

Poster Presentation at the International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterrey, May 22-25, 2006.

Optimization of Long Term Monitoring at Wood Treating Sites

Mark King (king@gwinsight.com; Groundwater Insight Inc.,
Halifax, Nova Scotia, CANADA)
Robert Anderson (BBL, Pittsburgh, Pennsylvania)
Kurt Paschl, Mike Bollinger, Mitch Brouman, Mike Helbling
(Beazer East Inc., Pittsburgh, Pennsylvania)
Jennifer Abrahams (Geotrans, Sacramento, California)
Rita Bauer (RETEC, Atlanta, Georgia)

ABSTRACT: This paper describes a Protocol to optimize long term groundwater monitoring at wood treating sites. Releases of creosote and other liquids are often sources of groundwater contamination at these sites and, regardless of the remedial approach used to address the dissolved phase plumes, there is almost always a requirement for long term monitoring. The Protocol described herein is based on the defining characteristics of wood treating operations including age, type of contamination, treatment methods and waste handling. The Protocol emphasizes monitoring to support MNA remedies, because experience has shown that MNA is an integral part of the dissolved phase remedy at most wood treating sites. The Protocol also considers the site-specific requirements of any active remedy components, and any outstanding aspects of the Site Conceptual Model that are not addressed by the presumptive specifications. The objectives of the Protocol are: 1) to ensure the efficient collection of data that directly supports ongoing evaluation of remedy effectiveness, and 2) to minimize the collection of extraneous data.

INTRODUCTION

A Protocol for Long Term Monitoring Optimization (LTMO) has been developed by Beazer, a company with environmental legacy interests at wood treating and coal tar sites across the United States. The Protocol is consistent with an industry-wide trend toward risk-based remedies where exposure potential is negligible but groundwater contamination will persist over the long term. The goal of the Protocol is to focus data collection on site-specific remedy performance objectives, and it emphasizes the development of a well understood Site Conceptual Model. The Protocol considers recent USEPA documents that address LTMO (e.g., USEPA 2004 and USEPA/US Army Corp of Engineers, 2005).

The Beazer LTMO Protocol is based on the defining characteristics of wood treating sites. It supports long term monitoring objectives for presumptive Beazer remedies on these sites, namely: source control (long term containment and DNAPL recovery), and Monitored Natural Attenuation (MNA). The Protocol provides a set of presumptive monitoring program specifications that are evaluated on a site-specific basis, and modified based on the judgment of Beazer,

the site consultant, and the site regulator(s). This group should include geologists and/or engineers with experience in assessing groundwater plumes on wood treating sites.

Regulatory Considerations. Beazer notes that regulatory monitoring requirements may vary greatly between sites, for a variety of reasons including the following:

- Varying interpretations by individual regulators regarding EPA's stated desire to return groundwater to its most "beneficial reuse";
- Poorly defined performance objectives and points of compliance;
- Inadequate development and/or understanding of the Site Conceptual Model;
- Presumptive regulatory resistance to monitoring program reductions;
- Varying regulatory emphasis on mass removal; and
- Varying regulatory interpretation of "reasonable timeframe" for MNA remedies.

The Beazer LTMO Protocol provides a consistent basis for addressing these sources of variability.

WOOD TREATING SITES – TYPICAL CHARACTERISTICS

Preservatives. The wood treating industry has operated in the US for more than 100 years, producing treated products such as railway ties, utility poles and fence posts (USEPA, 1995). Three main types of preservatives have been used over the years: creosote, pentachlorophenol and metals salts.

Creosote, the oldest of these, dates back to the earliest wood treatment operations and is still widely used today. It is a Dense Nonaqueous Phase Liquid (DNAPL) and is a mid-range distillate of coal tar consisting of more than 200 organic compounds, with the following typical composition: 85% Polycyclic Aromatic Hydrocarbons (PAHs), 10% phenolic compounds and 5% oxygen-, sulfur-, and nitrogen-heteroaromatic compounds (Mueller et al., 1989). The pure compound solubility of creosote compounds varies over several orders of magnitude.

Pentachlorophenol usage in wood treatment started around 1950. It is applied as a 5-7% solution within a petroleum oil solvent. Commercial grade pentachlorophenol contains 10% to 15% impurities, including tetra-chlorophenol, more highly chlorinated phenols (6% to 14%), and up to 0.1% polychlorinated dibenzo-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs). The dioxin of greatest toxicity and regulatory concern (2,3,7,8 TCDD) has not been detected in commercial grade pentachlorophenol produced in the US (USEPA, 1997).

The use of metal salts in wood preservation began in the 1970's and by the late 1990's this type of preservative was used for the majority of treated wood products. The most common formulation is chromate copper arsenate, or CCA (USEPA, 1997), which is typically applied in an aqueous solution.

