

Approach for Pump-and-Treat Performance Assessment at the Hanford Site

September 2016

M.J. Truex
C.D. Johnson

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <<http://www.ntis.gov/about/form.aspx>>
Online ordering: <http://www.ntis.gov>



This document was printed on recycled paper.

(8/2010)

Approach for Pump-and-Treat Performance Assessment at the Hanford Site

M.J. Truex
C.D. Johnson

September 2016

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The U.S. Department of Energy Hanford Site is applying pump-and-treat (P&T) remediation to control and diminish contaminant plumes. In the future, a remedial decision will need to be made to transition from P&T to remediation closure or to another approach to complete remediation. The recent document *Performance Assessment for Pump-and-Treat Closure or Transition*¹ provides a structured approach to assess P&T systems and support remedy decisions.

The purpose of this document is to identify how elements of the *Performance Assessment for Pump-and-Treat Closure or Transition* document can be applied to address performance assessment needs for Hanford Site P&T systems. The report is intended to be a resource for the site to develop a performance assessment approach and exit strategy for each P&T system. This report focuses on P&T assessment for transition to natural attenuation because 1) the 200-ZP-1 and 200-UP-1 operable unit P&T systems are part of remedies where transition to natural attenuation is identified in the Record of Decision and 2) the 100 Area systems target chromium plumes that are being diminished and are receding from the river such that natural attenuation may become a suitable polishing step to meet both aquifer concentration objectives and the more stringent river-protection standards. For decisions associated with Hanford P&T systems, performance assessment is expected to focus on several types of information. Because evaluation of plume attenuation will be important for shutdown decisions, examining historical plume data (and data from areas where monitored natural attenuation was selected as the remedy) could provide useful information to demonstrate why attenuation may be a suitable polishing step. The current monitoring and evaluation of the P&T system provide good baseline information for the assessment through quantification of mass removal trends and documentation of optimization decisions. The availability of numerical models and results (such as capture analyses) can facilitate other recommended assessment components. For instance, contaminant concentration trends at individual wells or for plumes can be interpreted in the context of capture analysis information to compare observed contaminant concentration responses to expected responses. Consideration of a zone where attenuation can be allowed to occur after a P&T is shut down will be important as part of managing natural attenuation as it reduces contamination to meet the remedial action objectives. With an appropriate attenuation zone established, incorporating attenuation capacity information into quantitative evaluation of fate and transport (e.g., using the models or other data evaluation techniques described herein) is expected to be a primary analysis supporting determination of whether P&T shutdown is acceptable. Importantly, the site should consider implementing rebound tests to provide information for the fate and transport analysis and as way to verify (or not) the expected plume response to shutdown of a P&T system.

Broadly, recommendations from this report include the following:

- Prepare an exit strategy for candidate P&T systems using this report and the *Performance Assessment for Pump-and-Treat Closure or Transition* document as resources, and incorporate this exit strategy into regulatory documents, as appropriate. This exit strategy could serve the same type of function as documents used to support the recent shutdown of the 200-PW-1 operable unit Soil Vapor Extraction system.^{2,3}
- Align the plume and P&T system monitoring approach with the performance assessment needs identified in the exit strategy. The decision about whether a P&T system can be shut down and

¹ Truex, MJ, CD Johnson DJ Becker, MH Lee, and MJ Nimmons. 2015. *Performance Assessment for Pump-and-Treat Closure or Transition*. PNNL-24696, Pacific Northwest National Laboratory, Richland, Washington.

² DOE. 2014. *Path Forward for Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*. DOE/RL-2014-18, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

³ DOE. 2016. *Endpoint Evaluation for the 200-PW-1 Operable Unit Soil Vapor Extraction System Operations*. DOE/RL-2014-48, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

transitioned to natural attenuation for final polishing to meet the remedial action objectives includes significant use of data collected during the P&T operational period.

- Plan and implement elements such as attenuation capacity evaluations (e.g., study of historical plume conditions), rebound testing, and persistent source assessments based on the needs identified in the exit strategy. These elements, along with P&T operational data, monitoring data, and modeling assessments, collectively are used to quantify plume dynamics and support predictions of plume behavior that are needed as part of the decision process.

Acknowledgments

This document was prepared by the Deep Vadose Zone – Applied Field Research Initiative at Pacific Northwest National Laboratory. Funding for this work was provided by the U.S. Department of Energy (DOE) Richland Operations Office. The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the DOE under Contract DE-AC05-76RL01830.

Acronyms and Abbreviations

CMD	contaminant mass discharge
COV	coefficient of variation
CSM	conceptual site model
DOE	U.S. Department of Energy
DVZ-AFRI	Deep Vadose Zone – Applied Field Research Initiative
EPA	U.S. Environmental Protection Agency
MCL	maximum contaminant level
MNA	monitored natural attenuation
P&T	pump-and-treat
PNNL	Pacific Northwest National Laboratory
QA	Quality Assurance
RAO	remedial action objective
ROD	Record of Decision

Contents

Summary	iii
Acknowledgments.....	v
Acronyms and Abbreviations	vii
1.0 Introduction	1
2.0 Resources for P&T Performance Assessment	3
2.1 Synopsis of P&T Performance Assessment Guidance.....	3
2.2 Synopsis of Plume Data Evaluation Approaches	6
2.2.1 Plume Analysis.....	7
2.2.2 Single-Well Attenuation Rate Analysis	16
2.2.3 Flow-Path Attenuation Rate Analysis	16
3.0 Performance Assessment Elements	21
3.1 Plume Dynamics	21
3.1.1 Operations Information	21
3.1.2 Additional Recommended Information and Analyses	22
3.2 Attenuation Capacity.....	27
3.3 Predicting Plume Behavior.....	29
4.0 Exit Strategy Development.....	31
4.1 Conceptual Site Model.....	31
4.2 Decision Logic for Performance Assessment	32
4.3 Documentation of Information.....	33
5.0 Quality Assurance.....	35
6.0 Conclusions and Recommendations	37
7.0 References	39

Figures

- Figure 1. Conceptual depiction (after Truex et al. 2015a) of the source flux zone being controlled by P&T and a downgradient attenuation zone, whose extent must be determined by the site decision makers. To support a decision to transition to a monitored natural attenuation remedy, the CMD from the source zone (or potentially an upgradient plume) must not be greater than the attenuation capacity in the attenuation zone under natural-gradient conditions. In this situation, the plume would stay within the limits defined by the site decision makers..... 4
- Figure 2. Primary elements of the decision logic used for the P&T assessment (after Truex et al. 2015a). The full decision logic (Figure 10 in Truex et al. 2015a) includes additional elements of the decision process, which are omitted here for brevity. 6
- Figure 3. Depiction of the types of quantities calculated from plume data, including plume maps, rate of change in overall plume concentration/mass, rate of change in point concentrations, and rate of change in concentration over distance along a flow path. 7
- Figure 4. Arbitrary example to illustrate the Delaunay triangulation (a) of the well locations and the corresponding Voronoi polygons (b). To calculate area for the Voronoi polygons, some clipping boundary must be applied, such as the convex hull of the well locations. 9
- Figure 5. Aggregation of data over 6-month time intervals. Individual sample results for two wells (dot and triangle points) are shown over time. For each 6-month interval, an average of all the data in that interval is calculated for each well (x and star points). Values shown here are for illustration only and do not represent actual data. 10
- Figure 6. Example of linear regression of (arbitrary) concentration data versus time to obtain a first-order (exponential) curve fit. Here, the attenuation rate (k) is 0.1777 yr^{-1} 12
- Figure 7. Depiction of a flow-path analysis to determine attenuation rate from concentration versus distance data in a steady-state plume. 17
- Figure 8. Depiction of the components for calculating a threshold concentration (C_{thresh}) based on the attenuation rate calculated from the flow-path analysis, the distance spanned (L), and the concentration goal at the downgradient well (C_{goal}). The contaminant plume with a concentration of C_{thresh} at the upgradient well will decrease in concentration to C_{goal} at the downgradient well as it passes through the attenuation zone between the wells. 19
- Figure 9. Depiction of the historical chromium plume in the 100D Area based on data from 2009. The plume image was obtained using the Plume Status feature of the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/apps/plumes/index.html>, accessed on 8/30/2016), which uses plume images from the annual Hanford Site groundwater monitoring reports. Wells selected for the example historical plume analyses are also shown. 23
- Figure 10. Conceptual depiction of a plume with P&T extraction and injection wells and corresponding idealized capture zones. With hydraulic analysis, the travel times t_{ie} and t_{im} or t_{pe} and t_{pm} can be calculated. The t_{ie} and t_{pe} can be calculated as a time for a pore volume to move within the capture zone. 25
- Figure 11. Conceptual depiction of a concentration trend at monitoring or extraction wells in relation to the computed travel times depicted on Figure 10. 26

Figure 12. Conceptual depiction of a concentration or mass discharge plot for a mass-based evaluation of a plume trend.	27
Figure 13. Conceptual depiction of how historical plume data can provide information to calculate a threshold concentration that will meet a specified downgradient concentration goal because the plume after P&T is shut down will be attenuated in the attenuation zone (see Figure 1) before reaching the target well.	30
Figure 14. Example decision logic for a Hanford P&T system performance assessment.	32

1.0 Introduction

The U.S. Department of Energy Hanford Site is applying pump-and-treat (P&T) remediation to control and diminish groundwater contaminant plumes. There are P&T systems in the 100 Areas (DOE 2015a) and 200 Area (DOE 2015b) currently operating to address aquifer contamination. Operational information for these systems is provided in annual summary reports (DOE 2015a, b). Groundwater monitoring information for the targeted plumes is compiled in the annual Hanford groundwater monitoring reports. In the future, a remedial decision will be needed to transition from P&T to remediation closure or to another approach to complete remediation (e.g., transition to natural attenuation). The recent document *Performance Assessment for Pump-and-Treat Closure or Transition* (Truex et al. 2015a) provides a structured approach to assess P&T systems and support remedy decisions. The overall guidance in Truex et al. (2015a) can be used to identify appropriate system-specific data and assessment approaches to support Hanford decisions on the P&T systems. In this way, the Hanford Site can plan for the upcoming decisions and focus on collecting and compiling appropriate data to support P&T system performance assessment.

The purpose of this document is to identify how elements of the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a) can be applied to address performance assessment needs for Hanford Site P&T systems. The report is intended to be a resource for the site to develop a performance assessment approach and exit strategy for each P&T system. For this effort, the individual P&T system design, application, and plume setting needs to be considered to define relevant and specific performance assessment approaches. Because the P&T performance assessment will need to be conducted in the future as part of formal operable unit activities, this current document focuses on identifying appropriate approaches that the operable unit staff and other decision makers can use as a resource for conducting the assessment. The report focuses on P&T assessment for transition to natural attenuation because 1) the 200-ZP-1 and 200-UP-1 operable unit P&T systems are part of remedies where transition to natural attenuation is identified in the Record of Decision (ROD) (EPA, DOE, and WDOE 2008, 2012) and 2) the 100 Area P&T systems target chromium plumes that are being diminished and are receding from the river (DOE 2015a) such that natural attenuation may become a suitable polishing step to meet aquifer concentration objectives and the more stringent river-protection standards. Thus, for P&T applications at Hanford, it is anticipated that a key element of P&T performance assessment will be to determine when a P&T system can be shut down and transitioned to natural attenuation for final polishing to meet the remedial action objectives (RAOs), with consideration of potential continued targeted treatment for areas of persistent contamination.

Section 2.0 of this document includes a synopsis of the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a) and other resources for analyzing contaminant plume dynamics. Section 2.0 also describes types of data and assessment approaches that could be applied for assessing the existing Hanford P&T systems. Section 3.0 provides information about primary performance assessment elements and how they can be applied for the Hanford P&T systems. Section 4.0 describes developing an exit strategy to guide the P&T performance assessment process. Conclusions are presented in Section 5.0.

2.0 Resources for P&T Performance Assessment

The *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a) was intended to provide a structure for conducting P&T performance assessment in a way that facilitates remedy decisions. Section 2.1 provides a synopsis of Truex et al. (2015a) as context for its use to support assessments for Hanford Site P&T systems. A key element of a performance assessment is quantifying contaminant plume dynamics. Section 2.2 describes relevant plume data evaluation approaches as resources for subsequent sections of this report.

2.1 Synopsis of P&T Performance Assessment Guidance

The performance assessment described in Truex et al. (2015a) is organized to use a set of *decision elements* to help decision makers distinguish among several categories of *decision outcomes* associated with optimization, transition, or closure of P&T systems. The decision elements are summarized below.

- *Contaminant concentrations and trends*: These data are used to evaluate whether the plume has declined during the P&T remedy and to provide input for the subsequent decision element assessments.
- *Contaminant mass discharge (CMD; mass/time)*: The CMD at a given location in a plume (or at the source) indicates the amount of contaminant mass migrating past that location over time. P&T system data can provide contaminant mass extracted over time, which is an indicator of extraction efficiency. With knowledge of the natural gradient at the site, the P&T data can be interpreted in terms of the CMD that would occur from the capture zone if P&T system operations were discontinued. This CMD information is useful when assessing performance and future plume behavior in comparison to factors related to the downgradient transport of the contaminants (e.g., the attenuation capacity, as described below and shown conceptually in Figure 1). It is also important to consider the variation in contaminant concentrations within the plume or source at locations upgradient of the CMD measurement location. When there are steep concentration gradients or an order-of-magnitude variation in concentrations across the plume width, concentration-based approaches (e.g., a threshold concentration approach as discussed below) may be more appropriate than spatially averaged mass-based approaches in evaluating downgradient transport and attenuation. For example, it may be necessary to specifically assess what happens with a high-concentration core of a plume (versus lower concentrations further from the plume core), because that portion of the plume will likely drive the need for remediation.

