Investigation Requirements for Ethanol-Blended Fuel Releases

Petroleum Remediation Program
Guidance Document 4-21

This guidance document describes site investigation requirements for ethanol-blended fuel releases for the Minnesota Pollution Control Agency's (MPCA) Petroleum Remediation and Emergency Response programs. An ethanol-blended fuel is defined as a fuel containing greater than 10 percent ethanol by volume (E10). This would include E85, denatured fuel-grade ethanol (E95), and other fuel blends greater than E10 such as E15 or E20. These requirements are for sites that had a confirmed ethanol-blended fuel release and for releases at facilities that store or have stored ethanol-blended fuel where the released product is unknown (potential release).

I. Introduction

Ethanol-blended fuel releases will require investigation beyond that described in Guidance Documents 4-01 *Soil and Ground Water Assessments Performed During Site Investigations*, 4-01a *Vapor Intrusion Assessments Performed During Site Investigations*, 4-02 *Potential Receptor Surveys and Risk Evaluation Procedures at Petroleum Release Sites*, and 4-05 *Ground Water Sample Collection and Analysis Procedures*. The degree of additional investigation may vary depending on if the release is confirmed or potential. Confirmed releases will generally require a Remedial Investigation (RI). For potential releases, ethanol release-specific data collected during the Limited Site Investigation (LSI) will be used to determine the need for additional investigation.

These requirements are necessary due to additional risk factors as well as the influence ethanol has on subsurface fate and transport of petroleum hydrocarbons. Ethanol poses additional environmental risks not typical or inherent with petroleum releases, such as:

- Ethanol degradation in the subsurface has the potential to produce large quantities of methane gas that could lead to explosive conditions. Methane generation may be delayed for months to years after a release and may persist for years after the ethanol is no longer present in groundwater. At some sites, methane might be the primary contaminant of concern and the risk driver for corrective action or long-term monitoring.
- Unlike conventional petroleum fuels, ethanol is miscible in water and, as a result, has implications for the distribution of contamination and occurrence of light non-aqueous phase liquid in the subsurface.
- Releases of ethanol-blended fuels to surface waters present several issues. These include phase separation and extreme dissolved oxygen demand that occurs during ethanol degradation, which could quickly lead to anoxic conditions resulting in significant fish and wildlife mortality. Extreme dissolved oxygen demand can also be an issue with disposal of recovered liquids.

The effect of ethanol on the fate and transport of petroleum hydrocarbons may affect site investigation and risk evaluation in the following ways:

- Natural attenuation of petroleum hydrocarbons can be delayed due to preferential biodegradation of ethanol. This may result in delayed aqueous phase plume stabilization or longer plumes, which could increase risk to groundwater receptors.
- Elongated petroleum plumes in groundwater may serve as a vapor source and present increased risk for the vapor intrusion pathway.
- The increased production of methane and carbon dioxide may strip petroleum hydrocarbons from groundwater and provide a pressure gradient to move vapor into receptors.
- Ethanol can remobilize preexisting, stable petroleum contamination, thus potentially increasing the risk.

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II. Investigation Requirements

A. Investigation considerations

1. **General considerations:** For confirmed releases, long-term monitoring of soil gas and groundwater via permanent monitoring points and wells is required because 1) the appearance of methane may be delayed and 2) ethanol degradation can prolong (or inhibit) attenuation and, thus, stability of the aqueous phase petroleum plume. In these cases, an LSI would not be sufficient because long-term monitoring is needed to assess potential methane generation, persistence, and associated risk as well as characterize the stability of the petroleum fraction.

2. **Historical product storage:** Prior to initiating LSI activities, the current and past storage of ethanol-blended fuels should be determined.

3. **Drilling safety:** Due to the potential for elevated methane gas levels, care should be exercised when drilling into areas with potentially high methane concentrations.

