_2 to form 2,4-Dinitrophenyl azide (DNPA).

DNPA coelutes with the formaldehyde-DNPH derivative.



DNPA



Formaldehyde

Several studies have capitalized on the formation of DNPA for the sampling of NO_2 , by altering/optimizing their HPLC gradient.

The use of KI scrubbers to limit O_3 interferences promotes NO_2 by the oxidation of NO.

TO11A does not reflect any of the aforementioned information.

Acetaldehyde

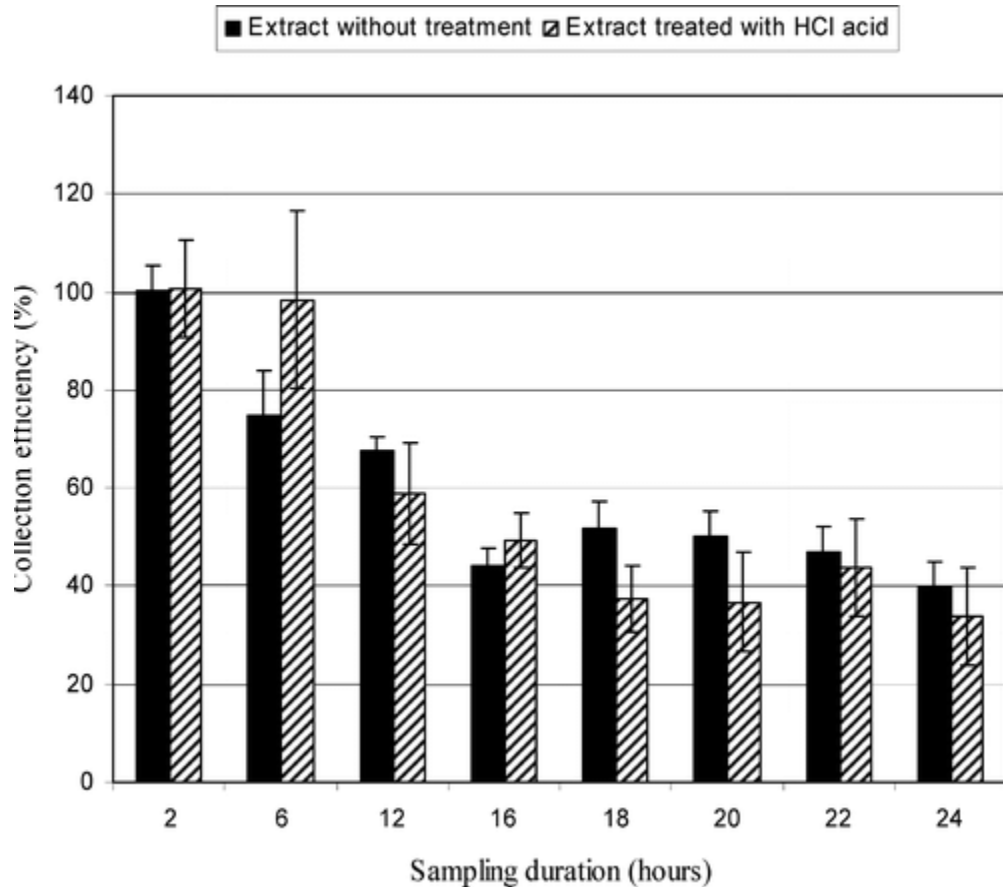
Through an extensive literature search, we were only able to find three studies during which carbonyls other than formaldehyde were evaluated on DNPH-coated solid sorbents for long-term sampling (i.e., 24 h or greater).

Lazarus (1999) reported low acetaldehyde collection efficiencies (CE); and Grosjean (1991), and Grosjean and Grosjean (1995) evaluated breakthrough of the collection media, which does not necessarily reflect CE.

Acetaldehyde

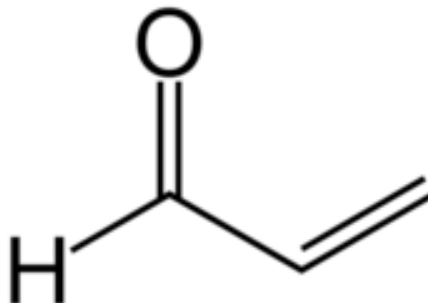
Experimental condition	Carbonyl	SUPELCO	WATERS	XPOSURE	HOUSE
3 hours at 30% RH	Formaldehyde	89 ± 10 ^c (3)			
	Acetaldehyde	93 ± 8 ^c (3)			
24 hours at 30% RH	Formaldehyde	83 ± 4 (3)	87 ± 11 (3)	111 ± 4 (3)	104 ± 25 (3)
	Acetaldehyde	39 ± 7 (3)	43 ± 3 (3)	62 ± 7 (3)	1 ± 2 (3)
48 hours at 30% RH	Formaldehyde	89 ± 8 (3)	93 ± 4 (3)	105 ± 19 (3)	14 ± 8 (3)
	Acetaldehyde	51 ± 22 (3)	43 ± 2 (3)	40 ± 11 (3)	0 (3)
24 hours at 60% RH	Formaldehyde	101 ± 8 (3)	101 ± 13 (3)	121 ± 32 (3)	133 ± 27 (3)
	Acetaldehyde	27 ± 4 (3)	29 ± 2 (3)	30 ± 2 (3)	9 ± 2 (3)

Acetaldehyde



- Herrington, J.; Fan, Z.; Liroy, P. J.; Zhang, J. Low acetaldehyde collection efficiencies for 24-hour sampling with 2,4-dinitrophenylhydrazine (DNPH)-coated solid sorbents. *Environ. Sci. Technol.* 2007, 41, 580-585.

