Texas Natural Resource Conservation Commission

INTEROFFICE MEMORANDUM

To: PST Corrective Action Coordinators
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Subject: Interim Guidance: Monitoring Natural Attenuation for Verification of Groundwater Plume Stability

The February 10, 1997 memorandum *Closure Process for Petroleum Hydrocarbon LPST Sites Exceeding Target Concentrations* highlights situations where natural attenuation should be evaluated as a remedial alternative for groundwater contamination. The memorandum also indicates situations where the stability of a groundwater plume should be verified prior to site closure. Plume stability is dependent on natural attenuation processes.

Responsible parties may include the collection of natural attenuation indicator information in proposals to verify plume stability or propose to use monitored natural attenuation as a corrective action plan (CAP). The recently implemented guidance *Operation, Monitoring and Performance of Remedial Systems* (RG-261) lists many natural attenuation indicators that can be evaluated to determine if natural attenuation is occurring at sites. The attached table lists the only natural attenuation indicators that should typically be monitored as a "first cut" evaluation of natural attenuation in groundwater. Do not require/preapprove the collection of additional natural attenuation indicators (e.g., methane, alkalinity, carbon dioxide, etc.) unless there is a site-specific basis for doing so (i.e., the indicators in the table have yielded equivocal information), or the additional indicator information can be obtained for no additional cost.

Proposals for verification of plume stability should provide for the collection of one or two rounds of the natural attenuation indicators and at least a total of three to four contaminant concentration monitoring events. The second round of natural attenuation indicator sampling may be necessary if no clear trends were identified from the first sampling event. If one round of contaminant concentration data has been collected, then only two or three more monitoring events may be needed. If no natural attenuation indicators are to be measured, then additional site concentration monitoring

events may be necessary. It is important that the natural attenuation indicator information be measured in wells which document background concentrations, and in wells within and beyond the plume. Optimally, the indicator information will be collected from a series of wells positioned along the axis of the contaminant plume (in the direction of plume migration) and transverse to the contaminant plume. Some additional monitoring wells sited specifically to collect critical natural attenuation information may be needed. Plume stability will be indicated when the extent of the contaminant plume appears to be stable or declining, and there is a clear trend with the indicator information which coincides with the location of the contaminant plume. If at the conclusion of this monitoring program, the results are equivocal (e.g., the indicator data do not confirm natural attenuation, or contaminant concentrations are highly variable across the sampling events), additional monitoring events may be warranted. If there is adequate historical contaminant concentration monitoring data to demonstrate a stable or declining plume, then the natural indicator information would not be needed.

Proposals for plume stability evaluations should be submitted as a groundwater monitoring proposal and not as CAPs. In addition to the information normally contained within groundwater monitoring proposals, the proposal should indicate the natural attenuation indicators that are to be measured, identify the wells to be sampled and frequency of sampling, and identify the sampling/analysis techniques for the natural attenuation indicators. If additional monitoring points are needed to support the evaluation, then a proposal should also be provided for well installation.

Only when further corrective action is needed to achieve a protective concentration at a point of exposure is a natural attenuation CAP necessary and appropriate. Natural attenuation CAPs should: identify the indicator information that is to be collected; detail the frequency of monitoring and sampling techniques; identify the wells that will be monitored; include a proposal for the installation of any additionally needed monitoring wells; contain an estimate of the degradation rate and remedial time frame based on prior monitoring; contain a contingency plan in case more aggressive actions are needed (for higher risk groundwater sites only); and include a description of how the data will be analyzed. To support development of a natural attenuation CAP, preliminary information such as that needed to support plume stability may need to be collected first. The guidance document *Corrective Action Plans for LPST Sites* (RG-41) provides additional guidance for developing a CAP.

The guidance provided herein is interim, pending completion of more thorough guidance. It is highly recommended that the attached article *A Practical Approach to Evaluating Natural Attenuation of Contaminants in Ground Water (McAllister and Chiang, 1994)* be studied. The article explains the typical plume behavior characteristics and data patterns that signal the occurrence of natural attenuation processes.

cc: Danny Neal, Manager, Reimbursement Section, PST Division

Attachment

Natural Attenuation Indicators: (The attached information was taken from the draft *ASTM Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Release Sites*, and from McAllister and Chiang, 1994.)

