Natural Attenuation of Contaminated Soil and Ground Water at Agricultural Chemical Incident Sites

Guidance Document 20

The MDA is committed to considering proposals for natural attenuation of agricultural chemicals at suitable incident sites. The following guidance document outlines MDA's approach for natural attenuation of contaminated soil and ground water at agricultural chemical incident sites in Minnesota.

The U.S. Environmental Protection Agency (EPA) defines monitored natural attenuation as (OSWER Directive 9200.4-17, 1997):

> *The term "monitored natural attenuation," as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to other methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and ground water. These in-situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants.*

Attenuation of pesticides and fertilizers can occur naturally in the environment, however, the process may be limited by local environmental conditions, high concentrations of the pesticides and/or fertilizers and mixtures of different chemicals. While much is known about the attenuation of individual pesticides at label application rates in agricultural field use settings, there is limited information available on the attenuation of individual agricultural chemicals or mixtures of agricultural chemicals above label rates in non-field settings.

The conditions suitable for natural attenuation, and the items that should be included in a proposal for natural attenuation of soil or water containing agricultural chemicals, are outlined below. All approvals for natural attenuation will be made on a site specific basis.

NATURAL ATTENUATION OF AGRICULTURAL CHEMICALS IN SOIL

A. Criteria for Evaluating When Natural Attenuation May Be Appropriate

A proposal for natural attenuation may be submitted to MDA staff if human health, surface water, ground water and the environment will not be significantly impacted by leaving the contaminated soil in place, and if natural attenuation can achieve the site cleanup goals within a reasonable timeframe. A proposal for natural attenuation must evaluate each of the following (the Contamination Impacts Survey completed during the Remedial Investigation will include much of the information that is described below):

<u>Threat to Human Health</u>
The proposal shall determine if contaminant concentrations in the soil exceed the human health based soil cleanup goals. In general, natural attenuation will not be allowed if contaminant levels in soil are above the applicable human health cleanup levels and access to the site is unrestricted. Natural attenuation may be allowed where the contaminant concentrations exceed human health based goals if access to the site is restricted. One method of restricting access to a site is the installation of a fence at least six feet in height which is locked when the site is not occupied. Other methods of restricting access to the contaminated soil may also be appropriate.

<u>Threat to Surface Water</u>
The proposal shall determine if a surface water body is present near the site and the potential for contaminated runoff from the site to reach this surface water body. In general, natural attenuation will not be allowed if contaminants are likely to migrate by runoff or erosion to surface water bodies at levels that may exceed applicable surface water standards.

In addition, the proposal shall determine the potential for contaminants from the site to migrate with ground water to adjacent surface water bodies at levels which will exceed applicable surface water standards for the water body. Natural attenuation of contaminated soil will not be allowed if contaminants from soil are likely to leach downward to ground water and then migrate with ground water flow to surface water bodies at levels which will exceed the applicable surface water standards.

Threat to Ground Water

The proposal shall determine if the contaminants will leach to ground water before degradation of the contaminants occurs. In general, natural attenuation is inappropriate in instances where contaminants are likely to migrate downward at levels which will exceed the ground water goals for the site. Ground water goals are established by MDA staff.

Threat to Other Potential Receptors

The proposal shall determine if there will be an impact to wildlife, vegetation or domesticated animals or if there will be migration to off-site locations via tile lines, utilities, and storm or drainage systems if the contaminants are left in place.

Timeframe and Cost Effectiveness of Natural Attenuation Approach

The proposal shall provide documentation that natural attenuation of the contaminants will achieve the site cleanup goals within a reasonable timeframe and in a cost effective manner when compared with other corrective actions. Since the use of natural attenuation requires that site cleanup goals be achieved within a reasonable timeframe, it may be necessary to use natural attenuation in conjunction with active remediation measures (for example, source control) or as a follow-up to active remediation measures which have already been implemented.

In addition, since natural attenuation requires extensive site characterization and long term monitoring, the costs of implementing natural attenuation shall be fully evaluated and compared with the costs of active remediation strategies which meet the site cleanup goals in a shorter timeframe.

B. Site Characterization Requirements

The suitability of a site for natural attenuation of agricultural chemicals should be based on the following site characteristics (Sims et al, 1993; U.S. Environmental Protection Agency (EPA) 1993; Cookson, 1995).

All of this information may not be required for every site, especially when contaminant levels barely exceed cleanup goals. Additional or alternative methods that could be used to characterize a pesticide contaminated site for natural attenuation may also be proposed.