Acrolein



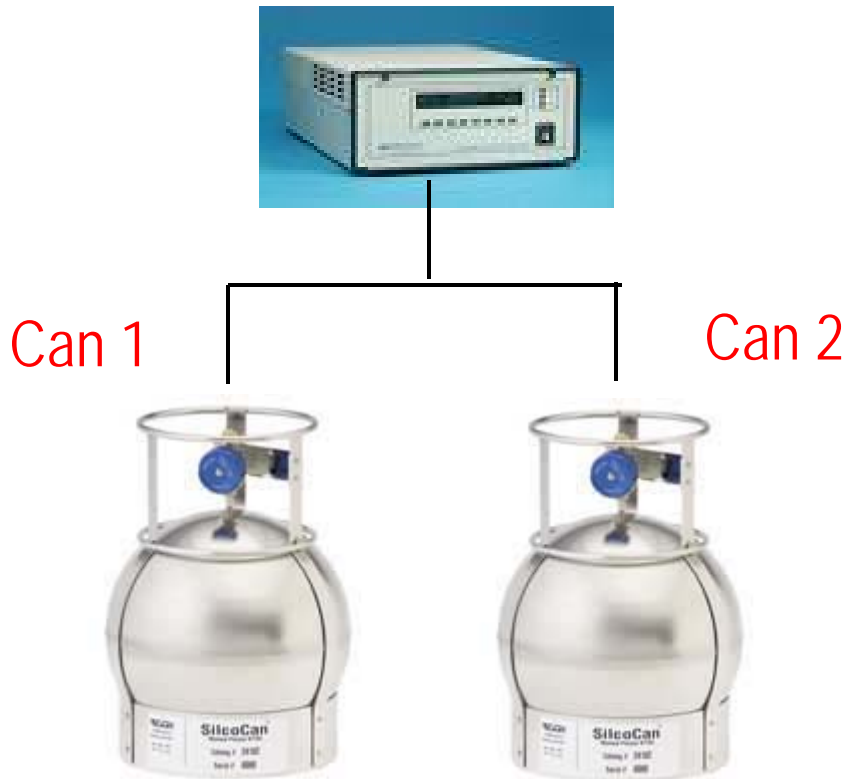
- L. Benning and A. Wahner, *J. Atmos. Chem.*, 1998, 31, 105–117.
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Acrolein by Canisters

- EPA Compendium Method TO-15
 - SUMMA Canisters
 - 24 hour samples
 - Analyzed by GC/MSD
- Recent work (*Heaton, Dann*) has demonstrated growth of acrolein within canisters.
- We designed a small study to investigate

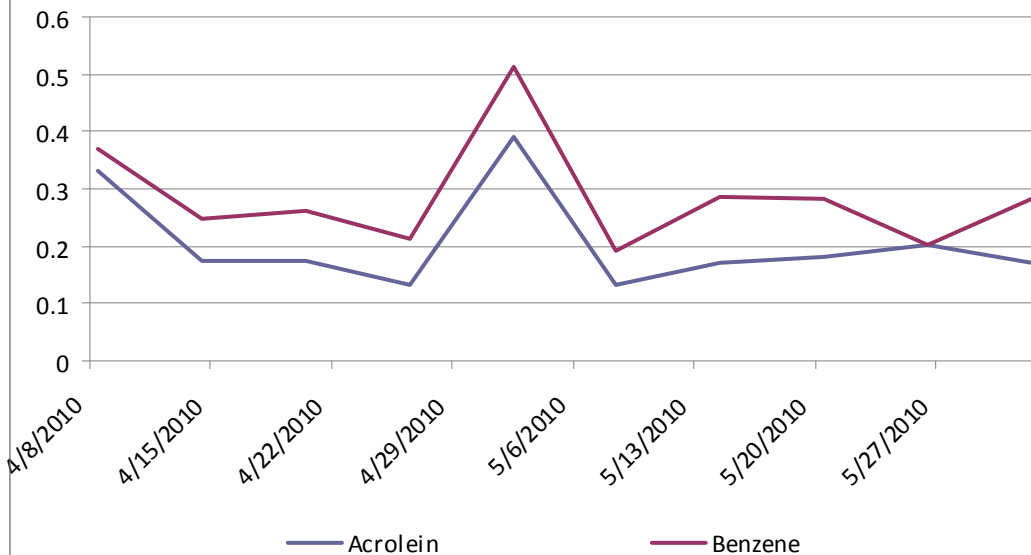
Collocation for Acrolein

Canister collocation



- Same Sample Split to 2 canisters
- 10 sampling events
- 2 different labs prepare and analyze canisters
- Site: Bronx NYC

