MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY

INTEROFFICE COMMUNICATION

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From: Vapor Intrusion TAPS Team
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SUBJECT: Evaluation of Possible Sources of Volatile Organic Compounds Detected in Helium Tracer Gas Samples and Tubing

I. Introduction

DEQ staff use helium for leak detection when collecting vapor samples from soil gas points and vapor pins. DEQ Standard Operating Procedures (SOPs) recommend using "Ultra High Purity" (UHP) grade helium for this purpose. Previous quality control testing revealed that all grades of helium, including UHP, may contain impurities that include Volatile Organic Compounds (VOCs), the subject of vapor intrusion investigations. Impurities from the helium may be at concentrations that identify that additional response activities are needed if they are not recognized as originating in the sampling process. Additionally, previous testing has also shown that certain kinds of tubing can potentially emit or adsorb VOCs that can similarly impact the results.

Therefore, the DEQ implemented the study described in this memo in an attempt to obtain a greater understanding of the potential for concentrations of VOCs that may be introduced from helium and or tubing using currently recommended vapor sampling SOPs. The previous investigation and testing referenced above was completed in July 2014 and the results are summarized in an Interoffice Communication to the VI TAPS Team dated January 28, 2015. It should be understood that the data set, on which these conclusions are based, is still relatively limited.

II. Objective

The objective of this study was to further evaluate the contribution of VOCs from sampling materials and processes:

1. Impurities in the helium used for leak detection.
2. Compounds emitted by tubing as received from the manufacturer or supplier.

III. Methods

This study used the same sampling protocols as those identified in the VI TAPS Team January 2015 communication. Data were generated from the analysis of air samples collected using methods that isolate the potential sources in question. Samples were submitted to either the DEQ Laboratory or Fibertec Environmental Services (Fibertec) for analysis of VOCs by Method TO-15. Duplicate samples were also collected. A brief description of each sampling protocol is described below:

Helium Sample Collection

Helium samples were collected by DEQ staff into DEQ lab-prepared bottle VACs directly from supply bottles at Purity Air, Inc., Lansing, Michigan. Four grades of helium were sampled: Industrial, High Pure, Ultra High Pure, and Zero air. Samples of helium gas were collected and analyzed by Fibertec to confirm initial helium gas sample results and establish an overall larger data set.

Tubing Sample Collection

Two types of samples were collected from the tubing. Samples were analyzed by the DEQ laboratory or by Fibertec. Both types of testing are described in more detail below.

Initially, samples were collected from three foot lengths of teflon, polyethylene, tygon, master flex, silicon, and nylflex tubing at 0, 5, 15, and 30 minutes after purging with nitrogen was initiated. Tubing was used, as received from the manufacturer or supplier, without any preparation or cleaning. The purge gas was then analyzed to determine the presence of contaminants desorbed from the tubing.

Following the initial testing, all tubing types (except Nylflex) were cleaned and additional tubing purge gas samples were collected for analysis to determine the effects of cleaning the tubing prior to use. (The tubing was cleaned by Fibertec and involved a nitrogren flush and baking in an oven to fully eliminate all of the VOC's from the manufacturing process.) A second component of this phase of the study was to evaluate for the presence of desorbed contaminants after the cleaned tubing was allowed to sit for 2, 13, and 30 days prior to use. This testing was done to evaluate the potential effects of storage since tubing is generally not used on the same day it is cleaned and/or purchased.

IV. Results

Helium Sample Results

The results of the helium testing are presented in Table 1. As can be seen in the table, various VOCs were detected in all the helium samples analyzed by DEQ laboratory. The compounds detected with some regularity include petroleum hydrocarbon compounds such as the trimethylbenzene isomers, benzene, toluene, ethylbenzene, and total xylenes, tetrachloroethylene, hexane, and styrene. The detected concentrations varied, but the frequency at which these compounds were detected was fairly consistent in samples analyzed by DEQ laboratory. In addition, Fibertec analyzed one sample of each of four different grades of helium. In two of the samples only two compounds were detected (benzene and styrene), in one sample only one compound was detected (styrene) and in the fourth sample three compounds were detected (benzene, xylenes, and styrene). For all compounds detected the reported concentrations were relatively low. In summary, although

the data from the DEQ laboratory and Fibertec showed some variability, the data appears to indicate all grades of helium contain some VOCs at various concentrations.

