U.S. Department of Energy Office of Environmental Management



# **Paducah Gaseous Diffusion Plant**

Review Report: Groundwater Remedial System Performance Optimization at PGDP, Paducah, Kentucky



Prepared for:

Office of Groundwater and Soil Remediation Office of Engineering and Technology

May 24, 2007

#### **EXECUTIVE SUMMARY**

The U.S. Army Corps of Engineers led a Remediation System Evaluation (RSE) of the Northeast and Northwest Extraction Systems at the Paducah Gaseous Diffusion Facility, Paducah Kentucky, from October 16-20, 2006. These extraction systems are currently operated by Paducah Remediation Services for U.S. Department of Energy (DOE) Paducah under a Comprehensive Environmental Response, Compensation, and Liability Act interim remedial action. DOE Paducah installed the two extraction systems in 1995 and 1997, to provide hydraulic control of the high concentration portion of the trichloroethylene and technetium-99 groundwater plume. The site exit strategy includes phase-out of the existing extraction systems through source treatment, containment, and in-situ treatment of the dissolved phase groundwater plumes. Optimization of the Northeast and Northwest Extraction Systems is prudent until such time that the systems are replaced and the source areas are treated.

The Review Team conducting the RSE made the following ten recommendations based on findings of the review report:

- 1) Place the Northeast Plume Extraction System on stand-by and develop an earlywarning detection strategy.
- 2) Characterize and evaluate the influence of source(s) near Solid Waste Management Units 30 and 7.
- 3) Modify the Northwest Plume Extraction System.
- 4) Consider innovative treatment approaches for discharge seeps along Little Bayou Creek.
- 5) Further characterize factors affecting migration of the Southwest Plume.
- 6) Update the site groundwater model and assess future plume migration.
- 7) Evaluate other potentially applicable remedial technologies.
- 8) Re-evaluate the basis for change-out of resins and carbon in the treatment train.
- 9) Reduce the frequency of process monitoring, as well as remote well and equipment checks.
- 10) Re-evaluate the approach to extraction well rehabilitation.

# **TABLE OF CONTENTS**

1.0	INTRODUCTION - PURPOSE AND PERSONNEL INVOLVED	1
1.1	Purpose	1
1.2	RSE Team Composition	1
1.3	Site Visit, Presentations, and Persons Contacted	2
1.4	Site Background	2
1.5	Previous Remedial Assessments of the Extraction Systems	8
1.6	Remediation System Evaluation Process	9
1.7	Positive Observations	9
1.8	Integration of Groundwater Strategy with Facility Programmatic Strategy	10
2.0	RECOMMENDATIONS	13
2.1	Place Northeast Plume Extraction System on Stand-by and Develop Early-	
	Warning Strategy	13
2.2	Investigate Possible Source Area Near SWMU 30 and 7	15
2.3	Modify Northwest Plume Extraction System	17
2.4	Consider Innovative Treatment Approach for Seeps Area along Little	
	Bayou Creek	22
2.5	Further Characterize Factors Affecting Migration of Southwest Plume	23
2.6	Update Site Groundwater Model and Reassess Plume Migration	25
2.7	Recommendations for Other Potentially Applicable Technologies	28
2.8	Re-evaluate Basis for Change-Out of Resins and Carbon	29
2.9	Reduce Frequency of Process Monitoring and Remote Well and	
	Equipment Checks	32
2.10	Re-evaluate Approach to Extraction Well Rehabilitation	34
3.0	SUMMARY	35
4.0	REFERENCES	36
Appe Resta	ndix - Potential Contingent Strategy for Northeast Plume Extraction System art	37
TAB	LES	
Table	e 1 – Summary of Recommendations	35
FIGU	JRES	
Figur	re 1 Trichloroethylene Plume Locations at PGDP	4
Figur	•	5
Figur		6
0	ii	