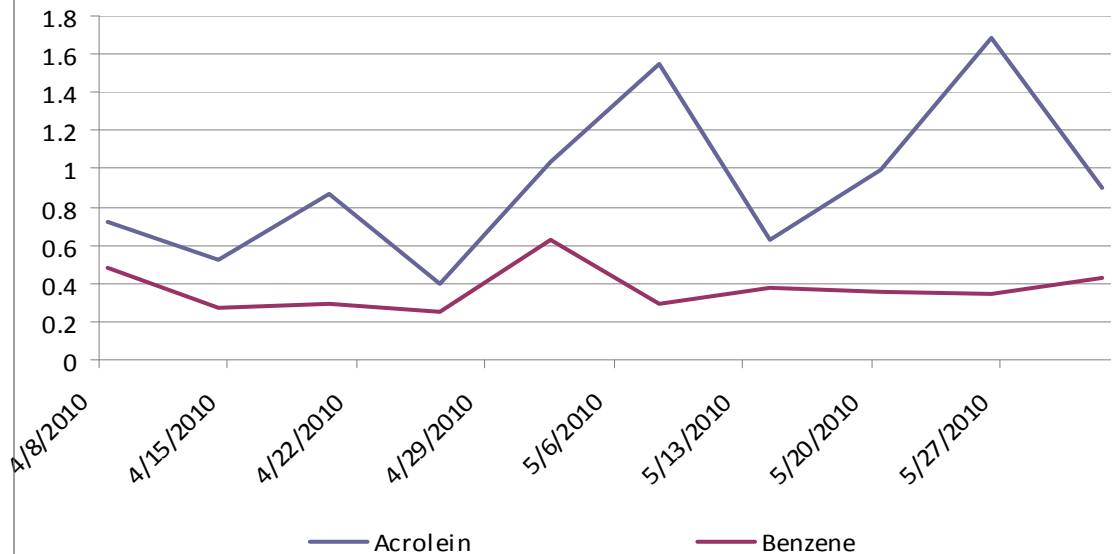
Canister 1 Time Series



- Acrolein - As a Mobile Source should track Benzene
- Typical Acrolein concentration should be lower than benzene

Not the case here –
Why? Canister is contributing to acrolein values.