4. **Monitoring well installation and sampling:** Research has shown that ethanol-blended fuels will eventually phase separate after contact with soil water, and that the ethanol fraction can move into and disperse within the capillary fringe. In addition, the high degradation rates and associated products will make monitoring well installation and sampling critical. Shorter screen lengths and multi-level wells may be required, and documentation of well installation and sampling methods may be critical to interpret results. Special care in groundwater sampling is critical to avoid volatilization losses, especially for methane.

5. **Soil sample analysis:** The Petroleum Remediation Program does not support the analysis of ethanol from soil samples; therefore, no additional soil analyses are required.

6. **High methane concentrations:** If at any point in the investigation high methane concentrations are detected in groundwater or soil gas, notification is required. Contact the MPCA Project Manager assigned to the release site if either of the following conditions are met.

   a. Groundwater: aqueous methane concentrations exceed 10,000 µg/L.

   b. Soil gas: methane concentrations exceed 10 percent of the lower explosive limit, or 0.5 percent methane by volume (5000 ppmv), within 100 feet of a receptor.

7. **Future requirements:** Acetate is a degradation product of ethanol and can be used to assess the potential long-term generation of methane in groundwater. Acetate and/or dissolved organic carbon analysis may be required upon MPCA request. The MPCA is evaluating if these analytes will become standard requirements.

B. Limited site investigation requirements:

These requirements pertain to both confirmed and potential ethanol-blended fuel releases. Samples will typically be collected from soil borings, temporary wells, and preliminary soil gas assessment probes.

1. **Groundwater investigation:** All groundwater samples must be analyzed for ethanol and methane. Quantify ethanol along with volatile organic compounds (VOCs). Quantify methane along with ethane and ethene.

2. **Soil gas investigation:** Soil gas sampling is required regardless if receptors are present. If receptors are present, follow Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations* for sample depth and location. If no receptors are present, source-area soil gas samples should be collected two feet above the water table but at least five feet below the surface.

   For confirmed releases, install one permanent soil gas monitoring point in the source area during the LSI. If possible, complete it as a multi-level monitoring point with two individual screened intervals. The deep screen interval should be placed two feet above the water table, and the shallow screen interval should be placed at least five feet below the surface, with a minimum separation distance of eight to ten feet between intervals. See *Vapor Intrusion Assessments Performed During Site Investigations* for more information regarding permanent soil gas monitoring point installation.

   Soil gas samples must be analyzed for the compounds in the Minnesota Soil Gas List (see *Vapor Intrusion Assessments Performed During Site Investigations*) and fixed gases. Ethanol is included in the Minnesota Soil Gas List. Fixed gases include methane, oxygen, carbon dioxide, and carbon monoxide. Fixed gases will require a separate analysis, but a single canister will supply enough sample volume to complete all required analyses.

C. Remedial investigation requirements: These requirements pertain to confirmed releases of ethanol-blended fuel.

1. Groundwater investigation

a. Investigation protocols*:* Groundwater samples will typically be collected from monitoring wells. Monitoring well construction during the RI should follow guidelines in Guidance Document 4-01 *Soil and Ground Water Assessments Performed During Site Investigations*. Following review of water table elevation conditions, additional monitoring wells with shorter well screens or multi-level wells may be required.

b. Sampling parameters*:* All groundwater samples must be analyzed for ethanol and methane as described herein and for natural attenuation parameters as described in Guidance Document 4-03 *Assessment of Natural Biodegradation at Petroleum Release Sites*. Acetate may be required on a site-specific basis. Specific parameters may be dropped from routine analysis from all or some wells based on investigation results.

2. Soil gas investigation

a. Investigation protocols: Permanent soil gas monitoring points are required as part of the RI regardless if receptors are present. If receptors are present, follow Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations* for sample depth and location. If no receptors are present, install one permanent soil gas monitoring point in the source area as described in Section II.B.2 above.

b. Sampling parameters: Samples must be analyzed for compounds in the Minnesota Soil Gas List and fixed gases. Specific parameters may be dropped from routine analysis from all or some monitoring points based on investigation results.

