City of Houston
Post-Harvey Monitoring
Houston, TX

October 3, 2017

TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

Background

Landfall of Hurricane Harvey on August 25, 2017, and subsequent stalling of the system over south Texas, caused unprecedented flooding in the Houston Region. As a result, several industrial facilities were damaged. An example of this includes the Valero Refinery near the Manchester Community. A floating roof tank suffered failure due to heavy rainfall experienced at the facility. This subsequently led to a spill of light crude from this tank; light crude is a mixture of volatile organic compounds (VOCs). Valero has reported to the Texas Commission on Environmental Quality (TCEQ) and United States Environmental Protection Agency (EPA) that it is removing residual crude material from the damaged tank. After the spill, Valero began spraying the exposed light crude with foam suppressant to minimize emissions from the VOCs. Cleanup and repairs are on-going.

City of Houston Mobile & Canister Data

The City of Houston used its Mobile Ambient Air Monitoring Laboratory (MAAML) vehicle to conduct mobile sampling in the Houston area, as well as investigator-collected canister samples. Specifically, the Manchester neighborhood in Houston was a particular focus of sampling efforts. Based on City of Houston Analytical Reports provided to TCEQ on September 14, 2017, the MAAML vehicle was stationed at five sampling locations in Houston, with three sampling events conducted in the Manchester neighborhood. Sampling was conducted in Kingwood and Magnolia on September 2, 2017 and Manchester September 4, 6, and 8, 2017. In addition, ambient air grab samples were collected via canisters on September 2 and 4, 2017 in the Manchester neighborhood in the afternoon/early evening.

TCEQ first became aware of City of Houston investigation data via news articles, such as the Washington Post article on September 4, 2017, *Chemical companies have already released 1 million pounds of extra air pollutants, thanks to Harvey*. While speaking with the City of Houston on September 6, 2017, the city provided some preliminary information on sampling they had conducted in the area (hand-held equipment from investigators); TCEQ also requested to receive the MAAML and canister data, once validated. On September 14, 2017, the TCEQ received the MAAML Analytical Reports (MAAML reports) for the Manchester area sampling from Valero. Upon review of the MAAML reports, the MAAML sampling times cannot be confirmed. The sampling times provided in the written portion of the reports do not match the sampling times listed with the data in the data tables. Also, the MAAML sampling locations in Manchester cannot be confirmed; two of the three latitude and longitude coordinates listed in the data tables do not map to, or near to, the Manchester area (see Appendix A: Discrepancies within the MAAML Reports for more detail).

Data Quality

The City of Houston analytical reports TCEQ received did not include a description of the quality processes used for the sampling conducted with the MAAML or by the City's investigators. To

fully understand the quality of the data provided in these reports, documented quality assurance/quality control (QA/QC) protocols that ensure the data generated from these field sampling activities are of known and acceptable quality should be described or referenced. Documents detailing sampling procedures, analytical protocols, data management, and data validation are the foundation of reliable environmental sampling and provide the details necessary to understand important limitations of the data. With respect to analytical data, a final report should, at a minimum, summarize data quality objectives identifying the standards for data accuracy, including bias and precision, and targeted data completeness; QA/QC checks performed; and the QA/QC results that were used to ensure these objectives are met. Further, any discussion of data quality should also include a description of any operational or sampling anomalies, such as equipment malfunctions, software malfunctions, or procedural deviations, and whether these impacted data collection, management, or reporting. In the absence of any discussion regarding the City's quality processes for at least the QA/QC of data collection, or validation, the TCEQ cannot draw any conclusions as to the quality of the data collected. The TCEQ's evaluation of the City's data should not infer any acceptance or concurrence of the data's quality.