Release Locations. Primary historical release locations on wood treating sites include: 1) former surface impoundments used for wastewater treatment and sludge storage (USEPA, 1997), 2) areas around the storage and treatment tanks and, 3) the drip tracks where wood is temporarily placed after preservative application. Releases are usually decades old, and related to outdated management practices that have since been mitigated. For example, surface impoundments have not been used on wood treating sites since 1988, and drip tracks are currently regulated under 40 CFR Part 264 Subpart S of the Resource Conservation and Recovery Act (RCRA) regulations.

Dominant Groundwater Constituents. The most common site-related constituents in groundwater at Beazer wood treating sites originate from creosote because: 1) creosote has been used longer than other common preservatives, 2) pollution control measures and environmental awareness were minimal in the early era of creosote usage, 3) creosote is a DNAPL and may migrate below the water table, and 4) the solubility of creosote constituents is large enough to allow transfer of environmentally significant dissolved phase mass, but small enough to allow long term source zone persistence.

The composition of groundwater affected by creosote is dominated by compounds of moderate molecular weight and solubility. The most common compound is naphthalene, followed by acenaphthene, methyl-naphthalene and phenanthrene. These mid-range compounds are more common than some of the high solubility creosote compounds (e.g., phenol) because most creosote sources have been in the subsurface for a prolonged period, allowing time for depletion of the latter.

At Beazer sites where pentachlorophenol has been used, it may be detected in groundwater but is typically less extensive than naphthalene and the other mid-range PAHs. This is likely due to the later introduction of pentachlorophenol and application within a petroleum oil carrier which limits the sources zones to near the water table. Other chlorinated phenols may also occur in groundwater, due to their presence as impurities in commercial formulations, but they tend to be much less extensive than pentachlorophenol. PCDDs/PCDFs are typically negligible in groundwater, due to their low solubility. If they are detected in groundwater at wood treating sites, it is often due to the introduction of formation solids (or NAPL) during sampling.

The use of CCA at Beazer sites is occasionally evident as elevated levels of metals in the vicinity of the source zones. The extent of the dissolved phase metal constituents is typically much less than naphthalene and other moderately soluble creosote constituents. Dissolved phase metals occur less frequently at wood treating sites because of the manner in which CCA is applied and the later introduction of this preservative.

The dissolved contaminant trends noted on Beazer sites are consistent with those described by Rosenfeld and Plumb (1991) in a study of five wood treatment facilities.

Conceptual Model for Plume Migration at Wood Treating Sites. The most mobile organic contaminants in groundwater at wood treating sites are considered to be biodegradable to some degree, as indicated by a variety of laboratory and field studies (e.g., Mueller, 1989; King and Barker, 2001). The potential effect of biodegradation on plume stabilization was evaluated as part of Protocol development. It is suggested that dissolved phase plumes at typical wood treating sites are stable, due to the combination of plume biodegradation and advanced plume age. Consequently, Monitored Natural Attenuation is almost always an integral component of the site remedy.

LTMO PROTOCOL SPECIFICATIONS

Overview. The Protocol provides a set of presumptive specifications that are based on the defining characteristics of wood treating sites. It is presumed that MNA is an integral part of the dissolved phase remedy, while the monitoring requirements of other remedy components are incorporated on a site-specific basis. Similarly, the Protocol presumes a relatively simple Site Conceptual Model, with more complicated aspects incorporated as required, on a site-specific basis. Data collection activities are designed on a two-tier system, where Tier 1 locations and analytical parameters are monitored more frequently than Tier 2. Any program optimized through the Protocol must be capable of the following, as stated by EPA (2004):

- Detecting changes in environmental conditions that may reduce remedy effectiveness;
- Identifying any potentially toxic and/or mobile transformation products;
- Verifying that the plume is not expanding above levels of concern;
- Assessing effectiveness of the cleanup or treatment system;
- Evaluating whether alternative technologies or approaches could improve the ability of a remedy to achieve cleanup goals;
- Verifying the absence of unacceptable exposures;
- Detecting new contaminant releases that could impact remedy effectiveness;
- Demonstrating the effectiveness of any institutional controls; and
- Verifying attainment of short-term, intermediate, or final goals.

Preliminary LTMO Tasks. These include the following:

- Revisit, or establish, cleanup objectives and appropriate points of compliance;
- Develop the timeframe for achieving objectives; and
- Establish the management decisions to be made with the monitoring data.

Monitoring Frequency. As previously discussed, it is expected that if changes occur to dissolved phase distributions at wood treating sites, they will occur slowly, due to the advanced age of the plumes. It is also expected that source zone depletion will be relatively slow. After an appropriate period of

confirmation, monitoring frequency should reflect these expected slow rates of change.