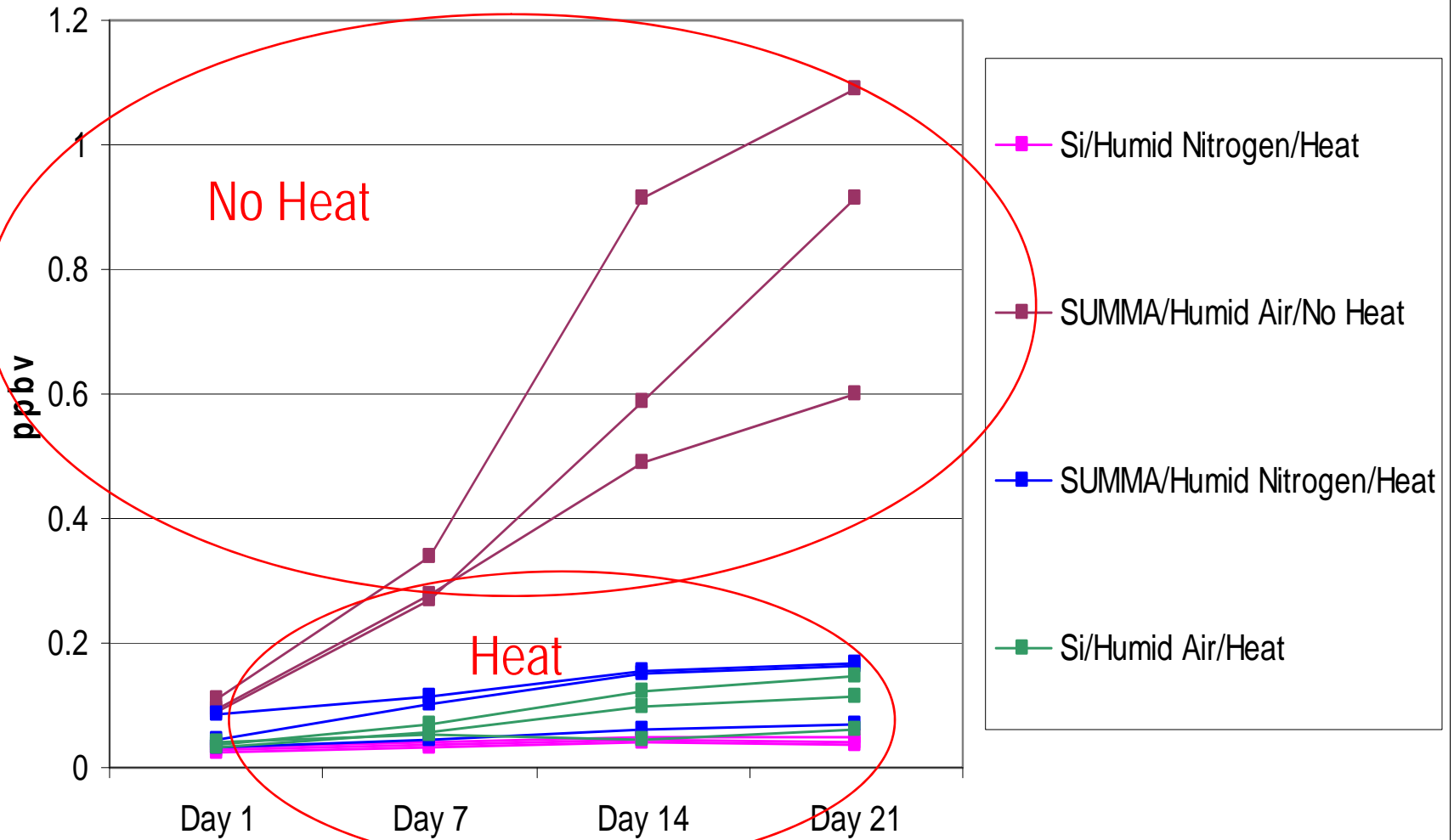
Canister 2 Time Series



Acrolein Study

- Experimental Design
 - Variables studied
 1. Canister type and prep (cleaning)
 - Heat vs No-Heat
 - Humidified Air vs Humidified Nitrogen
 - SUMMA canister vs Silco lined
 2. Lab analysis and calibration gas standards
- Test 1: Blank canisters analysis looking at Acrolein growth
 - Test for cleanliness over 21 days
 - Assumption – all SUMMA created equal

Phase 1 Test 1: Blank Canister Analysis for Acrolein (corrected values)



Recommendations

- Add heat to canister prep. At least 90°C.
- Start with fresh canisters and test **each** canister for cleanliness **over time** to ensure capability for use for Acrolein. (no growth)
- Collocate each sampling event.

Conclusions

- Laboratory staff need to be aware of DNPA and the possible coelution with the formaldehyde-DNPH derivative.
- Field sampling technicians need to be aware of acetaldehyde collections efficiencies beyond 6 hours of sampling.
- Acrolein-DNPH issues appear to be well known throughout the scientific community.
- Canisters must be cleaned with heat in order to attempt sampling acrolein.

APPENDIX B

E-MAIL COMMUNICATIONS

Vetrano, Karen

From: Meghan Kelley <mkelley@contestlabs.com>
Sent: Tuesday, November 28, 2017 12:33 PM
To: Vetrano, Karen
Cc: Lihzis, Melita
Subject: RE: Data package for Aluf

Hi Karen,

I just checked with our Lab Manager, this is not something we do here.

-Meghan

From: Vetrano, Karen [mailto:KVetrano@trcsolutions.com]
Sent: Tuesday, November 28, 2017 12:07 PM
To: Meghan Kelley <mkelley@contestlabs.com>
Cc: Lihzis, Melita <MLihzis@trcsolutions.com>
Subject: FW: Data package for Aluf
Importance: High

Hi Meghan!

I'm working with Melita Lihzis on the Orangetown Air Sampling program.

We have had some resident concerns regarding the detected concentrations of Acrolein.

I found this article from EPA regarding the DQE guidelines for Ambient Air Acrolein Measurements:
<https://www3.epa.gov/ttnamti1/files/ambient/airtox/20101217acroleindataqualityeval.pdf>

Can you let me know if ConTest follows these recommended practices for Acrolein. For example, did these canisters undergo specific preparation for Acrolein sampling and are your canisters tested for Acrolein "growth"?

Thanks so much!

Karen

Karen M. Vetrano, Ph.D.
Manager, Risk Assessment and Toxicology



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Vetrano, Karen

From: Gentile, Tom (DEC) <tom.gentile@dec.ny.gov>
Sent: Wednesday, November 29, 2017 10:47 AM
To: Vetrano, Karen
Cc: Lihzis, Melita; Felton, Dirk (DEC)
Subject: RE: Please 11/292017

Karen,

In short, your acrolein measurements as analyzed by Con-Test Analytical Laboratory are extremely suspect and problematic. I have serious concerns. Our lab has worked on this issue with EPA very intensively over the years. We believe our acrolein can measurements to be valid based on years of work with EPA and other States on this sampling method issue. We will need to have a discussion with your contract lab about how they handled and analyzed these samples. The EPA currently treats all acrolein results reported to the AQS as unverifiable. During the next round of sampling we will co-locate with you. I already asked Ms. Lihzis about your future sampling schedule in the community.
Tom

Thomas Gentile
Chief, Air Toxics Section
Bureau of Air Quality Analysis & Research
Division of Air Resources
New York State Department of Environmental Conservation
625 Broadway, Albany, NY 12233-3259
Phone: (518)402-8402
E-mail: Tom.Gentile@dec.ny.gov

From: Vetrano, Karen [mailto:KVetrano@trcsolutions.com]
Sent: Wednesday, November 29, 2017 10:29 AM
To: Gentile, Tom (DEC) <tom.gentile@dec.ny.gov>
Cc: Lihzis, Melita <MLihzis@trcsolutions.com>
Subject: FW: Please 11/292017

ATTENTION: This email came from an external source. Do not open attachments or click on links from unknown senders or unexpected emails.

Good Morning Tom,

I have a question regarding the analysis method used for measurements of Acrolein for the AQS VOC sampling.

