

Technical Memorandum

To: Montana Department of Environmental Quality (DEQ)
Remediation Division
Hazardous Waste Site Cleanup Bureau

From: Aimee Reynolds

Date: 10/22/2007

Re: Application of Massachusetts Method in Facility Characterization

This memo provides clarification of how the Hazardous Waste Site Cleanup Bureau will use the Massachusetts Method for volatile petroleum hydrocarbons (VPH) and extractable petroleum hydrocarbons (EPH) in facility characterization and confirmation sampling. The purpose of the VPH and EPH methods is to provide a breakdown of the petroleum compounds present in environmental media to allow for risk assessment and fate and transport analysis. However, based on guidance provided by the Massachusetts Department of Environmental Protection¹, it may not be necessary for all samples of all media at a given facility to be analyzed using these methods to achieve these goals. The following provides some direction regarding decisions about the frequency of VPH and EPH analysis but is only meant to be a guide to provide a basis for facility-specific decision-making.

SMALL RELEASES

For small facilities, such as small underground storage tank (UST) excavations, pipeline breaks, or truck spills without groundwater impacts, screening techniques are best used to direct soil removal operations, and identify areas for assessment and/or confirmatory laboratory analysis. The typical approach is to remove as much contaminated soil as possible, verify the adequacy of the cleanup visually and/or with field screening techniques like photoionization detectors (PIDs), flame ionization detectors (FIDs), ultraviolet fluorescence and absorbance, immunoassay test kits, or fiber-optic chemical sensors, or emulsion-based total petroleum hydrocarbon methods, and then collect soil confirmation samples for laboratory analysis. With the exception of mineral/dielectric oils and heavier wastes, **all** laboratory samples should generally be analyzed using VPH (including methyl-tertiary butyl ether, benzene, toluene, ethylbenzene, xylenes, and naphthalene (MBTEXN)). EPH-screen should be utilized for analysis on petroleum hydrocarbon products except for gasoline and aviation gas. For EPH-screened samples with concentrations greater than 200 mg/kg, fractionation is required. On a facility-specific basis, if the source of contamination is distinct, such as a single release from a fuel oil UST system, then a minimum of 20% of confirmation samples exhibiting the highest EPH-screen concentrations may be fractionated. For diesel range hydrocarbon contaminants that are heavier than diesel, fractionated EPH samples should include polycyclic aromatic hydrocarbon (PAH) analysis. If confirmation samples indicate that additional cleanup is necessary, a facility-specific determination must be made as to how to proceed.

LARGE RELEASES

1.0 Volatile Petroleum Hydrocarbons

Field screening techniques using PIDs, FIDs, ultraviolet fluorescence and absorbance, immunoassay test kits, or fiber-optic chemical sensors, may be appropriate for facilities with gasoline range contamination. In addition, total petroleum hydrocarbon (TPH) and gasoline range organic (GRO) laboratory analyses may also be appropriate as screening tools for facility characterization. Decisions about the number of samples requiring VPH analysis, including MBTEXN, should be made on a facility-specific basis. DEQ will consider the heterogeneity of facility conditions related to both the contaminant and the physical characteristics of the facility (such as soil type, stratigraphy, microbiology, source vs. migration areas, and degradability of the product, and the property usage). The responsible party or potentially liable person should demonstrate these facility-specific conditions to DEQ in its sampling proposal. For screening techniques that provide reliable quantitative results and that differentiate petroleum contamination from other compounds (e.g., GRO), fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific VPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results.

1.1 Soil and Waste

DEQ requires that a **minimum** of 20% (a higher percentage may be appropriate) of all samples collected for waste and soil be analyzed by a laboratory using the VPH method, including MBTEXN. Additional VPH analyses may be required on a facility-specific basis. Because of differences in mobility and degradation rates, the goal should be to collect samples from a variety of areas at the facility for VPH analysis rather than focusing on worst-case areas. For instance, depending on the number of samples being collected, VPH samples should be collected at the source and at the edge of the release with additional samples at midpoints along the axis of the release as necessary to determine the range of concentrations present and confirm the reliability of screening data over the range of concentrations. The more heterogeneous the products or physical characteristics of the facility, the more samples should be analyzed by using the VPH method. For example, if there are two distinct sources or soil types onsite, a **minimum** of 20% of samples from each source and/or soil type should be analyzed using the VPH method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific VPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the VPH analyses. Because the purpose of residential surface soil sample analyses is to calculate risk and because of the variability of residential surface soil conditions, **all** residential surface soil samples should be analyzed by a laboratory using the VPH method.

After cleanup has been conducted and verified visually and/or with qualitative field screening techniques, soil confirmation samples should be collected for quantitative field or laboratory analysis. **All** quantitative confirmation samples should be analyzed using a screening technique that provides reliable quantitative results and that differentiates petroleum contamination from other compounds (e.g., GRO) with a **minimum** of 20% of the samples analyzed using the VPH laboratory method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the

absence of facility-specific VPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the VPH analyses. Additional VPH analyses may be required on a facility-specific basis.