Measurements Collected

According to the analytical reports received by TCEQ, The City of Houston collected two types of measurements: (1) static, (2) grab. A Total of 10 static measurements were collected at three different locations via the MAAML vehicle. To do this, the MAAML vehicle is moved to a desired location and once in-place collects static measurements with the on-board instrumentation. The collection duration for volatile organic compounds (VOCs) was 1-hour. The MAAML measured a total of 62 VOCs. A total of four ambient air grab samples were collected by City of Houston investigators at four different sampling locations in the Manchester neighborhood. The duration of the grab samples collected ranged from 15 to 20 seconds, as stated in the chain of custody forms for three of the four the samples. One canister chain of custody only listed "sec" as the duration. While it is possible the sample was only 1-second, it is more likely that the sample was a 15-20 second duration sample, which would be consistent with the other two samples collected. As such, this sample was treated as a 15-20 second duration sample for this evaluation. The canister samples also measured a total of 62 VOCs.

Maximum (Max) measurement values for static and grab sampling are presented in Table 1. Max measurements were measured in the Houston area, specifically in/around the Manchester area near the damaged Valero tank.

Table 1. Max Values for Benzene and 1,3-Butadiene Measured during Static and Grab Monitoring.

	BENZENE		1,3-BUTADIENE	
MEASUREMENT TYPE	**Max Value (ppb)**	**Duration**	**Max Value (ppb)**	**Duration**
STATIC [1]	26.2	1-hr	1.1	1-hr
GRAB [2]	334.5	15-20 sec	10.3	15-20 sec

[1] *Max values are from 9/6/2017 at unverifiable time, at a location approximately 1,700 feet downwind of the damaged Valero tank (south of the Manchester neighborhood).*

[2] *Max values are from 9/4/2017 at unverifiable time, at a location approximately 690 feet northwest of the damaged Valero tank (inside the Manchester neighborhood).*

Evaluation of Data

TCEQ Air Monitoring Comparison Values (AMCVs)

The TCEQ 1-hour Air Monitoring Comparison Values (AMCVs) for the 62 VOCs sampled are presented in Table 2. AMCVs are chemical-specific screening levels for ambient air set to protect human health and welfare. Health-based AMCVs are safe levels at which exposure of similar duration is not expected to result in adverse health effects. AMCVs are used to determine if there is a potential concern. They are set at levels sufficiently below a level expected to cause adverse health effects so that, even when concentrations of a contaminant are somewhat above the AMCV, adverse health effects are not expected.

Table 2. TCEQ 1-Hour Health-based AMCVs.

Chemical	AMCV (ppb)	Chemical	AMCV (ppb)	Chemical	AMCV (ppb)	Chemical	AMCV (ppb)
Propylene	SA*	Trans-1,2-Dichloroethene	2000	Methyl Methacrylate	500	m-xylene	1700
Dichlorodifluoromethane	10000	Methyl Tert-Butyl Ether	500	1,4-Dioxane	200	p-Xylene	1700
1,2-Dichlorotetrafluoroethane	10000	1,1-Dichloroethane	1000	Bromodichloromethane	100	Bromoform	5
Methyl Chloride	500	Cis-1,2-Dichloroethylene	2000	methyl isobutyl ketone	200	Styrene	5200
Vinyl Chloride	27000	Vinyl Acetate	190	Trichloroethylene	100	o-Xylene	1700
1,3-Butadiene	1700	n-Hexane	5400	n-Heptane	8300	1,1,2,2-Tetrachloroethane	10
Bromomethane	30	methyl ethyl ketone	20000	Cis-1,3-dichloropropene	9.9	p-ethyltoluene	250
Ethyl Chloride	1000	Ethyl Acetate	4000	Trans-1,3-Dichloropropene	9.9	1,3,5-Trimethylbenzene	3000
Ethanol	10000	Chloroform	20	1,1,2-Trichloroethane	100	1,2,4-Trimethylbenzene	3000

Chemical	AMCV (ppb)	Chemical	AMCV (ppb)	Chemical	AMCV (ppb)	Chemical	AMCV (ppb)
Trichlorofluoromethane	10000	Tetrahydrofuran	500	methyl butyl ketone	10	Benzyl Chloride	10
isopropanol	2000	ethylene dichloride	540	Toluene	4000	1,3-Dichlorobenzene	500
Acetone	11000	1,1,1-Trichloroethane	1700	Dibromochloromethane	2.3	1,4-Dichlorobenzene	500
1,1-Dichloroethylene	180	Benzene	180	ethylene dibromide	0.5	1,2-Dichlorobenzene	500
Methylene Chloride	3400	Carbon Tetrachloride	20	Tetrachloroethylene	1000	1,2,4-Trichlorobenzene	50
1,1,2-Trichlorotrifluoroethane	5000	Cyclohexane	1000	Chlorobenzene	100		
Carbon Disulfide	8000	1,2-Dichloropropane	100	Ethylbenzene	20000		