Figure 4	Particle Tracking for the Southwest Plume at the PGDP	7
Figure 5	A Range of Technologies is Needed to Match Site Conditions	12
Figure 6	TCE Concentrations over Time in Northwest Plume Extraction We	lls
		13
Figure 7	TCE Concentrations over Time in Northeast Plume Extraction Wel	ls
_		14
Figure 8	Water Levels over Time in Monitoring Well 66	15
Figure 9	<b>Concentrations over Time of TCE and <sup>99</sup>Tc in Monitoring Well 66</b>	15
Figure 10	Location of Wells in the Vicinity of the Northwest Plume	18
Figure 11	TCE Concentrations over Time, Northern Extraction Wells	19
Figure 12	TCE Concentrations over Time, Southern Extraction Wells	20
Figure 13	<sup>99</sup> Tc Concentrations over Time in Southern Extraction Wells	22
Figure 14	Schematic of a Geosiphon	23
Figure 15	TCE Concentrations over Time in MW84	25
Figure 16	Effluent 99Tc Concentrations over Time from Lead Ion-Exchange	
	Vessel	30

# Acronyms

μg/L ATSDR	micrograms (10 <sup>-6</sup> grams) per liter Agency for Toxic Substances and Disease Registry
CERCLA	Comprehensive Environmental Response, Compensation, and Liablity Act
DoD	United States Department of Defense
DOE	United States Department of Energy
EM	Environmental Management
EPA	United States Environmental Protection Agency
ERDC	Engineer Research and Development Center, USACE
ES	EnergySolutions
EW	Extraction Well
ft	feet
GAC	granular activated carbon
GC	gas chromatograph
gpm	gallons per minute
HQ	Headquarters
HTRW CX	Hazardous, Toxic, and Radioactive Waste Center of Expertise, USACE
ITRC	Interstate Technology and Regulatory Council
KRCEE	Kentucky Research Consortium for Energy and the Environment
LLMW	low-level mixed waste
MCL	Maximum Contaminant Level
msl	mean sea level
MW	Monitoring Well
O&M	Operation and Maintenance
pCi/L	picocuries (10 <sup>-12</sup> Curies) per liter
PGDP	Paducah Gaseous Diffusion Plant
POC	point of compliance
POE	point of exposure
PRS	Paducah Remediation Services
RGA	Regional Gravel Aquifer
ROD	Record of Decision
RSE	Remediation System Evaluation
UCRS	Upper Continental Recharge System
SRNL	Savannah River National Laboratory
SWMU	Solid Waste Management Unit
<sup>99</sup> Tc	technetium 99
TCE	trichloroethylene
USACE	United States Army Corps of Engineers
VP	vapor phase

## 1.0 INTRODUCTION - PURPOSE AND PERSONNEL INVOLVED

# 1.1 Purpose

At the request of the U.S. Department of Energy (DOE), Headquarters' (HQ) Office of Environmental Management, the Office of Groundwater and Soil Remediation (EM-22) secured the services of the U.S. Army Corps of Engineers (USACE) to lead a Remediation System Evaluation (RSE) of the Northeast and Northwest Extraction Systems at the Paducah Gaseous Diffusion Plant (PGDP), Paducah Kentucky, from October 16-20, 2006. These extraction systems are currently operated by Paducah Remediation Services LLC (PRS) for DOE under a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) interim remedial action. DOE Paducah installed the two extraction systems in 1995 and 1997 to provide hydraulic control of the high concentration portions of the trichloroethylene (TCE) and technetium-99 (<sup>99</sup>Tc) groundwater plumes. The site exit strategy includes phase-out of the extraction systems through source treatment, containment, and in-situ treatment of the dissolved phase groundwater plumes. Optimization of the Northeast and Northwest Extraction Systems is prudent until such time that the systems are replaced and the source areas are treated.

# 1.2 RSE Team Composition

The team conducting the RSE consisted of the following individuals:

- Beth Moore, US DOE Headquarters; Hydrogeologist and Review Project Manager
- Dave Becker, USACE; Geologist and Review Team Leader
- Lindsey Lien, USACE; Environmental Engineer and Team Member
- Rob Greenwald, GeoTrans, Inc; Hydrogeologist and Team Member
- Brian Looney, Savannah River National Laboratory (SRNL); Geochemist and Team Member

# 1.3 Site Visit, Presentations, and Persons Contacted

The Review Team convened at DOE Paducah from October 16-20, 2006, to conduct a site visit and inspection of the remedial systems under evaluation. Presentations were given by PRS staff on October 17, 2006, as detailed below. The extraction systems were inspected by the Review Team on October 18, 2006. An outbriefing of initial RSE

observations and recommendations from the site visit was presented to DOE and PRS staff on October 19, 2006, by the Review Team Lead, Dave Becker.