I have discussed with a chemist that typical Summa canister sampling and TO-15 is not an appropriate method. In addition, I found the following EPA discussion regarding Acrolein data quality issues and the recommendation that the canisters be specifically cleaned and tested for "Acrolein growth". Can you provide any insight on the state's methodology?

Thanks!

Karen M. Vetrano, Ph.D.
Manager, Risk Assessment and Toxicology

APPENDIX C

DATA AND STATISTICAL ANALYSIS

**BLAUVELT INDIVIDUAL SAMPLES VS
COMPILED NEW YORK STATE MAXIMUM
DATA**

Blauvelt and Site Specific NYS DEC VOC Data Used for Statistical Comparisons

	Blauvelt (August 8, 14 and 20, 2017)			Pinnacle State Park (2013 - 2016)*			Whiteface Mountain Base (2008 - 2016)*		
	Benzene	Carbon Tetrachloride	Hexachlorobutadiene	Benzene	Carbon Tetrachloride	Hexachlorobutadiene	Benzene	Carbon Tetrachloride	Hexachlorobutadiene
	Individual Data Pts	Individual Data Pts	Individual Data Pts	max	max	max	max	max	max
	0.11	0.073	0	0.245	0.096	0.024	0.309	0.09	0.015
	0.23	0.07	0.044	0.227	0.095	0.012	0.177	0.094	0.009
	0.097	0.061	0	0.239	0.096	0.014	0.37	0.094	0.009
	0.1	0.076	0	0.232	0.107	0.015	0.434	0.111	0.008
	0.16	0.07	0				0.169	0.094	0
	0.1	0.058	0				0.199	0.1	0.003
	0.12	0.081	0				0.147	0.102	0.008
	0.25	0.072	0				0.255	0.1	0.01
	0.093	0.058	0				0.222	0.124	0.019
	0.11	0.076	0						
	0.17	0.075	0						
	0.094	0.062	0						
min ppb	0.093	0.058	0	0.227	0.095	0.012	0.147	0.09	0
max ppb	0.25	0.081	0.044	0.245	0.107	0.024	0.434	0.124	0.019
conversion factor	3.19	6.29	10.66	3.19	6.29	10.66	3.19	6.29	10.66
min ug/m3	0.297	0.365	0.000	0.724	0.598	0.128	0.47	0.57	0
max ug/m3	0.798	0.509	0.469	0.782	0.673	0.256	1.38	0.78	0.20

*Data ordered from most recent to oldest

Data obtained from: <http://www.dec.ny.gov/chemical/66478.html>

t-Test Blauvelt Benzene vs Pinnacle Benzene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:05:43 AM
 From File Air Quality Data ProUCL input.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Piinnacle

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	12	4
Number of Distinct Observations	10	4
Minimum	0.093	0.227
Maximum	0.25	0.245
Mean	0.136	0.236
Median	0.11	0.236
SD	0.0547	0.00789
SE of Mean	0.0158	0.00394

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	14	-3.548	1.761	0.998
Welch-Satterthwaite (Unequal Variance)	12.2	-6.120	1.782	1.000

Pooled SD 0.049

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 0.00299
 Variance of Sample 2 6.2250E-5

Numerator DF	Denominator DF	F-Test Value	P-Value
11	3	48.043	0.009

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

t-Test Blauvelt vs Whiteface Mountain Benzene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:08:02 AM
 From File Air Quality Data ProUCL input.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Whiteface Mntn

Raw Statistics

	Blauvelt Sample 1	Whiteface Mntn Sample 2
Number of Valid Observations	12	9
Number of Distinct Observations	10	9
Minimum	0.093	0.147
Maximum	0.25	0.434
Mean	0.136	0.254
Median	0.11	0.222
SD	0.0547	0.0984
SE of Mean	0.0158	0.0328

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	19	-3.492	1.729	0.999
Welch-Satterthwaite (Unequal Variance)	11.7	-3.224	1.782	0.996

Pooled SD 0.076

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 0.00299
 Variance of Sample 2 0.00969

Numerator DF	Denominator DF	F-Test Value	P-Value
8	11	3.241	0.075

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Pinnacle Carbon Tetrachloride Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:16:16 AM
 From File Air Quality Data ProUCL input_a.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Pinnacle

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	12	4
Number of Distinct Observations	9	3
Minimum	0.058	0.095
Maximum	0.081	0.107
Mean	0.0693	0.0985
Median	0.071	0.096
SD	0.00774	0.00569
SE of Mean	0.00223	0.00284

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	14	-6.876	1.761	1.000
Welch-Satterthwaite (Unequal Variance)	7.1	-8.067	1.895	1.000

Pooled SD 0.007

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 5.9879E-5
 Variance of Sample 2 3.2333E-5

Numerator DF	Denominator DF	F-Test Value	P-Value
11	3	1.852	0.671

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Whiteface Mntn Carbon Tetrachloride Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:18:05 AM
 From File Air Quality Data ProUCL input_a.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Whiteface Mntn

Raw Statistics

	Blauvelt Sample 1	Whiteface Mntn Sample 2
Number of Valid Observations	12	9
Number of Distinct Observations	9	6
Minimum	0.058	0.09
Maximum	0.081	0.124
Mean	0.0693	0.101
Median	0.071	0.1
SD	0.00774	0.0106
SE of Mean	0.00223	0.00354

