G R A D I E N T
TRENDS
Risk Science & Application

Spring 2009

DNAPL: Lessons Learned

By Neal C. Grasso, M.S., P.G.

Recognition of the unique challenges of DNAPL contamination is resulting in a gradual, but significant, shift in the approaches to managing this issue.

Over the last 25 years, billions of dollars have been spent studying and attempting to remediate dense non-aqueous phase liquid (DNAPL)-contaminated hazardous waste sites to drinking water standards (*e.g.,* maximum contaminant levels, or MCLs). Yet, according to a recent U.S. EPA-sponsored DNAPL expert panel (U.S. EPA, 2003), no DNAPL site in the U.S. has achieved the MCL goal. Moreover, current remedial goals may not be attainable at most DNAPL sites. Because of the stark impracticability of achieving drinking water standards, a slow but dramatic regulatory shift is occurring in the management and remediation of DNAPL-contaminated sites.

…DNAPLs are environmentally persistent, and they defy conventional remedial technologies, making the attainment of MCLs nearly impossible.

DNAPLs are liquids that are denser than, and relatively insoluble in, water, such as chlorinated solvents, coal tar, creosote, some pesticides, and polychlorinated biphenyls (PCBs). DNAPL sites are often challenging to characterize and remediate for several reasons. First, DNAPL is hard to find in the subsurface because it reaches out in "tentacles" through high-permeability layers. Second, it can persist, acting as an ongoing source of groundwater contamination for decades. For example, DNAPL still remains at "legacy" contamination sites, such as former manufactured gas plants, 50 to 100 years after site closure. Third, unlike light NAPL (LNAPL), which floats on water and moves with groundwater, DNAPL sinks in the subsurface, moving along the surface of less permeable underlying strata (U.S. EPA, 2007).

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I N S I D E

Letter to our Readers

May 2009

Dear Colleague,

In this issue, we address non-aqueous phase liquids (NAPL), both dense and light. Twenty-five years after the first identification of NAPL at hazardous waste sites, there are still fundamental misconceptions about its characterization, transport, and remediation. Today, *Trends* examines past and present scientific understanding on the topic.

Contributors to this issue include Neal C. Grasso, M.S., P.G., a Senior Geologist at Gradient Corporation; Andrew B. Bittner, M.Eng., P.E.; and Kurt D. Herman, M.Eng., P.G., both environmental engineers at Gradient. Joining us with an editorial are Kurt D. Herman and Elizabeth Allen, *Trends* editor, who discuss the potential impact of stimulus money from the 2009 American Reinvestment and Redevelopment Act on the U.S. EPA's major cleanup programs.

We hope that you find this issue of *Trends* informative about recent developments on a subject as important today as it was 25 years ago.

Yours truly,

Teresa S. Bowers, Ph.D.

Trends is a free publication of Gradient Corporation, a national leader in risk assessment and negotiation of risk-based remediation. If you have a colleague who would benefit from this publication, please contact Andrew Bisbas at (617) 395-5000 or email us at *trends@gradientcorp.com.*

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DNAPL: Lessons Learned

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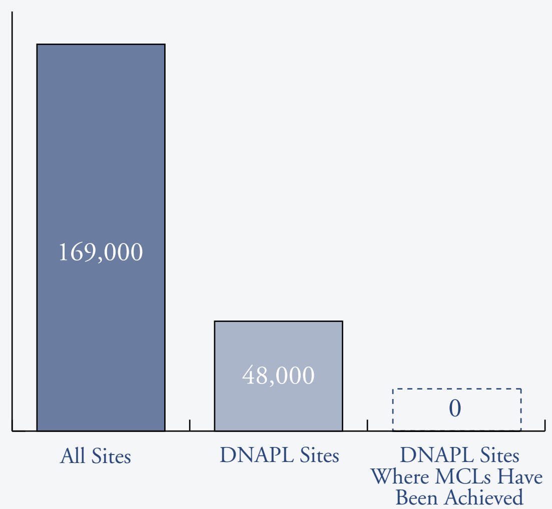
Since the advent of the modern environmental regulatory system in the 1970s, federal and state policy has traditionally required remediation of groundwater to drinking water standards. Throughout the 1970s and '80s, DNAPL site remediation focused on achieving these standards. However, DNAPLs are environmentally persistent, and they defy conventional remedial technologies, making the attainment of MCLs nearly impossible.

DNAPL SITE CLEANUP STATUS



Source: U.S. EPA, 2003, 2004.

