Air emission controls

Petroleum Remediation Program

This document describes the air emissions screening process used to determine if controls are required to address human-health risks associated with exposure to remediation system air emissions, particularly from soil vapor extraction systems, including vacuum-enhanced extraction systems and air strippers. The air emissions screening process involves emissions sampling and data evaluation throughout operation of a remediation system, from the design phase through the implementation phase, to evaluate acute and chronic risks. Air emissions sampling is also used to evaluate system effectiveness, which may include determining mass removal rates and trends, contaminant concentrations, waste treatment efficiency, and adherence to any permit requirements. The sampling requirements described below are designed to meet both risk assessment and system effectiveness objectives. See Corrective action design and implementation for more information about the corrective action design approval process and remediation system design requirements.

Please note: Soil vapor extraction (SVE) systems and air strippers (AS) are considered air emissions units. If you currently have an air emissions permit, or have other sources at your site that would trigger the need for an air emissions permit, you must include the remediation system in your air emissions permit. Please call the Minnesota Pollution Control Agency (MPCA) Small Business Assistance Helpline at 651-282-6143 if you need further information.

I. Overview

A. Air emissions screening process: Figure 1 depicts the steps of the screening process, which can be broken up into three distinct stages: pilot test, full-scale startup, and full-scale operation. Section II describes requirements for each stage. Pilot test and full-scale startup requirements are used to assess acute risk, whereas full-scale operation requirements are used to assess chronic risk and to determine if continued use of existing controls is required.

Acute risk is based on maximum one-hour average air concentrations compared to acute toxicity values. Similarly, chronic risk is based on maximum annual average air concentrations compared to chronic toxicity values, or inhalation unit risk for excess lifetime cancer risk. Air concentrations are determined by air dispersion modeling using emission rates that are appropriate for the given time frame.

B. Air emissions evaluation: The air emissions Risk assessment screening spreadsheet (RASS) is used to assess acute and chronic risks from remediation system air emissions. It can be used for SVE systems and AS, either individually or concurrently, to evaluate risk from individual and from a mixture of contaminants based on common toxicological endpoints, including excess lifetime cancer risk. The spreadsheet is flexible in that it allows users to alter system stack height, receptor distance, and flow rate to quickly evaluate how these changes affect the need for emission controls based on default air dispersion modeling conditions. In addition, the spreadsheet can accommodate site-specific air dispersion modeling if actual conditions vary significantly from default conditions. Site-specific modeling requires assistance from the MPCA. See the RASS for additional instructions.

C. **Air emission controls:** Air emission controls may consist of system controls that alter the exposure scenario such as raising the system stack height, relocating the discharge stack, or reducing subsurface extraction rates. Controls may also consist of treatment controls that reduce emission rates through chemical, physical, and biological treatment of waste streams prior to discharge. The chosen control should balance cost with impact to system operation. For example, reducing subsurface extraction rates may require longer system operation, thus offsetting costs saved by not treating the emissions. Air emission controls may be required for one or more stages of operation and may be required to address acute and/or chronic risks.

II. Air emissions screening process

A. **Pilot test:** Generally, air emission controls are not required during a pilot test. Under certain circumstances, however, controls may be required when sensitive receptors are present. A sensitive receptor is defined as an area or structure used or occupied by sensitive population groups, such as daycare facilities, schools, or nursing homes. Identify sensitive receptors as part of the receptor survey completed during the site investigation and risk evaluation; see Risk evaluation and site management decision at petroleum release sites. If a sensitive receptor exists within 500 feet of the air discharge point, air emission controls may be needed during the pilot test to address acute risk, with recommendations for controls made in Pilot test work plan.

During a pilot test, collect air emission samples one hour into each step test. If a step test lasts less than one hour, collect the sample at the end of the step test. If a step test exceeds one hour, collect a sample one hour into the step test and a second sample at the end of the step test if it exceeds two hours in duration.

Pilot test air emission samples are collected, in part, to determine if the full-scale system will require air emission controls for acute risk. Report results from a pilot test in the Pilot test report. If pilot test results confirm acute risk levels will or are likely to be exceeded, make recommendations for air emission controls during full-scale startup and operation in the Pilot test report. If controls are required for the full-scale start-up stage, incorporate them into the full-scale design presented in Remediation system detailed corrective action design (SDCAD) report.