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	19	-7.929	1.729	1.000
Welch-Satterthwaite (Unequal Variance)	14.0	-7.572	1.761	1.000

Pooled SD 0.009

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 5.9879E-5
 Variance of Sample 2 1.1250E-4

Numerator DF	Denominator DF	F-Test Value	P-Value
8	11	1.879	0.328

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Pinnacle Hexachlorobutadiene Comparison for Uncensored Full Data Sets without NDs*

***Blauvelt NDs treated as 0**

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:29:56 AM
 From File Air Quality Data ProUCL input_b.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Pinnacle

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	12	4
Number of Distinct Observations	2	4
Minimum	0	0.012
Maximum	0.044	0.024
Mean	0.00367	0.0163
Median	0	0.0145
SD	0.0127	0.00532
SE of Mean	0.00367	0.00266

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	14	-1.891	1.761	0.960
Welch-Satterthwaite (Unequal Variance)	12.7	-2.779	1.771	0.992

Pooled SD 0.012

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 1.6133E-4
 Variance of Sample 2 2.8250E-5

Numerator DF	Denominator DF	F-Test Value	P-Value
11	3	5.711	0.178

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Whiteface Mountain Hexachlorobutadiene Comparison for Uncensored Full Data Sets without NDs*

***Blauvelt NDs treated as 0**

User Selected Options

Date/Time of Computation ProUCL 5.111/30/2017 11:31:14 AM
 From File Air Quality Data ProUCL input_b.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt

Sample 2 Data: Whiteface Mntn

Raw Statistics

	Blauvelt Sample 1	Whiteface Mntn Sample 2
Number of Valid Observations	12	9
Number of Distinct Observations	2	7
Minimum	0	0
Maximum	0.044	0.019
Mean	0.00367	0.009
Median	0	0.009
SD	0.0127	0.00566
SE of Mean	0.00367	0.00189

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	19	-1.170	1.729	0.872
Welch-Satterthwaite (Unequal Variance)	16.0	-1.294	1.746	0.893

Pooled SD 0.010

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 1.6133E-4
 Variance of Sample 2 3.2000E-5

Numerator DF	Denominator DF	F-Test Value	P-Value
11	8	5.042	0.030

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

**BLAUVELT AVERAGE SAMPLING LOCATION
DATA VS COMPILED NEW YORK STATE
ANNUAL AVERAGES**

Blauvelt and Site Specific NYS DEC VOC Average Data Used for Statistical Comparisons

	Blauvelt (August 8, 14 and 20, 2017)			Buffalo, NY (2013 - 2016)			Pinnacle State Park (2013 - 2016)*			Whiteface Mountain Base (2008 - 2016)*		
	Benzene	Carbon Tetrachloride	Hexachlorobutadiene	Benzene	Carbon Tetrachloride	Hexachlorobutadiene	Benzene	Carbon Tetrachloride	Hexachlorobutadiene	Benzene	Carbon Tetrachloride	Hexachlorobutadiene
	Average	Average	Average	Average	Average	Average	Average	Average	Average	Average	Average	Average
	0.15	0.071	0.015	0.145	0.08	0.001	0.086	0.081	0.004	0.072	0.081	0.002
	0.12	0.073	0	0.158	0.081	0.002	0.114	0.082	0.003	0.075	0.081	0.002
	0.15	0.07	0	0.15	0.085	0.002	0.094	0.083	0.002	0.076	0.083	0.001
	0.12	0.072	0	0.911	0.1	0.004	0.101	0.084	0.001	0.083	0.083	0
										0.075	0.072	0
										0.083	0.07	0
										0.06	0.075	0
										0.079	0.084	0.001
										0.098	0.093	0.001
min ppb	0.12	0.07	0	0.145	0.08	0.001	0.086	0.081	0.001	0.06	0.07	0
max ppb	0.15	0.073	0.015	0.911	0.1	0.004	0.114	0.084	0.004	0.098	0.093	0.002
conversion factor	3.19	6.29	10.66	3.19	6.29	10.66	3.19	6.29	10.66	3.19	6.29	10.66
min ug/m3	0.383	0.440	0.000	0.463	0.503	0.011	0.274	0.509	0.011	0.19	0.44	0
max ug/m3	0.479	0.459	0.160	2.906	0.629	0.043	0.364	0.528	0.043	0.31	0.58	0.02

*Data ordered from most recent to oldest

Data obtained from: <http://www.dec.ny.gov/chemical/66478.html>

t-Test Blauvelt vs Buffalo Average Benzene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:16:45 PM
From File Air Quality Data ProUCL input_avg.xls
Full Precision OFF
Confidence Coefficient 95%
Substantial Difference (S) 0.000
Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt Average

Sample 2 Data: Buffalo Average

Raw Statistics

	Blauvelt Sample 1	Buffalo Sample 2
Number of Valid Observations	4	4
Number of Distinct Observations	2	4
Minimum	0.12	0.145
Maximum	0.15	0.911
Mean	0.135	0.341
Median	0.135	0.154
SD	0.0173	0.38
SE of Mean	0.00866	0.19