1.2 Groundwater

DEQ requires that a **minimum** of 20% (a higher percentage may be appropriate) of all samples collected for groundwater be analyzed by a laboratory using the VPH method, including MBTEXN. Additional VPH analyses may be required on a facility-specific basis to determine compliance with water quality standards. Because of differences in mobility and degradation rates, the goal should be to collect VPH samples from various portions of the plume. For instance, depending on the number of wells being sampled, VPH samples should be collected from wells at the source and at the edge of the plume with additional wells sampled at midpoints along the axis of the plume as necessary to determine the range of concentrations present and confirm the reliability of screening data over the range of concentrations (i.e., the axis of the plume should be characterized with VPH results). The more heterogeneous the products or physical characteristics of the facility, the more samples should be analyzed by the laboratory using the VPH method. For example, if there are two distinct sources or aquifers onsite, a **minimum** of 20% of samples from each source and/or aquifer should be analyzed using the VPH method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific VPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the VPH analyses. Because the purpose of residential groundwater sample analyses is to calculate risk, **all** residential groundwater samples should be analyzed by a laboratory using the VPH method.

As wells are sampled over time, initial VPH analyses should be used to direct future sampling requirements. For the first year of sampling VPH analyses are appropriate for a **minimum** of 20% of samples from each sampling event (either quarterly or semiannually). Additional VPH analyses may be required on a facility-specific basis to determine compliance with water quality standards. After the first year, if continued monitoring is required and the plume has stabilized, the number of wells sampled and the frequency of sampling may be decreased and the axis of the plume may become the focus of continued monitoring. A 20% **or higher** frequency of VPH analyses may continue to be appropriate but if the concentrations of the hydrocarbon ranges have stabilized, the percentage of VPH samples may be decreased. The responsible party or potentially liable person should provide the reasoning behind the proposed monitoring plan to DEQ in its sampling proposal.

1.3 Surface Water and Sediment

Because of the variability of the media and the potential sensitivity of aquatic organisms, DEQ requires that **all** surface water and sediment samples be analyzed by a laboratory using the VPH method, including MBTEXN.

1.4 Soil Gas and Air

Field screening techniques using PIDs or FIDs may provide some information regarding soil gas or air concentrations at the facility. However, because of the generally limited number of samples collected, the variability of the media, and the need for risk analysis, soil gas or air samples collected for laboratory analysis should be collected using SUMMA canisters and analyzed for volatile compounds including MBTEXN using EPA Method TO-15. The Air Phase Hydrocarbon (APH) Method developed by the MADEP should be used for determining the concentrations of the VPH fractions.

2.0 Extractable Petroleum Hydrocarbons

Field screening techniques such as ultraviolet fluorescence and absorbance, emulsion-based total petroleum hydrocarbon methods, immunoassay test kits, and fiber-optic chemical sensors, may also be appropriate for facilities with diesel range contamination. In addition, total petroleum hydrocarbon (TPH) and diesel range organic (DRO) laboratory analyses may also be appropriate as screening tools for facility characterization. Fractionated EPH analyses are performed to provide information necessary for risk assessment and fate and transport analysis. Decisions about the number of samples requiring laboratory analysis should be made on a facility-specific basis considering the heterogeneity of facility conditions related to both the contaminant and the physical characteristics of the facility (such as soil type, stratigraphy, microbiology, source vs. migration areas, and degradability of the product, and the property usage). The responsible party or potentially liable person should demonstrate these facility-specific conditions to DEQ in its sampling proposal.

2.1 Soil and Waste

DEQ requires that a **minimum** of 20% (a higher percentage may be appropriate) of all samples collected for waste and soil be analyzed using the EPH-screen method. EPH-screen should be utilized for analysis on petroleum hydrocarbon products except for gasoline and aviation gas. For EPH-screened samples with concentrations greater than 200 mg/kg, fractionation is required. If VPH compounds, including MBTEXN, are not present above screening levels, further VPH analyses should not be required. For diesel range hydrocarbon contaminants that are heavier than diesel, initial EPH samples should include polycyclic aromatic hydrocarbon (PAH) analysis. If PAHs are not present above screening levels, further PAH analysis should not be required. Because of differences in mobility and degradation rates, the goal should be to collect EPH samples from a variety of areas at the facility rather than focusing on worst-case areas. Again, depending on the number of samples required, EPH samples should be collected at the source, at the edge of the release and at midpoints along the axis of the release as necessary to determine the range of concentrations present and confirm the reliability of the screening data over the range of concentrations. The more heterogeneous the products or physical characteristics of the facility, the more samples should be analyzed using the EPH method. Again, for example, if there are two distinct sources or soil types onsite, a **minimum** of 20% of samples from each source and/or soil type must be analyzed using the EPH method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the EPH analyses. In the absence of facility-specific EPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. Because the purpose of residential surface soil sample analyses is to calculate risk and because of the variability of residential surface soil conditions, **all** residential surface soil samples should be analyzed by a laboratory using the EPH method.