B. **Full-scale startup:** If controls are not in place at startup, then acute risk assessment is required during startup. After the system is adjusted to its long-term operating configuration, operate the system continuously for one hour and then collect an air emission sample. Shut down the system following sample collection. Evaluate the one-hour startup sample results to assess acute risk. If acute risk is identified, controls may be required prior to restarting the full-scale system. If acute risk is not identified, the system may be restarted following MPCA approval. Contact the MPCA as soon as sample results are available to discuss if controls are required or if the system may be restarted.

If controls are in place to address acute risk at full-scale startup, a one-hour sample is still required to determine if the controls are meeting air emission expectations, but the system does not have to be shut down following sample collection.

The start-up requirements also apply when a full-scale system is reconfigured. System reconfiguration may consist of altering the active extraction well configuration, starting an air sparging system after an initial SVE operation period, or any action that is likely to result in a significant increase in emission rates. If a system is reconfigured, the one-hour sampling requirements described above are followed.

When prior controls are in place, a one-hour sample is required, but the system does not have to be shut down following sample collection. If no controls are in place, shut down the reconfigured system following sample collection until the results are evaluated and the MPCA approves system restart.

C. **Full-scale operation:** Sampling requirements during this stage for systems with and without controls in place will generally be similar. Conduct sampling monthly for the first twelve months of operation.

For systems without controls in place at startup, such as no controls required for acute risk, use monthly sampling results to assess chronic risk. If chronic exposure levels are exceeded for a continuous period of 3 months, controls may be required, which will require system shutdown until adequate controls are in place. Once controls are in place, resume monthly sampling.

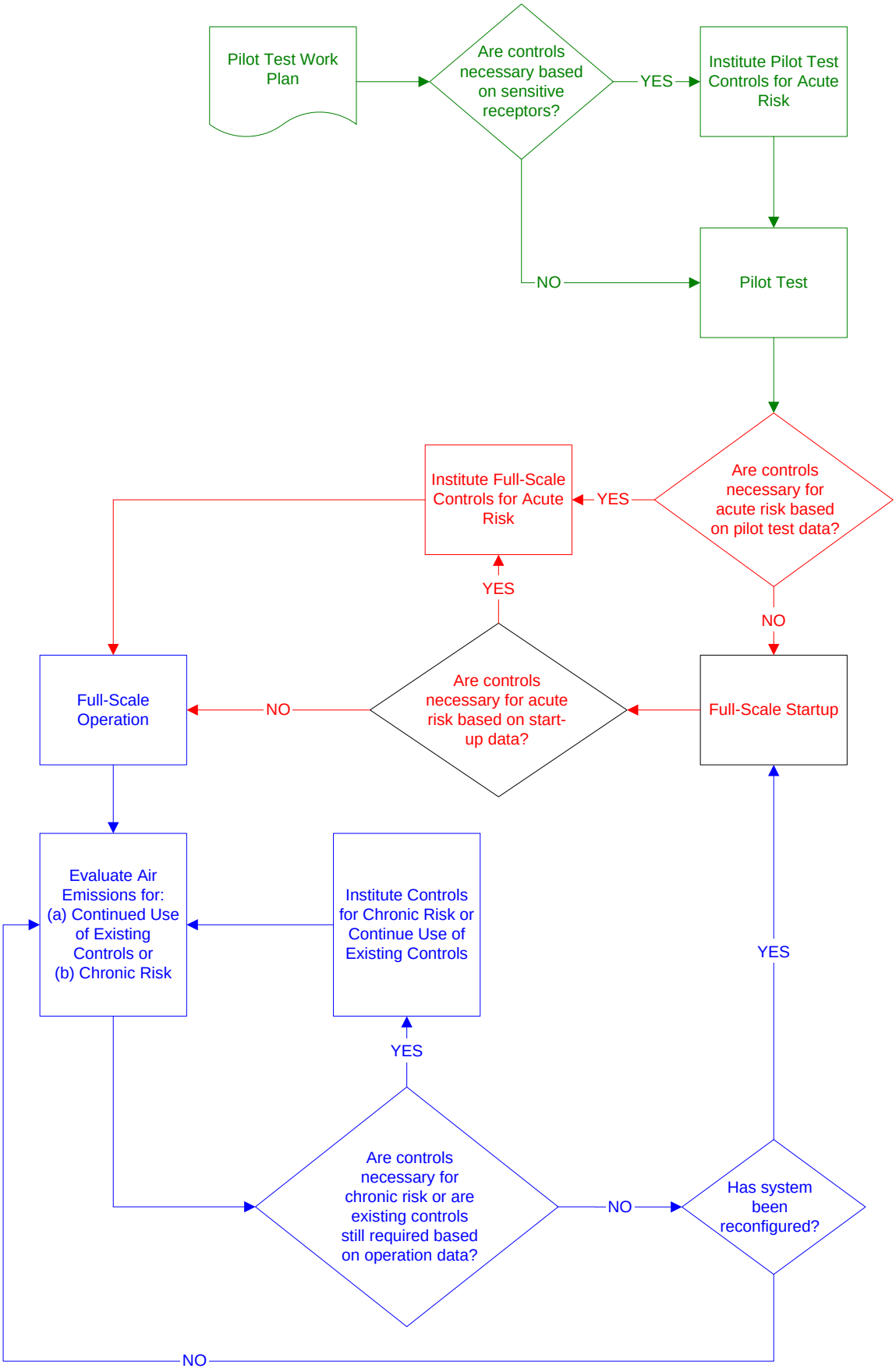
For systems with acute controls in place either at or following full-scale startup, controls may be discontinued upon MPCA approval once it can be demonstrated that acute exposure levels are no longer exceeded. Contact the MPCA as soon as sample results are available to discuss if controls may be discontinued. Use subsequent sampling to assess chronic risk. Controls may need to be implemented if chronic exposure levels are exceeded for a continuous period of three months according to the protocols listed above for systems without controls in place at startup.