If permanent soil gas monitoring points have been installed for long-term monitoring, a direct reading methane field instrument (e.g., landfill gas meter) may be used in lieu of laboratory analysis for fixed gases if a good correlation between two consecutive laboratory and field measurement events can be demonstrated. It is advised to quantify methane using the required lab analysis and a methane field instrument during the RI.

III. Sample Collection

A. Introduction: Guidance describing equipment decontamination, field procedures, sample collection, sampling event documentation, and required Quality Assurance/Quality Control (QA/QC) sampling should be followed according to Guidance Document 4-05 *Ground Water Sample Collection and Analysis Procedures* unless alternative procedures are specified below.

B. Ethanol in groundwater: Aqueous samples for ethanol analysis should be collected using laboratory-supplied 40-milliliter (ml) HCl-preserved purge-and-trap bottles in a manner that minimizes turbulence, air entrapment and overfilling. 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 ethanol sample is turbid and effervesces when water comes into contact with the bottle preservative, unpreserved samples should be collected and noted on the chain-of-custody form. Unpreserved samples must be analyzed within a seven day holding time. Samples should be stored at a temperature of 4 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. Samples should be submitted for ethanol in groundwater analysis following U.S. Environmental Protection Agency (EPA) method 8260 with modifications. Laboratory QA/QC procedures for ethanol in groundwater samples via EPA 8260 with modifications are described in Section IV below.

C. Methane in groundwater: Aqueous samples for methane, ethane, and ethene analysis should be collected using laboratory-supplied glass serum bottles. Samples should be preserved using a 1:1 hydrochloric or sulfuric acid to a pH less than 2. Preservative should be added to glass bottles using an appropriate dispensing device (e.g., dropper) prior to adding sample water. 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. Cap the bottle using an appropriate septum and aluminum crimp cap. After capping, invert the bottle and check for air bubbles. If bubbles are present, discard the vial and fill a replacement. Samples should be stored at a temperature of 4 degrees Celsius during transport to the analytical laboratory.

Samples should be collected, at a minimum, in duplicate sets or according to laboratory instructions in order to guard against loss by breakage and to allow for laboratory quality assurance. Samples should be submitted for RSK-175 analysis following the laboratory QA/QC procedures described in Section IV below.

D. Ethanol in soil gas: Soil gas samples for ethanol analysis should be collected using laboratory-supplied evacuated canisters. Samples should be collected according to the appropriate sampling procedures and QA/QC requirements outlined in Sections II and III of Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations.* Samples should be submitted for laboratory analysis of compounds on the Minnesota Soil Gas List using EPA method TO-15. Ethanol is included in the Minnesota Soil Gas List. Laboratory QA/QC procedures for TO-15 are described in Guidance Document 4-01a.

E. Fixed gases in soil gas: Soil gas samples for fixed gases (methane, oxygen, carbon dioxide, and carbon monoxide) analysis should be collected using laboratory-supplied evacuated canisters. Samples should be collected according to the appropriate sampling procedures and QA/QC requirements outlined in Sections II and III of Guidance Document 4-01a *Vapor Intrusion Assessments Performed During Site Investigations*. Samples should be submitted for laboratory analysis of fixed gases by EPA method 3C. Laboratory QA/QC procedures for EPA 3C are described in Section IV below.

When using a direct reading methane field instrument such as a landfill gas meter, care must be taken to avoid inference with petroleum VOCs. An in-line activated carbon filter should be used to remove VOCs so the meter is only reading methane.

F. Natural biodegradation parameters: Field parameters and terminal electron acceptors should be collected according to the procedures outlined in Guidance Documents 4-05 *Ground Water Sample Collection and Analysis Procedures* and 4-03 *Assessment of Natural Biodegradation at Petroleum Release Sites*, respectively.