The view of setting appropriate remedial goals began to shift in 1993, when the EPA published its guidance on "technical impracticability" (TI). The EPA recognized that "restoration to drinking water quality…may not always be achievable due to the limitations of available remediation technologies," resulting in the inability to remediate groundwater within "a reasonable time frame" (U.S. EPA, 1993). Although the EPA's TI guidance has been used to demonstrate that remediating a given site to MCLs is often not possible and that alternative remedial goals are needed, very few TI waivers have been granted, *e.g.,* only 77 through 2006 (Charsky, 2007).

While the EPA's TI guidance was intended for all types of hazardous waste sites, it also specifically acknowledged DNAPL, suggesting that DNAPL source zone delineation and removal should be performed in order to achieve a "significant reduction of current and future risk." This recognition of the importance of source zone reduction was a significant turning point. Since 2000, federal regulators have focused less on achieving MCL compliance and more on reducing the size of DNAPL source zones. A 2003 EPA panel, convened to provide guidance on DNAPL remediation, concluded that remediating source zones was important, as well as managing the dissolved plume (U.S. EPA, 2003). The panel stressed that attainment of MCLs as the single measure of success did not account for the potential benefits of source zone reduction, including reduced DNAPL mobility, reduced longevity of the plume, reduction in mass flux and discharge, and enhanced efficiency of containment technologies. These benefits far outweigh potentially adverse effects, such as re-mobilization of residual DNAPL, changes in DNAPL distribution, and alteration of the physical and chemical conditions in the aquifer, all of which can be managed by containing the dissolved phase plume (U.S. EPA, 2003).

Although many states have adopted non-degradation policies that stipulate groundwater remediation to drinking water standards, the shift toward source zone reduction is also occurring at a state level. The Texas Commission on Environmental Quality (TCEQ) now allows Plume Management Zones (PMZs), within which less stringent, but equally protective, cleanup objectives are established. If certain conditions are met, such as plume shrinkage or stabilization, site owners can designate a PMZ, even if traditional regulatory standards are not achieved (ESTCP, 2008).

While there has been considerable progress in understanding the complexities of remediating DNAPL, state and federal regulators have only recently focused on the benefits of source zone reduction and the need for alternatives to strict MCL compliance. The regulatory/policy framework is now catching up with the scientific understanding that the short-term goal of source reduction can bring a site closer to the long-term goal of achieving MCLs, and that setting such alternative remedial endpoints may be more realistic and feasible.

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Is Your NAPL Mobile?

By Andrew B. Bittner, M.Eng., P.E.

The extent to which a given NAPL source will be mobilized is determined by several hydrogeologic and compound-specific conditions.

Determining NAPL mobility at hazardous waste sites is one of the most important, yet often misunderstood, considerations in characterizing risks and selecting remedial alternatives. Since the term "NAPL" was coined at Love Canal over 25 years ago, many factors have been identified that influence the potential mobility of subsurface NAPL, including compound-specific characteristics (*e.g.,* viscosity) and soil-specific parameters (*e.g.,* soil particle size and porosity). However, there is still no inexpensive or *in-situ* test to determine whether NAPL is mobile; thus, a weight-of-evidence approach, relying on sound professional judgment, is required.

> ***…a weight-of-evidence approach, using routinely collected data and field observations, can provide a strong indication regarding NAPL mobility.***

Conceptually, understanding the presence and mobility of NAPL requires an evaluation of the environmental concentrations of the NAPL's key chemical constituents. A NAPL is present when the concentration of its constituents in soil exceeds a saturation threshold known as C_{sat}, the concentration at which groundwater and soil vapor are completely saturated. The mere presence of a NAPL does not make it mobile; NAPL is potentially mobile only when its concentration exceeds the residual saturation level, C_{res}, the point at which the gravitational forces upon the NAPL exceed the capillary retention forces. Many studies have been performed to define C_{res} for different NAPLs and soil types (Brost and DeVaull, 2000). By comparing measured concentrations to literature-reported C_{res} values, one can assess whether a NAPL is potentially mobile.

Determining whether NAPL is mobile at a specific site also requires consideration of the hydraulic gradient, the driving force that allows the NAPL to displace water within soil pores. If the driving force is large, NAPL may be mobilized. However, even the most inherently mobile NAPLs (*e.g.,* pooled gasoline in a sandy matrix) will not move if the hydraulic gradient is small. The hydraulic gradient of an LNAPL pool is related to the slope of the water table; for DNAPLs, it is controlled by the slope of a confining layer, such as clay or bedrock.