**SA = simple asphyxiant. A simple asphyxiant is an inert substance that can displace oxygen from air when present in sufficiently high concentrations causing unconsciousness or suffocation. These substances are relatively non-toxic and therefore do not have an AMCV.*

Data Usefulness

There are typically two types of ambient air data collected: (1) grab samples and (2) time-integrated samples. Grab samples provide data that are used for source identification. The short nature of the sample (generally with a duration measured in seconds), in conjunction with meteorological data, aids in the identification of potential sources of a contaminant plume. An example of this would be the EPA's use of their Trace Atmospheric Gas Analyzer (TAGA) bus. TAGA is a self-contained mobile laboratory capable of real-time sampling of outdoor air emissions while in motion. Use of the TAGA data, along with investigator hand-held response equipment, aided in the conclusion by EPA that the probable source of elevated benzene and VOC readings in the Manchester community was the roof failure and spill at that Valero facility.

Time-integrated samples provide data that can be used not only for source identification, but also for health effects evaluations. This method allows for a sample to be collected over a longer period of time (generally with a duration of 30 minutes or greater). A longer sample duration provides data that are sufficiently similar to the durations used to derive safe levels, such as AMCVs, for comparison.

The canister samples collected during this sampling effort falls into the grab sample category. Like TAGA data, these samples are useful for attempting to identify any potential sources of pollutants, but cannot reliably be used in human health assessment.

The MAAML samples collected fall into the category of time-integrated samples, which can be evaluated from a human health perspective. The max 1-hour value of benzene for those samples is 26.2 ppb (see Table 3), which was measured on September 6, 2017 and is approximately 7 times lower than the 1-hour health-based benzene AMCV of 180 ppb. Based

on these data, we would not expect adverse effects to occur as a result of exposure to these concentrations.

Table 3. MAAML Benzene Measurements in/near the Manchester Community.

Date	9/4/2017			9/6/2017				9/8/2017		
Sample*	1	2	3	1	2	3	4	1	2	3
Benzene (ppb)	5.2	6.7	8.1	26.1	16.3	14.5	**26.2**	1.1	0.8	0.7

**Samples are identified by order measured that day; times cannot be verified.*

Exceedances Do Not Equal Health Effects

As discussed above, health-based AMCVs are set to provide a margin of safety and are set well below levels at which adverse health effects are reported in the scientific literature. So, an exceedance of an AMCV by a sample of similar duration does not constitute a bright line where health effects would occur. Rather, an exceedance tells us that we need to look further and conduct a more in-depth review (e.g., location of population, potential for exposure, and frequency and magnitude of detections and how do they compare to levels at which health effects would be anticipated?).

In the case of benzene, the TCEQ short-term AMCV is set to protect against adverse blood changes, which was the most sensitive critical effect observed in the scientific literature. Effects associated with this critical effect were observed at concentrations of 10,200 ppb benzene in mice exposed for 6 hours a day over the course of 6 days. Adjusting just one of the 6-hour exposures to a 1-hour exposure results in a human equivalent concentration of 18,500 ppb. To put this into perspective, the health-based 1-hour AMCV for benzene is approximately 103 times lower than this level. In the context of hurricane damage, it is also noted that the 1-hour AMCV is approximately 290 times lower than the EPA 1-hour Acute Exposure Guideline Level (AEGL) of 52,000 ppb for emergency situations.