Tubing Sampling Results

The results of the tubing testing are presented in Tables 2, 3, and 4. As can be seen in the tables, VOCs were detected in all of the samples collected from the various types of uncleaned and as-shipped tubing. In general, the highest number of compounds and concentrations were detected in the zero minute flow samples, indicating that VOC concentrations decreased the longer the tubing was purged with nitrogen before collecting the sample. And, while there were observed similarities in the compounds detected in the helium and the tubing gas samples, additional/different compounds were present in the tubing off-gas samples. It should be noted: (1) none of the tubing types were cleaned prior to purging with nitrogen; (2) the Teflon tubing and the poly tubing 30 minute purge samples were not analyzed; and (3) the poly tubing zero minutes purge sample contained PCE, but the 5 and 15 minute purge samples were non-detect.

After being cleaned and allowed to sit for 2, 13, and 30 days, no impurities were detected in the samples collected from teflon, polyethylene, master-flex, and silicon tubing. However, in the tygon tubing sample (identified for use in DEQ's soil gas sampling SOP) a number of VOCs at various concentrations were detected. Nylflex tubing was not tested after cleaning.

V. Summary:

A. In all samples of helium gas collected and analyzed (2014 and 2015) numerous impurities (VOCs) are present. Both the number of detected compounds and their concentrations vary.

B. Tygon tubing desorbs a number of VOCs, but at seemingly low concentrations. Cleaning of the tubing appears to help reduce the number of VOCs detected, but does not eliminate them entirely.

C. Teflon was the only tubing that did not desorb VOCs, even at zero time interval. Cleaning of all types of sample tubing appears to be effective in reducing or eliminating the presence of VOCs.

D. Although the concentration of VOCs detected in the helium gas and tubing gas samples are relatively low, and it is expected that any impact or contribution to the samples would be very low concentrations, their presence has the potential to raise questions about the validity of low level concentrations identified in site-specific soil gas sample data. Therefore additional steps and care are necessary when using Helium as a tracer gas and modifications to further reduce this effect must be implemented.

E. The ongoing collection and analysis of helium and tubing gas samples is recommended to supplement the existing data set and allow for a more thorough assessment of the presence of contaminants/impurities and their effect on soil gas sample results.

F. It is recommended the use of tygon tubing be eliminated from the DEQ SOP for the collection of soil gas samples. Additionally, the effectiveness of other sample collection methods that do not require the use of helium as the tracer gas should be evaluated.

VI. Conclusion:

The results of this study underline the importance of planning when conducting a vapor intrusion investigation. The development and implementation of justifiable and appropriate Data Quality Objectives, field and laboratory Quality Assurance/Quality Control procedures, sampling methodologies, and an accurate Conceptual Site Model become very important in providing a context for the collection and evaluation of data from a vapor intrusion investigation. As with assessing the risk for the vapor intrusion pathway, the multiple lines of evidence approach to document sampling procedures and results can also be used to show that sample data is representative and accurately reflective of the vapor conditions at the site.

Attachments

Table 1: Summary of Helium Results
Table 2: Summary of Tubing Impurities- by compound
Table 3: Summary of Tubing Impurities- for Total VOC's
Table 4: Summary of Tubing Impurities After Cleaning and Retesting