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	6	-1.083	1.943	0.840
Welch-Satterthwaite (Unequal Variance)	3.0	-1.083	2.353	0.821

Pooled SD 0.269

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 3.0000E-4
Variance of Sample 2 0.144

Numerator DF	Denominator DF	F-Test Value	P-Value
3	3	481.429	0.000

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

t-Test Blauvelt vs Pinnacle Average Benzene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:18:15 PM
 From File Air Quality Data ProUCL input_avg.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Pinnacle - Average

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	4	4
Number of Distinct Observations	2	4
Minimum	0.12	0.086
Maximum	0.15	0.114
Mean	0.135	0.0988
Median	0.135	0.0975
SD	0.0173	0.0119
SE of Mean	0.00866	0.00594

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	6	3.453	1.943	0.007
Welch-Satterthwaite (Unequal Variance)	5.3	3.453	2.015	0.008

Pooled SD 0.015

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Reject H0, Conclude Sample 1 > Sample 2](#)

[Welch-Satterthwaite Test: Reject H0, Conclude Sample 1 > Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 3.0000E-4
 Variance of Sample 2 1.4092E-4

Numerator DF	Denominator DF	F-Test Value	P-Value
3	3	2.129	0.551

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Whiteface Mountain Average Benzene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:19:30 PM
 From File Air Quality Data ProUCL input_avg.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Whiteface Mntn - Average

Raw Statistics

	Blauvelt Sample 1	Whiteface Mountain Sample 2
Number of Valid Observations	4	9
Number of Distinct Observations	2	7
Minimum	0.12	0.06
Maximum	0.15	0.098
Mean	0.135	0.0779
Median	0.135	0.076
SD	0.0173	0.0102
SE of Mean	0.00866	0.0034

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	11	7.572	1.796	0.000
Welch-Satterthwaite (Unequal Variance)	4.0	6.138	2.132	0.002

Pooled SD 0.013

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Reject H0, Conclude Sample 1 > Sample 2](#)

[Welch-Satterthwaite Test: Reject H0, Conclude Sample 1 > Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 3.0000E-4
 Variance of Sample 2 1.0411E-4

Numerator DF	Denominator DF	F-Test Value	P-Value
3	8	2.882	0.206

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Pinnacle Average Carbon Tetrachloride Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:42:35 PM
 From File Air Quality Data ProUCL input_avg_a.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Pinnacle - Average

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	4	4
Number of Distinct Observations	4	4
Minimum	0.07	0.081
Maximum	0.073	0.084
Mean	0.0715	0.0825
Median	0.0715	0.0825
SD	0.00129	0.00129
SE of Mean	6.4550E-4	6.4550E-4

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	6	-12.050	1.943	1.000
Welch-Satterthwaite (Unequal Variance)	6.0	-12.050	1.943	1.000

Pooled SD 0.001

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 1.6667E-6
 Variance of Sample 2 1.6667E-6

Numerator DF	Denominator DF	F-Test Value	P-Value
3	3	1.000	1.000

Conclusion with Alpha = 0.05

[Two variances appear to be equal](#)

t-Test Blauvelt vs Whiteface Mountain Average Carbon Tetrachloride Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:45:13 PM
 From File Air Quality Data ProUCL input_avg_a.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Whiteface Mntn - Average

Raw Statistics

	Blauvelt Sample 1	Whiteface Mountain Sample 2
Number of Valid Observations	4	9
Number of Distinct Observations	4	7
Minimum	0.07	0.07
Maximum	0.073	0.093
Mean	0.0715	0.0802
Median	0.0715	0.081
SD	0.00129	0.00701
SE of Mean	6.4550E-4	0.00234

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	11	-2.411	1.796	0.983
Welch-Satterthwaite (Unequal Variance)	9.1	-3.596	1.833	0.997

Pooled SD 0.006

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 1.6667E-6
 Variance of Sample 2 4.9194E-5

Numerator DF	Denominator DF	F-Test Value	P-Value
8	3	29.517	0.018

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

t-Test Blauvelt vs Pinnacle Average Hexachlorobutadiene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:51:49 PM
 From File Air Quality Data ProUCL input_avg_b.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Pinnacle - Average

Raw Statistics

	Blauvelt Sample 1	Pinnacle Sample 2
Number of Valid Observations	4	4
Number of Distinct Observations	2	4
Minimum	0	0.001
Maximum	0.015	0.004
Mean	0.00375	0.0025
Median	0	0.0025
SD	0.0075	0.00129
SE of Mean	0.00375	6.4550E-4

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	6	0.329	1.943	0.377
Welch-Satterthwaite (Unequal Variance)	3.2	0.329	2.353	0.381

Pooled SD 0.005

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 5.6250E-5
 Variance of Sample 2 1.6667E-6

Numerator DF	Denominator DF	F-Test Value	P-Value
3	3	33.750	0.016

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

t-Test Blauvelt vs Whiteface Mountain Average Hexachlorobutadiene Comparison for Uncensored Full Data Sets without NDs