Since soil properties, NAPL constituent concentrations, and the hydraulic gradient can vary widely and be difficult to quantify, a weight-of-evidence approach, using routinely collected data and field observations, can provide a strong indication regarding NAPL mobility. The following factors should be considered in such an approach:

- *Measured Concentrations:* Concentrations of NAPL constituents in soil must exceed residual saturation levels; the higher the exceedance, the more likely it is that mobile NAPL is present.
- *Field Observations:* Dripping NAPL in soil borings, thick LNAPL accumulation in monitoring wells, and NAPL seeps along embankments can be indicators of mobile NAPL.
- *Release Timing*: Old NAPL releases are less likely to be mobile than recent releases. Migrating NAPL plumes are self-depleting; as a plume migrates, a footprint of residually impacted soils is left behind. Eventually, the NAPL plume becomes depleted and is no longer mobile.

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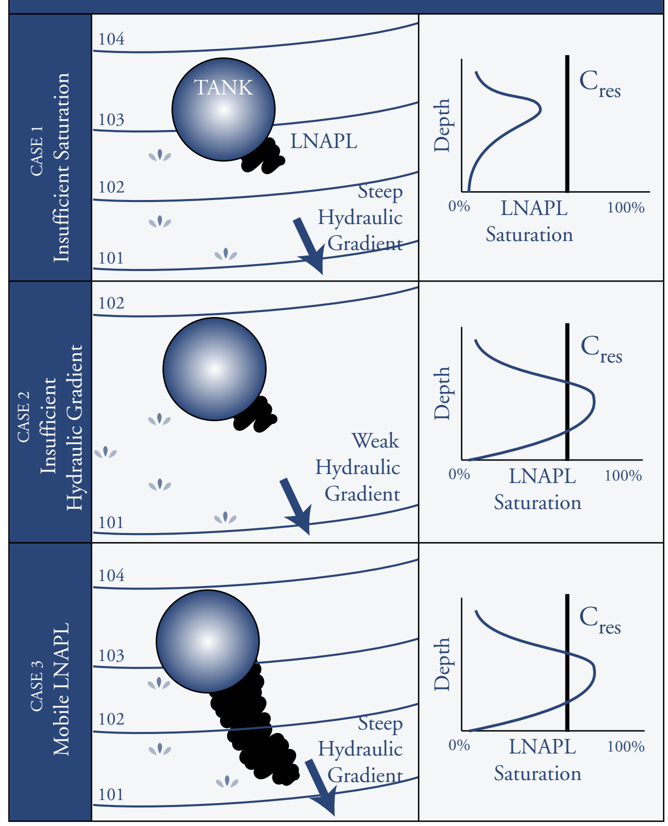
Is LNAPL From a Leaky Tank Mobile?



Both a steep hydraulic gradient **and** a concentration greater than residual saturation (C_{res}) are required for LNAPL migration.
Source: API, 2004.

Sediment DNAPL Challenges

By Kurt D. Herman, M.Eng., P.G.

The dynamic nature of sediment systems compounds the difficulty associated with DNAPL risk characterization and remediation in this medium.

While the technical understanding of sediment DNAPL contamination has evolved considerably since the Industrial Age began, the dynamic nature of sediments continues to pose a unique challenge to effective DNAPL risk characterization and remediation.

In the 1800s, awareness of sediment contamination was based on gross effects on aquatic life (*e.g.*, fish kills), nuisance complaints, and navigational impediment. Environmental remediation had not yet been coined as a "term of art." One early (1868) account of sediment DNAPL (tar) remediation is noteworthy because of its financial motivation (to recover tar for sale) and quick remediation time:

> ***…despite our increased understanding, sediment DNAPL remediation is often a complex, costly, and lengthy process.***

> A few weeks since, Mr. A. Lamprey…discovered a deposit of coal tar lying at a depth of several feet in the bed of a small creek…After prospecting a little, a long wooden pump and suitable staging apparatus were rigged, and, on Friday and Saturday last, upwards of four thousand gallons were raised and barrelled [for sale]. (*Manchester Union Democrat,* 1868)

In recent years, a more detailed and comprehensive understanding of trace chemical effects on aquatic ecosystems and humans has been developed. Laws and regulations provide additional criteria for implementing remediation, *e.g.*, natural resource recovery to "fishable/swimmable" conditions under the 1972 Clean Water Act. Tools such as sediment transport and food web models allow evaluation of contaminant risks to organisms throughout the ecosystem, accounting for contaminant bioavailability, environmental partitioning, and bioaccumulation. Improvements in sampling and analytical techniques (*e.g.,* SEM/AVS, diffusion samplers, bioassays) allow more accurate predictions of chemical effects. However, despite our increased understanding, sediment DNAPL remediation is often a complex, costly, and lengthy process.