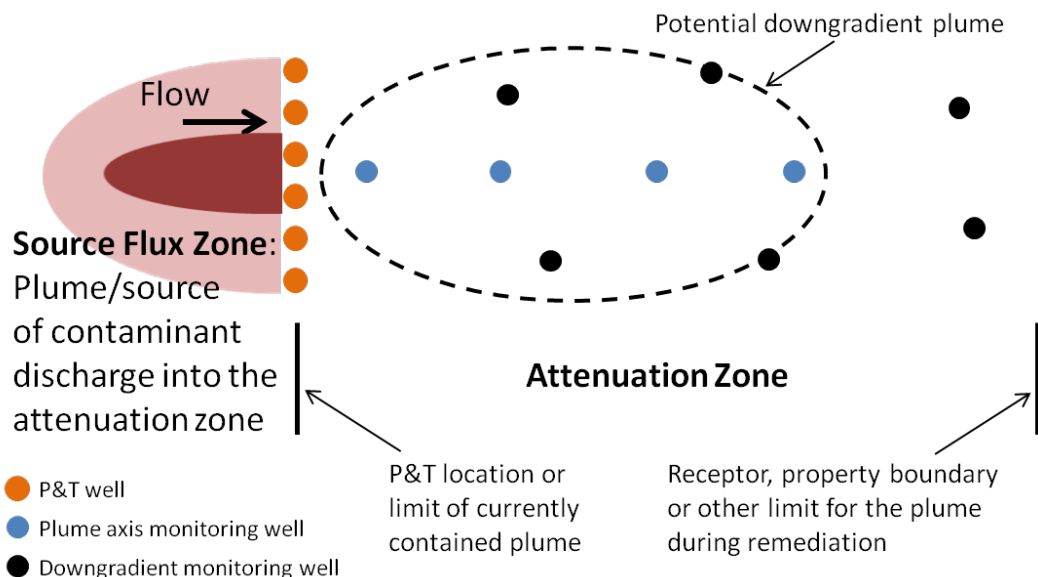


Figure 1. Conceptual depiction (after Truex et al. 2015a) of the source flux zone being controlled by P&T and a downgradient attenuation zone, whose extent must be determined by the site decision makers. To support a decision to transition to a monitored natural attenuation remedy, the CMD from the source zone (or potentially an upgradient plume) must not be greater than the attenuation capacity in the attenuation zone under natural-gradient conditions. In this situation, the plume would stay within the limits defined by the site decision makers.

- **Attenuation capacity (AC) of the aquifer:** The attenuation capacity is a way to quantify the ability of an aquifer (or portion of an aquifer) to decrease contaminant concentration over time without active remediation. There are multiple approaches to evaluating attenuation rates and mechanisms in the aquifer. These rates and mechanisms are important to assessing the role of natural attenuation during P&T or for transitioning P&T to monitored natural attenuation (MNA) (or another remedy that includes the contribution of natural attenuation). The attenuation capacity can be conceptually estimated as a decrease in contaminant mass over time within a given volume of the aquifer (shown in Figure 1) under natural-gradient conditions. Performance and future plume behavior can be assessed by comparing this attenuation capacity to the CMD (described above). In some cases, especially when there is a higher concentration plume core, it may be more appropriate to represent the attenuation capacity as an attenuation rate (change in concentration per time), using the threshold concentration approach (discussed below) for evaluating the concentration emanating from the source zone plume core.
- **Estimated future plume behavior and time to reach RAOs:** Like any remedy decision, predicting plume fate and transport and the time needed to reach the RAOs is an important part of P&T performance assessment. The plume behavior under continued P&T or MNA, or with application of other remedy components or alternative remedies, needs to be estimated. Key components of this decision element include evaluating protectiveness (e.g., controlling exposure during remediation) and estimating the time to reach the RAOs. For the plume behavior estimate, it is also important to consider the controlling features at the site (e.g., matrix diffusion) or source conditions that may extend the remediation timeframe. It is also important to consider the uncertainty associated with estimating future plume behavior and time to reach RAOs when using these estimates to support a remedy decision.

- *P&T system design, operational, and cost information:* As part of the performance assessment, information about the P&T design, operation, and cost are important to consider when assessing whether optimization would help performance or for comparison of P&T to other remediation alternatives.

The following categories of decision outcomes are included in the decision logic for the P&T performance assessment (Truex et al. 2015a).

- *Initiate P&T Remedy Closure:* If the site conditions meet RAOs, then an appropriate outcome of the analysis is to proceed with P&T remedy closure. Criteria used to evaluate whether RAOs have been met may have been established in site remedy decision documents. In some cases, a rebound study to assess concentration trends with the P&T system off may be needed as part of assessing whether concentration goals have been met. The U.S. Environmental Protection Agency (EPA) provides guidance (e.g., EPA 2011a, b, 2013, 2014a, b) for the remedy closure process.
- *Transition P&T to MNA:* This outcome is for sites where P&T has changed plume conditions such that RAOs can now be met with MNA.
- *Continue with Existing or Optimized P&T:* If P&T has diminished the plume, it may be appropriate to continue P&T or optimize the system and continue P&T, if it is practical to meet RAOs. As time progresses, the P&T system may need to be re-evaluated with respect to progress toward meeting the RAOs.
- *Supplement P&T with Other Treatment Technologies:* This outcome may be appropriate at sites where P&T has been inefficient or ineffective in progressing toward RAOs, but where a specific plume condition or feature can be addressed by a supplementary treatment (e.g., targeted treatment of a contaminant hot spot) such that RAOs can then be met with this combined approach. Some sites may have complexities that need to be considered in evaluating a supplemented P&T approach (NRC 2013; ITRC 2015). In this case, the site may need to consider adaptive remedy approaches and means to mitigate exposure while addressing contamination. It is also possible that, over time, the supplemented P&T system may need to be re-evaluated with respect to progress toward meeting the RAOs.
- *Transition to a New Remedy Approach:* At sites where P&T has been inefficient or ineffective in progressing toward RAOs, another remedy approach may be more cost effective. Some sites may have complexities that need to be considered in selecting the new remedy approach (NRC 2013; ITRC 2015). In this case, the site may need to consider adaptive remedy approaches and means to mitigate exposure while addressing contamination.

Figure 2 summarizes the decision logic described by Truex et al. (2015a) for the P&T performance assessment, incorporating the decision elements and the decision outcomes. After updating the conceptual site model (CSM) and assessing whether RAOs have been met, the decision logic consists of several primary assessments that distinguish between outcomes. The first assessment is based on whether the plume has declined during P&T operations. If the plume has declined, then an assessment is conducted to determine whether MNA is warranted. For the Hanford P&T systems, this assessment of potential transition to MNA is a primary need because this transition is either specified in the ROD (EPA, DOE, and WDOE 2008, 2012) or current performance shows declining plumes (DOE 2015a). If MNA is not appropriate, then the logic points to evaluating continued/optimized P&T. For plumes that have not declined during P&T or for situations where the plume has declined but RAOs cannot be practically reached with P&T or MNA, the decision logic points to evaluation of other approaches. In this case, the decision logic specifies either evaluating technologies to supplement P&T or switching to a remedy approach based on a different technology to address factors inhibiting remediation. Site decision makers may also consider ARAR (Applicable or Relevant and Appropriate Requirements) waivers or revisiting

RAOs (e.g., using approaches to define objectives, as described in the *Integrated DNAPL Site Strategy* document [ITRC 2011]) depending on the conditions driving the need for an alternative remedy approach to P&T.

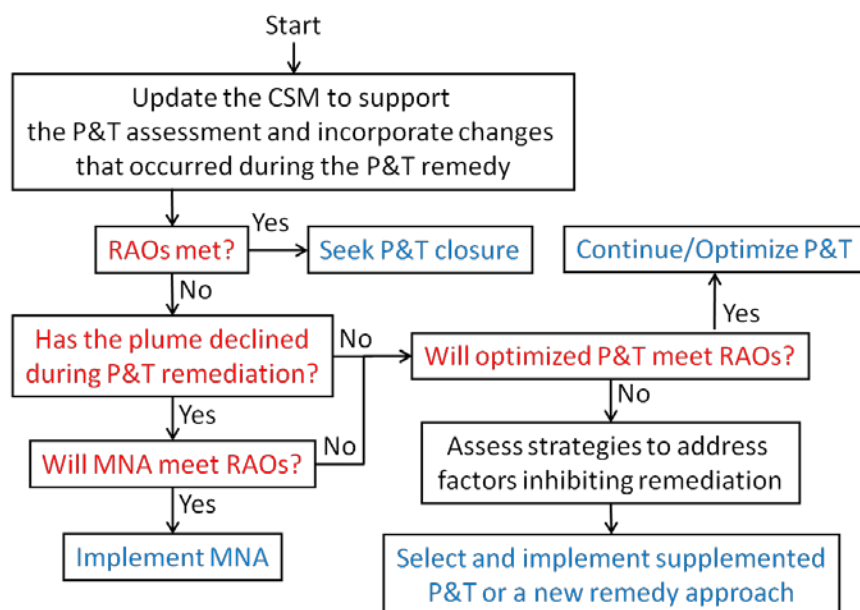


Figure 2. Primary elements of the decision logic used for the P&T assessment (after Truex et al. 2015a). The full decision logic (Figure 10 in Truex et al. 2015a) includes additional elements of the decision process, which are omitted here for brevity.

2.2 Synopsis of Plume Data Evaluation Approaches

Plume dynamics can be quantified using several different approaches, including analysis of observed contaminant data and predictive modeling (using either analytical or numerical modeling tools). Different types of plume dynamics evaluations provide specific types of insight into the current and predicted plume behavior, either with continued P&T operations or with discontinuation of P&T. Data-driven approaches include semi-quantitative and quantitative assessments that use either wells located across the entire plume or a subset of wells located in specific locations within the plume. Published EPA guidance (EPA 2002) discusses three types of quantitative analyses for estimating attenuation rates from observed data and the type of information that can be determined from each type of rate. Figure 3 conceptually depicts the types of plume data evaluation approaches, including evaluation of the whole plume (as a plume map or numerically from the data), changes in the source strength, and changes along a transect down the flow axis. Implementation of plume analysis is described in Section 2.2.1, analysis of point data is discussed in Section 2.2.2, and analysis of spatial data along a transect is discussed in Section 2.2.3. Sections 3.0 and 4.0 discuss how these approaches can be integrated into elements of a P&T performance assessment and used to develop an exit strategy.

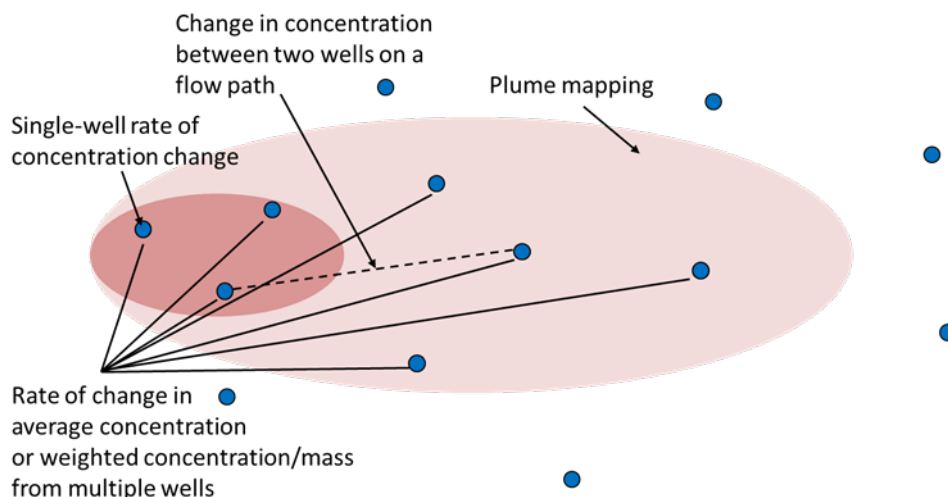


Figure 3. Depiction of the types of quantities calculated from plume data, including plume maps, rate of change in overall plume concentration/mass, rate of change in point concentrations, and rate of change in concentration over distance along a flow path.

2.2.1 Plume Analysis

2.2.1.1 Defining the Wells Used in the Plume Analysis

Plume analysis is based on evaluating temporal and spatial changes in groundwater monitoring data collected from a defined set of wells within the same hydrologic unit of the subsurface. That is, point data from wells are used to estimate characteristics of the contaminant plume (defined as the extent of contaminant concentration at or above the maximum contaminant level [MCL]). Preferably, the wells would be distributed across the extent of the contaminant plume in a relatively uniform fashion to obtain data representative of the plume. Depending on the contaminant migration characteristics, the preferred well distribution may include wells at downgradient locations to allow observation of plume movement over time. The set of wells actually available, however, is nearly always non-ideal with respect to spatial distribution and density. Well network selection should consider how well the network spans the plume and include “background” locations so that the plume extent can be estimated. To use P&T pumping wells for collecting data, the pumped wells should span the plume rather than being a source control or plume interception configuration. Available wells and data will need to be considered in the context of the uncertainty derived from the actual spatial distribution of the data.

Regardless of the spatial distribution of the wells, plume analysis requires data from the same set of wells over time. If data are irregularly collected (e.g., because wells are decommissioned, newly installed, or skipped in some sampling events), then temporal data interpretation becomes difficult or infeasible. Plume maps using different well sets for separate times will show variations in the plume extents that are artifacts of the different spatial distribution of data. Quantitative calculations are not meaningful when different sets of wells are used over time because there is a different basis used for the different times.

Given wells in the correct hydrologic unit and with coincident data in intervals over the timeframe of interest, one further spatial consideration is potentially relevant to the plume analysis. The question is whether to use wells only within the plume (plume wells) or to also include wells in “clean” portions of the aquifer that bound the extent of the plume (bounding wells). The approach used at a given site will depend on the nature of a given type of plume analysis and things like the aforementioned potential for plume movement. It is important to understand the implications of including bounding wells in quantitative calculations. While inclusion of bounding wells may make sense to capture concentration

changes resulting from plume migration, it may not make sense in other situations. If an average plume concentration is determined in the plume analysis, inclusion of bounding wells will result in a lower magnitude for that average plume concentration. However, inclusion of bounding wells should only have a minor effect on a plume mass estimate. The relative impact of bounding wells outside of the plume will also depend on plume core concentrations and variability of concentrations in the bounding wells. As the plume concentrations decrease, any bounding well concentrations detected below the MCL but above “non-detect” will have the potential to influence calculations more. Certain types of plume analysis results can also be affected by including bounding wells. Calculation of a plume attenuation rate is minimally affected (except perhaps when plume concentrations approach the MCL). However, a time to completion calculation based on an average plume concentration would be affected by the “dilution” of the magnitude of the average plume concentration when bounding wells are included. Thus, the time to remedy completion is better estimated based on plume mass or an average plume concentration derived from only wells within the plume.

Understanding the type of data needed with respect to spatial and temporal conditions is important for considering different variants of plume analysis. These factors can provide insight into uncertainty, data gaps, and future monitoring needs.

2.2.1.2 Plume Mapping

The most basic approach for evaluating the nature of a groundwater contaminant plume is the semi-quantitative interpretation of two-dimensional (2D) concentration contour plots. Contour plots are useful because they indicate the direction and extent of contamination spread. Temporal changes in plume contour plots can reveal information about plume stability (or lack of stability), effects of seasonal flow variations, and the impacts of remedial actions (whether from P&T, source treatment, or other remediation). However, care must be taken when assessing 2D plume contours because groundwater contamination is a three-dimensional (3D) phenomenon. The 3D nature of the plume needs to be kept in mind both when compiling the data that will be contoured and when interpreting the contour plots. Flattening all data, possibly collected at different elevations, into a single, flat 2D layer may not be representative of the plume, particularly if the data span across different hydrogeological units.

