Bioattenuation of Petroleum Hydrocarbon Vapors in the Subsurface

Update on Recent Studies and Proposed Screening Criteria for the Vapor-Intrusion Pathway

by Robin V. Davis

Subsurface sources of petroleum hydrocarbons emanating from leaking underground storage tank (LUST) systems typically do not result in the intrusion of associated vapors into overlying buildings. However, under certain circumstances, this type of vapor intrusion can occur. To better understand the conditions under which vapor intrusion may or may not occur, I have compiled data from well-characterized sites and studied bioattenuation of petroleum hydrocarbon vapors in the subsurface. I got started on this when regulators from USEPA's Office of Underground Storage Tanks (OUST) and several state LUST programs formed a Petroleum Vapor Intrusion Work Group that met from 2003 to 2005. Since then, I have independently expanded on the findings I reported in LUSTLine *#49 and #52. In this article, I summarize my findings and recommend screening criteria for both vapor-phase and dissolved-phase hydrocarbon contamination sources at well-characterized sites. I hope this will help my fellow LUST project managers make decisions about when to investigate the vapor-intrusion pathway at sites with petroleum hydrocarbon contamination.*

Background

The objectives of the Petroleum Vapor Intrusion Work Group were to study the behavior of soil vapors associated with subsurface petroleum sources, determine when the vapor-intrusion pathway may be complete, and develop petroleum-specific criteria to screen out sites where the pathway is not likely to be complete. We amassed peer-reviewed data from well-studied sites. As part of this team, I constructed a database that contained 29 benzene and 22 total petroleum hydrocarbon (TPH) subsurface soil-vapor sample events from 16 geographic locations in the United States and Canada.

The work group determined that more data were needed, and although the group was dissolved in 2005, I have continued to compile data from additional published literature and studies from contributing states. My findings, which are presented in this article, are my own, made independently of USEPA and the State of Utah, and based on my own analysis of my larger 2009 database.

In the two *LUSTLine* articles mentioned above, I reported on the earlier database contents and some key findings: (1) a few feet of clean soil overlying contaminant sources and an adequate subsurface oxygen supply are critical for attenuating petroleum vapors, and (2) a greater than ten-fold attenuation of contaminant vapor concentration was typical of sites with sufficient thickness of clean overlying soil and oxygen levels greater than four percent.

My expanded 2009 database contains peer-reviewed data for 259 benzene and 210 TPH vapor-sample events from 53 geographic locations in the United States and Canada. This database contains site-specific information including soil type, depth to groundwater, presence of free product, and concentrations of benzene and TPH in both the dissolved phase and the soil-vapor phase. This database reveals more definitive screening criteria for subsurface soil-vapor hydrocarbons and for hydrocarbon contaminants dissolved in groundwater.

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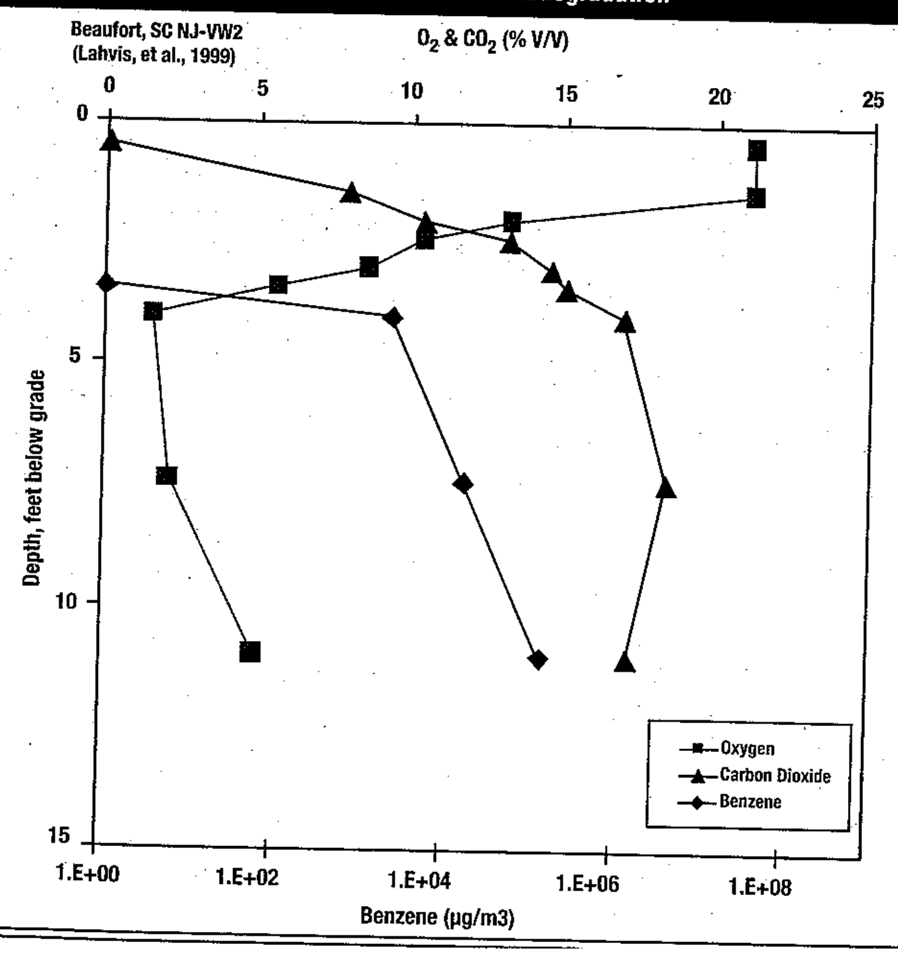
Figure 1: Soil Vapor Profile Showing Signature Characteristics of Aerobic Biodegradation