TABLE 1
SUMMARY OF HELIUM RESULTS

Project Name:	Former Marrah Carpet	Clarks 767 (Marshall)	Mulberry St.	Mulberry St.	Total Image Salon	US Aviex	Logan's Gas & Deli	US Aviex	US Aviex
Sample ID:	Equipment Blank Helium	Equipment Blank Helium	Helium Sample - A	Helium Sample - B	Helium Blank	Helium Blank	Helium Blank	Equipment Blank - 1	Equipment Blank - 2
Date:	9/16/2014	9/17/2014	9/22/2014	9/22/2014	10/20/2014	10/28/2014	11/6/2014	4/14/2015	4/14/2015
Lab:	DEQ	DEQ	DEQ	DEQ	DEQ	DEQ	DEQ	DEQ	DEQ
Analyte:									
1,1,1-TCA	--	--	--	--	--	1.8	--	--	--
1,2,4-TMB	65	54	190	29	74	63	100	7.2	2.3
1,3,5-TMB	16	15	52	7.6	20	17	25	1.7	--
2,2,4-Trimethylpentane	--	--	13	2.9	1.7	4.8	3.2	4	4.4
4-Methyl 2-pentanone	--	--	--	4	--	9.4	4.1	--	--
Benzene	3.3	1.9	23	8.3	7.5	20	8.5	4.4	4.8
dichlorodifluoromethane	--	--	--	2.1	--	--	--	--	--
Ethylbenzene	19	12	79	14	30	41	38	--	5
Hexane	--	--	18	9.4	5.3	18	5	2.8	4.6
Methylene Chloride	110	--	2	--	--	--	--	21.5	24
Xylenes	14	75	400	65	154	179	200	--	4.4
Styrene	38	8.2	37	5.3	8.5	20	18	88	140
Tetrachloroethylene	54	22	96	29	51	110	250	11	13
Toluene	--	34	230	62	87	190	110	--	--

All concentrations in ug/m3.
Ultra High Pure Helium was used for all blank samples.
All Sampling was conducted by RRD-DEQ Staff.

TABLE 1
SUMMARY OF HELIUM RESULTS

Project Name:	Helium Sample	Helium Sample	Helium Sample	Helium Sample
Sample ID:	Industrial Grade	High Pure	Ultra High Pure	Zero
Date:	4/25/2015	4/25/2015	4/25/2015	4/25/2015
Lab:	Fibertec	Fibertec	Fibertec	Fibertec
Analyte:				
1,1,1-TCA	--	--	--	--
1,2,4-TMB	--	--	--	--
1,3,5-TMB	--	--	--	--
2,2,4-Trimethylpentane	--	--	--	--
4-Methyl 2-pentanone	--	--	--	--
Benzene	1.7	--	2.1	2.6
dichlorodifluoromethane	--	--	--	--
Ethylbenzene	--	--	--	--
Hexane	--	--	--	--
Methylene Chloride	--	--	--	9.6
Xylenes	--	--	--	--
Styrene	41	18	47	48
Tetrachloroethylene	--	--	--	--
Toluene	--	--	--	--

All concentrations in ug/m3.
Ultra High Pure Helium was used for all blank samples.
All Sampling was conducted by RRD-DEQ Staff.