Aqueous samples for acetate analysis may be requested by the MPCA. If requested, samples should be collected using laboratory-supplied 125-ml unpreserved general bottles. Samples should be stored at a temperature of 4 degrees Celsius during transport to the analytical laboratory. Acetate samples can also be frozen allowing for a longer holding time.

IV. Required Laboratory Quality Assurance/Quality Control

A. Ethanol in groundwater: Aqueous samples may be analyzed for ethanol using the most recent version of EPA method 8260. The laboratory may need to modify the method to improve performance and optimize the instrument. Laboratories analyzing samples for aqueous phase ethanol shall follow the method as defined by the EPA in the EPA SW-846 8000 series methods dated December 1996 or later updates and by incorporating the following additional quality control procedures listed below.

1. The laboratory shall incorporate the following procedures for the analysis of ethanol in water by EPA method 8260:

a. Calibration solution standard: Calibration standard used for ethanol must be a water-based standard and not a methanol-based standard. Ethanol water-based standards should be stored at <4 degrees Celsius. Expiration date for stock standard is two years from opening or as stated on the vial, whichever is earlier. Intermediate dilution standards have an expiration date of two months.

b. Initial calibration: The initial calibration curve should contain at least five calibration points. The r^2 for each curve must be greater than or equal to 0.990. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and reanalyzed.

c. Continuing calibration verification: Analyze one low-level ethanol standard at the report level (RL) and one mid-level ethanol calibration verification standard at approximately 500 µg/L prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12 hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for ethanol in the low-level standard should be between 60 percent and 140 percent of the true value. The %R for ethanol in the mid-level standards should be between 70 percent and 130 percent of the true value (with a percent difference of less than or equal to 30 percent).

d. Initial demonstration of capability: Analyze 4-7 replicate check standards at a concentration of 500-1000 µg/L. Percent recovery (%R) must be equal to 80-120 percent. The percent relative standard deviation (%RSD) must be less than 20 percent.

e. Method detection limit/report level: Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven 50-ug/L standards. The RL should be three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 percent criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met. For Petroleum Remediation Program project sites, the RLs should be at or below 100 µg/L of ethanol.

2. The laboratory shall include the following QC procedures in the analysis of ethanol in water:

a. A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank, a Laboratory Control Sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a Laboratory Control Sample Duplicate (LCSD) is prepared and analyzed.

b. Method blanks/trip blanks: Analyze one method blank per QC batch of 20 samples or less. The concentration of ethanol in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a “B” to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

One trip blank should accompany every 20 environmental samples. The concentration of ethanol in the trip blank should be less than the associated report level. If ethanol is present in the trip blank, review the associated method blank. If a comparable level of ethanol is present in the method blank, the source of the contamination may be in the analytical system and measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a “B” to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

c. Samples: Absolute areas of the quantitation ions for the internal standard and surrogate must not decrease by more than 50 percent from the initial calibration.

d. Accuracy/precision: One MS and MSD is required per batch. The %R for ethanol in the MS/MSD must be between 70 percent and 130 percent with a relative percent difference (RPD) of less than or equal to 30 percent. The %R for ethanol in the LCS and LCSD should be between 70 percent and 130 percent with a RPD of less than or equal to 30 percent.

e. Special notes: The quantitation ion for ethanol is 45 atomic mass units (AMU). Confirmation ions are 46 AMU and 47 AMU. The presence of ethyl ether can cause an interference with the analysis. If ethyl ether is present in the sample, special care must be taken. Ethanol standards must be analyzed separately from the normal 8260 VOC list due to the interference from ethyl ether.

B. Methane in groundwater: Aqueous samples may be analyzed for methane using a headspace gas chromatography/flame ionization detector (GC/FID) technique based on a method developed by the EPA Robert S. Kerr Environmental Research Laboratory (Kerr Labs). The work is detailed in the Standard Operating Procedure from Kerr Labs (RSK-175) and in "Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Chromatographic Technique," Journal of Chromatographic Science, Vol. 36, May 1998. Since this analysis is a performance-based analysis, laboratories analyzing samples for aqueous-phase methane must also incorporate the following additional quality control procedures.