■ **Vapor-Intrustion Pathway Screening** *from page 11*

Causes of Vapor Intrusion by Petroleum Hydrocarbons

Vapor intrusion from subsurface petroleum sources occurs when free-phase product or very high dissolved sources (i.e., much greater than 1,000 µg/L benzene and 10,000 µg/L TPH) are in direct contact with, or very near, building foundations. The thousands of petroleum-contaminated sites that I and fellow project managers throughout the nation have supervised prove this fact, not to mention at least one published study (Sanders and Hers, 2006). There are no reported or published cases where vapor intrusion has occurred at low-dissolved sources (< 1,000 µg/L benzene; < 10,000 µg/L TPH) when clean soil and oxygen are present between the source and the receptor.

Bioattenuation of Subsurface Petroleum Hydrocarbon Vapors

Bacteria capable of degrading petroleum hydrocarbons are everywhere in the environment (USEPA, 1999), and a century of research and published studies shows that the subsurface is a highly efficient bioreactor that is capable of biodegrading petroleum sources, given adequate clean soil, moisture, and oxygen.

Aerobic biodegradation of petroleum hydrocarbon vapors is recognizable by the signature characteristics shown in Figure 1, where vapor concentrations are high near the source of contamination, accompanied by oxygen depletion and carbon-dioxide enrichment. Above the contaminated zone, oxygen and carbon dioxide rebound to near-atmospheric conditions. This example shows that benzene vapors associated with very high dissolved-contaminant concentrations, or "source strength," (benzene in groundwater 16,000 µg/L) are attenuated by a factor of about one million with seven feet of clean overlying soil.

Subsurface Attenuation Factors: Screening Criteria for Petroleum Vapors

The work group found that the magnitude of contaminant concentration reduction could be expressed as a subsurface vapor-attenuation factor (AF), which is simply the ratio of the shallow subsurface soil-vapor concentration divided by the deep-soil vapor concentration. Low AFs equate to significant attenuation. In *LUSTLine* #49 and #52, I reported that significant attenuation is represented by AFs between <0.05 and <0.1.

My larger 2009 database shows the same trend as my earlier analyses (≥0.1 represents insignificant AFs), but I now have a much clearer understanding of what this distribution of AFs means. Figure 2 shows the distribution of the magnitude of subsurface attenuation of benzene and TPH vapors from data in my 2009 database. This distribution shows that insignificant AFs ≥0.1 constitute the majority of events and that a nearly equal number of events exhibit significant attenuation with AFs ≤0.01.

To better understand why so many events exhibit insignificant AFs, I studied the data from each event line-by-line and depth-by-depth. My findings, shown in Figure 3, indicate three reasons for insignificant AFs: (1) insufficient clean soil, (2) low source strength, and (3) rapid attenuation near the source. My analysis of the data also show that high AFs do not necessarily mean that vapors are not attenuating.