Table 2

DEQ - Summary of Tubing Impurities

Flow rate:	Control Bottle						0 Minutes Flow						5 minutes flow						15 minutes flow						30 minutes flow					
Tubing type:	**Teflon**	**Poly**	**Tygon**	**Masterflex**	**Silicon**	**Nylflex**	**Teflon**	**Poly**	**Tygon**	**Masterflex**	**Silicon**	**Nylflex**	**Teflon**	**Poly**	**Tygon**	**Masterflex**	**Silicon**	**Nylflex**	**Teflon**	**Poly**	**Tygon**	**Masterflex**	**Silicon**	**Nylflex**	**Teflon**	**poly**	**Tygon**	**Masterflex**	**Silicon**	**Nylflex**
Results for VOCs in ppbv																														
Methyl isobutyl ketone	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**0.96**	<RL	**[0.57]**	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
Toluene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**0.93**	**0.98**	<RL	<RL	<RL	<RL	**[0.26]**	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
Tetrachloroethylene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**0.47**	**4.50**	<RL	<RL	<RL	<RL	<RL	**1.1**	<RL	<RL	<RL	<RL	<RL	**1.2**	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
Ethyl benzene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**0.54**	**[0.26]**	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
m&p Xylene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**2.20**	**1.2**	<RL	<RL	<RL	<RL	**0.58**	<RL	<RL	**0.62**	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
o-Xylene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**1.30**	**0.57**	<RL	<RL	<RL	<RL	**0.34**	<RL	<RL	**[0.25]**	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
1,3,5-Trimethylbenzene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**0.40**	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL
1,2,4-Trimethylbenzene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**1.80**	**0.95**	<RL	<RL	<RL	<RL	**0.72**	**0.3**	<RL	**0.52**	<RL	<RL	**0.41**	<RL	<RL	<RL	NT	NT	**[0.25]**	NT	<RL	<RL
1,3-Dichlorobenzene	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**1.2**	**9.8**	<RL	<RL	<RL	<RL	**0.42**	**5.5**	<RL	<RL	<RL	<RL	**[0.29]**	**4.8**	<RL	NT	NT	<RL	NT	**2**	<RL
Isopropyl Alcohol	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	**large**	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	<RL	NT	NT	<RL	NT	<RL	<RL

Control Bottle = Was cleaned at the same time as the other bottles then filled with nitrogen direct from canister cleaner.
0 Minutes Flow = This bottle was connected to the 3 foot of tubing and with nitrogen flowing, the sample was collected immediately.
5 Minutes Flow = This bottle was collected after 5 minutes of nitrogen flowing through the 3 ft of tubing.
15 Minutes Flow = This bottle was collected after 15 minutes of nitrogen flowing through the 3 ft of tubing.
<RL = Below reporting limit
NT = Not tested
Values in [ ] are trace levels below reporting limit.

Table 3

DEQ - Summary of Tubing Impurities

	Results for total VOCs ppbv				
Flow Rate:	**Control bottle**	**0 minutes flow**	**5 minutes flow**	**15 minutes flow**	**30 minutes flow**
Tubing Type					
Teflon	<RL	<RL	<RL	<RL	Not tested
Poly	<RL	**0.47**	<RL	<RL	Not tested
Tygon	<RL	**12.63**	**3**	**1.61**	**0.25**
Masterflex	<RL	**5.16**	**0.45**	**0.29**	Not tested
Silicon	<RL	**10.37**	**5.5**	**4.8**	**2**
Nylflex	<RL	<RL	**1.39**	<RL	<RL

Control Bottle = Was cleaned at the same time as the other bottles then filled with nitrogen direct from canister cleaner.
0 Minutes Flow = This bottle was connected to the 3 foot of tubing and with nitrogen flowing, the sample was collected immediately.
5 Minutes Flow = This bottle was collected after 5 minutes of nitrogen flowing through the 3 ft of tubing.
15 Minutes Flow = This bottle was collected after 15 minutes of nitrogen flowing through the 3 ft of tubing.
<RL = Below reporting limit
NT = Not tested
Values in [ ] are trace levels below reporting limit.

Table 4

DEQ - Summary of Tubing Impurities After Cleaning and Retesting

	Result for total VOCs ppbv		
Time passed after initial testing:	**2 days**	**13 days**	**30 days**
Tubing Type			
Teflon	NT	NT	**<RL**
Poly	NT	**<RL**	NT
Tygon	**7.35**	NT	NT
Masterflex	**<RL**	NT	NT
Silicon	**<RL**	NT	NT
Nylflex	NT	NT	NT

Control Bottle = Was cleaned at the same time as the other bottles then filled with nitrogen direct from canister cleaner.
0 Minutes Flow = This bottle was connected to the 3 foot of tubing and with nitrogen flowing, the sample was collected immediately.
5 Minutes Flow = This bottle was collected after 5 minutes of nitrogen flowing through the 3 ft of tubing.
15 Minutes Flow = This bottle was collected after 15 minutes of nitrogen flowing through the 3 ft of tubing.
<RL = Below reporting limit
NT = Not tested