# Public Discussion Draft RSR Wave 2 - Potential Changes to RSRs Monitored Natural Attenuation Class C Cleanup August 8, 2013

The Department of Energy and Environmental Protection is developing "public discussion drafts" of ideas for potential future amendment to DEEP regulations, or new provisions for regulations, to address remediation of releases and sites where hazardous substances have been released. Many of the subject matters for these drafts grew out of the Cleanup Transformation workgroup recommendations from November 2012. The purpose of the public discussion drafts is to provide more detail to the concepts set forth in the November 2012 Workgroup reports and the February 2013 Cleanup Transformation draft report. As a discussion draft, the language is not structured to read exactly as regulation language would, and does not attempt to propose section and subsection outline format. Also, this discussion draft is not a public hearing draft of a proposed regulation; DEEP will further shape and refine the discussion draft after considering public feedback, before proposing any formal proposed regulation for amendment/adoption and before initiating the formal regulation adoption process.

### **Purpose:**

The purpose of this proposal is to establish the requirements of monitored natural attenuation (MNA) of groundwater as a remedial option to achieve a Class C Cleanup. A Class C Cleanup, as recommended in DEEP's February 2013 Cleanup Transformation draft proposal, would be a new endpoint category for remediation of releases/sites, where:

- the selected long-term groundwater remedy is in operation but has not achieved the remediation standards of groundwater,
- the estimated duration of such remedy is known,
- there is an ongoing operation and maintenance requirement, and
- there is no current or near future exposure pathway to drinking water or volatilization receptors within the timeframe modeled for MNA.

This proposed provision would be a self-implementing option and would allow MNA as an accepted remedial approach using natural processes to address plumes under specific conditions. The proposal outlines the technical pre-requisites necessary to consider MNA a self-implementing remedial alternative and establishes an acceptable duration for a MNA program of up to 20 years. Alternative provisions are also proposed for SWPC and GWPC. For SWPC, a dilution factor would be allowable provided that no sensitive receptors are affected.

## **Natural Attenuation Evaluation and Implementation:**

Selection of MNA for a groundwater remedy to achieve a Class C Cleanup would include an evaluation of downgradient receptors and off-site issues, along with a periodic progress evaluation to demonstrate that attenuation is in fact occurring within a finite time frame. As long as MNA is occurring and there is a non-conforming groundwater plume, the plume shall be registered with the DEEP.

This section is subdivided in two stages. Stage A intends to address the regulatory pre-requisites for MNA. Stage B proposes the operation and maintenance requirements.

**STAGE A1 - General Pre-Requirements:** For MNA to be considered, the following pre-requisites must be met:

- Source contaminant must be removed. If the source cannot be removed, the minimum requirement is to control the source. Plume above criteria cannot be expanding or moving off-site or to sensitive receptors.
- Soil remediation has been completed and is in compliance with the residential direct exposure criteria and the pollutant mobility criteria for the applicable groundwater classification.
- No migrating or mobile LNAPL is present.
- MNA is not a DNAPL remedial option since compliance with groundwater is unlikely to occur in less than 20 years.
- MNA cannot be implemented if the concentration at the surface water discharge boundary is above 10 times the acute toxicity level. [DEEP may propose rules for when/where MNA might be allowable if the plume exceeding SWPC is breaking out into surface water; specific suggestions for rules are sought as part of the feedback.]
- MNA cannot be implemented if anyone is being currently exposed to the groundwater that exceeds GWPC or Volatilization Criteria.

**STAGE A2 - Site-Specific Evaluation Requirements**: To select MNA as the groundwater remedy, the following must be performed:

- Develop a robust Conceptual Site Model to identify attenuation mechanism appropriateness and demonstrate the degree of understanding regarding site processes.
- Evaluate onsite and downgradient receptors and off-site issues for the MNA duration.
- Identify the degradable contaminant(s) or COCs for the period of time the MNA is in place.
- Delineate the plume size and migration pattern as a function of time.

- Discuss in detail how the contaminant is going to be attenuated and how the plume is going to be controlled:
  - a. Plume history (to demonstrate loss of contaminant mass that leaves the source),
  - b. Geochemical indicators and rates (to demonstrate conditions are favorable for mass loss), and
  - c. Computer modeling (to demonstrate that the site data are consistent with loss via natural attenuation).
- Present rationale supporting sustainability of attenuation.
- Explain risks associated with contaminants and natural attenuation processes.
- Assess toxicity of transformation products and the potential they may exceed concentrations of the parent compound.
- Generate a long-term groundwater monitoring plan.
- Ensure any plume breaking out into surface water is not negatively impacting the local aquatic life, and will not do so for the MNA duration.

**STAGE A3 - Decision Points:** For MNA to be used, all requirements presented in Stage A1 and Stage A2 must be met. Also, the following must be demonstrated:

- Plume spatial area above criteria must be shrinking in size based on existing groundwater data.
- Plume concentration above criteria must not be migrating.
- Natural attenuation must be sustainable.
- MNA maximum duration cannot exceed 20 years.

#### **STAGE B - Minimum Monitoring Requirements:**

Performance monitoring is required as long as contaminant levels remain above required cleanup levels at any portion of the site. Once a plume has been shown to be shrinking and if the concentrations are all below risk based levels, and if no off-property issues or discharge issues are present, then intensive long-term monitoring need not extend for years and years. Groundwater sampling should be done quarterly for the first two years, semiannually for the next three years, and then annually for the following years unless an alternative is approved by the Commissioner. Sampling frequency should be reset at year 10 if calibration audit finds the predicted concentration is lower than the actual concentrations of the substance. Different types of geochemical analysis and different types of solute transport models may be required for fuels versus solvent metals plumes.