1. **Initial calibration:** An external standard calibration technique is used. The concentration of the target analyte is calculated from the average response factor or from a standard curve.

   The initial calibration curves should contain at least five calibration points. The %RSD for average response factors must be less than or equal to 30 percent or the r^2 value for the curve must be greater than or equal to 0.995. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curve shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and reanalyzed. If the instrument calibration results are outside the acceptance criteria, a number of actions can be taken:

   a. Check the instrument operating conditions. Instrument maintenance may be required.

   b. Review the response at each calibration level to insure that the problem is not associated with one standard. If the problem appears to be associated with one of the standards, that standard can be re-injected. If the problem persists, remake the standard and reanalyze it.

   c. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of a calibration point from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing calibration points. If the top point is removed, the need for diluting samples and reanalyzing will occur at a lower concentration level. If the low point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change.

2. **Continuing calibration:** The initial calibration curves are verified at the beginning and ending of an analytical sequence and every 12 hours by analyzing a mid-level standard. The drift must be within 70 percent to 130 percent. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Reanalyze the calibration standard. If the calibration criteria are still not met, a new initial calibration must be performed. All samples that were analyzed since the last passing calibration standard must be reanalyzed. There is one exception allowed for this QC criterion. If the recovery of the calibration verification standard is >130 percent of the true value and the environmental samples show no detection of the analyte, the "less than" value can be reported without reanalysis.

3. **Method validation:** The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

   The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven laboratory control samples near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses must be ≥70 percent and ≤130 percent (with a relative standard deviation of ≤30 percent).

4. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. Contact

the MPCA Project Manager for any required report level for each project. RLs depend on program needs. They can change as new information becomes available. RLs are verified after each calibration and at least monthly. For Petroleum Remediation Program project sites, the RLs should be at or below 1,000 µg/L of methane.

5. **Batch QC:** A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a LCS/LCSD pair.

   The concentration of methane in the method blank must be less than one-half of the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

   Methane is to be spiked into the LCS and LCSD. The spiking levels should be five to ten times the report levels. The LCS is made from reagent-grade water that has been demonstrated to be methane-free. In a water matrix, the percent recovery of methane in the LCS or LCSD must be ≥70 percent and ≤130 percent. The RPD between the LCS/LCSD pairs in water must be ≤30 percent.

   If prepared, the RPD between water sample duplicate pairs must be must be ≤50 percent.

   Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.

C. Fixed gases in soil gas: Soil gas samples may be analyzed for methane using a GC/FID. Other fixed gases including oxygen, carbon dioxide, and carbon monoxide may be analyzed using a GC/TCD (Thermal Conductivity Detector) technique based on EPA method 3C. Laboratories analyzing samples for fixed gases in soil gas must also incorporate the following additional quality control procedures.

1. **General considerations:** Helium is used to prepare calibration gases. Use sample collection procedures described in EPA method 3C or 25C. The sample loop must be Teflon or stainless steel tubing of the appropriate diameter. Peak height or peak area can be used for quantitation.

   EPA 3C requires that each sample must be analyzed in duplicate to calculate the average response. For the purposes of the MPCA Petroleum Remediation Program, a single analysis will be adequate.

2. **Initial calibration:** An external standard calibration technique is used. The concentration of the target analyte is calculated from the average response factor or from a standard curve.

   The initial calibration curves should contain at least five calibration points. The % RSD for average response factors must be less than or equal to 30 percent or the r^2 value for the curve must be greater than or equal to 0.995. The recovery (accuracy) for each point in the curve must be 70 percent to 130 percent except for the lowest point in the curve which must be 60 percent to 140 percent. The lowest calibration point in the curve shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, a smaller sample volume is injected into the GC and reanalyzed. If the instrument calibration results are outside the acceptance criteria, a number of actions can be taken:

   a. Check the instrument operating conditions. Instrument maintenance may be required.

   b. Review the response at each calibration level to insure that the problem is not associated with one standard. If the problem appears to be associated with one of the standards, that standard can be reinjected. If the problem persists, remake the standard and reanalyze it.

   c. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of a calibration point from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing

calibration points. If the top point is removed, the need for diluting samples and reanalyzing will occur at a lower concentration level. If the low point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change.

