U.S. Chemical Safety and Hazard Investigation Board

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Response to Philip C. Price, PhD Petition for Correction – November 1, 2016
Final Investigation Report – Freedom Industries Investigation Report, 2014-01-I-WV

This document is in response to questions and comments raised by Philip C. Price, the petition requester. Among a number of issues raised in the petition, the requestor states that, "I would hope that the CSB would follow its *Final Data Quality Guidelines,* p7, and more fully apply 'commonly accepted scientific... standards' to its work."

The Freedom Industries (Freedom) investigative team used root cause analysis tools and followed accepted scientific standards and practices throughout the investigation and production of the Freedom report, including standardized test methods for metallurgical examination, and protocols for internal and external review for thoroughness, confidential business information, factual accuracy, and technical and logical correctness. With the response to this petition, the CSB will also be releasing four CSB contractor reports on the metallurgical evaluation of tank 396 and the inspections of tanks 395, 396 and 397. These are:

> Metallurgical Evaluation of Tank Coupon T396, Anamet, Inc.
> API653 Inspection Report of Tank 395, Powers Engineering and Inspection, Inc.
> API653 Inspection Report of Tank 396, Powers Engineering and Inspection, Inc.
> API653 Inspection Report of Tank 397, Powers Engineering and Inspection, Inc.

The other issues and questions raised in the petition are addressed below.[1]

- **What chemicals were spilled?**

The CSB reviewed multiple sources of information to determine the chemicals most likely released as a result of the Freedom incident. One of the sources was CSB interviews with Freedom personnel who stated that crude methylcyclohexanemethanol (MCHM) and polyglycol ethers (PPH, Stripped) were the only materials added to the storage tank that leaked (tank 396). Beyond interviews, the CSB partnered with the U.S. Occupational Safety and Health Administration's (OSHA) area office to collect a sample of material from the leaking storage tank for further chemical analysis.

[1] The Freedom Investigation Report will be revised to include additional information provided in the petition responses.

Shortly after the leak was discovered on the morning of January 9, 2014, Freedom arranged for the remaining contents of tank 396 to be removed and stored at Freedom's Poca Blending facility.[2] The tank 396 sample obtained by the CSB and OSHA for chemical analysis was taken from the storage container at the Poca Blending facility on January 17, 2014. The CSB found through interviews that the vacuum trucks used to remove the contents of tank 396 were not cleaned prior to their use during the leak response and remediation efforts. Further, the CSB could not verify that the storage tanks at Poca Blending were clean prior to receiving the material from tank 396. Ultimately, the possibility exists that the sample of tank 396 contents may have been contaminated by remnant chemicals in either the vacuum trucks and/or the Poca Blending facility storage tanks.

The sample of tank 396 material referenced in the CSB report was sent to OSHA's Salt Lake City Test Center where the chemical composition was analyzed on January 27, 2014, using gas chromatography-mass spectrometry (GC-MS), followed by a quantitative GC analysis on February 24, 2014. In both instances, OSHA used standard internal protocols to conduct the tests, which included extracting bulk liquid samples with isopropyl alcohol (IPA). A summary of the reported analytes and their percent concentrations is given in Table 1.

Table 1. Summary of reported qualitative and quantitative chemical analyses of tank 396 contents.

	Qualitative GC-MS	*Quantitative GC (% composition)*
Reported analytes and their percent	Major analytes detected: • 4-methylcyclohexanemethanol • 2-methylcyclohexanemethanol (2-MCHM)* Minor analytes detected: • Methanol • Cyclohexanemethanol • Propylene glycol phenyl ether (PPH and/or isomer) • Unknowns	• 4-methylcyclohexanemethanol (81.1 %) • Methanol (1.42%) • Cyclohexanemethanol (0.15 %) • Propylene glycol phenyl ether (PPH and/or isomer) (0.83%) • Unknowns (16.5%)

*The indication of 2-MCHM was most likely the result of a misidentification of the peak by a mass spectral library that OSHA uses to aid in the identification of unknowns. See text below for full explanation.