Mapping plume concentrations as isosurfaces (i.e., 3D contours) provides improved understanding over interpretation of 2D plume contours. Isosurfaces show the volume and depth elements that are missing from the 2D contour depictions. To make meaningful isosurfaces, sufficient data density is required both laterally (x and y directions) and vertically. While high-resolution characterization approaches can provide data with good vertical resolution, most sites do not have monitoring well networks with the necessary data density to effectively map isosurfaces from observed data. In contrast, results from numerical groundwater models are inherently suitable for creating isosurface depictions. If available, isosurfaces lead directly to calculation of plume mass.

2.2.1.3 Approach to Plume Analysis

The EPA guidance on attenuation rate calculation (EPA 2002) discusses quantitative plume analysis using mass and concentration data over space and time. A mass-based analysis applies well-specific weighting factors to the temporal concentration data from a selected set of wells that are representative of the spatial extent of the plume, giving rise to an estimated attenuation rate for the whole plume. Temporal concentration data may come from monitoring wells or from pumped wells, though pumped well concentration data reflect a capture zone that is a function of aquifer properties and pumping rate. The weighting factors equate to the representative volume for each well and are multiplied times the concentration at each well to give an estimate of plume mass. Selection of equal weighting equates to using an average plume concentration to estimate the plume attenuation rate. A plume attenuation rate

can be used to estimate the time for remedy completion. Plume attenuation rate estimates are more resilient against errors caused by changes in flow direction (e.g., from seasonal variations).

2.2.1.4 Weighting Approaches for Determining Plume Mass

There are two typical approaches to the weighting factors for each well: using a representative area based on 1) Voronoi polygons (also referred to as Thiessen polygons) or 2) applying equal weighting (same area for each well). The spatial density and distribution of wells across the plume/site will be a factor in determining the type of weighting that makes sense for estimating plume mass. A relatively dense well network that includes “background” wells bounding the plume extents is probably well suited for Voronoi polygon weighting. Equal weighting may be more appropriate for a sparse or skewed well network.

Voronoi polygons (Figure 4) provide a method of attributing an effective area to each well as the weighting factors for calculating plume mass. Standard computational methods (Fortune 1987^a; Tipper 1991; Hjelle and Dæhlen 2006) can be used to calculate the extent of the Voronoi polygons (e.g., from circumcenters of the Delaunay triangulation, which is the mathematical dual of the Voronoi polygons). There are several aspects to consider when using Voronoi polygons for weighting factors, including how to handle well clusters or spatially proximate wells and defining an outer boundary to constrain edge polygons.

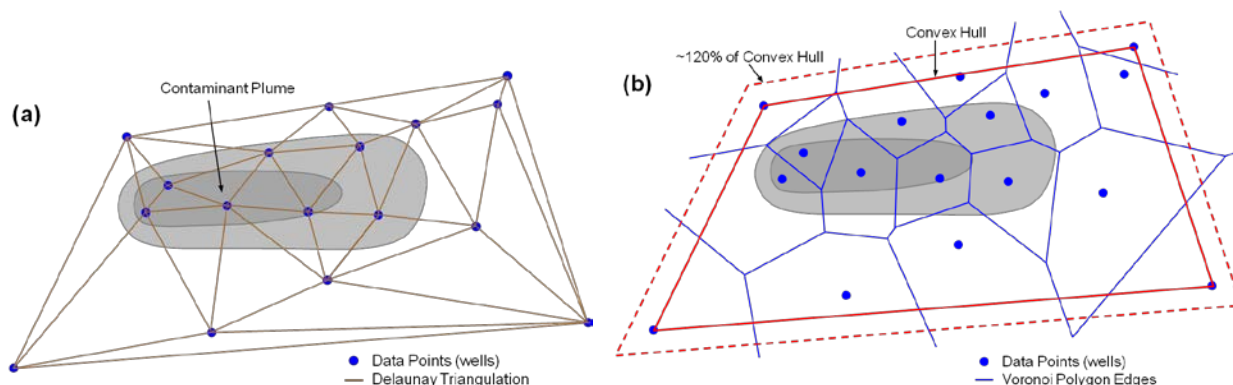


Figure 4. Arbitrary example to illustrate the Delaunay triangulation (a) of the well locations and the corresponding Voronoi polygons (b). To calculate area for the Voronoi polygons, some clipping boundary must be applied, such as the convex hull of the well locations.

An approach for handling wells located close together may be required when using Voronoi polygon weighting. Nested wells or well clusters will typically represent different elevations in the subsurface at the nominal “same” lateral location. If clustered wells represent different hydrologic units, then they will naturally be in separate well groups for plume assessment. If they represent different elevations within the same hydrologic unit, then the data should be averaged or only one elevation should be used in the analysis (e.g., select the elevation with the highest concentrations). If only one elevation is used, the maximum of all wells in the cluster could be used (meaning variation in the represented elevation over time) or one specific well (elevation) could be used every time (which could mean that changes in vertical distribution of contamination may not be represented). Even when wells are not a cluster at the same nominal location, they may be relatively close in the context of the entire plume, making it necessary to consider how best to represent the concentration and weighting in that vicinity.

^aA fast JavaScript implementation of Fortune’s algorithm is available at <http://www.raymondhill.net/voronoi/rhill-voronoi.html> (accessed September 16, 2016). The D3 JavaScript library (<https://d3js.org/>) has Voronoi polygon functionality (<https://github.com/d3/d3-voronoi>) that is based on Raymond Hill’s work.

When using Voronoi polygons to apply weighting for calculating plume contaminant mass, a boundary for outer edge polygons will be required. Voronoi polygons on the outer edge of a well network are often either open polygons (i.e., have infinite area) or are closed polygons encompassing a large area. Such characteristics of the edge polygons would lead to a greater weighting of concentrations at outer wells. If all such outer wells represent, over the entire time of interest for the plume analysis, background conditions of non-detects or concentrations less than the MCL, then the choice of a boundary and the magnitude of the weighting factors are less critical because a very small number times a large factor still gives a small number. If however, outer boundary polygons correspond to wells representing concentrations within the plume, then the choice of enclosing boundary has more impact on the magnitude of the plume mass estimate. Regardless, the impact on assessing plume attenuation is minimal because the same set of wells is used in the analysis of concentrations at any given time and because the weighting factors will remain the same. A typical outer boundary would be the convex hull around the wells or some buffer beyond the convex hull (e.g., 120% expansion of the convex hull).

The other typical approach for weighting factors is to use equal weighting for all wells, which may make more sense than Voronoi polygon weighting for some sites. Equal weighting would apply the same area to each well, likely being based on a typical distance between wells. As shown in the calculation section below, the equal weighting approach is equivalent to the average plume concentration approach with respect to the plume attenuation rate.

2.2.1.5 Temporal Aggregation

The practical logistics of groundwater sampling can lead to sample collection from individual monitoring wells in a given well network taking place on different dates (perhaps even different months in a quarter or year). Similarly, pumped wells may be sampled at different times, or perhaps more frequently than monitoring wells. Because of variations in sample event timing, it may make sense to aggregate (combine) data across a broader monthly, quarterly, semi-annual, or annual interval for use in a plume analysis. For each sample aggregation time interval, an average concentration at each well would be calculated based on all the sample events within that time interval and all the replicates from each sample event (i.e., an average of all the discrete sample results). This set of averaged concentrations for each well in each time interval is subsequently used in the plume analysis. Figure 5 depicts arbitrary data for two wells over time that is aggregated into 6-month time intervals that start in February or August. All values within a given interval (including multiple sample events and replicates) are averaged for each well.

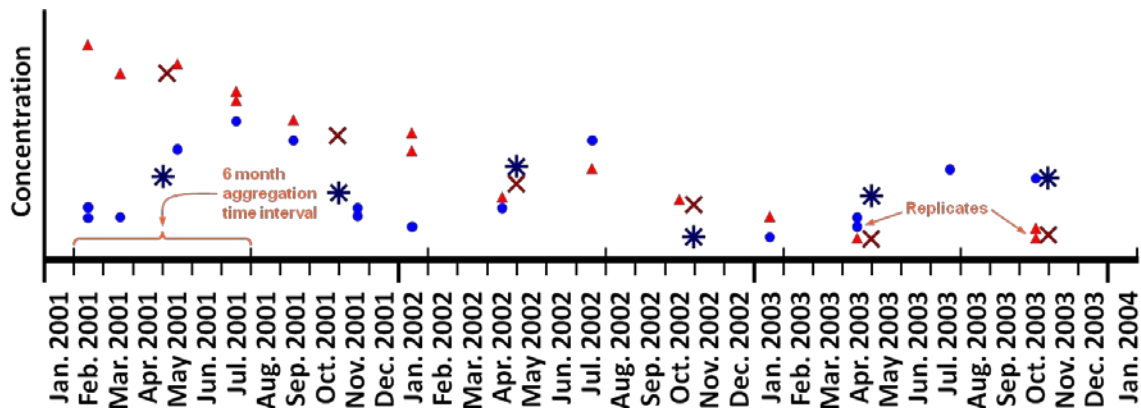


Figure 5. Aggregation of data over 6-month time intervals. Individual sample results for two wells (dot and triangle points) are shown over time. For each 6-month interval, an average of all the data in that interval is calculated for each well (x and star points). Values shown here are for illustration only and do not represent actual data.

It is worth noting that other factors may affect the temporal aggregation or size of time intervals. Seasonal variations may affect groundwater concentrations. For example, monitoring locations near a river may be seasonally diluted when the river is at a high stage versus low stage conditions. An understanding of seasonal variability in concentration data should be applied to select the data most representative of the contaminant plume.

2.2.1.6 Plume Analysis Calculations

As mentioned above, quantitative plume analysis looks at the rate of change in plume mass (or average plume concentration) over time, i.e., the plume attenuation rate (EPA 2002). The calculation approach for determining a plume attenuation rate is described here.

After considering the factors described above, the set of n wells, the time interval ($t_{interval}$) for data aggregation, and the type of weighting are defined for use in the analysis.

Given the area of the Voronoi polygon for the i^{th} well ($A_{Voronoi,i}$), the aquifer thickness at the i^{th} well (B_i), the aquifer porosity (θ), the site-specific representative area for all wells (A_{Equal}), and/or the constant aquifer thickness for all wells (B), calculate the weighting factors (V_i) as shown in Equation 1.

$$\begin{aligned}
 V_i &= A_{Voronoi,i} \cdot B_i \cdot \theta && \text{(for Voronoi polygon weighting)} \\
 \text{or} \\
 V_i &= A_{Equal} \cdot B \cdot \theta = V_{well} && \text{(for equal weighting)} \\
 \text{or} \\
 V_i &= 1.0 = V_{well} && \text{(for equal weighting, equating to average plume concentration)}
 \end{aligned} \tag{1}$$

Calculate the average groundwater concentration ($C_{i,j}$) for the i^{th} well during the j^{th} time interval from the $N_{samples,i,j}$ individual sample results from all the sample events during the j^{th} time interval at the i^{th} well, including same-date replicate samples, as shown in Equation 2.

$$C_{i,j} = \frac{\sum_{p=1}^{N_{samples,i,j}} C_{i,j,p}}{N_{samples,i,j}} \tag{2}$$

To estimate the mass in the plume (m_j) for the j^{th} time interval, sum the weighting factor (V_i) times the average groundwater concentrations of that interval ($C_{i,j}$) for all N_{well} wells, per Equation 3.

$$m_j = \sum_{i=1}^{N_{well}} V_i \cdot C_{i,j} \tag{3}$$

When the weighting factor is based on equal weighting, a constant weighting factor (V_{well}) is used. The weighting factor (volume over which the well data is representative) is then related to the total volume by $V_{total} = N_{well} \cdot V_{well}$ and Equation 3 simplifies to Equation 4, which is based on the average plume concentration (C_{avg}) for the j^{th} time interval.

$$m_j = \sum_{i=1}^{N_{well}} V_{well} \cdot C_{i,j} = V_{well} \cdot \sum_{i=1}^{N_{well}} C_{i,j} = V_{total} \cdot (\text{Avg. Plume Concentration}) = V_{total} \cdot C_{avg,j} \tag{4}$$

The plume attenuation rate is assumed to be a first-order process (i.e., a function of mass or concentration, equivalent to exponential decay for a declining trend) and is thus determined from linear regression of natural log-transformed data. The linear regression determines the plume attenuation rate (k) corresponding to the best-fit, first-order curve (Equation 5). The regression is typically depicted with a plot of the

plume mass (or average concentration) data for all time intervals in the time span of interest (e.g., Figure 6). The use of average plume concentration data alone (equal weighting with $V_{well} = 1.0$) does not impact calculation of the plume attenuation rate (i.e., the data are just scaled by a constant weighting factor so the attenuation rate is unchanged, even though the magnitude of the data changes). The linear regression algorithm (e.g., equivalent to the LINEST function in Microsoft® Excel®) should return the regression curve, the calculated attenuation rate (k , the negative of the regression slope), and statistics about the regression, including the coefficient of determination (r^2).

$$\begin{aligned} m_{plume} &= m_0 \cdot e^{-k \cdot t} & \text{equates to} & \ln(m_{plume}) = \ln(m_0) - k \cdot t = b - k \cdot t \\ C_{avg} &= C_0 \cdot e^{-k \cdot t} & \text{equates to} & \ln(C_{avg}) = \ln(C_0) - k \cdot t = b' - k \cdot t \end{aligned} \quad (5)$$

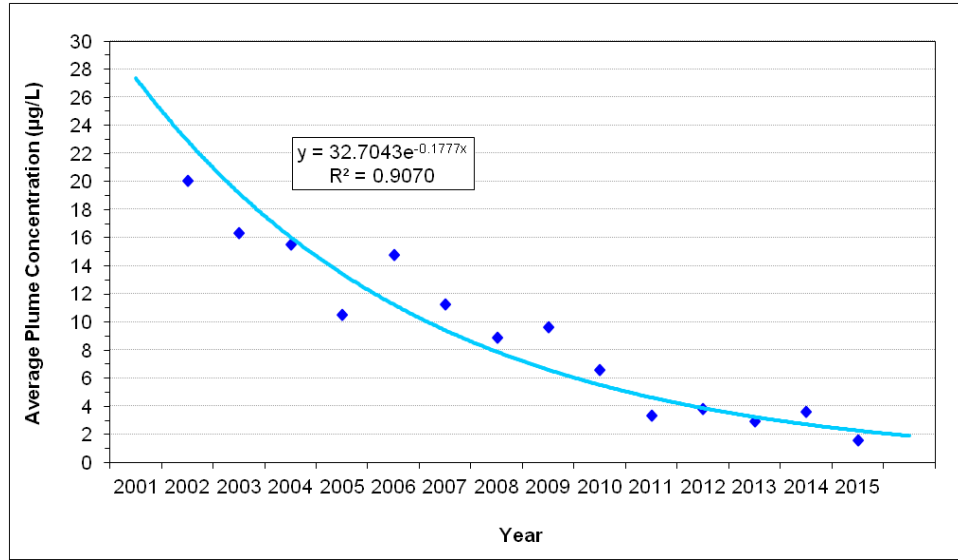


Figure 6. Example of linear regression of (arbitrary) concentration data versus time to obtain a first-order (exponential) curve fit. Here, the attenuation rate (k) is 0.1777 yr^{-1} .