One key challenge is posed by the fundamentally dynamic nature of sediments. Both natural and anthropogenic forces, such as waves, currents, and boat propeller wash, act upon and shift contaminated sediments over time, affecting exposure potential. Minimizing total risk requires evaluation of multiple effects that occur over a wide spectrum of time scales, including:

- periodic – *e.g.*, salmon spawning, annual snow pack melt, tidal effects;
- occasional, chaotic – *e.g.*, 100-year flood;
- occasional, planned – *e.g.*, navigational dredging;
- constant – *e.g.*, methane generation.

There is a tension between balancing short- and long-term risks when selecting a sediment remedy. A risk *vs.* depth trade-off exists, particularly with DNAPL, which sinks downward when mobile. Short-term risks from shallow sediment exposures are balanced against long-term potential exposures to deeper, sequestered sediment DNAPL. For example, dredging for remediation may actually cause more short-term risks (*e.g.*, stirring up sediment, creating preferential pathways for DNAPL migration), but may reduce total long-term risk. Consequently, there is often a preference to not actively dredge the areas of contamination because of this short-term risk potential.

Dynamic effects must be considered in remedy design to avoid sediment recontamination and costly "re-remediation." For example, neglecting to account for methane generation when designing a sediment cap remedy can lead to a blown cap. Failure to adequately contain an upland DNAPL source can lead to recontamination of clean sediments from ongoing DNAPL migration. Thus, while there are several techniques – capping, dredging, stabilization – for actively remediating DNAPL-contaminated sediments, the devil is in the details for successful remedy implementation.

The author can be reached at kherman@gradientcorp.com.

For Additional Information:

U.S. EPA. 2005. Contaminated Sediment Remediation Guidance for Hazardous Wastes Sites. Office of Solid Waste and Emergency Response. 236p., December.

What's New at Gradient

Recent Awards and Appointments

Teresa S. Bowers has been named a member of the NIEHS Superfund Basic Research Program External Advisory Panel.

Julie Goodman has been elected to the Nominating Committee of the Society of Toxicology.

Chiharu Mori, **Sagar Thakali,** Ann Tarrant, **Manu Sharma, Tim Verslycke,** and Harry Yekel won the Perry J. Gehring Best Abstract Award in the 2009 Society of Toxicology (SOT) Risk Assessment Specialty Section for their abstract entitled "Translating *In Vitro* Estrogenic Assay Results to Ecological Risk Assessment."

Cathy Petito Boyce, Ari Schoen Lewis, Sonja N. Sax, M. Eldan, S.M. Cohen, and **Barbara D. Beck** won the *Human and Ecological Risk Assessment*'s 2008 Best Paper of the Year for their article entitled "Probabilistic analysis of human health risks associated with background concentrations of inorganic arsenic: Use of a margin of exposure approach." *Hum. Ecol. Risk Assess.* 14(6):1159-1201.

Recent Publications

Bowers, T.S. 2009. Improbable blood lead concentration - IQ relationships. *J. Pediatr.* 154:465.

Goodman, J.E., L.A. Beyer, and **B.D. Beck.** 2009. Comment on "Evaluation of evidence for infection as the mode of action for induction of rat lymphoma" by Caldwell *et al.* *Environ. Mol. Mutagen.* 50(1):4-5.

Langseth, D.E. 2009. Remedial cost allocation cash out valuation under uncertainty. *Environ. Claims J.* 21(1):62-72.

Hesterberg, T.W., **C.M. Long**, W.B. Bunn, **S.N. Sax**, C.A. Lapin, and **P.A. Valberg**. 2009. Non-cancer health effects of diesel exhaust: A critical assessment of recent human and animal toxicological literature. *Crit. Rev. Toxicol.* 39(3):195-227.

Rhomberg, L.R. 2009. Commentary: Risk assessment in the 21st century: Changes wrought by changing science. *Risk Anal.* 29(4):488-489.

Soin, T., **T. Verslycke**, C. Janssen, and G. Smagghe. 2009. Ecdysteroids and their importance in endocrine disruption research. In *Ecdysone: Structures and Functions.* (Ed.: Smagghe, G.), Springer, Netherlands, p539-549.

Upcoming Presentations

Kansas City, KS. May 17-21, 2009. David Langseth. American Society of Civil Engineers World Environmental & Water Resources Conference: "Spreadsheet Method for Solute Flux Rate Uncertainty Evaluation at a Monitored Boundary."