For the qualitative tests, OSHA relied upon a mass spectral library to tentatively identify the components of the tank 396 sample. After the initial data collection, OSHA purchased an analytical standard of 4-MCHM that contained both *cis*- and *trans*-4-MCHM isomers to calibrate its GC data. Results from the analytical standard indicate that the mass spectral library had misidentified the 2-MCHM and in fact OSHA was observing *cis*- and *trans*-4-MCHM isomers in its own GC data. The percentage of 4-MCHM reported in Table 1 is a summation of both the cis-

[2] U.S. Chemical Safety and Hazard Investigation Board. Freedom Industries Incident Investigation Report. Section 1.0, Page 1. Freedom Industries Chemical Release - Investigations | the U.S. Chemical Safety Board (Accessed December 11, 2016).

and trans-4-MCHM isomers observed by OSHA in the tank 396 sample.

The objective of OSHA's analyses was limited to compliance purposes and, as a result, did not address the identification of the unknown chemicals in the sample tested. The CSB did not pursue any additional testing and cannot report any findings beyond what OSHA provided. The CSB recognizes that there is uncertainty in determining the exact composition of chemicals in tank 396 at the time of the release.

OSHA reported a pH in the range of 4.5-5 for the tank 396 sample. To obtain this result, OSHA used a pH testing strip intended for aqueous solutions. As this sample is a non-aqueous mixture, the reported pH should be considered a relative value for comparison to other samples, rather than a direct correlation with an aqueous pH value. The pH value is not an indication that acid was added to the tank, and should not be interpreted as such. See below for comment on possible addition of acid to tank 396.

- **How much of each chemical was spilled?**

Tank 396 had an inventory of about 30,906 gallons on January 8, 2016. The CSB measured the Baker storage container's level on January 16, 2016, and estimated a volume of about 20,000 gallons of recovered material from tank 396, resulting in a net loss of about 11,000 gallons.

The CSB estimates the released volume of chemicals from tank 396 by subtracting the recovered volume of tank 396 contents as measured at Poca Blending on January 16, 2016 (~20,000 gallons) from Freedom's last recorded inventory of tank 396 on January 8, 2016 (~31,000 gallons). This results in an estimated net loss of about 11,000 gallons of material. To estimate the amount of individual chemicals released, the CSB uses OSHA's quantitative chemical analysis results to estimate the following release volumes:

Chemical	***Estimated Volume Released (gallons)***[3]
4-Methylcyclohexanemethanol	8,900
Methanol	160
Cyclohexanemethanol	17
Propylene glycol phenyl	91
Unknowns	1,800
Total Estimated Volume	10,967

[3] Calculated by multiplying 11,000 (estimated gallons released) by the percent compositions listed in Table 1.

- **When did the spill happen? How long was MCHM flowing into the water intake? Is it possible the tank was leaking, undetected, for a very long time?**

The CSB considered two possible leak scenarios:

a) the leak began, more or less, instantaneously and was soon discovered;
b) the leak persisted over some extended time period, but went unnoticed by either the general public or Freedom officials.

To assess these two scenarios, the CSB estimated potential flow rates from the two holes discovered at the bottom of tank 396 and considered other qualitative evidence. The following assumptions were made for leak flow rate calculations:

- due to the presence of highly permeable gravel beneath the tank, there was essentially no resistance inhibiting flow from the tank;
- the edges of the two holes were sharp;
- the soil-side hole diameter was equal to the interior-side hole diameter;
- the coefficient of velocity (C_v) is assumed to be 0.98;
- the coefficient of contraction (C_c) is assumed to be 0.63;
- the tank (20 ft. diameter x 20 ft. tall) held ~31,000 gallons of material at the start of the leak;
- approximately 11,000 gallons of material leaked from the tank before the leak was stopped.

The time for 11,000 gallons to drain from the tank, assuming leakage through the 0.4-inch hole, the 0.75-inch hole, or both holes, is approximated below:[4]

Leak size	***Time to drain 11,000 gallons***
0.4-inch diameter	~28 hours
0.75-inch diameter	~8 hours
Both 0.4 and 0.75-inch holes open	~6 hours

The CSB notes that air quality complaints from the public began around 10:00 am and that the material was removed from tank 396 at around 1:00 pm.[5] Considering that the smell of the contaminated water was detectable by humans at concentrations in water as low as one part per trillion (ppt),[6] it seems unlikely the leak occurred through the 0.4-inch hole for a 28-hour period

[4] $t = 2A_t(\sqrt{(z_1)} - \sqrt{(z_2)})/[C_d A_o \sqrt{(2g)}]$, where A_t is the cross-sectional area of the tank, z_1 is the height of the fluid in the tank at the start of the leak, z_2 is the height of the fluid when flow from the tank is stopped, C_d is the coefficient of discharge (in this case assumed to be 0.62), A_o is the area of the leak orifice, and g is gravitational acceleration.