Figure 2: Magnitude of Subsurface Soil Vapor Attenuation

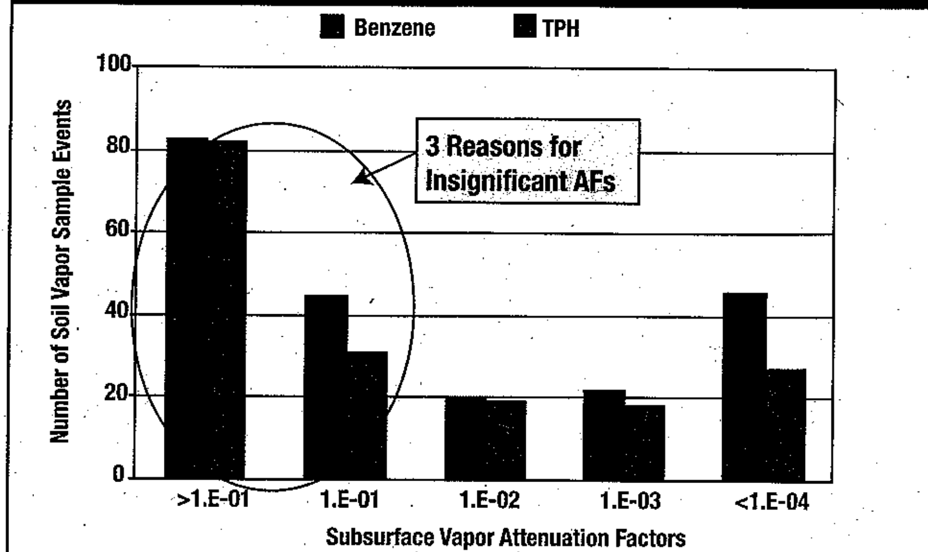
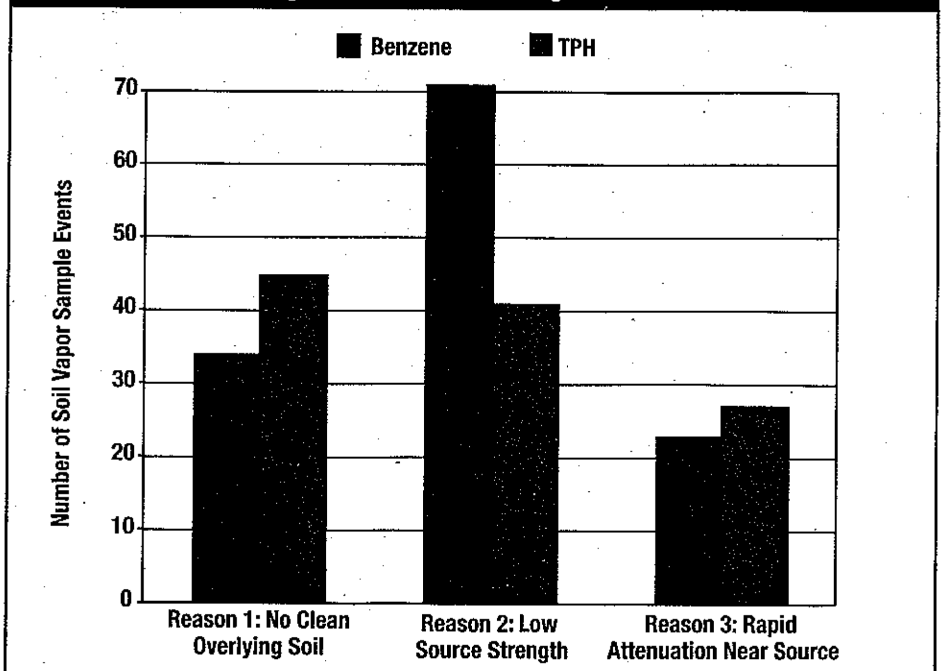


