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Delivered by Email

Elizabeth J. Callahan
Department of Environmental Protection
Bureau of Waste Site Cleanup
One Winter Street
Boston, MA 02108

Re: Response to Request for Public Comments
On Proposed MCP Amendments

Dear Ms. Callahan:

I would like to take this opportunity to provide you with some comments regarding new regulations the Massachusetts Department of Environmental Protection (MADEP) has proposed for investigating and remediating sites affected by releases of non-aqueous phase liquids (NAPLs).   My interest in this stems from my work at a site in Massachusetts for UniFirst Corporation, on whose behalf these comments are submitted. I regularly provide short course instruction to State environmental agencies, the United States Environmental Protection Agency (USEPA), and professional associations, including the Massachusetts Licensed Site Professional (LSP) Association, on subsurface contaminant behavior, site investigation techniques and subsurface remediation.   My research program at Queen's University is focused on the subsurface behavior and remediation of NAPLs, including both light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs).

It is great to see that MADEP is considering revision of its MCP given that new developments are continuously taking place in the area of contaminant hydrogeology.   I trust that the following comments will be useful. I would be pleased to discuss them further with you and others if you feel that this would be beneficial.

Sincerely yours,

Bernard H. Kueper, Ph.D., P. Eng.
Professor

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Dr. B.H. Kueper comments regarding proposed MCP amendments

Definition of Non-Stable NAPL:

"Non-Stable NAPL means a NAPL that is: (a) migrating along or within a preferred flow path; (b) discharging or periodically discharging to a subsurface structure, utility or surface water body; or (c) spreading or expanding laterally or vertically as a bulk fluid through or from the subsurface strata".

Comment:

The above definition is reasonable and technically justified. Condition (b) is relatively straight forward to assess through visual observation. Assessment of conditions (a) and (c) are not as straight forward to assess.

MADEP also may consider adopting a definition of Stable NAPL, which may be characterized by the following conditions:

(i)   No ongoing releases of NAPL to the subsurface, from a tank, impoundment, piping or other structure;

(ii)   Stable or decreasing aqueous phase concentrations in monitoring wells located in the vicinity of the NAPL source zone;

(iii)   The presence of NAPL at residual saturations, or above residual saturations if it has been demonstrated that the NAPL is not migrating; and

(iv)   An assessment of NAPL mobility based on a conceptual site model, historical data, and screening level calculations if appropriate, that indicates cessation of NAPL movement.

MADEP may want to consider using the new definition of Non-Stable NAPL as the standard for determining when NAPLs constitute "uncontrolled sources." In addition to the Non-Stable NAPL criterion, MADEP has proposed to use the 1% solubility rule-of-thumb, which is one line of evidence for determining whether groundwater may have come into contact with NAPL at some point in time. The 1% rule-of-thumb is not sufficient, by itself, to determine whether NAPL is currently present in the subsurface. This is discussed as a separate point later in this comment document.

Definition of Residual LNAPL Saturation:

"Residual LNAPL Saturation means the range of LNAPL saturations greater than zero up to the LNAPL saturation at which LNAPL capillary pressure equals pore entry pressure. It includes the maximum LNAPL saturation below which LNAPL is discontinuous and immobile under the applied gradient".

Comment:

My recommendation is that this definition should not make use of the terms "capillary pressure" and "pore entry pressure". To be technically correct, use of the term "capillary pressure" would need to distinguish between LNAPL-air capillary pressure and LNAPL-water capillary pressure. Within the capillary fringe and below the watertable, LNAPL is typically non-wetting with respect to water and it would be the LNAPL-water capillary pressure that is of interest. Above the capillary fringe in regions of low moisture content, LNAPL is wetting with respect to air and it would be the LNAPL-air capillary pressure that is of interest. Above the capillary fringe in regions of moderate moisture content the system gets more complicated in that a three-phase system would need to be considered.