Taking time (t) as the independent variable (x) and either mass (m_{plume}) or concentration (C_{avg}) as the dependent variable (y), the following equations are used to calculate regression related quantities, including the slope (m) and intercept (b or b' , both represented by a generic b). Here, n is the number of data points, \bar{x} and \bar{y} are the averages of the independent and dependent variables respectively, and $conf$ is the user-specified confidence level (e.g., 95%).

$$S_{xx} = \sum_{i=1}^n x_i^2 - \frac{\left(\sum_{i=1}^n x_i \right)^2}{n} \quad (6)$$

$$S_{yy} = \sum_{i=1}^n y_i^2 - \frac{\left(\sum_{i=1}^n y_i \right)^2}{n} \quad (7)$$

$$S_{xy} = \sum_{i=1}^n x_i \cdot y_i - \frac{\left(\sum_{i=1}^n x_i\right) \cdot \left(\sum_{i=1}^n y_i\right)}{n} \quad (8)$$

$$m = \frac{S_{xy}}{S_{xx}} \quad (9)$$

$$b = \bar{y} - m \cdot \bar{x} \quad (10)$$

$$r^2 = \frac{S_{xy}^2}{S_{xx} \cdot S_{yy}} \quad (11)$$

$$SS_{regr} = \frac{S_{xy}^2}{S_{xx}} \quad (12)$$

$$SS_{resid} = S_{yy} - SS_{regr} \quad (13)$$

$$df = n - 2 \quad (14)$$

$$se_y = \sqrt{\frac{SS_{resid}}{df}} \quad (15)$$

$$se_m = \frac{se_y}{\sqrt{S_{xx}}} \quad (16)$$

$$t - statistic = \left| \frac{m}{se_m} \right| \quad (17)$$

$$\alpha = 1 - conf \quad (18)$$

The coefficient of determination (r^2) value for the regression indicates the proportion of the variance in the dependent variable that is predictable from the independent variable. Values closer to 1.0 indicate that the regression line better represents the data.

The p -value associated with testing whether the regression slope is different from zero is obtained by look-up in a t distribution table for a t-statistic value (as calculated by Equation 17), the degrees of freedom (df), and a 2-tailed test. This p -value look-up is equivalent to the Excel function TDIST(t -statistic, df , 2). If the p -value is less than the significance level (α), then we reject the null hypothesis (that $m = 0$) and conclude that there is a meaningful non-zero slope.

The estimated mass or concentration is calculated from the regression slope and intercept per Equation 19, which gives the regression line.

$$\hat{y} = m \cdot x_p + b \quad \text{for any time value, } x_p \quad (19)$$

Confidence intervals describe the interval within which the true regression line would fall at a *conf* percent confidence (e.g., 95% confidence). For *conf* = 95% there is a 95% probability that the true linear regression line of the population lies within the confidence interval of the regression line calculated from the sample data. The prediction interval is the interval, within which a new value would be expected to lie at a *conf* percent confidence (e.g., 95% confidence). Confidence and prediction intervals are calculated from Equations 20 and 21 using the *t-critical* value. The *t-critical* value is determined from a t-distribution look-up for the significance level (α) and the degrees of freedom (*df*). The *t-critical* value look-up is equivalent to the Excel function TINV(α , *df*).

$$\text{confidence interval} = \hat{y}_p \pm (t - \text{critical}) \cdot se_y \cdot \sqrt{\frac{1}{n} + \frac{(x_p - \bar{x})^2}{S_{xx}}} \quad \text{for any time value, } x_p \quad (20)$$

$$\text{prediction interval} = \hat{y}_p \pm (t - \text{critical}) \cdot se_y \cdot \sqrt{1 + \frac{1}{n} + \frac{(x_p - \bar{x})^2}{S_{xx}}} \quad \text{for any time value, } x_p \quad (21)$$

The coefficient of variation (COV) indicates how individual data points vary about the mean value, with a value ≤ 1.00 indicating a relatively close group around the mean and a value > 1.0 indicating more scatter around the mean. The COV is calculated from the standard deviation of the mass or concentration data (s_y) and the average of the mass/concentration data (\bar{y}).

$$s_y = \sqrt{\frac{S_{yy}}{n-1}} \quad (22)$$

$$COV = \frac{s_y}{\bar{y}} \quad (23)$$

In addition to looking at regression statistics, the Mann-Kendall statistic (*S*) is a non-parametric approach to evaluating data for trends. A positive *S* indicates an increasing trend and a negative value indicates a decreasing trend, with stronger trends having larger magnitude *S* values. *S* values closer to zero have little or no trend. The Mann-Kendall statistic is useful for analyzing data that do not follow a normal distribution. That is, there are no distribution assumptions and (as with linear regression) measurements at irregular intervals are acceptable. The Mann-Kendall analysis is more robust when outliers are present versus any bias that outliers may impart on the linear regression statistics. When doing Mann-Kendall calculations, data must be organized in temporally sequential order. The Mann-Kendall statistic is a summation of the signs of the differences between data values, as shown in Equation 24 (where *y* represents plume mass or concentration). The Mann-Kendall statistic gives an indication of how strongly the data exhibit a trend. Further analysis can be performed by comparing the statistic to corresponding probability tables that indicate whether the statistic is significant or not for a given confidence level.

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \text{sgn}(y_j - y_i) \quad \text{where, } \text{sgn}(x > 0) = 1, \text{sgn}(x = 0) = 0, \text{ and } \text{sgn}(x < 0) = -1 \quad (24)$$

2.2.1.7 Interpreting the Plume Attenuation Rate

The calculations described above provide quantitative measures of whether a trend in the data exists and an estimate of the plume attenuation rate (the k from Equation 5). The plume attenuation rate can be used to determine whether the plume is growing, shrinking, or stable and to estimate the time to remedy completion.

In general, the plume attenuation rate will account for dispersion, reaction (biodegradation or abiotic transformation), source strength decline, and migration of the plume outside the domain of the wells. Migration outside the observed zone depends on the distribution of observation wells relative to the plume extent and rate of migration. For plumes whose migration is slow enough to stay within the well network, the plume attenuation rate would not include a component attributable to migration. Migration outside the observed zone is more of an issue when the plume is disconnected from the source (i.e., the source has been depleted or removed), because as a disconnected plume migrates beyond the well network, the plume mass naturally decreases. This situation gives an accelerated plume attenuation rate (over the rate attributable to just dispersion, reaction, and source decline processes alone) and the plume strength is not representative for calculating a time to completion.

The plume attenuation rate indicates a growing, stable, or shrinking plume. An increase in plume mass (or average concentration) gives a negative rate and indicates that the plume has not reached a steady state and continues to expand. A plume attenuation rate near zero and the lack of a trend in the plume mass/concentration indicate a stable plume. The stable plume may be the result of very little attenuation (i.e., if the source has been removed) or the result of a balance between a continuing source and the plume attenuation processes. A positive plume attenuation rate indicates that the plume is declining (and may be shrinking) because attenuation processes have greater capacity than the source flux or because the source itself is declining in strength.

The plume attenuation rate, in units of “per time,” can be converted to a half-life ($t_{1/2}$) using Equation 25, providing another way to think about the plume attenuation. A half-life can be easier to understand because it simply describes the time it will take for the starting amount of material to decrease by half. However, the half-life (by itself) does not provide information about the magnitude of the change in the amount of material.

$$t_{1/2} = \frac{\ln(2)}{k} \quad (25)$$

When assessing plume attenuation, an estimate of the remedy timeframe may be of interest. The remedy timeframe can be estimated from the plume attenuation rate (k), and both a mass or concentration goal (X_{goal}) and starting point (X_0), as shown in Equation 26. As discussed above, the basis for the attenuation rate can affect the suitability of using that rate for estimating a remedy timeframe. A plume attenuation rate determined from average plume concentrations for a well network with boundary wells outside the plume or from a plume that migrates outside of the defined well network will tend to underpredict the remedy timeframe. The time to remedy completion is better estimated from plume attenuation rates derived from plume mass or from an average plume concentration where the wells are all within the plume.

$$\text{Time Goal is Met} = \text{Starting Time} + \frac{\ln(X_{goal}/X_0)}{-\ln(2)/t_{1/2}} = \text{Starting Time} + \frac{\ln(X_{goal}/X_0)}{-k} \quad (26)$$

The mass-based assessment of plume attenuation rate demonstrates whether contaminants are being attenuated, indicates the plume trend (stable, shrinking, or expanding), and provides a good indicator of how long the plume will persist.

2.2.2 Single-Well Attenuation Rate Analysis

Analysis of a single well proceeds much as described for the plume analysis in Section 2.2.1, except that most often the analysis uses concentration data alone (not mass). The well selection, weighting, and mapping aspects of the plume analysis are not relevant to a single-well analysis. However, the temporal aggregation considerations (Equation 2) are the same as for the plume analysis. Single-well attenuation rate analysis uses the same linear regression (Equation 5, but using C_{ij} for the one well being analyzed instead of the plume C_{avg}) and trend assessment (Equation 24) as those used for the plume analysis.

While there are many similarities in the calculation approach, analysis of a single well provides different information than a plume analysis. In general, the point attenuation rate from single-well data indicates the potential plume lifetime at that location (whether due to attenuation processes or migration), but interpretation of the analysis depends on the location of the well within (or outside of) the plume. If a well is located in an evolving portion of the plume or even in a downgradient (or transverse) location outside of the plume, then the single-well analysis can indicate how the plume is migrating/expanding. However, it is often not possible to separate out any attenuation effects from the migration effects for such locations. If a well is located within the source area, then the single-well analysis provides an indication of the persistence of the source and the timeframe for reaching cleanup goals. The single-well analysis in the source area may indicate a rate of source depletion or may show little or no change in the source. Single-well analysis for a group of wells could potentially be collectively evaluated to interpret plume trends, though interpretation of the mass-based plume attenuation rate (Section 2.2.1) is likely to be more straightforward.

There are two considerations when estimating the time for remedy completion (plume persistence) based on a single-well analysis for a location in the source area. If the source area well is not in the strongest part of source, the analysis may lead to underestimation of time for remedy completion. Assessing multiple source area wells or the well with the highest concentration will help avoid underestimating the plume persistence. If the contaminant has characteristics of high water solubility and low degradability, the source may be depleted faster than the rate of attenuation for the dissolved-phase plume. The single-well analysis in such a case would also lead to underestimation of the time for remedy completion from single-well analysis of a source area well.

2.2.3 Flow-Path Attenuation Rate Analysis

The third approach to estimating attenuation rates for a plume is based on concentration or mass flux changes over distance (e.g., from near the source to a downgradient location) along a flow path within the plume (Figure 7). Such an analysis with distance in the direction of flow can indicate whether attenuation is occurring and the attenuation rate (or attenuation capacity). A flow-path analysis uses data from a particular time from different locations in the plume, and hence does not provide information about remedy completion time. Rather, the flow-path analysis provides an attenuation rate that accounts for all attenuation processes (dispersion, adsorption, biotic and abiotic transformation, etc.) over the distance spanned. The attenuation rate can then be applied in the context of terminating P&T operations by determining a concentration threshold (i.e., what concentration can remain at the end of P&T operations such that natural attenuation will meet a concentration goal at a specific downgradient distance). The approach to performing a flow-path analysis and the information it provides will depend upon the nature of the plume, the stage of plume evolution, and the available monitoring locations.

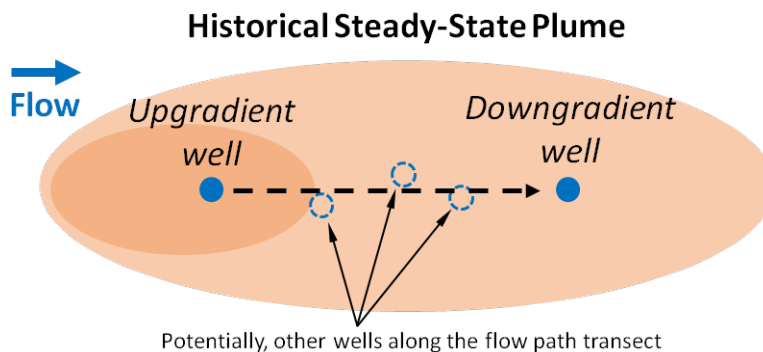


Figure 7. Depiction of a flow-path analysis to determine attenuation rate from concentration versus distance data in a steady-state plume.

As with the plume and single-well analyses, the selection of wells for use in a flow-path analysis is important because aspects such as the source zone, plume evolution, remedy (e.g., P&T) implementation, and seasonal effects can influence the analysis results. At its simplest, a flow-path analysis involves data from a transect of wells along the flow path of the plume. That is, concentrations from an observation location outside of the source (either near the source or further out in the plume) plus one or more observation locations at points further downgradient in the direction of groundwater flow are analyzed to determine the attenuation rate over the distance encompassed (which can be equated to the attenuation capacity). Wells should not be located within the source area to avoid misrepresenting the length of the attenuation zone and any effects related to changes in the source strength. Using data from multiple wells provides more detail about the change in plume concentrations over distance, but a two-point analysis is also adequate to assess the attenuation capacity. Wells that are not along the flow path will likely lead to misestimating the attenuation rate. For example, if the flow direction is due east, but the transect of wells falls along an east-by-north line, the actual data may have the wrong progression of concentrations over distance.

The selected wells need to span a zone of the contaminant plume that is at steady state, not still evolving. If the zone assessed includes portions of the plume that are still evolving, then the attenuation rate will be skewed because it will also include contaminant migration effects. For example, an analysis that uses a point near the source area and a point at the leading edge of an evolving plume would indicate a larger attenuation capacity (attenuation rate) than an analysis of the same locations when the plume had reached steady state at both locations. Application of a P&T remedy affects the plume dynamics and generally represents conditions unsuitable for a flow-path analysis. While a pseudo-steady state may be achieved during P&T operations, such disturbed conditions are not representative of the natural conditions for which attenuation rate information is typically desired. There will also be a period of time after cessation of P&T operations where the plume is in a transient state while it recovers back to natural conditions. The flow-path analysis either needs to be performed using data prior to disturbance from a remedy or after a remedy has been terminated and the plume has been allowed to re-attain steady state conditions under natural flow.