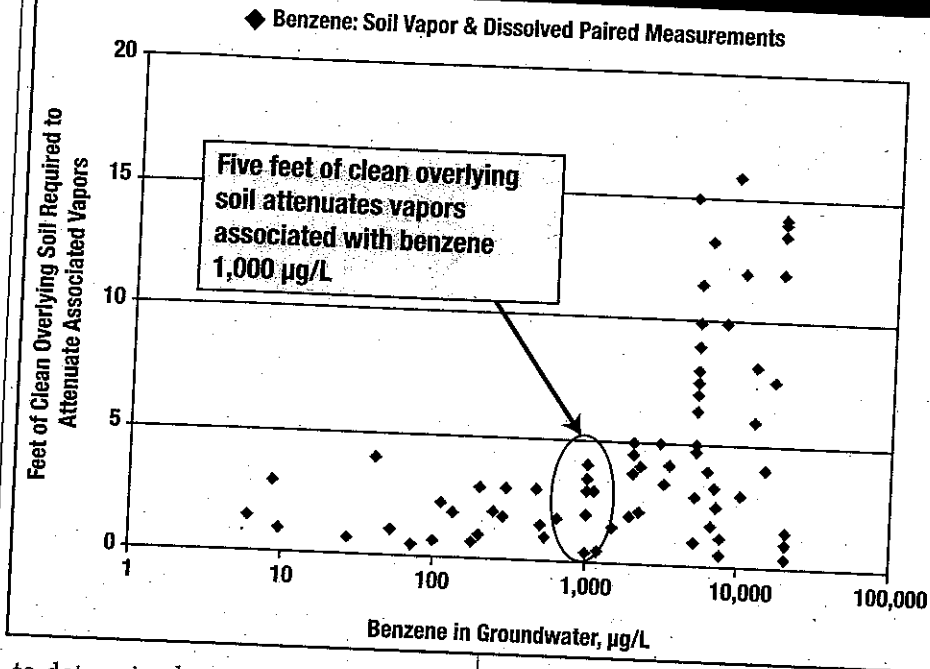
Figure 3: Sample Events from Figure 2 with AFs >0.1 Showing Three Reasons for Insignificant Attenuation



Conditions characteristic of reason #1 should definitely be known at the earliest stages of site investigation and characterization, and cleanup or mitigation should generally be the first course of action. As for reason #2 (and the primary reason why I am writing this article), many vapor-intrusion investigations have taken place at sites where source strengths are so low that vapors are barely detectable, much less a potential vapor-intrusion problem. Reason #3 sites are generally characterized by very high dissolved-contaminant concentrations and should therefore be subject to vapor-intrusion investigations as a matter of course.

Figure 4 shows the distribution of vapor-sample events that exhibit significant attenuation. The cases are characterized by the presence of sufficient thickness of clean overlying soil. While most of the sites exhibit AFs greater than 10,000-fold contaminant reduction (AF<1E-04), 100-fold attenuation is a safe and reasonable assumption and in my opinion, a reasonable screening criterion to apply to subsurface petroleum vapors, and an accurate but conservative representation of subsurface bioattenuation of soil vapors.

Figure 5: Thickness of Clean Overlying Soil Required to Attenuate Benzene Soil Vapors Associated with Various Dissolved Source Strengths (all soil types)



Screening Criteria for Dissolved Petroleum Sources

My 2009 database contains a subset of 127 events where dissolved- and vapor-phase benzene and TPH were measured at about the same location at about the same time. I performed a line-by-line evaluation of this subset to determine how much clean soil is required to attenuate vapors associated with various dissolved-source strengths and in different soil types. My review followed strict evaluation criteria: (1) dissolved sources only with no known vadose-zone contamination, and (2) subsurface vapors attenuate completely.

Figures 5 and 6 are plots of benzene and TPH data for all soil types. Figure 5 shows that although five feet of clean overlying soil attenuates vapors associated with dissolved benzene sources up to approximately 6,000 µg/L, a more cautious screening criterion to use would be 1,000 µg/L as the maximum concentration. Figure 6 shows that about five feet of clean overlying soil attenuates vapors associated with dissolved TPH sources up to approximately 10,000 µg/L.

Due to space constraints in this article, I cannot show my data analysis according to soil type, but I did categorize and analyze these data according to their respective soil types. The data show that for benzene, five feet of clean sand/gravel; fine sand/silty sand/silt; and silty clay/clay attenuate vapors associated with 6,000 µg/L; 3,000 µg/L; and 2,000 µg/L, respectively. TPH data show a similar trend of vapor attenuation according to soil type, where 10,000 µg/L TPH is a conservative maximum concentration in a silty clay/clay soil type.