As a starting point in frequency optimization, existing site data should be evaluated for trends relevant to the remediation and monitoring objectives. Where the existing data support less than two years of trend evaluation, quarterly monitoring frequency would be adopted for initial monitoring of both Tier 1 and Tier 2 locations and parameters. The quarterly frequency is intended to generate sufficient seasonal results to enable the use of trend statistics, such as the Mann-Kendall test. Subsequent decreases in frequency would be contingent upon ongoing compliance with performance goals.

For Tier 1 components:

- After four quarterly events, monitoring frequency would decrease according to the following progression: semi-annual for two events, every two years for two events, every five years for two events and every 10 years thereafter.
- Monitoring would continue at a minimum frequency of every 10 years, until site-specific remedial objectives are met.

For Tier 2 components:

- After four quarterly events, monitoring frequency would decrease according to the following progression: every two years for two events, every five years for two events, and every 10 years thereafter.
- Monitoring would be discontinued after two monitoring events at the 10 year frequency.

For MNA and/or engineered containment remedies, it is expected that Tier 1 monitoring would continue as long as the source remains in place. Given the expected slow rate of change in plume and source status at wood treating sites, it is reasonable to expect that the monitoring program could last for decades. The requirement for modifications to the presumptive monitoring frequencies would be based on the professional judgment of Beazer, the site consultant and the site regulator(s).

The presumptive frequency starts with a widely accepted quarterly interval and then the duration between sampling events is extended as the data record accumulates. Quantitative statistical and geostatistical methods were evaluated for setting frequencies, but were determined to be impractical for broad presumptive application. In practice, site-specific frequencies would be evaluated and assigned based on professional judgment.

Analytical Parameters. Low molecular weight PAHs are considered Tier 1 presumptive analytical parameters because of their relative potential for migration in groundwater. Any of these constituents that were not detected in groundwater in excess of regulatory criteria during site characterization and design activities would be excluded from the list. Pentachlorophenol and any wood preservative metals (e.g., originating from CCA) would be included as Tier 1 parameters if they were identified as site-specific issues during site investigations or early

monitoring. Field parameters are also assigned a Tier 1 priority because they are required to support sampling protocols and they provide data that may contribute indirectly to monitoring of site constituents.

Several common electron acceptors and metabolic by-products are considered Tier 2 presumptive parameters because they provide ongoing data for performance monitoring of natural attenuation and indirect information on plume status. For example, movement in the sulfate-reducing zone (either advancing or receding) within a plume may indicate similar movement in the distribution of dissolved phase organic contaminants. These parameters would initially include all major electron acceptors and metabolic by-products, including dissolved oxygen (obtained as a field parameter), nitrate, sulfate, manganese, iron and methane. After four monitoring events this list would be modified to include only those parameters that are identified as having site-specific significance.

Microbial parameters are excluded from the presumptive list because their distribution tends to be highly variable and insensitive to the types of small changes that are of interest for long term plume monitoring. Furthermore, a unique relationship between microbial activity and adequate natural attenuation cannot be defined. Microbial activity will vary throughout the plume, depending on a range of factors such as electron acceptor distribution and proximity to the source zone. Microbial parameters would be considered for inclusion at sites where the remedy includes a component of engineered bioremediation.

Monitoring Locations. The selection of monitoring locations must support the evaluation of remedy progress. At most Beazer sites, the groundwater cleanup objective is to contain the dissolved phase plume by natural attenuation and/or engineered corrective actions. This scenario has different monitoring requirements than one where the goal is return groundwater to its maximum beneficial reuse. The presumptive monitor well locations and priorities for containment-type remedies are as follows:

- *Upgradient of the source* – The purpose of this location is to define groundwater chemistry before the source is contacted. The Protocol presumes that a single location will be sufficient for this purpose. Site-specific modifications would be considered where there is significant vertical, horizontal or temporal variability in the chemistry of groundwater approaching the source zone. This location is assigned a Tier 2 priority, due to the expected absence of long term changes.
- *Within the plume source zone* – The purpose of this location is to enable evaluation of the gradual decrease in source strength. The Protocol presumes a single location will be sufficient for this purpose, and it should target the approximate location of maximum dissolved phase concentrations, while avoiding monitor wells containing NAPL. Site-specific modifications would be considered if multiple source zones exist. This location is assigned a Tier 2 priority, due to the expected slow rate of change in source composition.
- *Downgradient, within the plume* – The purpose of this location is to enable evaluation of plume status (i.e., advancing, stable or receding) within the main

body of the plume. The target zone is where concentrations are one to two orders of magnitude less than the source zone concentration. The Protocol presumes that the plume is well characterized and relatively uniform and, therefore, that one location near the central axis of the plume is adequate. Site-specific modifications would be considered where the plume is irregularly distributed or occurs at significant concentrations in more than one hydrostratigraphic unit. This location is assigned a Tier 1 priority, because it provides direct evidence of plume status.