If a plume is subject to seasonal variations in flow direction, using concentrations from a single transect of wells along a flow path may not be the most suitable approach for a flow-path analysis. An approach to overcome variations in flow direction involves using two or more transects of wells perpendicular to the flow direction and wide enough to encompass plume variations as the flow direction changes. These perpendicular transects would be located at multiple distances downgradient from the source and would provide mass flux data to use in place of the flow-path transect concentration data.

2.2.3.1 Flow-Path Analysis Calculations

The calculations for a flow-path analysis are very similar to those for the plume analysis (Section 2.2.1.6) except that the first-order attenuation rate is described by Equation 27, with distance (d) as the independent variable (x) and concentration (C_i) (or mass flux) as the dependent variable (y).

$$C = C_0 \cdot e^{-m \cdot d} \quad \text{equates to} \quad \ln(C) = \ln(C_0) - m \cdot d = b - m \cdot d \quad (27)$$

The concentration (or mass flux) data need to come from effectively the same time. However, there may be small variations in actual date and there may be replicate samples at some wells, meaning that some aggregation may be required. For the selected time, calculate the average groundwater concentration (C_i) for the i^{th} well from the $N_{\text{samples},i}$ individual sample results from that well, as shown in Equation 28.

$$C_i = \frac{\sum_{p=1}^{N_{\text{samples},i}} C_{i,p}}{N_{\text{samples},i}} \quad (28)$$

Linear regression is then applied to these concentrations for wells along a transect, with the furthest upgradient well at a distance (d) of zero, and all other wells located at a positive distance downgradient from $d = 0$.

Regression-related quantities, including the slope (m) and r^2 , can be calculated for the set of independent and dependent data using Equations 6 through 18.

The flow-path attenuation rate (k) is equal to the regression slope (m) times the contaminant velocity (v_{contam}) as shown in Equation 29, where v_{gw} is the average linear groundwater velocity, R is the contaminant retardation factor, q is the Darcy “velocity”, and θ is the effective porosity.

$$k = m \cdot v_{\text{contam}} = \frac{m \cdot v_{\text{gw}}}{R} = \frac{m \cdot q}{\theta \cdot R} \quad (29)$$

As with the plume analysis, Mann-Kendall statistic can be used to determine if the flow-path concentration data have a trend. Equation 24 (where y represents concentration) can be applied to calculate the Mann-Kendall statistic after ordering the data in spatial order from $d = 0$ to the largest distance value.

2.2.3.2 Interpretation of the Flow-Path Analysis

The above linear regression calculations determine an attenuation rate (k) for the flow-path analysis, which can be used to determine a threshold value as input for a P&T performance assessment. Given a concentration goal (C_{goal}) at some distance (L) downgradient of a point in the plume (e.g., location of a contaminant concentration proposed to remain after P&T is terminated), a threshold concentration (C_{thresh}) can be calculated using Equation 30. This threshold concentration represents the concentration that must be reached at the selected point in the plume for the concentration goal to be achieved through attenuation at the distance L downgradient. Figure 8 depicts the scenario for interpreting a threshold concentration based on the calculated attenuation rate (Equation 29). The threshold concentration provides a metric for termination of a P&T system, though the potential for rebound after halting P&T must also be considered.

$$C_{\text{thresh}} = \frac{C_{\text{goal}}}{e^{-m \cdot L}} = \frac{C_{\text{goal}}}{e^{-k \cdot R \cdot L / v_{\text{gw}}}} \quad (30)$$

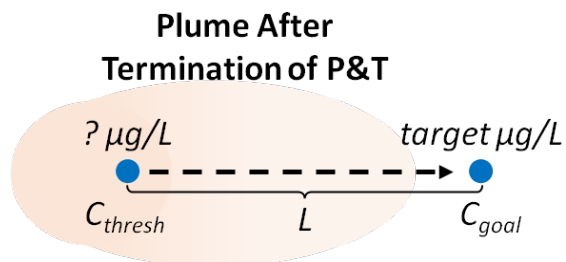


Figure 8. Depiction of the components for calculating a threshold concentration (C_{thresh}) based on the attenuation rate calculated from the flow-path analysis, the distance spanned (L), and the concentration goal at the downgradient well (C_{goal}). The contaminant plume with a concentration of C_{thresh} at the upgradient well will decrease in concentration to C_{goal} at the downgradient well as it passes through the attenuation zone between the wells.

3.0 Performance Assessment Elements

Unless a P&T system is operated until groundwater contaminant concentrations reach a final RAO (such as the drinking water or other standard), information about transition to MNA or transition to another treatment process is relevant. For all of the Hanford P&T systems, transition to MNA is important to consider. For the Central Plateau, transition from P&T to MNA was included as part of the current remedies, for instance, in the ROD for the 200-ZP-1 and 200-UP-1 operable units (EPA, DOE, and WDOE 2008, 2012). For the 100 Areas, natural attenuation may be a viable polishing step as a way to reach aquifer objectives and be protective of the Columbia River after plumes have been diminished by P&T. A key for these systems will be determining an appropriate plume condition for these transitions. Additionally, performance assessment should include collecting information to determine whether there are zones of persistent contamination that would be better addressed by a treatment technology other than P&T, or by a focused P&T system rather than a large system.

Evaluation of transitions for Hanford P&T systems is expected to include 1) quantification of contaminant plume dynamics from historical and current data (Section 3.1), 2) description and quantification of the attenuation capacity within an attenuation zone appropriate for the plume setting (Section 3.2), and 3) prediction of plume behavior after P&T is terminated (Section 3.3). These items, along with the other elements identified in the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a), are integrated into an exit strategy for the P&T system, as described in Section 4.0.

3.1 Plume Dynamics

Quantifying how the plume behaved prior to P&T and how it changed over time during P&T provides information to support decisions about when shutdown may be appropriate. The following sections describe several types of information and analyses that can be compiled to evaluate plume dynamics in this context.

3.1.1 Operations Information

During operations, monitoring and evaluation of plume dynamics are used to support operational decisions. For the Hanford P&T systems, the annual summary reports for the P&T systems (e.g., DOE 2015a, b) describe the information collected and actions taken. Elements of this type of plume dynamics evaluation include 1) contaminant conditions at locations of groundwater discharge to the Columbia River are used to demonstrate protection of the river; 2) plume distribution and trends (including plume maps) are used to quantify plume changes, support plume capture assessment, and support P&T optimization decisions; 3) plume distribution and trends combined with information from other investigations for source identification and quantification are used to determine P&T and other remedy actions; and 4) treatment system performance measures for flow rate, extraction volumes, and contaminant mass extraction are used to support operational decisions and, in conjunction with other data, to quantify plume changes and demonstrate progress toward contaminant reduction objectives. Each Hanford P&T system has been collecting and reporting this information. This information about plume dynamics and associated efforts to diminish the plume is important for supporting P&T transition or closure decisions, as recognized by the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a). Transition decisions are facilitated by compiling this information for use in updating the CSM and to provide evidence of plume decline and quantification of persistent contaminant sources.

3.1.2 Additional Recommended Information and Analyses

Several types of information and analysis are recommended to improve quantification of plume dynamics in support of a transition decision and to facilitate future monitoring design for natural attenuation. Plume dynamics need to be quantified in relation to the attenuation capacity (Section 3.2) and as input to the assessment of plume behavior (Section 3.3). The following sections summarize the recommended approaches.

3.1.2.1 *Historical Source/Plume Evaluation*

Historical source/plume evaluation gives useful input to the CSM by providing context for origins of the plume (i.e., sources and driving forces that produced the plume), establishing plume migration pathways that were present prior to remediation, and potentially providing information to interpret concentration changes with distance from sources. While multiple sources, complex flow patterns, and evolving monitoring well networks may hinder these assessments, historical data should be evaluated as part of updating the CSM and providing a context for interpreting plume dynamics.

In the 100 Area, historical records of chromium plumes, especially when augmented with more recent knowledge that identified key source areas, can be used to evaluate plume migration pathways and potential attenuation after P&T systems are terminated. As an example, historical data for the 100 D Area chromium plume that existed in the vicinity of the transect associated with wells 199-D5-122, 199-D5-39, and 199-D5-38 (Figure 9) show a relatively stable plume condition from 2000 through about 2010, when P&T was initiated in this area. Based on recent information, the chromium source near the upgradient portion of the plume was identified and addressed, causing plume concentrations to decline over the last few years. Prior to that time, it is likely that the source was relatively constant for an extended time. For this situation, it may be useful to examine the concentration trends in wells along a transect downgradient of the source (i.e., wells 199-D5-122, 199-D5-39, and 199-D5-38) to quantify the rate of concentration decline downgradient from a constant source. This information (e.g., with data from the Hanford Environmental Information System) can provide context for estimating the attenuation capacity in this area of the aquifer for the chromium plume, as shown in the example in Section 3.2.

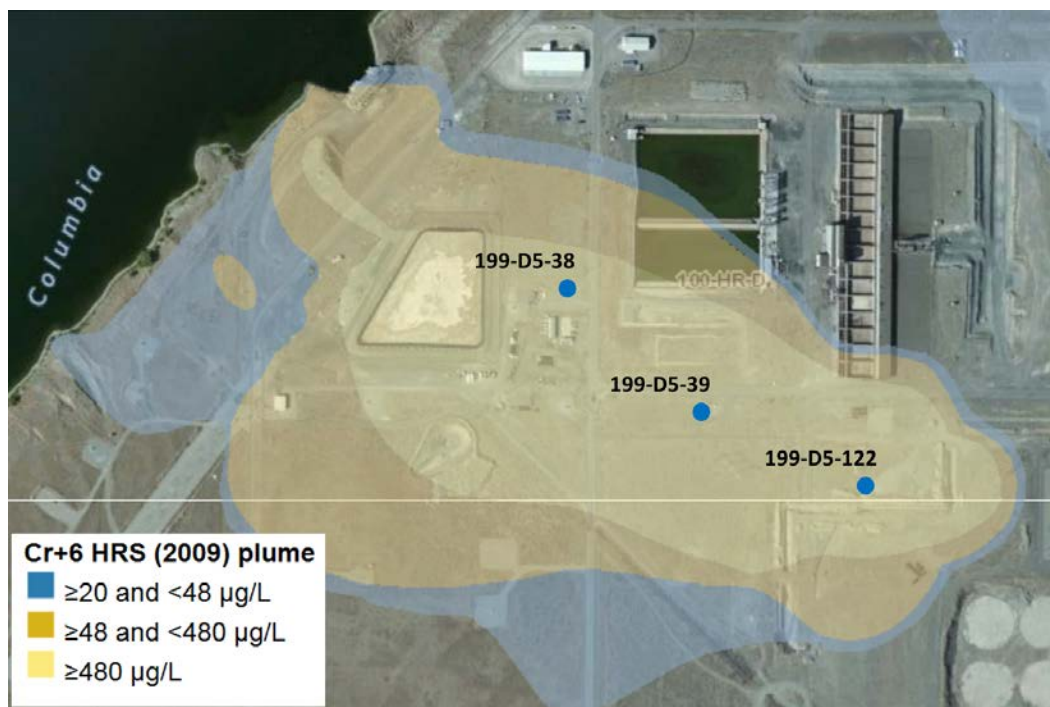


Figure 9. Depiction of the historical chromium plume in the 100D Area based on data from 2009. The plume image was obtained using the Plume Status feature of the PHOENIX web-based data tool for the Hanford Site (<http://phoenix.pnnl.gov/apps/plumes/index.html>, accessed on 8/30/2016), which uses plume images from the annual Hanford Site groundwater monitoring reports. Wells selected for the example historical plume analyses are also shown.

Source dynamics are complex in the 200 Area because of the thick vadose zone, variety of contaminant sources, and large variations in hydraulic conditions (i.e., the large hydraulic mounding of water due to aqueous discharges during the operational period in the 200 Areas) during and after waste discharges, which makes it more difficult to interpret the historical plume conditions. However, information compiled about plume conditions prior to initiating P&T operations provides context for interpreting plume changes induced by P&T.

3.1.2.2 Potential Continuing Source Evaluation

Groundwater monitoring data provide one means to evaluate whether a source is present and impacting the plume. In some cases, contaminants in the vadose (unsaturated) zone may be poised to become a contaminant source to groundwater, or to change the current contaminant discharge from a source area. Thus, to evaluate P&T shutdown or transition to natural attenuation, the expected future discharge of contaminants from vadose zone sources to the groundwater needs to be quantified. The results of this evaluation (e.g., an estimate of CMD of the source area) would be integrated into an assessment of predicted plume behavior (Section 3.3).

Truex and Carroll (2013) and Truex et al. (2015b) provide approaches for conducting vadose zone source assessments relevant to the Hanford Site. Truex et al. (2015c) and Oostrom et al. (2016) provide an example of this type of assessment at the SX Tank Farm in the Hanford 200 West Area. This assessment provides expected temporal profiles of contaminant discharge to the groundwater. Some of the vadose zone contaminants are currently causing an expanding contaminant plume. Additional vadose zone contaminants are expected to arrive at the groundwater in the future because the driving force for their transport through the vadose zone is different than the driving force for the contaminants already causing

a plume. A study using the same type of approach was applied to assess the source areas for the 200-UP-1 operable unit I-129 plume (Truex et al. 2016). This assessment estimated that the vadose zone would likely not be a continuing future source for the plume, which is consistent with the current groundwater data.

3.1.2.3 Plume/Source Dynamics during P&T

Groundwater monitoring during P&T operations is used to quantify P&T performance in diminishing contaminant plumes and provides data to quantify the plume conditions as part of assessing the potential to shut down or supplement the P&T system. The data are used to interpret plume conditions and changes during P&T and to identify zones of persistent contamination (e.g., potential continuing sources or zones that are more slowly treated). Items currently reported in the annual summary reports for the P&T systems (Section 3.1.1) provide some useful indicators of P&T performance. Several additional types of data analysis would enhance the performance assessment and be useful for optimization and in developing an exit strategy for the P&T system.

Individual Well Trends

Figure 10 shows a generic representation of extraction, injection, and monitoring wells within a plume. For Hanford P&T systems, models of predicted groundwater capture zones are available and provide flow direction and rate information that can be coupled with well concentration data for interpretation of P&T performance (DOE 2015a, b). Updating these capture zones is important for ongoing interpretation of the well concentration data. The capture analysis provides estimates of contaminant travel times between locations. Times t_{ie} and t_{im} in Figure 10 are the travel times of a clean-water front from an injection well to an extraction well and monitoring well, respectively. Times t_{pe} and t_{pm} in the figure are the travel times of groundwater from the outer/upgradient bounds of a concentration contour to a monitoring and extraction well, respectively, that are located inside the plume. These times can be calculated to represent predictions of when concentrations at the wells are expected to significantly change if conditions were similar to the ideal extraction of a dissolved contaminant plume with only equilibrium partitioning (i.e., K_d) and no contaminant sources within the capture zone. These estimates will not be exact because the value for contaminant partitioning (i.e., K_d) relevant for the travel path can only be estimated. However, the range of likely variations can be incorporated into interpretation of the travel times and well concentration data. In addition, calculation of t_{ie} and t_{pe} needs to consider the overall capture pattern and may be best quantified as a time for movement of a pore volume through the capture zone between the selected upgradient location and the extraction well.