Regardless of whether the LNAPL acts as wetting fluid, a non-wetting fluid, or an intermediate wetting fluid (and regardless of whether it occurs above or below the watertable), a practical definition of residual LNAPL saturation would be as follows:

Residual LNAPL saturation refers to the presence of LNAPL in the form of disconnected blobs and ganglia of organic liquid trapped in the pore space. Under typical hydraulic gradients, residual LNAPL saturations correspond to LNAPL saturations less than approximately 25% of pore space.

The above definition does not require LSPs and regulators to understand capillary pressure concepts and does not compel them to measure pore entry pressure. Pore entry pressure is not a standard laboratory measurement and the use of it in a definition of residual LNAPL saturation is complicated by the fact that pore entry pressure is a function of intrinsic permeability, which can vary by orders of magnitude over small distances at most sites. There is no need to refer to pore entry pressure because regardless of the pore entry pressure, residual LNAPL saturations typically correspond to LNAPL saturation of less than approximately 25% of pore space.

To assist in determining what the LNAPL saturation is at a site on the basis of soil sample results, the following simple calculation can be employed (USEPA, 2009):

$$C_D = \frac{S_r \phi \rho_N 10^6}{\rho_b} + C^T$$

where C_D is the soil concentration (mg/kg) corresponding to a specified LNAPL saturation, S_r is the specified maximum residual LNAPL saturation (unitless), ϕ is the porosity (unitless), ρ_N is the LNAPL density (g/cc), ρ_b is the dry soil bulk density (g/cc), and C^T is the theoretical maximum possible amount of chemical (mg/kg) present in the soil sample in the aqueous, vapor, and sorbed phases. The term C^T can be evaluated using a separate equation in USEPA (2009), but I suggest that the term be ignored because (i) it is small compared to the first grouping of terms on the right hand side of the

above equation, and (ii) by omitting the term, a conservative (slightly lower) soil concentration is calculated indicating the presence of LNAPL saturation above residual levels.

As an example, consider soil having a porosity of 0.30 and a dry bulk density of 1.9 g/cc, and an LNAPL having a density of 0.85 g/cc. Setting the maximum residual LNAPL saturation to 0.25 (25% of pore space), the resulting LNAPL soil concentration (as determined by the sum of all detected LNAPL constituents in a sample, including BTEX, F1, F2, F3 and F4 hydrocarbon fractions; or alternatively including GRO, DRO and ORO fractions), is calculated to be 33,600 mg/kg. If the sum of all detected LNAPL constituents in a soil sample is less than 33,600 mg/kg, then it can be concluded that the sample did not contain LNAPL above residual saturation.

Of note is that the above calculation procedure can be applied equally to dense, non-aqueous phase liquids (DNAPL) to determine, on the basis of soil sample results, whether the DNAPL is present below or above the maximum residual saturation.

Releases which require notification within 72 hours:

"(1) a release to the environment indicated by the presence of Non-aqueous Phase Liquid (NAPL) in a groundwater monitoring well, excavation, or subsurface depression at a measured thickness equal to or greater than 1/8 inch".

Comment:

My only comment regarding the above is that it may be difficult, in practice, to measure NAPL accumulations as thin as 1/8 inch. NAPL thickness is typically measured using either recovery in a bailer, or using an interface probe. With respect to LNAPLs, it is of note that the thickness of LNAPL in the well is always greater than the thickness in the formation (this arises from capillary effects in the formation, which are absent in the well). The finer grained the porous medium, the more pronounced the amplification is. I would suggest that the ½ inch criterion was adequate given this fact and the potential impracticability of being able to accurately measure NAPL accumulations as small as 1/8 inch.

Related to the above and as discussed further on in the proposed document, the presence of NAPL (LNAPL or DNAPL) in a well does not necessarily correspond to migration of NAPL (non-stable NAPL) in the formation. The presence of NAPL in a well indicates that a pool of NAPL (possibly a stable, non-migrating pool) has been intersected by the well.