Available Soil Water

The water content of unsaturated soil varies over time and with precipitation events. Adequate water content is required to sustain microbial activity in soil at agricultural chemical incident sites. The water holding capacity is defined as the change in water content in a unit volume of soil per unit change in matric potential (Hillel, 1982, p. 221). The optimum water holding capacity for promoting microbial activity is 25-85% of -0.01 M Pa water content (Sims et al, 1993; U.S. EPA 1993). Methods for determining the available soil water can be found in Klute, 1986.

Oxygen

The presence of oxygen is required in the pore spaces of soil to act as an electron acceptor for aerobic biodegradation of contaminants. The minimum air-filled pore space (see Hillel, 1982, pg. 11 and 16) of the contaminated soil should be 10% for aerobic degradation (Sims et al, 1993; U.S. EPA 1993). Methods for determining the air-filled pore space can be found in Klute, 1986. Soil samples for the air-filled pore space measurements should be collected by thin-walled (Shelby Tube) sampling methods (ASTM D1587).

Hydraulic Conductivity

The soil must have adequate hydraulic conductivity to allow the movement of moisture, nutrients and gases through the soil system. Ideally, the hydraulic conductivity of an unsaturated zone soil should be greater than 1.00E-04 cm/sec (Cookson, 1995).

Measurements of hydraulic conductivity of unsaturated soil should be conducted with either constant head or falling head permeameters, whichever is appropriate for the soil type (see Klute, 1986 and American Society of Testing Materials (ASTM) methods). Soil samples for the hydraulic conductivity measurements should be collected by thin-walled (Shelby Tube) sampling methods (ASTM D1587).

Soil pH

The pH of a soil is an indicator of the activity of the hydrogen ion in the soil. The soil pH should be in the range of 5-9 to promote optimal biodegradation (Sims et al, 1993; U.S. EPA 1993; Cookson, 1995).

There are several methods for determining soil pH (Sparks et al, 1996; U.S. EPA SW-846, Method 9045).

Redox Potential

In aerobic degradation, energy is obtained from the oxidation of reduced materials. The redox potential of a soil is a measure of the electron density of the soil system. As oxygen becomes depleted in aerobic degradation, other substances are used as terminal electron acceptors and this results in a progressive increase in electron density or a negative potential.

For aerobic degradation, the soil should have a positive Eh value of at least 50 millivolts (mV). Optimum aerobic degradation is achieved at Eh values greater than 400 mV (Sims et al, 1993; U.S. EPA 1993; Cookson, 1995). There are several methods for determining the redox potential of soil (Weaver et al, 1994).

Availability of Nutrients

Carbon (C), nitrogen (N) and phosphorus (P) are essential nutrients for microbial energy and growth. At agricultural chemical incident sites, nitrogen and phosphorus may be present in abundant amounts as a result of the release of fertilizers. The presence of high amounts of nitrogen and phosphorus may aid or inhibit microbial growth, depending on the concentrations of these nutrients and the degradation processes occurring at the site.

The suggested C:N:P ratio is 100:10:1, although this ratio may need to be modified based on the concentrations of contaminants present and the conditions of the site (Sims et al, 1993; U.S. EPA 1993). Total organic carbon (TOC) should be analyzed in soil samples using either EPA SW-846 Method 9060 or EPA 415.1. Ammonia nitrogen should be analyzed using EPA 350.1, nitrate nitrogen should be analyzed using EPA 353.2, and nitrite nitrogen should be analyzed using EPA 353.2. Available phosphorus should be analyzed using Olsen phosphorus method for soils with a pH >7.2 and the Bray P-1 method for soils with a pH <7.2 (North Central Regional Publication No. 221, 1988).

Enumeration Studies

Microbial enumeration studies or plate counts should be conducted on site soils. Plate counts may be used to quantify the number of bacteria able to grow on a specific set of nutrients and substrates immobilized in a solid medium (National Research Council, 1993). Since laboratory conditions may be more favorable than field conditions for biodegradation, these studies may be more useful as qualitative measures of degradation potential.

Total heterotrophic plate count (TPC) analyses are reported as a number of colony-forming units (CFUs) per gram of soil or per milliliter of water. Agricultural soil may have plate counts between 10^9 to 10^{12} CFU/g while a bulk soil with little root mass may have plate counts closer to 10^7. Petroleum contaminated soils have been found to have plate counts in the range of 10^4 to 10^6 CFU/g (Hemming and Milke, 1996). Soil with CFUs below 10^3 CFU/g may indicate generally toxic conditions for soil microbes (Cookson, 1995) or a lack of appropriate substrates, nutrients, oxygen and so forth.