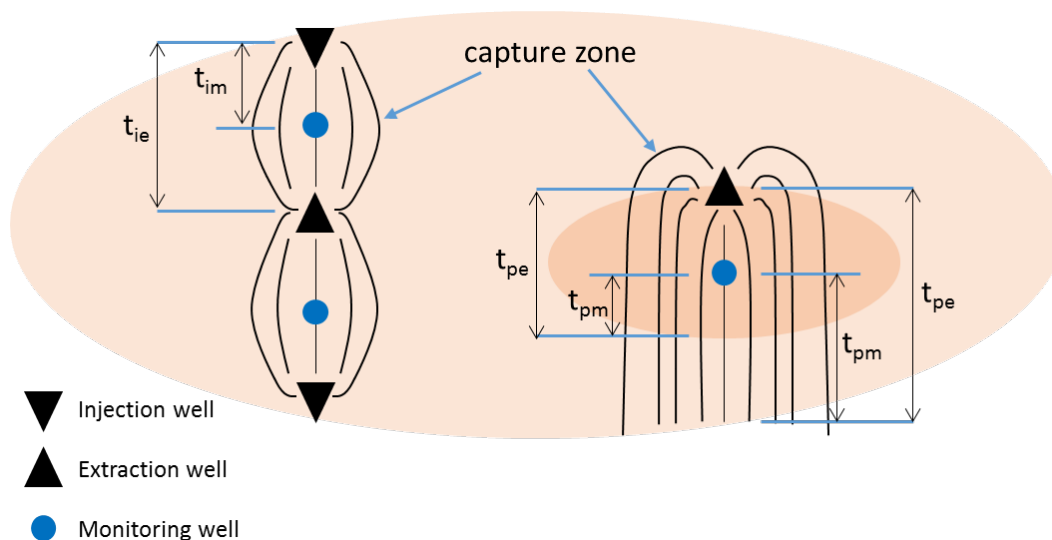


Figure 10. Conceptual depiction of a plume with P&T extraction and injection wells and corresponding idealized capture zones. With hydraulic analysis, the travel times t_{ie} and t_{im} or t_{pe} and t_{pm} can be calculated. The t_{ie} and t_{pe} can be calculated as a time for a pore volume to move within the capture zone.

At extraction and monitoring wells, data plots of the extracted concentration as a function of time describe changes in concentration associated with the groundwater flow to or past those locations. There are several basic patterns of concentration response, as shown conceptually in Figure 11. Over time (e.g., after initial dynamics, such as increases due to the relative location of wells and plume “hot spots”), well concentration profiles may follow three categories of patterns. Well data showing concentrations that remain essentially constant longer than the relevant computed travel time from Figure 10 are indicating that a continuing contaminant source(s) (primary or secondary [such as matrix diffusion]) is upgradient of the well or that the plume CSM needs to be re-evaluated. Well data showing concentrations that decline at a time consistent with the relevant computed travel time from Figure 10 but then stabilize at a higher-than-expected concentration are indicating that a continuing contaminant source(s) (primary or secondary [such as matrix diffusion]) is upgradient of the well or that the plume CSM needs to be re-evaluated. Well data showing concentrations that decline at a time consistent with the relevant computed travel time from Figure 10 and show continued decline to expected concentration levels are consistent with the plume CSM and assumption of a dissolved contaminant plume with only equilibrium partitioning and no contaminant sources within the capture zone. The above interpretations link the well concentration profile data to expected performance and provide insight into the potential for continuing sources and the validity of the CSM for the plume.

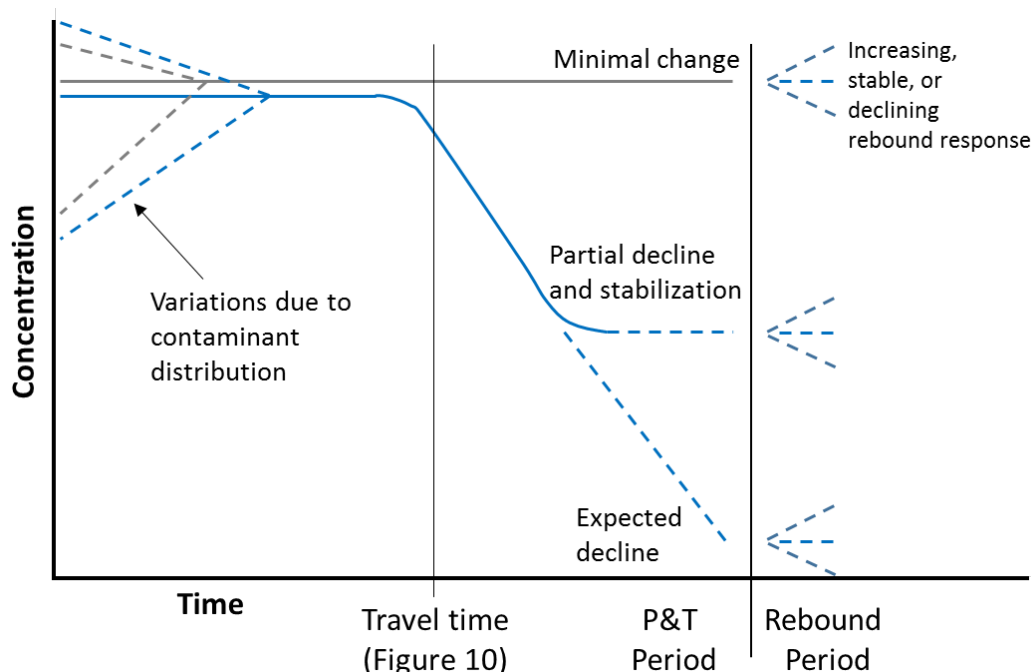


Figure 11. Conceptual depiction of a concentration trend at monitoring or extraction wells in relation to the computed travel times depicted on Figure 10.

Over time, data trends may suggest that it is appropriate to begin considering P&T shut down. As shown in Figure 11, conducting a rebound test (shutting off the P&T temporarily) is useful to confirm that concentrations measured under P&T operational conditions are not biased low due to the induced flow conditions. During a rebound test, each basic trend profile may show either an increase, decrease, or no change in concentration associated with 1) the uniformity of contaminant concentrations near the monitoring or extraction well, 2) changes in induced-flow versus natural flow pathways, and/or 3) mass-transfer/rate-limited processes (e.g., matrix diffusion or dissolution). Observed concentration changes during the rebound period need to be evaluated in terms of the plume CSM and potential impact on how the plume is quantified for comparison to objectives or for input to evaluation of natural attenuation (see Section 3.3).

At extraction and monitoring wells, actual concentration profiles will show variations associated with plume variability and seasonal changes in groundwater flow. Thus, interpretation will need to account for these variations. In particular, for wells near the river, river stage may need to be used to identify periods where well data do not represent plume conditions (e.g., these data would be removed from the plots used to interpret plume dynamics). Because of concentration variability, visual interpretation of trends should be augmented with quantitative analysis of trends to determine the slope and whether it is statistically upward, level, or downward (see Section 2.2.1.6).

Paired Well Trends

Spatial evaluation of well data may also be important to test aspects of the CSM. For instance, trends at wells near expected current or past sources can be compared to nearby upgradient and downgradient well trends. These comparisons can help with interpretation of whether the data support the CSM. However, as with the Individual Well Trend approaches above, the groundwater flow patterns and capture zones need to be considered for this assessment. This type of analysis would be useful to provide confidence that specialized conditions in the aquifer are understood sufficiently to take them into account when evaluating ongoing P&T performance or considering P&T shut down.

Plume Trends

Examination of the overall changes in the plume during P&T can be used to evaluate plume decline compared to expectations. Plume maps over time are the baseline approach for this type of assessment. Mass-based plume evaluation may also be useful to complement plume mapping. This mass-based approach (described in Section 2.2.1) enables plotting of overall plume trends, as shown conceptually in Figure 12. During P&T remediation, plumes would be expected to decline, but the rate of decline may help indicate the overall effectiveness of P&T in diminishing the plume, identify opportunities for optimization, and be used as a trigger for when transition to natural attenuation may be appropriate to consider (e.g., as is used in the 200-ZP-1 operable unit ROD). A mass-based plume analysis could be conducted using data from monitoring wells or extraction wells. For the extraction well analysis, it may be better to use mass-discharge rather than concentration data from each well so that variations in extraction flow rate over time and difference between extraction wells in the network can be incorporated into the mass assessment.

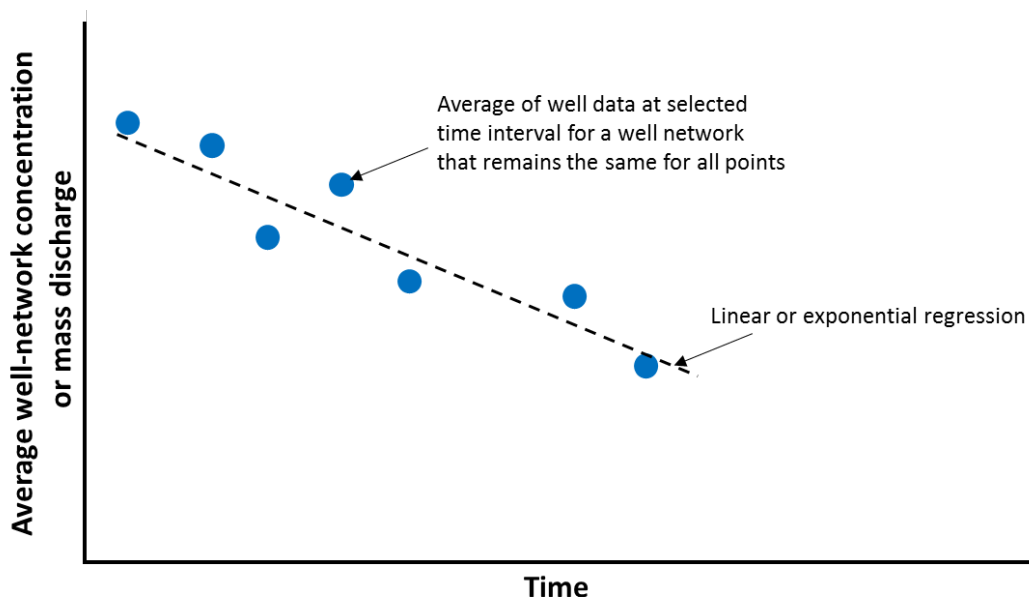


Figure 12. Conceptual depiction of a concentration or mass discharge plot for a mass-based evaluation of a plume trend.

3.2 Attenuation Capacity

All Hanford plumes being treated by a P&T system could potentially have the P&T system shut down prior to reaching RAOs, letting natural attenuation occur until these objectives are met. This transition from P&T to natural attenuation is currently included, for instance, in the ROD for the 200-ZP-1 operable unit (EPA, DOE, and WDOE 2008). The EPA has established directives and guidance for MNA (e.g., EPA 1998, 1999, 2002, 2003, 2004, 2007a, 2007b, 2010, 2011c, 2015) and there are useful resources available from other sources (e.g., ITRC 1999a, b, 2008; Truex et al. 2006, 2011, 2015a). For transition from a P&T remedy to reliance on natural attenuation as all or part of a subsequent remedy step, evaluation of natural attenuation must consider that P&T operation has altered the plume and it is difficult to directly apply some of the approaches identified for evaluating natural attenuation by EPA and others. For this condition of a transient plume, the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a) recommends that information be gathered to quantify the attenuation capacity within the portion of the aquifer where natural attenuation can be applied to stabilize

the plume and reach RAOs. This portion of the aquifer is termed the attenuation zone. It includes the existing plume footprint under P&T operations and the portion of the aquifer downgradient of this plume where, once the P&T is terminated and the plume responds to natural gradient conditions, it is acceptable for the plume footprint to adjust within this zone (i.e., temporarily expand) as natural attenuation prevents the plume from reaching receptors or a point of compliance. It would be expected that, over time, natural attenuation would then stabilize and shrink the plume to reach RAOs. The predicted plume behavior under these conditions is discussed in Section 3.3. To support those predictions, an accurate measure of the attenuation capacity is needed.

There are several methods to assess attenuation capacity. As described in Section 3.1.2.1, analysis of historical plumes may provide useful information. As an example, historical data for the concentration trends in wells along a transect downgradient of a chromium source (i.e., wells 199-D5-122, 199-D5-39, and 199-D5-38, Figure 9) can be evaluated to quantify the rate of concentration decline downgradient from this constant source. The azimuth of the path from well 199-D5-122 to well 199-D5-39 is 297° , the azimuth of the path from well 199-D5-122 to well 199-D5-38 is 303° , and the azimuth of the path from well 199-D5-39 to well 199-D5-38 is 309° . These azimuths are close to the flow path direction described by Truex et al. (2009) that occurs 10 months of the year in this area at an azimuth of 317° (average of 2007 and 2008 data). Chromium concentration data for wells in this area show a relatively stable plume condition from 2000 through about 2010, when P&T was initiated in this area. A flow-path analysis, as described in Section 2.2.3, can be conducted for well pair 199-D5-122/199-D5-39 and for well pair 199-D5-39/199-D5-38 using chromium concentration data from 2009, groundwater velocity from Truex et al. (2009, calculated from 2007-2008 hydraulic head data for the well triangle of 199-D4-20, 199-D5-43, and 199-D5-38), and a well-to-well distance measurement. This approach results in estimated first-order attenuation rate constants along this flow path of 0.68 and 0.24 yr^{-1} for the well pairs 199-D5-122/199-D5-39 and 199-D5-39/199-D5-38, respectively. This estimate accounts for any attenuation along this flow path (e.g., dilution, dispersion, or other processes) and provides a field estimate of attenuation in this zone downgradient of a source. Closer to the source, which is limited in areal extent, the attenuation rate is higher, likely due to significant dispersion. Farther downgradient, attenuation is less because lateral and vertical dispersion would be less in the more developed portion of the plume. Use of these attenuation rate estimates in a “threshold” flow-path concentration analysis is described in Section 3.3.