Figures 5 and 6 show some interesting features where many paired measurements line up along the 5,000 to 7,000 µg/L benzene concentration and the 70,000 µg/L TPH concentration. My database shows that these are measurements from sites dominated by silty clay/clay, soil types that are likely to have thick zones of soil contamination near the water table. These zones are commonly referred to as "smear-zone soils" and should be identified and characterized during initial, routine site investigations.

Figure 4: Distribution of Significant Attenuation

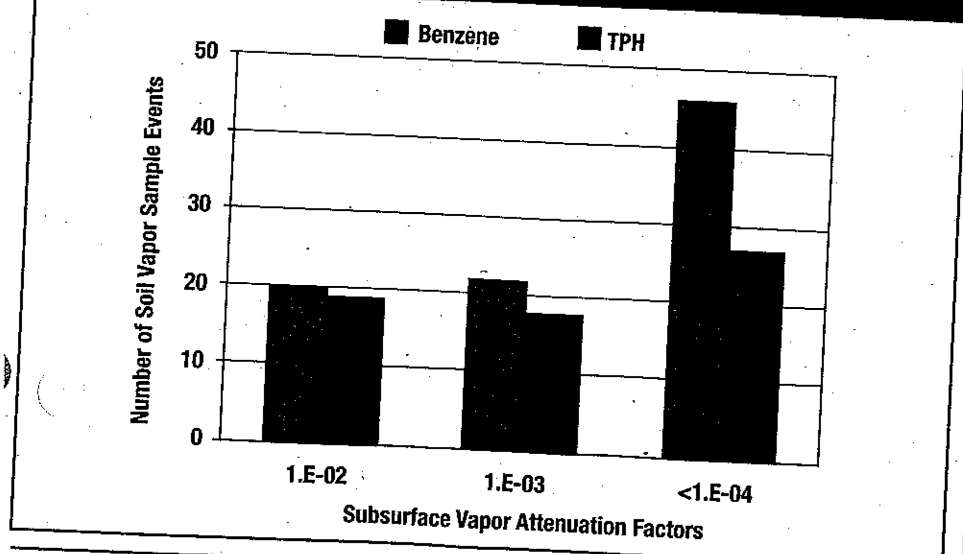


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Figure 6: Thickness of Clean Overlying Soil Required to Attenuate TPH Soil Vapors Associated with Various Dissolved Source Strengths