For systems with controls in place for chronic exposure, controls may be discontinued upon MPCA approval, once it can be demonstrated that chronic exposure levels are no longer exceeded. Contact the MPCA as soon as sampling results are available to discuss if controls may be discontinued.

D. Reporting requirements: Complete all pilot test reporting using Pilot test work plan and Pilot test report. Make recommendations for full-scale controls prior to startup in the Pilot test report, with specific details presented in Remediation system detailed corrective action design (SDCAD) report. Report startup and operation results using Remediation system operation monitoring (RSOM) report.

One-hour sampling results, either from full-scale startup or reconfiguration, and any sampling results that are used to determine the need for or discontinuance of air emission controls should be discussed with the MPCA as soon as they are available, with formal reporting completed in a subsequent RSOM.

Figure 1. Air emissions screening process



E. Sampling requirements

1. **Soil vapor extraction and vacuum-enhanced extraction systems:** Collect time-weighted air emission samples after the blower and any dilution valves at a location where accurate airflow measurements can be taken. If air treatment controls are present, collect samples before and after treatment at locations where accurate airflow measurements can be taken. Convert airflow measurements to standard conditions that are consistent with the standard conditions used by the laboratory to report analytical results, which Section IV defines below. Record airflow temperature and pressure at all measurement locations.

   Submit samples for laboratory analysis of compounds on the Minnesota soil gas list and for total hydrocarbons (THC). Vapor intrusion assessments performed during site investigations contains the Minnesota soil gas list.

2. **Air strippers:** Calculate air stripper (AS) emissions using an average water flow rate through the AS and contaminant concentrations in pre- and post-treatment water samples, influent and effluent, respectively. It is not necessary to directly measure AS airflow rates or collect air emission samples for laboratory analysis. Collect influent and effluent water samples along with water flow rate. Analyze samples for volatile organic compounds (VOCs). Additional analytes may be required based on site-specific circumstances or permit requirements. Groundwater sample collection and analysis procedures contains the list of required VOCs in groundwater.

III. Sample collection

A. Introduction: Unless alternative procedures are specified below, follow Vapor intrusion assessments performed during site investigations and Groundwater sample collection and analysis procedures guidance describing equipment decontamination, field procedures, sample collection, sampling event documentation, and required quality assurance/quality control (QA/QC) sampling.

B. Volatile organic compounds and total hydrocarbons in air emissions: Use the following procedures for collecting air emission samples using an evacuated canister.

1. Install a sampling port with a valve on the system piping after the blower and adjacent to where accurate airflow measurements are collected, including associated air temperature and pressure.
2. Fit the sampling port with inert tubing, such as polyethylene, stainless steel, or Teflon® of the appropriate size.
3. Install an in-line particulates trap to prevent particulates and moisture from entering the canister.
4. Affix an appropriate air restriction device such as a flow controller or critical orifice to the canister prior to sampling to allow for a time-weighted sample. Collect the time-weighted sample over a two to five minute period to account for short-term airflow and contaminant mass variability, with the objective being to collect a more representative sample.
5. Collect a sample by attaching the top end of the tubing to a sampling canister instrumented with a vacuum gauge and air restriction device.
6. Note and record the initial vacuum gauge reading and the system airflow, system air temperature, and system air pressure at the sampling location. Open the sampling canister valve and monitor the vacuum gauge to check progress of canister filling.
7. After the appropriate time has passed (two to five minutes), close the valve on the canister and record the time on the sampling form and on the chain-of-custody form.
8. Transport the canister and flow controller to the laboratory.