Modeling, with comparison to observed pre-P&T field data, can also be used to evaluate the attenuation capacity in the aquifer. As an example, the modeling applied in the 100-BC-5 remedial investigation/feasibility study document effectively quantified expected attenuation of the plume (in the absence of P&T). Similar modeling could be applied to historical plumes prior to P&T, if sufficient data were available to estimate plume behavior and the extent of attenuation in these plumes prior to P&T. It should be recognized that this attenuation was not sufficient to meet RAO objectives for the initial plume conditions (resulting in implementation of a P&T remedy). However, after the plume is diminished by P&T, this “attenuation capacity” may be suitable to polish the remaining contamination and meet RAOs.

Laboratory studies can also be applied to estimate attenuation capacity or provide evidence of attenuation processes to support attenuation evaluation. Because sorption retards contaminant transport, it can lead to some attenuation capacity, and Hanford-specific laboratory estimates for this parameter are important resources (e.g., DOE 2005, 2012; Fayer and Keller 2007; Last et al. 2006, 2009). Biogeochemical processes that sequester, remove, or degrade contaminants have also been studied and quantified in laboratory efforts and are the subject of ongoing research. As an example, laboratory studies were conducted to quantify the abiotic hydrolysis rate of carbon tetrachloride (Amonette et al. 2012) as an attenuation mechanism relevant for the 200-ZP-1 operable unit. Similarly, attenuation and transport mechanisms relevant to the Hanford Site have been evaluated for some inorganic contaminants (e.g., Truex et al. 2015d, 2016).

3.3 Predicting Plume Behavior

As with any remedy decision for groundwater, a prediction of how a plume is expected to behave after shutting down a P&T for transition to closure or natural attenuation is needed to support acceptance of the proposed action. Prediction of plume behavior requires setting a context for this assessment, defining an appropriate approach or approaches to make the prediction, and determining what type of verification for the prediction will be implemented either before or after the action is taken.

The context for a decision to shut down a P&T system for transition to closure or natural attenuation includes defining the plume and source conditions at the time of the transition, defining the hydraulic conditions (e.g., natural gradient) expected in the future, and identifying an attenuation zone (if the transition is to natural attenuation). For instance, as described in Section 2.1 (Figure 1) and Section 3.2, defining the acceptable “attenuation zone” for a transition approach is important because when P&T is shut down, the plume will no longer be manipulated (i.e., contained within a capture zone) by the induced hydraulic gradients of the pumping wells. Predictions are needed to show that, with P&T termination, the plume will stay within the existing plume area and/or within the attenuation zone. Thus, for the 100 Areas, transition of P&T to natural attenuation will be most appropriate for remnants of the plume that are inland away from the river. In this case, there is distance and time in the aquifer for attenuation to occur and meet both aquifer and surface water RAOs. In the 200 Area, hydrologic boundaries or administrative boundaries may be used to define the attenuation zone.

There are several types of approaches for predicting plume behavior after termination of P&T. Numerical modeling is the most robust approach and is appropriate given the existence of suitable models that can be adapted for this type of assessment. A key element in using a model is determining and justifying the configuration, assumptions, and input parameters. Data and analyses from the other sections of this report are targeted at developing suitable input information. It may also be useful to compile complementary data and analyses that help demonstrate the suitability of the model and/or corroborate the model results. Modeling of historical plume behavior, as discussed in Section 3.2, could be one way to complement predictive modeling. Use of a “threshold” flow-path analysis based on historical plume analysis may also be useful (Figure 13). One example stems from the flow-path analysis example discussed in Section 3.2 that resulted in estimated first-order attenuation rate constants along this flow path of 0.68 and 0.24 yr⁻¹ for the well pairs 199-D5-122/199-D5-39 and 199-D5-39/199-D5-38, respectively. Applying a “threshold” analysis as described in Section 2.2.3 estimates that a hexavalent chromium concentration of 230 µg/L at well 199-D5-122 would result in a concentration of 10 µg/L at well 199-D5-39 under natural gradient conditions, with a distance of about 175 m between these wells. For the well pair 199-D5-39/199-D5-38, more central to the former plume where attenuation processes may be more representative of post-P&T conditions (e.g., less vertical and lateral dispersion than occurred near the source area prior to P&T), a hexavalent chromium concentration of 30 µg/L at well 199-D5-39 would result in a concentration of 10 µg/L at well 199-D5-38 under natural gradient conditions, with a distance of about 190 m between these wells.

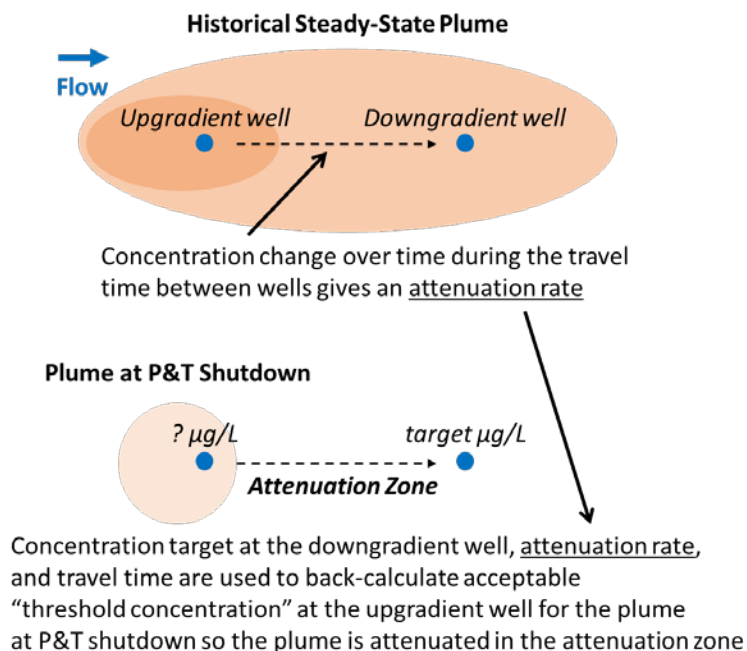


Figure 13. Conceptual depiction of how historical plume data can provide information to calculate a threshold concentration that will meet a specified downgradient concentration goal because the plume after P&T is shut down will be attenuated in the attenuation zone (see Figure 1) before reaching the target well.

Use of predictions to support a remedy decision will typically need to involve verification of predicted plume behavior. For P&T shutdown and transition, a rebound test can provide this type of verification and will supply data that can be used to refine the predictions prior to the final system shutdown. For a rebound test, the P&T system is shut down for a specified period of time, with monitoring used to 1) evaluate the response at individual wells within the plume as described in Section 3.1.2.3, and 2) monitor for plume movement based on wells within and downgradient of the plume. Collectively, these data can be compared to predicted plume behavior under natural gradient conditions. The data may also be useful to evaluate the selection of the attenuation zone. The timeframe for a rebound test can be selected based on the predicted extent of plume movement during the shutdown period to be 1) short enough that receptors are not impacted and the plume doesn't move outside capture zones for restart and 2) long enough that a change in the plume can be observed. Rebound testing in the 100 Area may be more constrained to shorter times due to the proximity of the river. However, it is expected that a rebound test would be conducted to assess the possibility that the remaining contamination inland from the river will be naturally attenuated, not for contamination adjacent to the river. Rebound time periods in the 200 West Area could be longer due to slower flow and less propensity of the plume to move outside the capture zone.

Post-decision monitoring is another approach to verify plume behavior predictions. Available natural attenuation guidance provides significant resources for designing appropriate monitoring. Key elements for a transition from P&T to natural attenuation will be use of monitoring well transects along flow paths within and just downgradient of remnant plumes that are left after P&T and are expected to naturally attenuate. By comparing the near-term responses of these plumes to expectations, predictions can be verified or questioned prior to these plumes reaching areas of concern, that is, the verification would be applied at the upgradient portion of the attenuation zone.

4.0 Exit Strategy Development

The concepts and approaches outlined in this report may be best applied prior to a proposed P&T system shutdown, in essence developing an exit strategy so that data collection relevant to making a shutdown decision begins prior to proposing the decision. Some of the analyses would only be applied near or at the time of the proposed decision. The procedures for these analyses can be included in the exit strategy to help obtain concurrence to begin the shutdown analysis process. This type of approach was previously applied at Hanford to support the shutdown of the 200-PW-1 operable unit Soil Vapor Extraction system (DOE 2014, 2016). The following sections describe the elements important to preparing an exit strategy, consistent with the guidance in the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a). For the Hanford P&T system applications, it is anticipated that the primary assessment need is to determine when a P&T system can be shut down and the remedy can be transitioned to natural attenuation for final polishing to meet the RAOs. This assessment, however, may also need to determine whether any continuing P&T or alternative treatment for persistent source areas is needed in conjunction with the natural attenuation approach.

4.1 Conceptual Site Model

A description of the CSM is important as context to support the P&T performance assessment and decisions for potential shutdown and transition to natural attenuation or other alternative approaches. As described in the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a), the CSM should be focused on the decision elements that will be needed when conducting the performance assessment. For the Hanford P&T systems, decisions are anticipated to be associated with transition to natural attenuation with consideration of potential continued targeted treatment for areas of persistent contamination.

For the 100 Area and 200 Area P&T systems, existing CSMs are available as resources to generate a CSM appropriate for supporting an exit strategy. As with the exit strategy developed for the 200-PW-1 Soil Vapor Extraction system (DOE 2014, 2016), preparing a CSM description is an important part of the exit strategy. The following are key elements of this exit-strategy CSM.

- Description of the plume setting in terms of hydrogeology, physical boundaries, and biogeochemistry affecting contaminant transport needs to be focused on elements important for interpreting plume behavior and identifying a potential attenuation zone. Information that highlights contaminant sources, natural gradient migration pathways, and attenuation mechanisms should be included.
- An assessment of historical plume dynamics (such as the example provided in Section 3.0) can be used to support the plume setting description and potentially to provide estimates of attenuation rate/capacity.
- A timeline of remedial actions (e.g., source reduction, P&T) can be interpreted in terms of how these actions relate to evolution of the plume and sources over time. This description should include a discussion of how these changes have led, or are leading to, conditions appropriate for considering P&T shutdown or transition.
- Quantitative descriptions of the plume/source distribution and contaminant transport parameters are needed to support plume analyses and modeling efforts that form the technical basis for the performance assessment decisions.

4.2 Decision Logic for Performance Assessment

A key element in developing an exit strategy for a targeted system will be to define the specific decision logic and supporting information that will be used by the decision makers. For the 100 Area and 200 Area applications of P&T systems at Hanford, decisions are anticipated to be associated with transition to natural attenuation, with consideration of potential continued targeted treatment for areas of persistent contamination. For this situation, the following example decision logic (Figure 14) adapted from the decision logic presented in the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a), may be a suitable starting point for developing the site-specific decision logic.

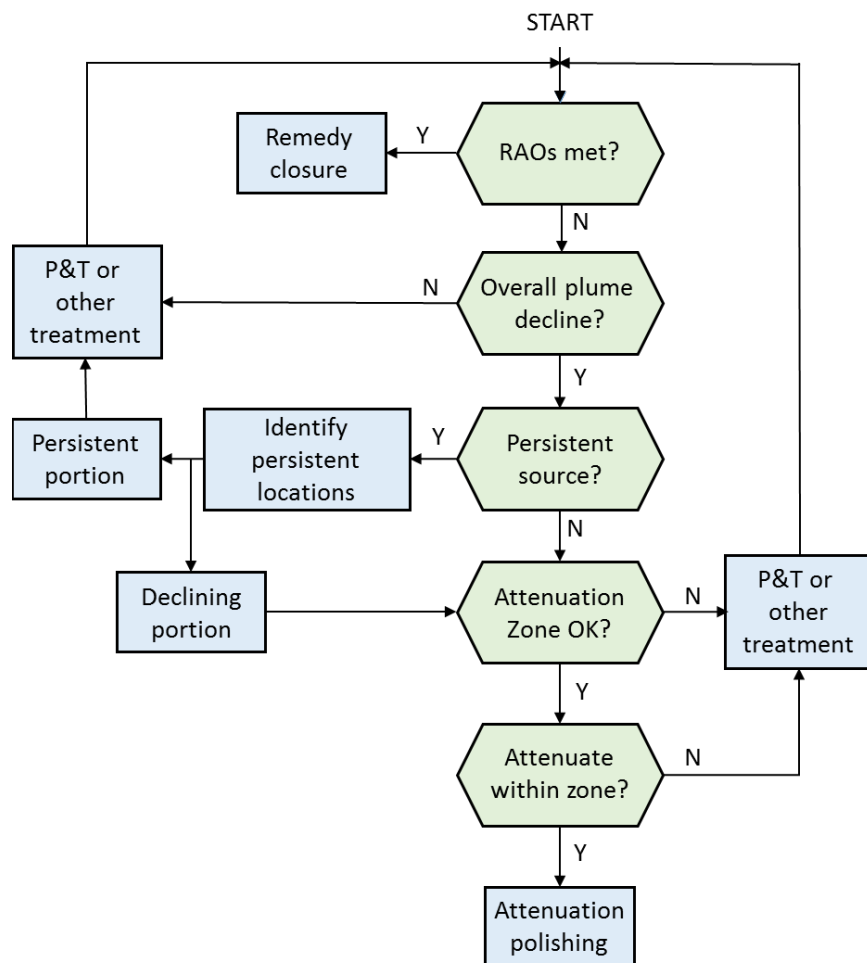


Figure 14. Example decision logic for a Hanford P&T system performance assessment.

As described in this document and by Truex et al. (2015a), the primary information need to support this decision logic includes evidence of plume decline, an assessment of plume “strength,” and assessment of continuing sources (e.g., vadose zone sources in the 200 Area or chromium calcite-dissolution sources in the 100 Area), suitable information to justify (or not) use of an attenuation zone, quantitative information about contaminant fate and transport (including attenuation capacity) under post-P&T conditions, and information about the P&T system and its performance during operations. The description of decision logic in the exit strategy should include discussion of how this type of information will be collected and used to support the decisions.

4.3 Documentation of Information

Preparing the exit strategy as a document that is reviewed and receives concurrence from the decision makers for the targeted P&T system may facilitate the processes. This type of approach was successfully used for evaluation and subsequent shutdown of the 200-PW-1 operable unit Soil Vapor Extraction system (DOE 2014, 2016). It may also be necessary to prepare additional technical documents that describe the data analysis methods and results in support of the decision logic defined in the exit strategy. However, each operable unit will need to determine the most appropriate documents to support remedy decisions associated with a P&T system performance assessment.