Representative soil samples should be collected for the microbial enumeration studies from the most highly contaminated soils and from uncontaminated soil so that bacterial counts in both contaminated and uncontaminated settings can be compared. Soil samples for microbial enumeration studies must be collected aseptically to avoid introducing nonindigenous bacteria into the samples. Sterilized soil sampling equipment should be used. Typically soil samples from split spoons or Shelby tubes are obtained and the outer few centimeters as well as the top and bottom of these core samples are removed with an alcohol-sterilized spatula. Only the center portion of the core is used in the enumeration study. In addition, soil samples should be cooled to 4 degrees centigrade but should not be frozen (Wisconsin Department of Natural Resources, 1994).

Methods for conducting total heterotropic plate counts can be found in Weaver et al (1994).

C. Monitoring Requirements

A monitoring plan is generally required for natural attenuation sites. The monitoring plan shall include monitoring procedures which will confirm that: 1) passive biodegradation is occurring; 2) contaminant concentrations are decreasing over time, and 3) contaminant decreases are due to attenuation and not migration of the contaminants. At a minimum, the contaminant concentrations shall be monitored periodically to establish that concentrations are decreasing over time. In addition, uncontaminated soil at depths of approximately 1-3 feet below the contaminated soil shall be monitored to assure that contaminants are not leaching downward. Ground water monitoring below the contaminated soil may also be appropriate.

We recommend that soil monitoring be conducted at a minimum of twice a year. Soil monitoring will generally be required until contaminant levels reach site cleanup goals.

The monitoring plan shall include a description of the sampling locations, sampling methods, a list of analytes appropriate for the site, including degradation products, if possible, and analytical methods.

NATURAL ATTENUATION OF AGRICULTURAL CHEMICALS IN GROUND WATER

A. Criteria for Evaluating When Natural Attenuation May Be Appropriate

Natural attenuation may be appropriate for contaminated ground water if there will not be an adverse impact on human health, surface water or other potential receptors and if natural attenuation of the contaminated ground water can achieve the site cleanup goals within a reasonable timeframe. These requirements will typically require that natural attenuation be used in conjunction with active remediation of the source of the ground water contamination. Any proposals for natural attenuation of contaminants in ground water must evaluate each of the following:

<u>Threat to Humans from Contaminated Ground Water</u>
The proposal shall determine if the ground water below the site is currently used for a water supply. The proposal shall determine the likelihood that contaminated ground water will migrate to: 1) currently used aquifers; 2) aquifers that are not currently used but could be used in the future, and 3) other formations which are connected to useable aquifers.

In general, natural attenuation of contaminants in ground water is inappropriate in instances where it is likely that ground water will become contaminated above ground water cleanup goals or in instances where the ground water contaminant plume is not stable and is continuing to migrate downgradient.

<u>Threat to Surface Water</u>
The proposal shall determine if a surface water body is present near the site and the potential for contaminated ground water to reach this surface water body. In general, natural attenuation of contaminated ground water is inappropriate if the contaminant plume is likely to migrate to the surface water body and cause contamination of the surface water body above applicable surface water standards.

<u>Threat to Other Potential Receptors</u>
The proposal shall determine the potential impact to wildlife, vegetation or other sensitive receptors if the contaminants are left to passively degrade in ground water. In addition, the proposal shall determine if the contaminants will migrate to off-site locations via tile lines, utilities, and storm or drainage systems.

<u>Timeframe and Cost Effectiveness of Natural Attenuation Approach</u>
The proposal shall provide documentation that natural attenuation of the contaminants will achieve the site cleanup goals within a reasonable timeframe and in a cost effective manner when compared with other corrective actions. Since the use of natural attenuation requires that site cleanup goals be achieved within a reasonable timeframe, it may be necessary to use natural attenuation in conjunction with active remediation measures (for example, control of the source of the ground water contamination) or as a follow-up to active remediation measures which have already been implemented.

In addition, since natural attenuation requires extensive site characterization and long term monitoring, the costs of implementing natural attenuation shall be fully evaluated and compared with the costs of active remediation strategies which meet the site cleanup goals in a shorter timeframe.

B. Site Characterization and Monitoring Requirements

A great deal of information concerning the natural attenuation of petroleum contaminants in ground water has been published recently (see reference list). Very little information exists and even less has been published regarding the natural attenuation of agricultural chemicals in ground water. As a result, the MDA suggests that proposals for site characterization and monitoring of passive degradation of agricultural chemicals in ground water be based on the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (EPA, 1998), as well as other appropriate references.

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