3. **Continuing calibration:** The initial calibration curves are verified at the beginning and ending of an analytical sequence. The drift must be within 70 percent to 130 percent. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Reanalyze the calibration standard. If the calibration criteria are still not met, a new initial calibration must be performed. All samples that were analyzed since the last passing calibration standard must be reanalyzed. There is one exception allowed for this QC criterion. If the recovery of the calibration verification standard is >130 percent of the true value and the environmental samples show no detection of the analyte, the "less than" value can be reported without reanalysis.

4. **Method validation:** The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

   The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven laboratory control samples near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses must be ≥70 percent and ≤130 percent (with a relative standard deviation of ≤30 percent).

5. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60 percent to 140 percent criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. Contact the MPCA Project Manager for any required report level for each project. RLs depend on program needs. They can change as new information becomes available. Report levels (RLs) are verified after each calibration and at least monthly. For most analytical work for the MPCA, the RLs should be at or below 1 percent for reported fixed gases. The MPCA requires that final results be reported as a percentage for fixed gases.

6. **Batch QC:** A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a LCS/LCSD pair.

   The concentration of methane in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

   Methane is to be spiked into the LCS and LCSD. The spiking levels should be five to ten times the report levels. The LCS is made from reagent-grade helium that has been demonstrated to be methane-free. In a soil gas matrix, the percent recovery of methane in the LCS or LCSD must be ≥70 percent and ≤130 percent. The RPD between the LCS/LCSD pairs in water must be ≤30 percent.

   Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report and corrective actions detailed (along with an explanation of the impact on data quality) in the case narrative.

V. Who to Contact

Minnesota statute requires that spills and releases of all grades and types of fuel greater than five gallons be reported to the Minnesota State Duty Officer (800-422-0798 or 651-649-5451) upon discovery. Releases that are not reported immediately may result in penalties or a reduction in Petrofund reimbursement if applicable. See Guidance Document 2-01 *Reporting of Petroleum Releases* for more information regarding when and how to report a release.

When reporting releases of ethanol-blended fuels to the State Duty Officer, the caller should specifically identify the fuel ethanol concentration. When reporting a release of any fuel type at facilities storing ethanol-blended fuel, the caller should specifically indicate the presence of these storage tanks on site. Depending on the nature of the release, the caller may be immediately contacted by the MPCA, or a written response may be issued.

Any questions regarding investigation of ethanol-blended fuel releases from storage tank systems may be directed to MPCA Petroleum Remediation Program staff. Any questions regarding spills and emergency response-related issues may be directed to MPCA Emergency Response Program staff. Please call the MPCA at 800-657-3864 or 651-296-6300 and request the appropriate staff.

Web pages and phone numbers

MPCA staff	http://www.pca.state.mn.us/pca/staff/index.cfm
MPCA phone	**651-296-6300 or 1-800-657-3864**
Petroleum Remediation Program web page	http://www.pca.state.mn.us/programs/lust_p.html
MPCA information request	http://www.pca.state.mn.us/about/inforequest.html
MPCA VIC Program	http://www.pca.state.mn.us/cleanup/vic.html
MPCA Petroleum Brownfields Program	http://www.pca.state.mn.us/programs/vpic_p.html
Petrofund web page	http://www.state.mn.us/cgi-bin/portal/mn/jsp/content.do?id=-536881377&agency=Commerce
Petrofund phone	**651-215-1775 or 1-800-638-0418**
State Duty Officer	**651-649-5451 or 1-800-422-0798**