Source elimination or control:

"(5) Source Elimination or Control. A Permanent or Temporary Solution shall not be achieved unless and until each Source of OHM Contamination:

(a) for a Permanent Solution, is eliminated or controlled;

(b) for a Temporary Solution, is eliminated or controlled, to the extent feasible;

(c) Parties conducting response actions shall seek to eliminate each Source of OHM Contamination. In cases where such elimination is not feasible, response actions shall control each Source of OHM Contamination. For the purposes of 310 CMR 40.1003(5), control of each Source of OHM Contamination requires:

1. the absence of unpermitted releases of OHM to the environment;
2. the absence of any Non-Stable NAPL;
3. the removal of any LNAPL to the extent feasible, based upon cost-benefit analysis using current LCSM principles which may include, but are not limited to, Transmissivity, Residual Saturation, and/or decline-curve analysis;
4. the absence of any DNAPL constituent concentration greater than 1 percent of its solubility limit; and
5. demonstration that OHM plumes in any environmental media are not expanding".

Comment:

It is good to see use of the words "to the extent feasible" in the above. However, as proposed, this provision would require that remediation proceed at all sites until concentrations in groundwater are below 1% of solubility, even if it has been demonstrated that the source is stable and the groundwater plume is not expanding. It is well recognized that removal of NAPL (particularly DNAPL) from the subsurface is often technically impracticable. Also of note, but not mentioned above, is that attempts to remove NAPL can worsen the extent of contamination at some sites depending on site-specific geology, NAPL architecture, and the type of remediation technology.

With respect to point (c) 4: "the absence of any DNAPL constituent concentration greater than 1 percent of its solubility limit", it is not clear to me why there would be a "concentration threshold" required to satisfy "control of each Source of OHM Contamination". Control of a source can be achieved without lowering DNAPL constituent concentrations in groundwater to less than 1 percent of solubility. I would suggest that the key requirements constituting "control of a source" include:

1. the absence of ongoing unpermitted releases of OHM to the environment;
2. the absence of any Non-Stable NAPL;
3. the absence of increasing trends in aqueous phase concentrations in the vicinity of the source; and
4. demonstrating that OHM plumes in any environmental media are not expanding.

In connection with my recommendation of removing the requirement of not exceeding 1 percent solubility in groundwater in order to satisfy source control, please consider the following:

1. If constituent concentrations in groundwater exceed 1% solubility, it cannot be concluded with certainty that DNAPL is present in the subsurface. As DNAPL source zones age with time, a significant amount of mass may be sequestered in low permeability materials such as silts, clays, and the bedrock matrix. After natural dissolution of all the DNAPL, constituent concentrations in groundwater exceeding 1 percent effective solubility may be sustained by back-diffusion from these low permeability zones.

2. The "1% rule-of-thumb" dates back to the early 1990s when practitioners recognized that DNAPL could be present in the subsurface even though constituent concentrations in groundwater are well below 100% of solubility. The intent of the 1% rule-of-thumb was simply to alert investigators of the possible presence of DNAPL should constituent concentrations in groundwater exceed this limit. There never was a technical basis for the exact 1% value. It is a very rough guide to simply alert investigators that if 1% solubility is exceeded, it is possible that the groundwater flow path leading to the monitoring well in question may have contacted DNAPL at some point in time, and at some location up-gradient or side-gradient of the monitoring point in question. The distance to the DNAPL cannot be determined on the basis of aqueous phase concentrations, and it is well known that 1% solubility can be exceeded both within the DNAPL source zone and well beyond it (USEPA, 2009). Some investigators in the 1990s made the mistake of assuming that DNAPL is present out to the 1% solubility contour in groundwater, therefore greatly overestimating the size of the DNAPL source zone. This mistake is less commonly made today. If MADEP were to adopt this 1% rule-of-thumb as a proxy both for the presence of DNAPL and Non-Stable DNAPL, it would serve only to perpetuate the error.

References:

USEPA, 2009. Assessment and delineation of DNAPL source zones at hazardous waste sites. United States Environmental Protection Agency, Publication EPA/600/R-09/119.