

Leading Indicator Process Development Report (PNNL-25533)

This is a summary of the [PNNL-25533 Leading Indicators Process Development](#) report, developed to provide an overview to inform and educate the reader of the report contents and a list of frequently asked questions on the subject matter.

Tank farm vapors are a mix of gases, and some gases in the mix are more easily detected than others. The more easily detected gases can be monitored by Industrial Hygiene technicians in real-time using handheld instruments. Monitoring for one or two chemicals (a leading indicator also referenced as a limiting chemical) can indicate the presence of other chemicals that cannot be monitored in real-time. It is possible to protect against potentially harmful tank vapors by monitoring for leading indicators. A recent study, (PNNL-25533), concluded that two tank farm gases, ammonia and nitrous oxide, were the best candidates to use as leading indicators. The analysis will be updated next year after more data is collected.

Leading Indicator FAQ

1. What causes the dirty socks or locker room smell?

Tank waste contains a small amount of decomposing organic material. Occasionally, a smell similar to dirty socks or rancid butter has been described by workers. These smells can be attributed to trace organics (carboxylic acids, aldehydes, ketones) often found in tank farm vapors and gases (see [Environmental Odors and Organic Compounds and their Smells](#)). Although some chemicals have a bad smell, they are not harmful until higher concentrations are reached.

2. What about chemicals you can't smell or detect?

Most tank farm gases and vapors are at concentrations well below what we can smell, or have no odor. Sampling can detect chemicals well below their odor thresholds. Laboratory analyses are capable of detecting chemical concentrations well under 1 part per million (ppm) and some compounds as low as 1 part per trillion (that is 1 in 1,000,000,000,000).

3. Why can you sometimes smell something, but the real-time monitors show nothing?

A few tank farm vapors can be smelled at below harmful concentrations and below what real-time instruments can detect. An excellent example of this is ammonia. Ammonia can be smelled at concentrations as low as 0.04 ppm and some monitors that we use only detect it when it is above about 1 ppm. The OEL for ammonia is 25 ppm, higher than the odor threshold of 0.04 to 20 ppm.

4. Today, what compounds are being monitored with direct reading instruments and used as leading indicators?

Ammonia and volatile organic chemicals (VOC) are being routinely monitored by direct reading instruments (DRI). Action levels have been established for each indicator. Action levels serve as a screening indicator of emissions that could impact workers' health. Ammonia is a prevalent chemical of potential concern (COPC) in tank headspace and readily monitored with DRIs. A wide range of tank COPCs are VOCs, and many can be detected using photoionization detector (PID)-based DRIs. Both ammonia and VOCs are good indicators of potential tank vapor emissions, but are not proven to be effective at detecting, quantifying, or serving as a leading indicator for every tank COPC. Because DRIs serve an important role in emissions screening, the leading indicator effort is focused on expanding the use and confidence in DRI monitoring and leading indicators for a larger set of COPCs.

5. Why weren't total volatile organic compounds (VOCs) included in the report as a leading indicator?

VOC monitoring can be used to indicate whether COPCs are present ([see Direct Reading VOC Action Level Evaluation](#)). VOC monitoring is routinely performed. However, there were no sample results for VOCs and COPCs taken at the same time. Without those sample result, no statistical comparison could be performed. The plan is to update this analysis after more VOC/COPC data is collected.

6. What does near real-time monitoring mean?

Real-time monitoring means that if a chemical is present in the worker breathing zone, it can be detected by instruments while workers are still in the field. When an instrument has a delayed response to a change (usually less than a second), it is called near real-time.

7. Does a leading indicator mean there are other chemicals?

Detecting a leading indicator means there might be other chemicals of potential concern (COPC) present. If a specific level for a leading indicator is detected, then a conservative safety response will be taken. Conservative safety responses are actions such as moving away and upwind of the source or donning appropriate personal protective equipment (PPE).

8. How do you know a chemical wouldn't come out by itself?

Tank headspaces and ventilation exhaust stacks contain gas mixtures which will not naturally separate into layers ([PNNL-14831](#)). The behavior of gas mixtures has been studied for more than 150 years and the science behind these conclusions is strong (entropy and the second law of thermodynamics). Thousands of tank headspace, ventilation exhaust stack, and worker breathing zone samples confirm that tank farm vapors and gases exist as gas mixtures.

9. What is the overall goal of leading indicators?

Leading indicators, combined with real-time monitoring, allows industrial hygiene to be proactive when responding to potential changing conditions. IH has responsibilities and leading indicators can tell you when enhanced Personal Protective Equipment (PPE) might be needed. Leading indicators also help determine what data should be collected and which real-time monitoring equipment should be selected.