In another example to help put acute benzene exposure into perspective, in January of 2010, the TCEQ conducted a gasoline VOC study in an effort to characterize VOC emissions from gasoline during vehicle refueling. Instantaneous (i.e., grab) measurements from that study showed benzene concentrations as high as 11,000 ppb at the fuel tank and 250 ppb five feet downwind, when a vapor recovery system (VRS) is not in place. Most newer-model vehicles are equipped with a VRS, but any time an individual interacts with gasoline (e.g., filling a lawn mower, etc.), they are potentially, acutely, exposed to relatively high levels of benzene. We are all exposed to varying levels of chemicals throughout the day, some relatively higher and some lower. Acute, transient, exposures to elevated levels are not of a health concern, as long as they are not of sufficient duration and magnitude to produce adverse health effects.

Conclusions

While the canister data are of the grab sample category and cannot be used for human health assessment, they do provide vital data to aid in source identification. Source identification aids in the rapid response to fix any potential issues. Concentrations from the 1-hour time-integrated samples, which can be used for human health evaluation, were all well below their respective health-based AMCVs. Based on these data, we would not expect adverse effects to occur as a result of exposure to these concentrations.

Appendix A: Discrepancies within the MAAML Reports

September 4, 2017 MAAML Report

Sampling Time

Under the Outcome section in the MAAML Report, it states:

> *The monitoring period ran from 15:00 to 18:00 CST on September 4, 2017…*

The data table listed in the back of the report provides the following information:

Date	Time (CST)
9/4/2017	9:00
9/4/2017	10:00
9/4/2017	11:00

Based on these two conflicting sets of times, TCEQ is unable to verify the specific time sampling took place.

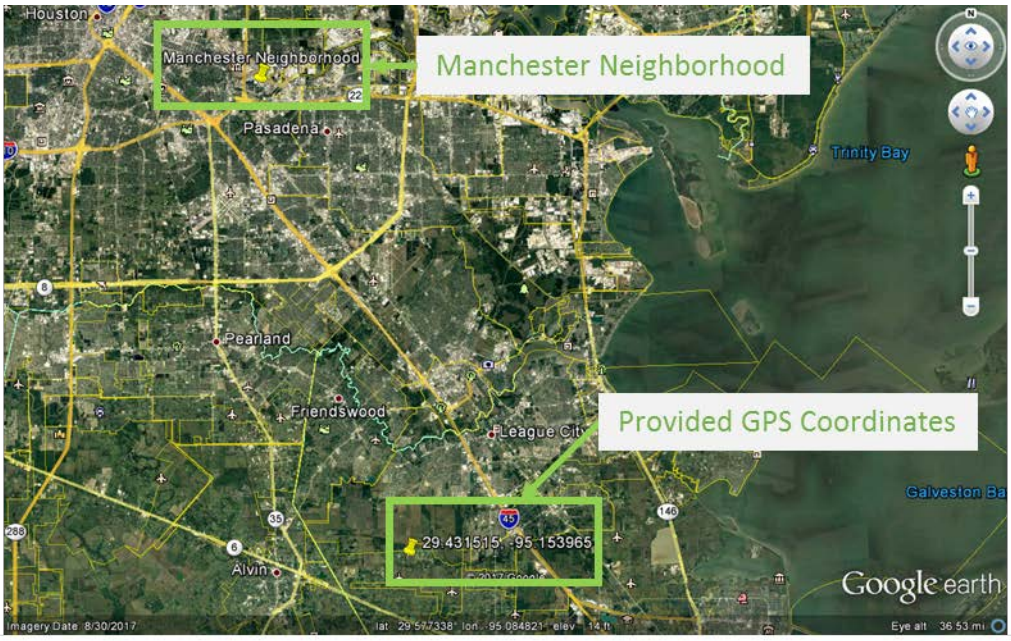
Sampling Location

The data table listed in the back of the report provides the following information:

Date	Location	Latitude	Longitude
9/4/2017	Manchester Park	29.431515	-95.153965

While Figure 1 in the Outcome section of the report provides a visual map of the MAAML location, the provided GPS coordinates do not match this location (see Map below).

The MAAML Figure 1 names Hartman Community Center as the sampling location, in the northern portion of the Manchester neighborhood. However, with contradictory data and inaccurate GPS coordinates, the location of sampling cannot be verified.