Amherst, MA. June 9-11, 2009. Mark Nascarella, Barbara Beck, and Edward Calabrese. International Conference on the Environmental Implications and Applications of Nanotechnology: "Quantifying Hormetic (Biphasic) Dose-Responses in the Assessment of Nanoparticle Toxicology."

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Is Your NAPL Mobile?

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- *Soil Type*: NAPL is more likely to be mobile in coarse-grained deposits (*e.g.,* gravel) than in fine-grained deposits (*e.g.,* clay).
- *NAPL Type*: Highly viscous NAPLs migrate less readily than NAPLs with lower viscosity.
- *Release Type*: A subsurface release is more likely to result in a mobile NAPL plume than a surface release because it has a large driving head concentrated over a small area. Similarly, large volume releases are more likely to cause NAPL mobility.
- *Groundwater Fluctuations*: Vertical groundwater fluctuations immobilize LNAPL because they create a large zone of residually saturated soils (*i.e.,* smear zone).

All of these criteria provide an indication of whether NAPL is likely to be mobile. Furthermore, at most sites, many of these data are commonly available. While no single criterion on this list can definitively be used to determine NAPL mobility, together these criteria can cost-effectively be used to assess the likelihood that NAPL is mobile.

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American Petroleum Institute (API). 2004. API Interactive NAPL Guide. Version 2.0. August.

Brost, E.J. and G.E. DeVaull. 2000. Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil. API Soil & Groundwater Research Bulletin No. 9. Accessed on October 30, 2006 at http://www.api.org/ehs/groundwater/upload/09_Bull.pdf, 9p.

Editorial: Will $900 Million Make the Environment Any Cleaner?

By Kurt D. Herman, M.Eng., P.G. and Elizabeth Allen

President Obama's infusion of cash into the U.S. EPA is aimed to provide new jobs, new site cleanups, and a faster pace for existing site cleanups. But will it work?

On February 17, 2009, President Obama signed the American Recovery and Reinvestment Act (ARRA) into law.

> ***Will the equivalent of $1.2 million per day over two years result in a cleaner, safer environment?***

This legislation provided a two-year $900 million "shot in the arm" capital infusion to the U.S. EPA for several of its main hazardous waste site cleanup programs. Two-thirds ($600 million) was allotted for the EPA's Superfund program, $200 million to the EPA's underground storage tank (UST) program, and the remaining $100 million went to its Brownfields program. Will the equivalent of $1.2 million per day over two years result in a cleaner, safer environment?

There is general agreement that many scientific and environmental agencies were under-funded during the Bush administration. With the trillions of dollars being bandied around the financial and auto-making industries, well-deserved funding for scientific research and environmental protection is a welcome and refreshing change. However, such a large amount of money being introduced in such a short timeframe poses unique challenges for the EPA in ensuring that the money is used effectively. Is the EPA prepared for such an influx of cash?

The EPA is currently deciding how to invest the Superfund money, and expects that its priorities will be job creation, initiating new cleanups, and speeding up existing cleanups. The main challenge is the time frame, since ARRA specifies that these funds must be used within a brief span of just two years. Two months of the two years have already expired, and Superfund cleanups often take decades, not months.

Accelerating UST site cleanup may also prove to be a challenge. The EPA has normally used a (lengthy) competition to determine which states will receive UST cleanup grants. As of March (the latest date for which information was available), the EPA was still in talks with state officials to determine how stimulus money could be used to remediate leaking USTs. Again, the clock is ticking.

Brownfields money will be placed in a nationwide competitive grant program. Supporters claim that these grants could stimulate work at existing sites and prompt towns and states to prioritize sites for cleanup when the economy improves. However, a lackluster property market makes it tough to unload even uncontaminated properties right now, let alone contaminated real estate.

Although this one (relatively) small piece of President Obama's "New Deal"-style legislation has promise for large short-term impacts on hazardous waste site cleanup and redevelopment, the impact of this funding on cleaning up the environment remains to be seen. Priorities and metrics for achieving success should be clearly defined and negotiated by the EPA, since time is quickly passing.

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By The Way...

The former president of Massachusetts' largest asbestos removal training school has the dubious distinction of being the first woman listed on the EPA's "environmental fugitive" web site.

Source: The Boston Globe, April 2, 2009 (http://www.boston.com/news/world/europe/ articles/2009/04/02/mass_woman_on_environmental_fugitive_web_site/).

In the next issue:

Overview: Gene-Environment Interactions

Genetic Susceptibility and Risk Assessment

Communicating Genetic Susceptibility

Guest Editorial: Genetics and the Law

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