C. **Volatile organic compounds in remediation system influent/effluent groundwater:** Collect aqueous samples for VOC analysis using laboratory-supplied 40-milliliter hydrochloric acid (HCL)-preserved purge-and-trap bottles in a manner that minimizes turbulence, air entrapment, and overfilling. Fit the system piping with appropriate sampling ports with valves before and after individual treatment units. Fill the bottle completely, leaving a positive meniscus at the top of the vial and avoid turbulence and aeration by tilting the bottle while filling. After capping, invert the bottle and tap with a finger to check for air bubbles. If bubbles are present, discard the vial and fill a replacement. If the VOC sample is turbid and effervesces when water contacts the bottle preservative, unpreserved samples should be collected and noted on the chain-of-custody form. Analyze unpreserved samples within a seven day holding time. Store samples at a temperature of four degrees Celsius during transport to the analytical laboratory.

Collect multiple bottles according to laboratory instructions to guard against loss by breakage and to allow for laboratory quality assurance. Submit samples for VOC in groundwater analysis following U.S. Environmental Protection Agency (EPA) method 8260. Groundwater sample collection and analysis procedures describes laboratory QA/QC procedures for VOCs in groundwater samples via EPA method 8260.

If a permit requires VOCs to be analyzed by a method other than EPA method 8260, such as EPA method 624 used for wastewater, use the permit-required method for system influent and effluent samples in lieu of method 8260.

IV. Required laboratory quality assurance/quality control

A. **Volatile organic compounds and total hydrocarbons in air emissions:** Each laboratory analyzing samples by method TO-15 shall follow the method as defined by the EPA in the EPA/625/R-96/010b dated January 1999 or updates.

1. The laboratory must supply the following data with each report:
    a. Method blank (zero canister): All results from analysis of the method blank should be less than the reporting limits. If reported concentrations are above the reporting limits, the laboratory will document this occurrence within the narrative and flag any concentration reported above the reporting limit for this compound up to 10 times the level measured in the blank. The area responses for the internal standards (ISs) must be within ± 50% of the area response of the ISs in the mid-point standard of the most recent initial calibration. The retention time for each IS must be within ± 0.33 minutes between the blank and the most recent calibration. Run method blanks every 20 environmental samples or once per day, whichever is more frequent.
    b. Laboratory control sample: The laboratory will report the percent recoveries from all analytes spiked into the laboratory control sample. Run one laboratory control sample within each 24-hour period of TO-15 samples analyzed.
    c. The narrative of the laboratory report will define if the initial calibration curve, continuing calibration check sample (when appropriate), and internal quality assurance (such as internal standards, blanks, etc.) met the method requirements for each report.
    d. Submit the chromatogram for each analysis with the data and have the compounds identified in the Minnesota soil gas list clearly labeled on the chromatogram. The Minnesota soil gas list is located in Vapor intrusion assessments performed during site investigations.
    e. The laboratory shall report the results using the field sample identification and the associated laboratory sample number.
    f. The laboratory shall report all compounds in units of micrograms per cubic meter ($\mu g/m^3$).

g. The laboratory report must contain the following information: Coversheet with signature of a laboratory supervisor or designee, a narrative discussing the sample results and any irregularities that were found during the analysis, chain-of-custody and sample-condition-upon-receipt forms, tables containing the VOCs, chemical abstracts service number of each reported compound, measured concentration in µg/m^3, reporting limit, date of analysis, labeled sample chromatograms, method blank data for the batch, and a summary of applicable quality control.