User Selected Options

Date/Time of Computation ProUCL 5.112/1/2017 12:53:41 PM
 From File Air Quality Data ProUCL input_avg_b.xls
 Full Precision OFF
 Confidence Coefficient 95%
 Substantial Difference (S) 0.000
 Selected Null Hypothesis Sample 1 Mean <= Sample 2 Mean (Form 1)
 Alternative Hypothesis Sample 1 Mean > the Sample 2 Mean

Sample 1 Data: Blauvelt - Average

Sample 2 Data: Whiteface Mntn - Average

Raw Statistics

	Blauvelt Sample 1	Whiteface Mountain Sample 2
Number of Valid Observations	4	9
Number of Distinct Observations	2	3
Minimum	0	0
Maximum	0.015	0.002
Mean	0.00375	7.7778E-4
Median	0	0.001
SD	0.0075	8.3333E-4
SE of Mean	0.00375	2.7778E-4

Sample 1 vs Sample 2 Two-Sample t-Test

H0: Mean of Sample 1 - Mean of Sample 2 <= 0

Method	DF	t-Test Value	Critical t (0.05)	P-Value
Pooled (Equal Variance)	11	1.243	1.796	0.120
Welch-Satterthwaite (Unequal Variance)	3.0	0.790	2.353	0.243

Pooled SD 0.004

Conclusion with Alpha = 0.050

[Student t \(Pooled\) Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

[Welch-Satterthwaite Test: Do Not Reject H0, Conclude Sample 1 <= Sample 2](#)

Test of Equality of Variances

Variance of Sample 1 5.6250E-5
 Variance of Sample 2 6.9444E-7

Numerator DF	Denominator DF	F-Test Value	P-Value
3	8	81.000	0.000

Conclusion with Alpha = 0.05

[Two variances are not equal](#)

APPENDIX D
RISK EVALUATION

Site-specific

Resident Equation Inputs for Air

Variable	Value
ED _{res} (exposure duration) years	26
TR (target risk) unitless	1.0E-6
THQ (target hazard quotient) unitless	1
LT (lifetime) years	70
EF _{res} (exposure frequency) days/year	350
ED _{n,1} (mutagenic exposure duration first phase) years	2
ED _{2,6} (mutagenic exposure duration second phase) years	4
ED _{6,16} (mutagenic exposure duration third phase) years	10
ED _{16,26} (mutagenic exposure duration fourth phase) years	10
EF _{n,1} (mutagenic exposure frequency first phase) days/year	350
EF _{2,6} (mutagenic exposure frequency second phase) days/year	350
EF _{6,16} (mutagenic exposure frequency third phase) days/year	350
EF _{16,26} (mutagenic exposure frequency fourth phase) days/year	350
ET _{res} (exposure time) hours/day	24
ET _{n,1} (mutagenic exposure time first phase) hours/day	24
ET _{2,6} (mutagenic exposure time second phase) hours/day	24
ET _{6,16} (mutagenic exposure time third phase) hours/day	24
ET _{16,26} (mutagenic exposure time fourth phase) hours/day	24

Site-specific

Resident Screening Levels (RSL) for Air

Key: I = IRIS; P = PPRTV; D = DWSHA; O = OPP; A = ATSDR; C = Cal EPA; X = APPENDIX PPRTV SCREEN (See FAQ #27); H = HEAST; F = See FAQ; J = New Jersey; E = see user guide Section 2.3.5; L = see user guide on lead; M = mutagen; S = see user guide Section 5; V = volatile; R = RBA applied (See User Guide for Arsenic notice) ; c = cancer; n = noncancer; * = where: n SL < 100X c SL; ** = where n SL < 10X c SL; SSL values are based on DAF=1; m = Concentration may exceed ceiling limit (See User Guide); s = Concentration may exceed Csat (See User Guide)

Chemical	CAS Number	Mutagen?	VOC?	Inhalation Unit Risk (ug/m ³) ⁻¹	IUR Ref	Chronic RfC (mg/m ³)	Chronic RfC Ref	Carcinogenic SL TR=1.0E-6 (ug/m ³)	Noncarcinogenic SL THI=1 (ug/m ³)	Screening Level (ug/m ³)
Benzene	71-43-2	No	Yes	7.80E-06	I	3.00E-02	IR	3.60E-01	3.13E+01	3.60E-01 ca*
Carbon Tetrachloride	56-23-5	No	Yes	6.00E-06	I	1.00E-01	IR	4.68E-01	1.04E+02	4.68E-01 ca
Hexachlorobutadiene	87-68-3	No	Yes	2.20E-05	I	-		1.28E-01	-	1.28E-01 ca

Site-specific

Resident Risk for Air

Chemical	Inhalation Unit Risk (ug/m ³) ⁻¹	IUR Ref	Chronic RfC (mg/m ³)	Chronic RfC Ref	Concentration (ug/m ³)	Carcinogenic Risk	Noncarcinogenic HI
Benzene	7.80E-06	I	3.00E-02	IR	4.46E-01	1.24E-06	1.43E-02
Carbon Tetrachloride	6.00E-06	I	1.00E-01	IR	4.36E-01	9.32E-07	4.18E-03
Hexachlorobutadiene	2.20E-05	I	-	-	3.80E-01	2.98E-06	-
<i>*Total Risk/HI</i>	-	-	-	-	-	<i>5.15E-06</i>	<i>1.84E-02</i>