After cleanup has been conducted and verified visually and/or with qualitative field screening techniques, soil confirmation samples should be collected for quantitative field or laboratory analysis. **All** quantitative confirmation samples should be analyzed using a screening technique that provides reliable quantitative results and that differentiates petroleum contamination from other compounds (e.g., DRO) with a **minimum** of 20% of the samples analyzed using the EPH laboratory method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific EPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the EPH analyses.

1.5 Groundwater

DEQ requires that a **minimum** of 20% (a higher percentage may be appropriate) of all samples collected for groundwater be analyzed by a laboratory using the EPH-screen method. For EPH-screened samples with concentrations greater than 500 µg/L, fractionation is required. VPH analyses are also required for all EPH-screen samples if the suspected release is of diesel (#1 and #2), waste oil, crude oil, and jet fuel/kerosene samples or from an unknown source. If VPH compounds including MBTEXN are not present above screening levels in two consecutive rounds of sampling, further VPH analyses should not be required. If VPH compounds are present above screening levels, additional VPH analyses may be required on a facility-specific basis to determine compliance with water quality standards. For diesel-range hydrocarbon contaminants that are heavier than diesel, initial EPH samples should include PAH analysis using EPA method 625. If PAHs are not present above screening levels in two consecutive rounds of sampling, further PAH analysis should not be required. Because of differences in mobility and degradation rates, the goal should be to collect EPH samples from various portions of the plume. For instance, depending on the number of wells being sampled, EPH samples should be collected from wells at the source and at the edge of the plume with additional wells sampled at midpoints along the axis of the plume as necessary to determine the range of concentrations present and confirm the reliability of screening data over the range of concentrations (i.e., the axis of the plume should be characterized with EPH results). The more heterogeneous the products or physical characteristics of the facility, the more samples should be analyzed using EPH. For example, if there are two distinct sources or aquifers onsite, a **minimum** of 20% of samples from each source and/or aquifer must be analyzed using the EPH method. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific EPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the EPH analyses. Because the purpose of residential groundwater sample analyses is to calculate risk, **all** residential groundwater samples should be analyzed by a laboratory using the EPH method.

As wells are sampled over time, initial EPH analyses should be used to direct future sampling requirements. If a Tier 2 type of risk analysis is not contemplated and the cleanup goal will be 1,000 µg/L, additional EPH fractionation may not be necessary. However, if further risk analysis is appropriate, EPH analyses may be appropriate for a **minimum** of 20% of samples from each sampling event (either quarterly or semiannually). After the first year, if continued monitoring is required and the plume has stabilized, the number of wells sampled and the frequency of sampling may be decreased and the axis of the plume may become the focus of continued monitoring. A 20% **or higher** frequency of

EPH analyses may continue to be appropriate but if the concentrations of the hydrocarbon ranges have stabilized, the percentage of EPH samples may be decreased. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific EPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the EPH analyses. The responsible party or potentially liable person should provide the reasoning behind the proposed monitoring plan to DEQ in its sampling proposal.

1.6 Surface Water and Sediment

Because of the variability of the media and the potential sensitivity of aquatic organisms, DEQ requires that **all** surface water and sediment samples be analyzed by a laboratory using the fractionated EPH method, VPH including MBTEXN or PAHs as appropriate.

1.7 Soil Gas and Air

Field screening techniques using PIDs or FIDs may provide some limited information regarding soil gas or air concentrations at the facility. However, because of the generally limited number of samples collected, the variability of the media, and the need for risk analysis, if soil gas or air samples are required, **all** samples collected for laboratory analysis should be analyzed using the fractionated EPH method, VPH including MBTEXN or PAHs as appropriate.

3.0 Facilities with Both Gasoline and Diesel Range Contamination

For facilities with both gasoline and diesel range contamination, a **minimum** of 20% of samples from each source should be analyzed for VPH or EPH or both as appropriate. VPH including MBTEXN and PAH analysis should be conducted as indicated above. If distinct source areas and plumes are present, a **minimum** of 20% of the samples collected from the gasoline source area should be analyzed using the VPH method and a **minimum** of 20% of the samples collected from the diesel source area should be analyzed using the EPH method. If the sources areas or plumes are commingled, it may be possible to analyze a **minimum** of 20% of the samples for both VPH and EPH. Decisions regarding the frequency of VPH/EPH analysis must be made on a facility-specific basis. Fraction concentrations from unfractionated results may be estimated by applying conservative fraction percentages from fractionated sample results to quantitative total petroleum hydrocarbon results. In the absence of facility-specific EPH analysis, conservative generic assumptions included in the Massachusetts Department of Environmental Protection¹ guidance may be applied to quantitative screening results. The responsible party or potentially liable person should present screening data with a breakout of the estimated fraction percentages based on the EPH analyses.

¹ Massachusetts Department of Environmental Protection, Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of MADEP VPH/EPH Approach, Final Policy, 2002, pp. 17-18.