- Bryan Clayton, PRS; Introduction, Regulatory Drivers and Actions, Source Areas, and Modeling Design Basis
- Fraser Johnstone, PRS; System Design, Modification, Operation, Performance, and Assessment
- Ken Davis, PRS; Groundwater Monitoring Reports

The following individuals were contacted during the RSE to obtain their observations and input on the conduct of groundwater and systems operations, as well as conceptual and mathematical model development.

- Steve Golian, DOE HQ
- David Dollins, DOE Paducah
- Rich Bonczek, DOE Paducah
- Karen Vangelas, SRNL
- Bruce Phillips, Navarro
- Al Laase, PRS
- John Morgan, PRS
- Chris Richards, PRS
- Joe Tarantino, PRS
- Dave Ashburn, PRS
- Stan Knaus, PRS
- Mike Clark, PRS
- Tracy Brindley, PRS
- Michelle Hope Lee, Northwind, Inc.

#### **1.4** Site Background

The Paducah site has soil and groundwater contamination by chlorinated solvents, principally trichloroethylene (TCE; Figure 1), as well as technetium-99 (<sup>99</sup>Tc; Figure 2). Contaminated groundwater extends beyond the plant boundaries, with some discharge to surface waters downgradient, primarily Little Bayou Creek to the west and northeast of the DOE property boundaries, respectively. To date, the principal offsite risk is due to TCE, and the predominant source of TCE is south and southeast of Building C 400. Building C 400 is coincident with the highest TCE concentrations (i.e., the centroid) in the northwest plume (Figure 1). A source of <sup>99</sup>Tc contamination in groundwater is also in the C 400 area. The site also has numerous hazardous and radioactive burial grounds, some of which are confirmed sources contributing contaminants, primarily TCE and <sup>99</sup>Tc,

to soil and groundwater. The burial grounds are likely future sources of solvents, metals, and radioisotopes that may further contaminate the soil and groundwater.

The subsurface of the site has three principal zones (Figure 3): 1) the Upper Continental Recharge System (UCRS is 0-50 feet deep at C 400); 2) the Regional Gravel Aquifer (RGA is 50-100 feet deep); and 3) the underlying McNairy Formation. Contaminants (TCE and <sup>99</sup>Tc primarily) have been detected in all three zones. To the north of the plant, TCE and <sup>99</sup>Tc are present in the RGA beyond the DOE property boundary. <sup>99</sup>Tc is migrating offsite primarily via the Northwest Plume (Figure 2), and to a lesser degree, via the Northeast Plume. TCE and <sup>99</sup>Tc (Figures 1 and 2, respectively) are also found in RGA groundwater of the Southwest Plume that is migrating in a west-northwest direction. The Southwest Plume is believed to be contained within the DOE property boundary. Particle tracking of the Southwest Plume (Figure 4) indicates that a portion of the plume may migrate to the northwest, and then to the north; another portion of plume may merge into the Northwest Plume before reaching the Ohio River and/or associated river deposits. It is important to note that source areas for the Northwest and Northeast Plumes are also potential sources for the Southwest Plume.

In 2002, the Agency for Toxic Substances and Disease Registry (ATSDR) published a Public Health Assessment for the PGDP, and concluded that "the facility poses no apparent public health hazard for the surrounding community from exposure to groundwater, surface water, soil, biota, or air." The following select ATSDR recommendations are pertinent as background information:

- o Prevent installation of new wells in the contaminated groundwater plume areas through institutional controls.
- o Prevent the future use of contaminated wells by disconnecting water pipes to homes or businesses and plugging or dismantling wells.
- o Continue groundwater monitoring, including monitoring in areas possibly affected by the plumes and areas near Little Bayou Creek and Bayou Creek, and the North-South Diversion Ditch.
- o Ensure that detection limits of degradation products of TCE, such as vinyl chloride, in the groundwater analyses are low enough to determine whether concentrations exceed health-based guidelines.
- o Continue monitoring the McNairy Aquifer wells to detect possible migration of contaminants from the RGA—if monitoring wells do not create a conduit for vertical migration.
- o Continue to restrict access to Little Bayou Creek, the outfalls, and the North-South Diversion Ditch. Determine if the existing signage adequately restricts public access to the southwest inactive landfill and the adjoining area.
- o Continue monitoring biota to ensure that it is safe to consume.