5.0 Quality Assurance

The Pacific Northwest National Laboratory (PNNL) Quality Assurance (QA) program is based upon the requirements as defined in the DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, Quality Assurance Requirements. PNNL has chosen to implement the following consensus standards in a graded approach:

- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, Part 1, Requirements for Quality Assurance Programs for Nuclear Facilities.
- ASME NQA-1-2000, Part II, Subpart 2.7, Quality Assurance Requirements for Computer Software for Nuclear Facility Applications, including problem reporting and corrective action.
- ASME NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

The procedures necessary to implement the requirements are documented through PNNL's "How Do I...? (HDI), a system for managing the delivery of laboratory-level policies, requirements and procedures.

The *DVZ-AFRI Quality Assurance Plan* (QA-DVZ-AFRI-001) is the minimum applicable QA document for DVZ-AFRI projects under the NQA-1 QA program. This QA Plan also conforms to the QA requirements of DOE Order 414.1D, *Quality Assurance*, and 10 CFR 830, Subpart A, *Quality Assurance Requirements*. The Deep Vadose Zone – Applied Field Research Initiative (DVZ-AFRI) is subject to the *Price Anderson Amendments Act*.

The implementation of the DVZ-AFRI QA program is graded in accordance with NQA-1-2000, Part IV, Subpart 4.2, Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development.

Three technology levels are defined for this DVZ-AFRI QA program. Within each technology level, the application process for QA controls is graded such that the level of analysis, extent of documentation, and degree of rigor of process control are applied commensurate with their significance, importance to safety, life cycle state of a facility or work, or programmatic mission.

The work for this report was performed under the technology level of Applied Research. Applied Research consists of research tasks that acquire data and documentation necessary to assure satisfactory reproducibility of results. The emphasis during this stage of a research task is on achieving adequate documentation and controls necessary to be able to reproduce results.

6.0 Conclusions and Recommendations

Performance assessment of a P&T system to support a decision about whether it is appropriate to shut down the system can be facilitated by using the approach described in the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a). The Truex et al. (2015a) document provides recommendations for the primary decision elements and the type of information that supports these decisions.

This Hanford-specific report focuses on P&T assessment for transition to natural attenuation because 1) the 200-ZP-1 and 200-UP-1 operable unit P&T systems are part of remedies where transition to natural attenuation is identified in the ROD (EPA, DOE, and WDOE 2008, 2012) and the 2) 100 Area systems target chromium plumes that are being diminished and are receding from the river such that natural attenuation may become a suitable polishing step to meet aquifer concentration objectives and the more stringent river-protection standards. Thus, for the applications of P&T at Hanford, it is anticipated that the decision process will focus on determining whether a P&T system can be shut down and transitioned to natural attenuation for final polishing to meet the RAOs, with consideration of potential continued targeted treatment for areas of persistent contamination. The contents of this report provide recommendations and resources to support this type of assessment at the Hanford Site.

For the Hanford P&T applications and associated decisions, performance assessment is expected to focus on several types of information. Because evaluation of plume attenuation will be important for Hanford P&T shutdown decisions, examining historical plume data (and data from areas where MNA was selected as the remedy) could provide useful information to demonstrate why attenuation may be a suitable polishing step. The current monitoring and evaluation of the P&T system provide a good set of baseline information for the assessment by quantifying mass removal trends and documenting optimization decisions. The availability of numerical models and results such as capture analyses can facilitate other recommended assessment components. For instance, contaminant concentration trends at individual wells or for plumes can be interpreted in the context of capture analysis information to compare observed contaminant concentration responses to expected responses. Consideration of a zone where attenuation can be allowed to occur after a P&T is shut down will be important as part of managing natural attenuation as it reduces contamination to meet the RAOs. With an appropriate attenuation zone established, incorporating attenuation capacity information into quantitative evaluation of fate and transport (e.g., using the models or other data evaluation techniques described herein) is expected to be a primary analysis supporting determination of whether P&T shutdown is acceptable. Importantly, the site should consider implementing rebound tests to provide information for the fate and transport analysis and as way to verify (or not) the expected plume response to shutdown of a P&T system.

Broadly, recommendations from this report include the following:

- Prepare an exit strategy for candidate P&T systems using this report and the *Performance Assessment for Pump-and-Treat Closure or Transition* document (Truex et al. 2015a) as resources, and incorporate this exit strategy into regulatory documents, as appropriate. This exit strategy could serve the same type of function as documents used to support the recent shutdown of the 200-PW-1 operable unit Soil Vapor Extraction system (DOE 2014, 2016).
- Align the plume and P&T system monitoring approach with the performance assessment needs identified in the exit strategy. The decision about whether a P&T system can be shut down and transitioned to natural attenuation for final polishing to meet the RAOs includes significant use of data collected during the P&T operational period.

- Plan and implement elements such as attenuation capacity evaluations (e.g., study of historical plume conditions), rebound testing, and persistent source assessments based on the needs identified in the exit strategy. These elements, along with P&T operational data, monitoring data, and modeling assessments collectively are used to quantify plume dynamics and support predictions of plume behavior that are needed as part of the decision process.

7.0 References

- 10 CFR 830, *Energy/Nuclear Safety Management*. Code of Federal Regulations, as amended.
- Amonette, JE, PM Jeffers, O Qafoku, CK Russell, DR Humphrys, TW Wietsma, and MJ Truex. 2012. *Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Final Report*. PNNL-22062, Pacific Northwest National Laboratory, Richland, Washington.
- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Application*. American Society of Mechanical Engineers, New York, New York.
- DOE. 2005. *Technical Guidance Document for Tank Closure Environmental Impact Statement Vadose Zone and Groundwater Revised Analyses, Final Rev. 0*. U.S. Department of Energy, Richland, Washington. Available at <http://www.hanford.gov/files.cfm/TCEIS-Vadose.pdf>.
- DOE. 2012. *Final Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington*. DOE/EIS-0391, U.S. Department of Energy, Richland, Washington.
- DOE. 2014. *Path Forward for Future 200-PW-1 Operable Unit Soil Vapor Extraction Operations*. DOE/RL-2014-18 Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE. 2015a. *Calendar Year 2014 Annual Summary Report for the 100-HR-3 and 100-KR-4 Pump and Treat Operations, and 100-NR-2 Groundwater Remediation*. DOE/RL-2015-05, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE. 2015b. *Calendar Year 2014 Annual Summary Report for the 200-ZP-1 and 200-UP-1 Operable Unit Pump and Treat Operations*. DOE/RL-2015-06, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE. 2016. *Endpoint Evaluation for the 200-PW-1 Operable Unit Soil Vapor Extraction System Operations*. DOE/RL-2014-48, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE Order 414.1D, *Quality Assurance*. U.S. Department of Energy, Washington, D.C.
- EPA. 1998. *Technical Protocol for Evaluation Natural Attenuation of Chlorinated Solvents in Groundwater*. EPA/600/R-98/128, U.S. Environmental Protection Agency, Washington, D.C.
- EPA. 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*. OSWER Directive 92000.4-17P, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.
- EPA. 2002. *Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies*. EPA/540/S-02/500, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio.
- EPA. 2003. *Performance Monitoring for Natural Attenuation Remedies in Ground Water*. EPA/540/R-03/004, U.S. Environmental Protection Agency, Washington D.C.

EPA. 2004. *Performance Monitoring of MNA Remedies for VOCs in Ground Water*. EPA/600/R-04/027, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, Ohio.

EPA. 2007a. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water - Volume 1, Technical Basis for Assessment*. EPA/600/R-07/139, U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2007b. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water – Volume 2, Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel, Nitrate, Perchlorate, and Selenium*. EPA/600/R-07/140, U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2010. *Monitored Natural Attenuation of Inorganic Contaminants in Ground Water – Volume 3, Assessment for Radionuclides Including Tritium, Radon, Strontium, Technetium, Uranium, Iodine, Radium, Thorium, Cesium, and Plutonium-Americium*. EPA/600/R-10/093, U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2011a. *Groundwater Road Map: Recommended Process for Restoring Contaminated Groundwater at Superfund Sites*. OSWER 9283.1-34, U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2011b. *Close Out Procedures for the National Priorities List Sites*. OSWER 9320.2-22, U.S. Environmental Protection Agency, Washington, D.C.

EPA. 2011c. *An Approach for Evaluating the Progress of Natural Attenuation in Groundwater*. EPA/600/R-11/204, U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Ada, Oklahoma.

EPA. 2013. *Guidance for Evaluating Completion of Groundwater Restoration Remedial Actions*. OSWER 9355.0-129, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

EPA. 2014a. *Groundwater Remedy Completion Strategy*. OSWER 9200.2-144, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

EPA. 2014b. *Recommended Approach for Evaluating Completion of Groundwater Restoration Remedial Actions at a Groundwater Monitoring Well*. OSWER 9283.1-44, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

EPA. 2015. *Use of Monitored Natural Attenuation for Inorganic Contaminants in Groundwater at Superfund Sites*. OSWER Directive 9283.1-36, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

EPA, Ecology, and DOE. 2008. *Record of Decision Hanford 200 Area 200-ZP-1 Superfund Site, Benton County, Washington*. U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy, Olympia, Washington.

EPA, Ecology, and DOE. 2012. *Record of Decision for Interim Remedial Action, Hanford 200 Area Superfund Site, 200-UP-1 Operable Unit*. U.S. Environmental Protection Agency, Washington State Department of Ecology, and U.S. Department of Energy, Olympia, Washington.

Fayer MJ, and JM Keller. 2007. *Recharge Data Package for Hanford Single-Shell Tank Waste Management Areas*. PNNL-16688, Pacific Northwest National Laboratory, Richland, Washington.

Fortune S. 1987. "A Sweepline Algorithm for Voronoi Diagrams." *Algorithmica* 2:153-174.

Hjelle Ø and M Dæhlen. 2006. *Triangulations and Applications*. Springer-Verlag, Berlin. 234 pp.

ITRC. 1999a. *Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices*. ISB-3, Interstate Technology and Regulatory Council, Washington, D.C. Available at <http://www.itrcweb.org/GuidanceDocuments/ISB-3.pdf>.

ITRC. 1999b. *ITRC/RTDF Training Course: Natural Attenuation of Chlorinated Solvents in Groundwater*. ISB-7, Interstate Technology and Regulatory Council, Washington, D.C. Available at <http://www.itrcweb.org/GuidanceDocuments/ISB-7.pdf>.

ITRC. 2008. *Enhanced Attenuation: Chlorinated Organics*. EACO-1, Interstate Technology and Regulatory Council, Washington, D.C. Available at <http://www.itrcweb.org/GuidanceDocuments/EACO-1.pdf>.

ITRC. 2011b. *Integrated DNAPL Site Strategy*. IDSS-1, Interstate Technology and Regulatory Council, Washington, D.C. Available at: http://www.itrcweb.org/GuidanceDocuments/IntegratedDNAPLStrategy_IDSSDoc/IDSS-1.pdf.

ITRC. 2015. *Remediation Management of Complex Sites*. Interstate Technology and Regulatory Council, Washington, D.C. Available at <http://www.itrcweb.org/Team/Public?teamID=64>.

Last, GV, EJ Freeman, KJ Cantrell, MJ Fayer, GW Gee, WE Nichols, BN Bjornstad, and DG Horton. 2006. *Vadose Zone Hydrogeology Data Package for Hanford Assessments*. PNNL-14702, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Last, GV, ML Rockhold, CJ Murray, and KJ Cantrell. 2009. *Selection and Traceability of Parameters to Support Hanford-Specific RESRAD Analyses, Fiscal Year 2008 Status Report*. PNNL-18564, Pacific Northwest National Laboratory, Richland, Washington.

NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*. American Society of Mechanical Engineers, New York, New York.

NRC. 2013. *Alternatives for Managing the Nation's Complex Contaminated Groundwater Sites*. National Academy of Sciences, Washington, D.C.

Oostrom M, M. Truex, GV Last, CE Strickland, and GD Tartakovsky. 2016. "Evaluation of Deep Vadose Zone Contaminant Flux into Groundwater: Approach and Case Study." *Journal of Contaminant Hydrology* 189:27-43.

Tipper JC. 1991. "FORTRAN programs to construct the planar Voronoi diagram." *Comp. Geosci.* 17(5):597-632.

Truex MJ, CJ Newell, BB Looney, and K Vangelas. 2006. *Scenarios Evaluation Tool for Chlorinated Solvent Monitored Natural Attenuation*. WSRC-STI-2006-00096, Washington Savannah River Company, Aiken, South Carolina.

Truex, MJ, VR Vermeul, BG Fritz, RD Mackley, DP Mendoza, RP Elmore, AV Mitroshkov, DS Sklarew, CD Johnson, M Oostrom, DR Newcomer, FJ Brockman, CL Bilskis, SS Hubbard, JE Peterson, KH Williams, E Gasperikova, and J Ajo-Franklin. 2009. *Hanford 100-D Area Biostimulation Treatability Test Results*. PNNL-18784, Pacific Northwest National Laboratory, Richland, Washington.

Truex MJ, PV Brady, CJ Newell, M Rysz, M Denham, and K Vangelas. 2011. *The Scenarios Approach to Attenuation Based Remedies for Inorganic and Radionuclide Contaminants*. SRNL-STI-2011-00459, Savannah River National Laboratory, Aiken, South Carolina. Available at www.osti.gov, OSTI ID 1023615, doi: 10.2172/1023615.

Truex MJ and KC Carroll. 2013. *Remedy Evaluation Framework for Inorganic, Non-Volatile Contaminants in the Vadose Zone*. PNNL-21815, Pacific Northwest National Laboratory, Richland, Washington.

Truex MJ, CD Johnson DJ Becker, MH Lee, and MJ Nimmons. 2015a. *Performance Assessment for Pump-and-Treat Closure or Transition*. PNNL-24696, Pacific Northwest National Laboratory, Richland, Washington.

Truex MJ, M Oostrom, and GD Tartakovsky. 2015b. *Evaluating Transport and Attenuation of Inorganic Contaminants in the Vadose Zone for Aqueous Waste Disposal Sites*. PNNL-24731, Pacific Northwest National Laboratory, Richland, Washington.

Truex, MJ, M Oostrom, GV Last, CE Strickland, and GD Tartakovsky. 2015c. *Evaluating Contaminant Flux from the Vadose Zone to the Groundwater in the Hanford Central Plateau: SX Tank Farms Case Study*. PNNL-23737, Pacific Northwest National Laboratory, Richland, Washington.

Truex MJ, JE Szecsody, NP Qafoku, R Sahajpal, L Zhong, AR Lawter, and BD Lee. 2015d. *Assessment of Hexavalent Chromium Natural Attenuation for the Hanford Site 100 Area*. PNNL-24705, Pacific Northwest National Laboratory, Richland, Washington.

Truex MJ, BD Lee, CD Johnson, NP Qafoku, GV Last, MH Lee, and DI Kaplan. 2016. *Conceptual Model of Iodine Behavior in the Subsurface at the Hanford Site*. PNNL-24709, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.



Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

U.S. DEPARTMENT OF
ENERGY

www.pnnl.gov