Parameter	Field or Lab Method	Analytical Method	Comments	Use of Data
Dissolved Oxygen (D.O.)			With all D.O. methods extra care must be taken to avoid aeration during all steps of the analysis including well purging and sample collection.	An inverse correlation of D.O. to BTEX concentrations indicates aerobic biodegradation is occurring. This relationship may also be expressed as depressed or non-detectable levels through the plume. Generally 1-2 mg/l D.O. is required to sustain aerobic degradation. Verify that groundwater beyond the plume has at least this D.O. concentration.
	Field	Meter or Probe	Use a flow thru cell with a dissolved oxygen electrode. Other parameters such as temperature, pH, oxidation reduction can be measured simultaneously. If an oxygen consuming probe is used, then care must be taken to ensure sufficient and continuous flow from the well thru the cell.	D.O. measurements should be measured in monitoring wells inside and outside the plume including upgradient of the plume.
	Field	ASTM D888-92 Winkler Titration	Field kits for performing Winkler titrations can be used as the primary method of D.O. measurement or to confirm meter measurements. A combination of both methods can be used to ensure data quality.	D.O. measurements should be measured in monitoring wells inside and outside the plume including upgradient of the plume.
	Field	Down hole probe	If an oxygen consuming probe is used down hole, then gentle agitation of the probe is required. Vigorous agitation should be avoided to prevent aeration. This technique is recommended only in low permeability conditions where continuous well purging is not possible	D.O. measurements should be measured in monitoring wells inside and outside the plume including upgradient of the plume.
Ferrous Iron (Fe II)				Increased concentrations of Fe (II) may indicate Fe (III) is being used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons.
	Field	Colorimetric Standard Methods 18th Edition. Method 3500-Fe D	Collect 100 ml of water in glass container. Filter sample with 0.2µ filter.	Measure inside and outside of plume.
	Field	Hach 25140-25	Filter sample with 0.2µ filter.	Measure inside and outside of plume.

Parameter	Field or Lab Method	Analytical Method	Comments	Use of Data
Oxidation Reduction Potential				Defines region of the plume under oxidizing and reducing conditions. Evaluates potential for biologically mediated redox reactions to occur and helps validate the D.O. measurements
	Field	Ion Selective Electrode	Oxidation Reduction Potential probe can be inserted into flow thru cell and reading obtained simultaneously with D.O., pH, and temperature Can be taken down hole if necessary	Measure inside and outside of plume.
	Field	Direct reading meter	Oxidation Reduction Potential probe can be inserted into flow thru cell and reading obtained simultaneously with D.O., pH, and temperature	Measure inside and outside of plume.
	Field	ASTM D 1498-93	Can be taken down hole if necessary	Measure inside and outside of plume.
pH				Difference in pH between contaminated and uncontaminated groundwater may be an indicator that biological activity is occurring and may confirm the oxidation reduction potential results.
	Field	EPA Method 150.1 or SW-9040	Can be analyzed in flow thru cell or collect 100-200 ml of water in glass or plastic container and analyze immediately. Calibration should be conducted using manufactures standard solutions.	Measure inside and outside of plume.
	Field	Direct reading meter	Calibration should be conducted using manufactures standard solutions.	Measure inside and outside of plume.
	Field	ASTM D 1293-84	.Calibration should be conducted using manufactures standard solutions.	.Measure inside and outside of plume.

Parameter	Field or Lab Method	Analytical Method	Comments	Use of Data
Nitrate				Decreased nitrate concentrations in the anaerobic portion of the plume may indicate use of nitrate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Field	Colorimetric field kit	Collect 100 ml of water in a glass container.	Measure inside and outside of plume.
Sulfate				Decreased sulfate concentrations in the anaerobic portion of the plume may indicate use of sulfate as an electron acceptor for anaerobic biodegradation of petroleum hydrocarbons.
	Field	Colorimetric field kit	Collect 100 ml of water in a glass or plastic container, cool to 4°C, analyze immediately.	Measure inside and outside of plume.