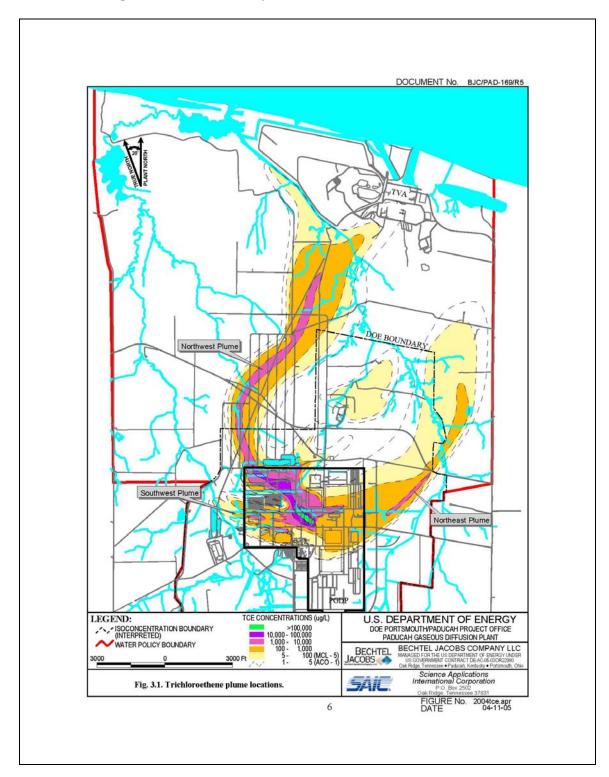


Figure 1. Trichloroethylene Plume Locations at the PGDP.

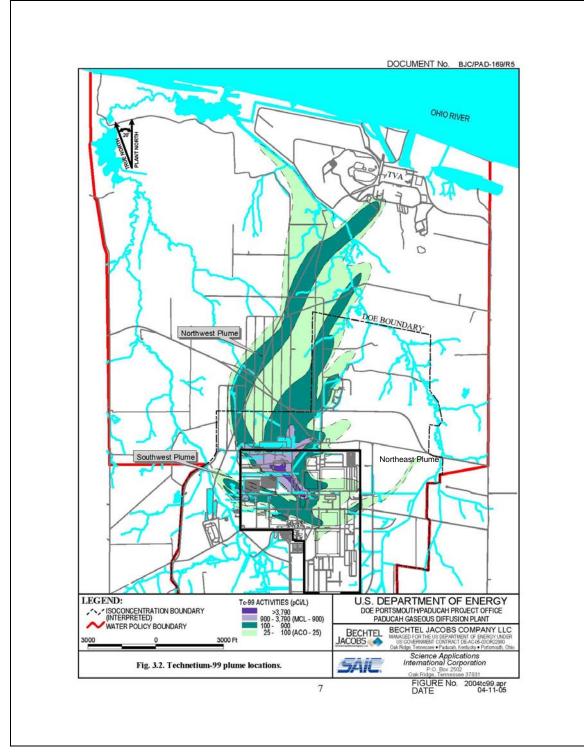


Figure 2. Technetium-99 Plume Locations at the PGDP.

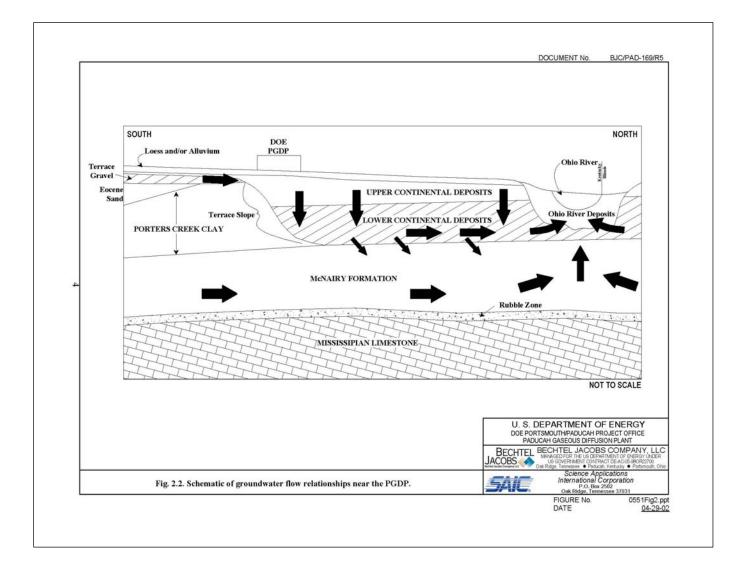


Figure 3. Schematic of Conceptual Site Model Near the PGDP.