## General Background and Guidance:

## Specific Requirements:

After a Class C Cleanup verification is filed, the components of a future (Wave 2) regulation will require that the Party must monitor the groundwater to determine the effectiveness of the selected MNA remedy and demonstrate the MNA's sustainability. Three lines of evidence can be employed to evaluate the effectiveness of remediation by natural attenuation. These are classified as Primary, Secondary, and Optional.

Primary: For the primary line of evidence, current and historical groundwater monitoring data are analyzed to establish the relationship of constituent concentration over time. "Historical groundwater and/or soil chemistry data must demonstrate a clear and meaningful trend of declining contaminant mass and/or concentrations at appropriate monitoring or sampling points" (EPA, 1999). At some petroleum release sites, evaluation of historical data may be sufficient to indicate stable or diminishing plume area and constituent concentration. In other cases, the secondary and optional lines of evidence are developed to adequately demonstrate that natural attenuation is effectively controlling plume growth.

Secondary: The secondary line of evidence consists of (1) an evaluation of chemical indicators of biodegradation (e.g. the consumption of electron acceptors), and (2) calculation of lumped attenuation rate calculations. "Hydrogeologic or geochemical data can be used to indirectly demonstrate the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels" (EPA, 1999).

Optional: The optional and third line of evidence entails construction of comprehensive calibrated site models to quantify natural attenuation processes, including the combined effects of physical processes (e.g. dispersion and dilution), chemical processes (e.g. sorption), and biological processes (including both aerobic and anaerobic processes). "Data from field or microcosm studies that directly demonstrate the occurrence of a particular natural attenuation process at a site" (EPA, 1999).

# Modeling Tools:

As mentioned before, to select MNA as the Class C groundwater remedy, the Party must demonstrate natural attenuation is occurring, and three key elements must be considered:

- 1) Plume history (to demonstrate loss of contaminant mass that leaves the source). Analysis of plume history is intended to define a groundwater plume as stable, shrinking, or expanding. Natural attenuation is appropriate at sites with shrinking or stable plumes if the remediation and time frame are consistent with the expected performance of natural attenuation at the site. Methods to analyze plume history are shown in Table 1. At some sites, the plume status may be apparent from a visual inspection of the contour maps or concentration and plume length graphs. However, at many sites a statistical evaluation of the historical monitoring data may be desired to provide an objective measure of plume status or to resolve differences in interpretation of the data.
- 2) *Geochemical indicators and rates* (to demonstrate conditions are favorable for mass loss): It provides supplemental information that natural attenuation processes are active at the site. There are three general types of geochemical indicators:
  - 1. Consumption of electron acceptors used for direct oxidative reactions (for petroleum hydrocarbons but not for chlorinated solvents) (see Table 2 and Table 3). The apparent loss of dissolved oxygen, nitrate, and sulfate in the plume area is typically used as a geochemical indicator of direct oxidation of petroleum hydrocarbons, but does not relate to the direct loss of chlorinated solvents.
  - 2. Production of metabolic by-products. At petroleum hydrocarbon sites, ferrous iron and methane are typically used as indicators of anaerobic biodegradation of dissolved petroleum hydrocarbon contaminants. At chlorinated solvent sites, the presence of daughter products needs to be evaluated.
  - 3. Presence of appropriate redox/microbial environments. At some chlorinated solvent sites, dissolved hydrogen is measured to indicate whether the site is under nitrate reducing, iron reducing, sulfate reducing, or methanogenic conditions. Biodegradation of chlorinated solvents via reductive dechlorination (the most important dechlorination reaction for many chlorinated solvents) is favored in sulfate reducing and methanogenic environments.
- 3) Computer modeling (to demonstrate that the site data are consistent with loss via natural attenuation).

Table 1 Methods to Analyze Plume History Data to Determine Plume Stability				
SCOPE AND DATA REQUIREMENTS: Involves graphical analysis of historical plume concentration measurements to define plume status as either stable, shrinking, or expanding. Requires data from multiple well locations, over 4 or more sampling episodes. Methods include:				
Plume contour maps	Plot plume contours over time to illustrate stable, shrinking, or expanding condition.			
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Well concentration plots	Plot concentration vs. time data for individual monitoring wells, and provide linear regression to define concentration trend. When performed in source areas, an estimate of the lifetime of the source can be derived.			
Average plume concentration plots	Define average plume concentration vs. time based on data collected from several monitoring wells.			
Statistical trend analysis	Quantify groundwater concentrations trends using Mann-Whitney or Mann-Kendall statistical methods.			

The Mann-Kendall test is a non-parametric statistical test that can be used to define the trends in data using a ranking procedure. Future guidance will include more information on this test.

Table 2 Geochemical Indicators at Petroleum Hydrocarbon (Fuel) Sites with NA Biodegradation				
Geochemical Indicator	Geochemical Indicator Concentration			
	Inside of Plume	Outside of Plume		
Dissolved Oxygen	Low	Higher		
Nitrate	Low	Higher		
Manganese	Higher	Low		
Dissolved Ferrous Iron	Higher	Low/ND		
Sulfate	Low	Higher		
Methane	Higher	Low/ND		
		ND: Non-detect		

Table 3 Geochemical Indicators at Sites with Chlorinated Solvents and NA via Reductive Dechlorination				
Geochemical Indicator	Geochemical Indicator Concentration			
	Inside of Plume	Outside of Plume		
Dissolved Oxygen	Low	Higher		
Nitrate	Low	Higher		
Manganese	Higher	Low		
Dissolved Ferrous Iron	Higher	Low/ND		
Sulfate	Low	Higher		
Methane	Higher	Low/ND		
<b>Daughter Products</b>	Present	ND		
Dissolved Hydrogen	Higher	Low/ND		
		ND: Non-detect		

Guidance on geochemical indicators at sites with metals will be available in future guidance.