[5] According to CSB interviews, the odor was noticed at the Interstate 77 and 79 split in Charleston, about 1 mile from the Freedom facility.

[6] U.S. Chemical Safety and Hazard Investigation Board. Freedom Industries Incident Investigation Report. Section 1.0, Page 1. Freedom Industries Chemical Release - Investigations | the U.S. Chemical Safety Board (Accessed December 11, 2016).

without public notice the previous day. Instead, a leak through either the 0.75-inch hole or both the 0.75- and 0.4-inch holes seems plausible because the leak could have started in the early morning hours, but was not noticed or reported by local residents until later in the morning on the day of the incident.

Finally, the soil beneath the gravel base for the tank was clay, and as a result the lowest resistance flow path for a leak should have been through the gravel and then along the ground surface. Interviews with Freedom officials and employees indicated they never noticed such a leak prior to the incident.

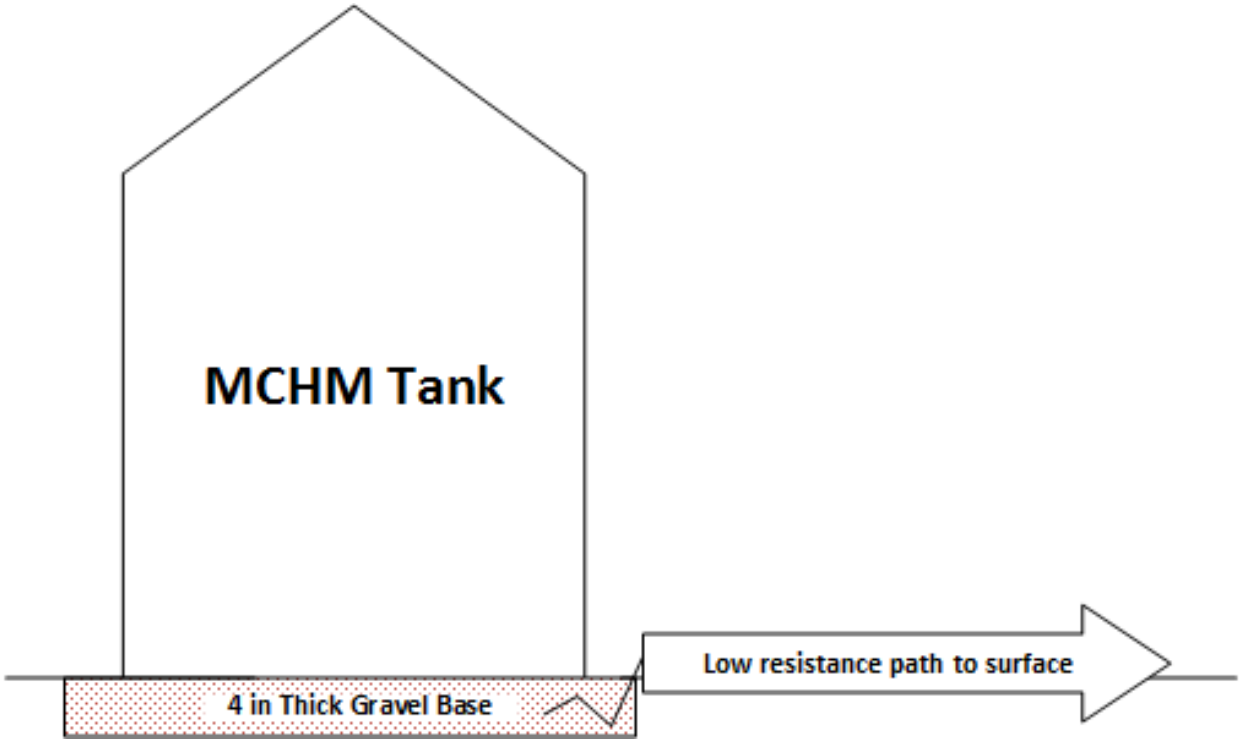

Figure 1. Low resistance flow path provided by the gravel base.