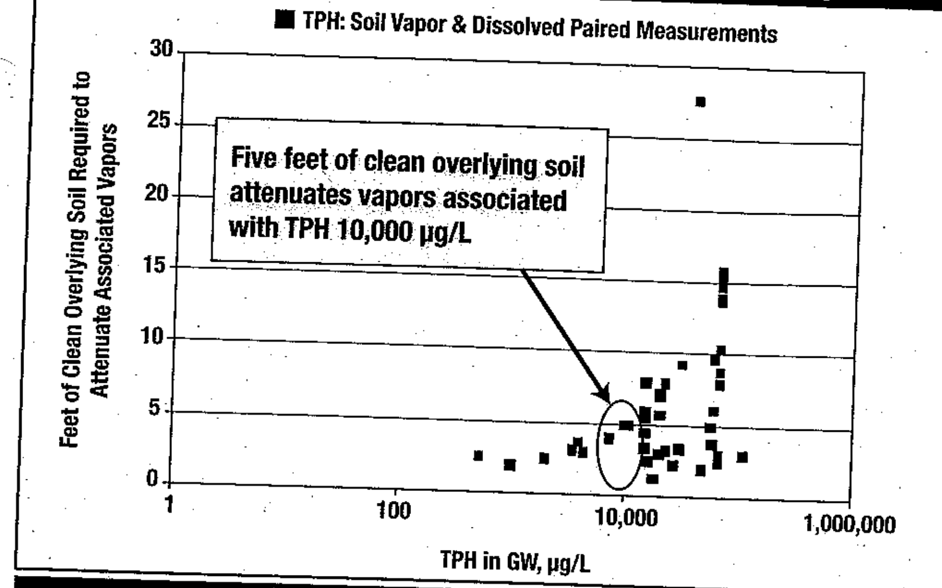
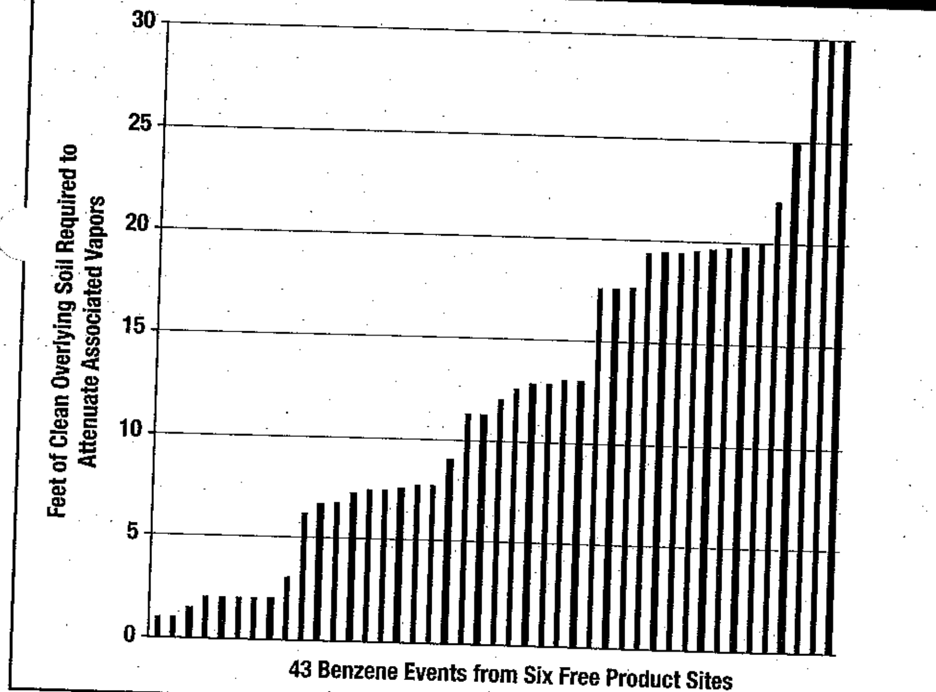


Figure 7: Thickness of Clean Overlying Soil Required to Attenuate Benzene Soil Vapors Associated with Free Product



■ Vapor-Intrusion Pathway Screening *from page 13*

Smear-zone soils can be notorious for releasing high dissolved-contaminant concentrations, depending on the relative position of the groundwater level. Therefore, regardless of soil type, the data indicate that five feet of any type of clean soil attenuates vapors associated with dissolved concentrations of 1,000 µg/L benzene and 10,000 µg/L TPH.

Figure 7 shows data from 43 benzene events where free product is reported. The data indicate that vapors associated with free product are fully attenuated with approximately 30 feet of clean overlying soil.

Absent emergency conditions such as reports of petroleum odors in buildings that must be abated and mitigated, I propose the following methods for evaluating sites to determine if vapor-intrusion investigations are necessary:

- Fully characterize sites by determining the full extent and degree of contamination.
- Fully characterize and understand dissolved-contaminant concentrations and presence of free product in response to temporal fluctuations of depth to groundwater.
- If five feet of clean soil consistently overlie dissolved sources where benzene is ≤1,000 µg/L and TPH is ≤10,000 µg/L, a vapor-intrusion investigation is not necessary.
- If 30 feet of clean soil overlie free-product sources, a vapor-intrusion investigation is not necessary.

In my opinion, these are reasonable methods and criteria to use to screen out sites with groundwater contaminated by petroleum hydrocarbons in the assessment of the vapor-intrusion pathway.

I Hope This Helps

A hard look at the data in my 2009 database has helped me better manage my petroleum cases by ensuring that vapor-intrusion investigations take place where they need to—at sites with free-phase petroleum and high-dissolved sources in close proximity to buildings. I hope this information helps others who are developing or rethinking their screening criteria for the vapor-intrusion pathway. ■

Robin Davis is Project Manager for the Utah Department of Environmental Quality, Leaking Underground Storage Tank program. She specializes in fate and transport of petroleum hydrocarbons and data acquisition and analysis, most recently for the vapor-intrusion exposure pathway. Robin can be reached at rvdavis@utah.gov.

Disclaimer: Any opinion expressed herein is that of the author and does not represent the State of Utah, USEPA, or the authors cited.

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