- *Downgradient, at or just beyond the plume front* – The purpose of this location is to enable evaluation of plume status at the front of the plume and to evaluate whether cleanup objectives are being achieved at the Point of Compliance. The location would target the downgradient zone where concentrations of the most extensive contaminant (likely naphthalene) are near or below the regulatory standard. The Protocol presumes that the plume is well characterized and relatively uniform and therefore that one location along the projected central axis of the plume is adequate. Site-specific modifications would be considered where the plume is irregularly distributed or occurs at significant concentrations in more than one hydrostratigraphic unit. This location is assigned a Tier 1 priority because it provides direct evidence of plume status and is the most important location type, on a technical and regulatory basis.
- *Cross-gradient from the plume* – The purpose of this location is to provide ongoing definition of lateral plume extent and to evaluate whether the other monitoring locations are appropriately placed. The Protocol presumes that this type of location will not be required, due to the mature nature of plumes on wood treating sites. Site-specific modifications would be considered if site corrective actions alter the natural direction of plume development, for example, where groundwater pumping and re-injection is conducted to enhance DNAPL recovery. If required, this location would be assigned a Tier 1 priority because, by definition, there would be increased potential for short term changes in plume distribution.
- *Groundwater level and NAPL thickness* – Groundwater level monitoring should be conducted at sufficient locations to provide ongoing groundwater flow characterization throughout the plume and source zones. Monitoring of NAPL thickness should be conducted in all wells in the vicinity of the NAPL source zone. These locations are considered Tier 1 components.

Modifications to the presumptive monitoring locations would be based on the professional judgment of Beazer, the site consultant and the site regulator(s).

Data Evaluation and Management Decisions. Monitoring data should be evaluated on an ongoing basis, to support management decisions regarding the continued effectiveness of the remedy. Methods will include a combination of the following:

- Graphical presentation of time series data for each well;

- Statistical analysis of time series data, using Mann-Kendall or other methods;
- Potentiometric surface maps;
- Maps showing changes in DNAPL presence and thickness;
- Maps showing changes in geochemical indicators;
- Maps and cross-sections showing changes in contaminant concentrations;
- Assessment of concentrations approaching asymptotic conditions; and
- Assessment of remedy effectiveness.

These interpretations would be used for ongoing refinement of the Site Conceptual Model and, if required, recommendations for further program modifications would be made to the regulatory agency.

SUMMARY

An LTMO Protocol has been developed, based on the defining characteristics of wood treating sites. The Protocol provides a set of presumptive specifications that would be evaluated and modified, based on professional judgment. The objectives of the Protocol are: 1) to ensure the efficient collection of data that directly supports ongoing evaluation of remedy effectiveness on wood treating sites, and 2) to minimize the collection of extraneous data.

ACKNOWLEDGMENTS

The authors would like to thank the group that peer reviewed the full Protocol document, from which this paper has been excerpted: Mike Basel, Murray Einarson, Jim Erickson, Mike Gefell, Ian Hutchinson, Alison Jones, Mike Kavanaugh, Dave Lipson, Jim Mercer, Neale Misquitta and Jim Mueller.

REFERENCES

- King, M.W.G., and J. Barker. 1999. "Migration and natural fate of a coal tar creosote plume 1. Overview and plume development." *Journal of Contaminant Hydrology*, 39:249-279.
- Mueller, J.G., P.J. Chapman, and P.H. Pritchard. 1989. "Creosote-contaminated sites—their potential for bioremediation." *Environmental Science and Technology*, 23:1197–1201.
- Rosenfeld, J.K., and R.H. Plumb, Jr. 1991. "Ground Water Contamination at Wood Treating Facilities." *Ground Water Monitoring and Remediation*, Winter:133-140.
- United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. December, 1995. *Presumptive Remedies for Soils, Sediments, and Sludges at Wood Treater Sites*. EPA/540/R-95/128.
- United States Environmental Protection Agency, Office of Research and Development. October, 1997. *Treatment Technology Performance and Cost Data for Remediation of Wood Preserving Sites*. EPA625/R-97/009.
- United States Environmental Protection Agency, Office of Solid Waste and Emergency Response. January 2004. *Guidance for monitoring at hazardous*

waste sites: framework for monitoring plan development and implementation.
Directive No. 9355.4-28.

United States Environmental Protection Agency and US Army Corps of Engineers. May 2005. *Road Map for Long Term Monitoring Optimization.*
EPA42-R-05-003.