- **Is it possible the spill was significantly larger?**

As indicated above, the CSB bases its estimate on the volume of material released on the last recorded inventory of tank 396. If this value is incorrect, it is conceivable the release could have been larger. The CSB did not discover any evidence to indicate that the inventory logs were incorrect, but the CSB cannot definitively rule it out. Additionally, it seems plausible based on leak rate modeling, that 11,000 gallons could have escaped overnight before it was discovered and then throughout the morning before the tank was emptied.

- **How did the spill happen?**

The release occurred because the tank contents were able to pass to the outside through holes caused by pitting corrosion at the bottom of the tank. It is uncertain when those holes were created and if previous owners had been aware of their existence. It could not be determined through interviews, documentation, or post-incident evaluations, whether the presence of polyvinyl acetate (PVA) found on the bottom of the tank was the result of mitigation efforts before the pitting actually formed holes. If this were the case, then the corrosion would have to have continued under the PVA after its application. It was also impossible to conclude whether the holes had been previously discovered and the PVA had been used to plug the holes and prevent further degradation. Finally, it was not possible to determine if the PVA had been put into place to prevent corrosion, but had been damaged at some point, exposing the bottom of the tank to a corrosive environment where the holes were able to form. In this latter scenario, debris and other material may have plugged the holes preventing tank contents from escaping until some event dislodged the debris. Frost heave, caused by weather conditions, may have initiated the release by dislodging PVA remnants or debris covering the holes on the day of the incident.

Ultimately however, the lack of a systematic inspection program, including commonly accepted guidance found in standards such as API-653, led to the tanks not being evaluated for potential failure due to corrosion, which would have easily been detected under such a regimen.

- **What was the source of the acid that corroded the tank?**

The CSB could not come to a definitive conclusion as to when the holes in the bottom of the tank formed. As a result, the CSB also could not conclude whether acid played a role in the corrosion and ultimate loss of containment in tank 396.

Although the CSB found evidence that the prior owner, Etowah River Terminal (ERT) added hydrochloric acid to the contents of tank 397 in 2012,[7] CSB did not find evidence of any such addition to tank 396. If ERT officials added hydrochloric acid to tank 396 or lowered the pH of the tank with some other chemical, this could have initiated the corrosion or accelerated the corrosion rate of the tank interior. As stated above, the reported pH of the tank contents should not be taken as evidence that acid was added to the tank.

- **Without a clear definition of what the public was exposed to, how can one evaluate public health effects? How is it possible for the NTP to do "toxicology testing"?**

The CSB understands the concerns of the petitioner and his family in light of the inhalation irritation and dermal rashes experienced after the release. We understand that many residents of the nine counties still have questions regarding the toxicity of the released material that permeated the West Virginia American Water (WVAW) filters into the drinking water supply. The CSB recognizes the need for more toxicological information to determine exposure thresholds for all the chemicals that made up the released material as well as the thousands of

[7] Etowah River Terminal Plant Manager, email message to Laboratory Manager, "8.08.12 Neutralization of Tank 397." August 8, 2012.

uncharacterized hazardous chemicals currently in use throughout industry. The CSB decided to stay abreast of the work being done by designated federal and state public health agencies to evaluate public health effects rather than undertake its own toxicological analyses.

The Freedom Investigation Report acknowledges the deficiencies in risk communication to the public and lack of toxicological information at the onset of the incident, which led the West Virginia Bureau of Public Health (WVBPH) to establish conservative levels for water consumption. Because the Centers for Disease Control (CDC), including the Agency for Toxic Substance and Disease Registry (ATSDR), the National Toxicological Program (NTP), and the WVBPH and Kanawha Putnam Health Department, all gathered toxicological information and/or conducted toxicological studies of this incident, the CSB used its limited resources to focus instead on root cause analysis.

NTP conducted nine toxicological studies and presented them in, *West Virginia Chemical Spill: Collective NTP Findings and Supporting Files*[8] from 2014 to 2015. This was in response to a nomination by the CDC/ATSDR in July 2014. The purpose of these tests was to evaluate the adequacy of CDC's drinking water screening level. As in the case of CSB and OSHA, NTP was unable to obtain an unadulterated sample and therefore unable to test the actual contents of tank 396. NTP acquired chemicals for these toxicological studies from a variety of sources.[9] Initial and subsequent updated component parts in the studies are listed below.