2. The laboratory is required to maintain the data for a minimum of ten years with the ability to reconstruct the data either electronically or on paper.
3. Laboratories must verify their reporting limits by running a standard at the reporting limit once every month. The recovery of the reporting limit shall be ± 40% of the true value.
4. Laboratories shall verify their calibration curve a minimum of every 24 hours. The 24-hour clock will begin at the injection of a standard for tuning the instrument; bromofluorobenzene is the suggested tuning standard. The calibration verification standard must be at the midpoint (or lower) of the calibration curve. The standard must meet TO-15 or laboratory generated limits for the compounds of interest/target compounds (as identified on the chain of custody), not a set of continuing calibration check compounds. If no direction is given to the laboratory for check compounds, then the laboratory standard operating procedures shall be followed.
5. Laboratories should run 10% laboratory duplicates. Duplicate samples should have less than or equal to 25% Relative Percent Difference or corrective action should be initiated.
6. The MPCA accepts a holding time of 14 days for the TO-15 analysis.
7. Dilute samples with concentrations that exceed the calibration range to fall within the calibration range. Make reasonable effort to get the majority of target analytes within the mid-range to upper-half of the calibration range for diluted samples. Only report values exceeding the calibration range with documented approval of the MPCA project manager or of the party for whom the data is being produced. Samples analyzed at dilutions that cause target analytes to be present in the lower third of the calibration range must be reanalyzed so the majority of the positive responses are in the upper half of the calibration range, unless there are documented extenuating circumstances explained in the narrative. Data from samples that are routinely analyzed at only one dilution that are above the calibration range will be rejected. Target analyte data from diluted samples that are in the lower third of the calibration range resulting in unnecessarily elevated reporting limits may be rejected.
8. Standard temperature and pressure: For the TO-15 analysis, the MPCA defines standard temperature as 25 degrees Celsius (77 degrees Fahrenheit, 298.15 K) and standard pressure as one atmosphere (14.7 pounds per square inch, 29.92 inches of mercury, 760 millimeters of mercury).
9. Retention time window and quantitation for THC: The retention time window is defined as beginning approximately 0.1 minutes before the onset of the first target analyte peak in the TO-15 calibration run and ending 0.1 minutes after the conclusion of the last target analyte peak in the TO-15 calibration run. The laboratory must use the target analyte list defined in Appendix A of Vapor intrusion assessments performed during site investigations for setting the retention time window.

   Quantitation is based on a single-point direct comparison of the total area within the retention time window to the total area of the total ion chromatogram for the continuing calibration verification standard. In calculating parts per billion by volume (ppbv), laboratories should use an average molecular weight of 100 g/mol.

   The laboratory must verify the placement of the retention time window at the beginning of each day and whenever a new gas chromatograph column is installed or when significant retention time shifts occur. This can be part of the calibration check.

Integration must be "baseline to baseline" as opposed to "valley to valley." Baseline to baseline is defined here as a flat baseline drawn parallel to the x-axis of the chromatographic graph that includes all responses within the retention time window. The correct baseline placement would be a horizontal line drawn through the lowest point in the chromatogram (before the end of the window). The lowest point may be within the window, outside the window (on the early end of the window), or before the solvent front. Placement of the baseline is determined for each sample.

10. Canisters: The laboratory providing sampling canisters shall verify each batch of 20 canisters by analyzing one container after cleaning. The canister chosen for post-cleaning analysis shall be the canister with the highest recorded VOC concentration from prior analyses. Verify the container by charging the canister with clean zero air, analyzing the container by TO-15, and verifying no compounds are found above the reporting limits required by the MPCA. Additionally, the supplier of summa canisters is expected to verify the operability of the canisters. The TO-15 standard operating procedures (or equivalent) describe the preventative maintenance performed on the canisters. One-hundred percent certified canisters may be required upon request.
11. Whenever a high concentration sample is analyzed, such as a sample with concentrations outside the calibration curves, a zero canister analysis should be performed to check for carryover. If carryover is detected, column bake out shall be performed.
12. Lab certification: Certification is available for the TO-15 method through the Minnesota Department of Health Environmental Laboratory Certification Program.
13. Perform method detection limit studies at least annually.
14. Analyze field samples after successfully meeting all criteria established for instrument performance checks, calibrations, and blanks. All target analyte peaks should be within the initial calibration range. The retention time for each internal standard (IS) must be within ± 0.33 minutes of the IS in the most recent calibration. The area response for the ISs must be within ± 50% of the area response of the ISs in the mid-level standard of the most recent initial calibration.
15. Analyze the daily check standard every 24 hours. This standard is at the mid-point of the calibration curve (10 ppbv suggested). The calculated concentration value for each target analyte must be within ± 30% of the true concentration value for each target analyte. Maintain control charts for the daily check standard.
16. Internal standard (IS): A suggested internal standard mixture of bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene will be added to each sample as standard. The resulting concentrations are at 10 ppbv (suggested).

B. Volatile organic compounds in remediation system influent/effluent groundwater: Groundwater sample collection and analysis procedures describes laboratory QA/QC procedures for VOCs in groundwater samples via EPA method 8260.