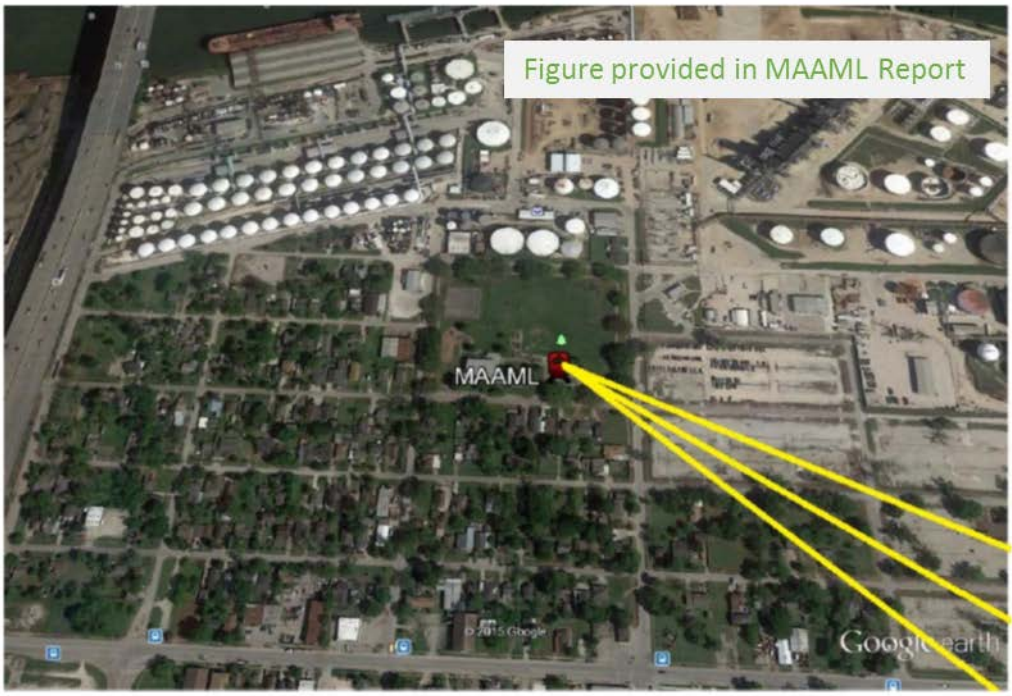


Figure 1: MAAML location and prevailing wind – Hartman Community Center (09/04/17)

September 6, 2017 MAAML Report

Sampling Time

Under the Outcome section in the MAAML Report, it states:

The monitoring period ran from 11:00 to 16:00 CST on September 6, 2017…

The data table listed in the back of the report provides the following information:

Date	Time (CST)
9/6/2017	11:00
9/6/2017	12:00
9/6/2017	13:00
9/6/2017	14:00

Based on these two conflicting sets of times, TCEQ is unable to verify the specific time sampling took place.

Sampling Location

Provided GPS coordinates in this MAAML Report appear to be accurate.

September 6, 2017 MAAML Report

Sampling Time

Under the Outcome section in the MAAML Report, it states:

The monitoring period ran from 10:00 to 13:00 CST on September 6, 2017…

The data table listed in the back of the report provides the following information:

Date	Time (CST)
9/8/2017	9:00
9/8/2017	10:00
9/8/2017	11:00

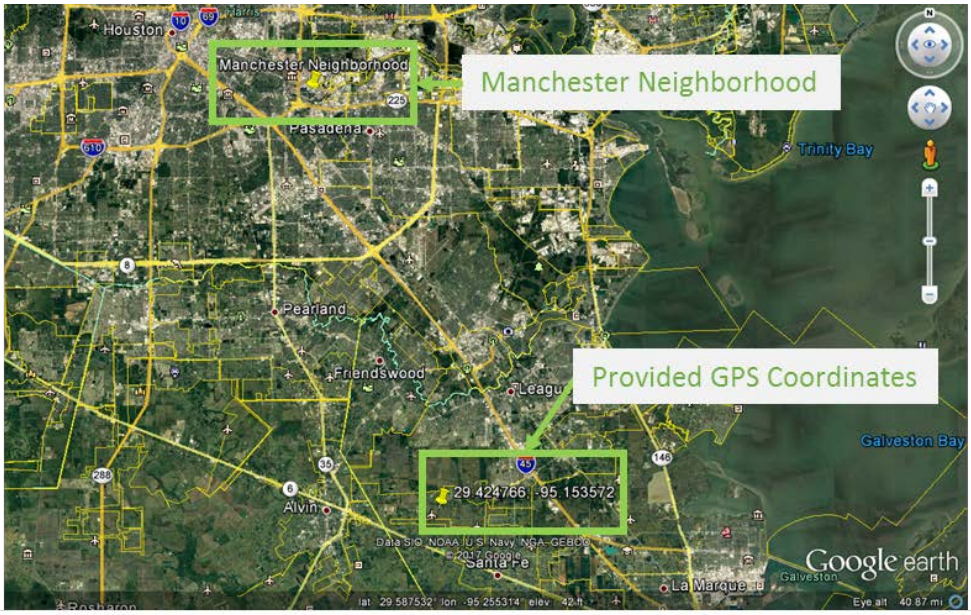
Based on these two conflicting sets of times, TCEQ is unable to verify the specific time sampling took place.

Sampling Location

The data table listed in the back of the report provides the following information:

Date	Location	Latitude	Longitude
9/4/2017	Near Lawndale and Central	29.424766	-95.153572

While Figure 1 in the Outcome section of the report provides a visual map of the MAAML location, the provided GPS coordinates do not match this location (see Map below). With contradictory data and inaccurate GPS coordinates, the location of sampling cannot be verified.



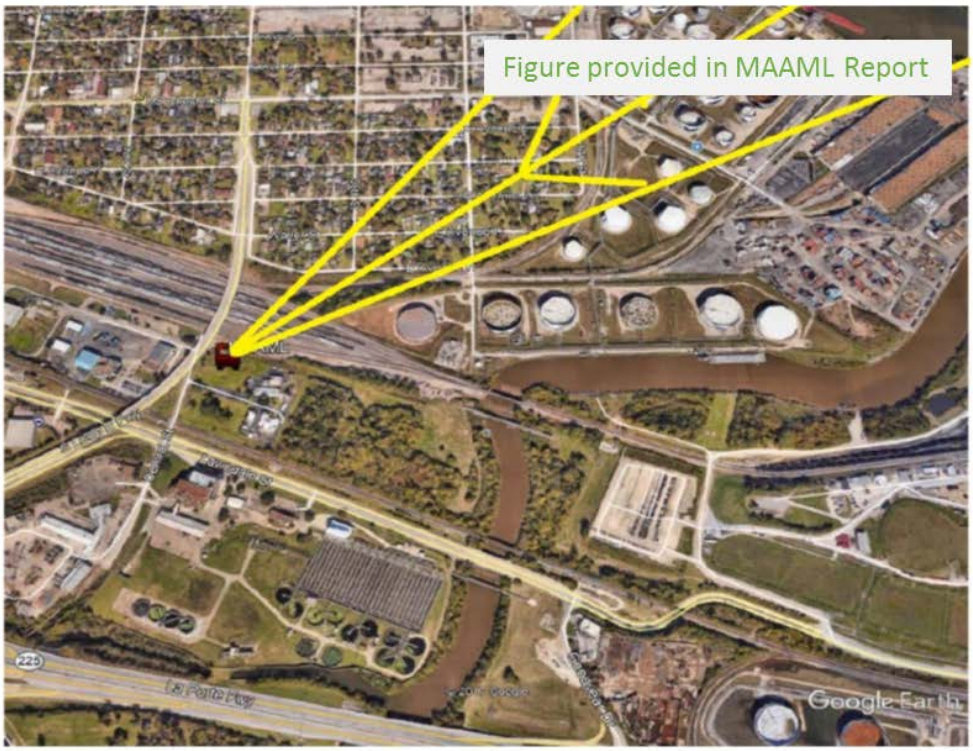


Figure 1: MAAML location and prevailing wind – Manchester (09/08/17)