1. Final NTP Update
2. Bacterial mutagenicity
3. High throughput screening assays
4. Mouse dermal irritation and hypersensitivity
5. Nematode (Caenorhabditis elgans) toxicity
6. Rat 5-day toxicogenomic
7. Rat prenatal developmental toxicity
8. Structure-activity relationship analysis
9. Zebrafish developmental toxicity and photomotor response

- **Do we understand where the spill plume spread, and levels of human exposures? Who received what relative exposures? (which residents' neighborhoods, census tracts)**

No. The CSB did not examine the size of the plume and its impact on human exposures. Though this type of inquiry was beyond the scope of CSB's investigation into the Freedom incident, we became aware of work done by other organizations in response to the Elk River release. The U.S. Geological Survey collected a limited number of water samples on the Elk, Kanawha, and Ohio

[8] *West Virginia Chemical Spill: Collective NTP Findings and Supporting Files*. http://ntp.niehs.nih.gov/results/areas/wvspill/collective.html (Accessed January 7, 2017).
[9] Chemical Methods – WV Chemical Spill NTP Studies. https://tools.niehs.nih.gov/cebs3/wvspill/index.cfm?action=main.download&bin_id=790&library_id=3686&fileIdsSelected=1de2c1a655b4e6290155c1127d210078 (Accessed January 24, 2017).

Rivers, and tap-water samples at several locations in the Charleston area for determination of 4-MCHM.[10,11] The CSB also learned from the Ohio River Valley Water Sanitation Commission (ORSANCO) that 4-MCHM was monitored at a number of water intakes from Paducah, KY to Pittsburgh, PA.[12]

- **The petitioner states, "…the CSB report only makes 3 formal recommendations (pages 113-4). This seems to indicate the CSB did not fully understand the chain of events that led to this spill's negative impacts on Kanawha Valley residents. Blame is not productive, but specific actions to prevent a future event are needed."**

The CSB's procedure for recommendations development includes root cause analysis, internal and external reviews, and meetings with proposed recommendations recipients. Consistent with agency policy, the CSB met with all potential recommendations recipients (with a focus on reaching the largest number of entities possible) and, as stated in the Final Investigation Report, found that many of the recipients had already established requirements and implemented practices that addressed many of the gaps that the CSB identified. Accordingly, additional lessons learned were identified in conjunction with the development of recommendations.

- **The petitioner states, "Part 3 of R2 (to American Water Works) suggests "as modeled by WVAW's Kanawha Valley Water System June 2016 Source Water Protection Plan". Obviously, the CSB never examined this document. It has not been approved, and has obvious deficiencies. A more egregious example is the omission of Yeager Airport as a water risk."**

With respect to Part 3 of R2, the CSB thoroughly examined WVAW's Kanawha Valley Water System, June 2016 Source Water Protection Plan and recognized it was submitted to WVBPH for approval. CSB found the components of the document to be thorough, and inclusive of source water monitoring. WVBPH submitted comments regarding WVAW's Kanawha Valley Water System June 2016 Source Water Protection Plan and WVAW responded on August 24, 2016, about a month prior to the CSB's Public Meeting in Charleston, WV.[13] As stated in this document, WVAW did consider the impact of the [Yeager] airport as a priority Potential Source of Significant Contamination.

Thank you for your petition and for your interest in the work of the CSB.

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[10] Determination of (4-methylcyclohexyl) methanol isomers by heated purge-and-trap GC/MS in water samples from the 2014 Elk River, West Virginia, chemical spill. (Accessed January 7, 2017).

[11] Chemicals in Elk River Spill Lingered Longer, Traveled Farther https://www.usgs.gov/news/chemicals-elk-river-spill-lingered-longer-traveled-farther (Accessed January 11, 2017).

[12] *Source Water Protection on the Ohio River: Working Together to Protect Drinking Water*. http://www.onewaterohio.org/docs/1000_ohio_river_valley_water_sanitation_commission_overview.pdf. (accessed January 7, 2017)

[13] *SWPP Supplement, West Virginia American Water Kanawha Valley Water System*, Updated August 2016 https://www.wvdhhr.org/oehs/eed/swap/documents/Grants/2016_Grant_Application.pdf (Accessed January 11, 2017)