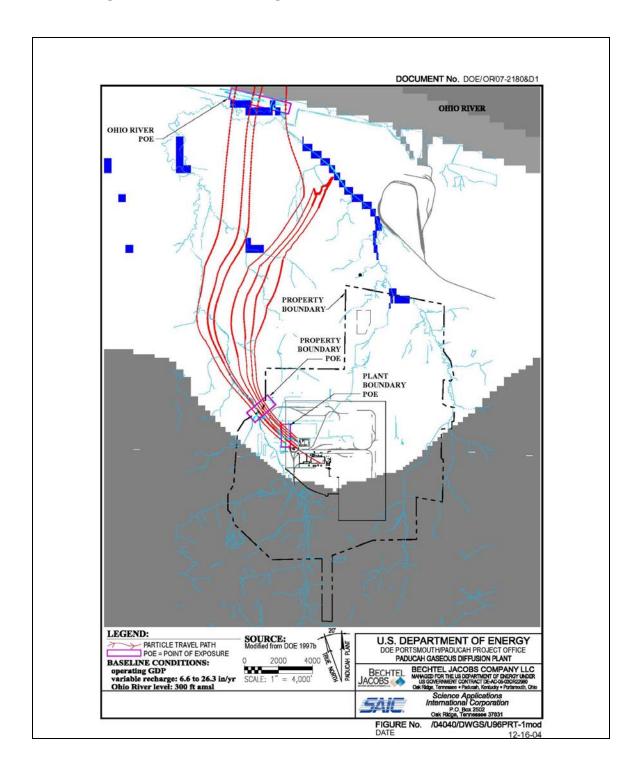


Figure 4. Particle Tracking for the Southwest Plume at the PGDP.

#### 1.5 Previous Remedial Assessments of the Extraction Systems

CERCLA requires periodic effectiveness reviews to assess remedial progress and, if necessary, to apply lessons learned and evolving knowledge to refine remedial action objectives (RAOs), and the means of attaining RAOs. In February-March 2006, DOE HQ conducted a Site Wide Remedy Review at the PGDP, including an assessment to identify any potential barriers to success for full implementation of the CERCLA Interim Record of Decision (ROD) for TCE source removal at Building C 400. The 2006 Site Wide Remedy Review constitutes an effectiveness review, and generally follows the Remedial Process Optimization (RPO) guidance published by the Interstate Technology & Regulatory Council (ITRC, 2004).

Recommendations of the Site Wide Remedy Review Report corroborate, at a minimum, the "Recommendations and Follow-up Actions" for the CERCLA Five-Year Review Report issued by DOE in December 2003. That is, page xiv of the CERCLA report specifically recommends evaluation of extraction well optimization for the Northwest Plume pump-and-treat system until a final remedy is determined. One reason given for this follow-up action is that the high concentration core of the Northwest Plume (at the north extraction well field) has migrated eastward and is bypassing the capture zone of the well field. It is consistent with the ROD and the Five-Year Review findings to modify the remedy in order to provide more cost-effective capture of the plumes.

For the Northeast Plume, it is noted that <sup>99</sup>Tc contamination may migrate into the area of the extraction well field (DOE, 2003). The Northeast Plume Containment System is not capable of removing <sup>99</sup>Tc extracted from the Regional Gravel Aquifer (RGA), thereby requiring a contingency plan for early-warning detection and trend analysis of <sup>99</sup>Tc at upgradient Monitoring Well (MW) 292. The contingency plan states that should <sup>99</sup>Tc be confirmed in MW292, DOE Paducah will have to provide treatment capabilities. Some of the monitoring wells upgradient of the Northeast pump-and-treat system have shown increasing <sup>99</sup>Tc trends (e.g., MW256), though the concentrations are still well below the groundwater cleanup goal of 900 pCi/L.

The CERCLA 2003 Five-Year Review report further states that the interim pump-andtreat remedies implemented for the Northwest and Northeast Plume Interim Actions are not protective over the long term. Both the Northeast and Northwest Containment Systems were approved as interim actions and are meant to limit the contaminant migration, with anticipated shutdown and replacement by other treatment systems, such as an in situ permeable reactive barrier. It is likely to require several years before shutdown and replacement can be accomplished for the Northwest Plume system. The Review Team recognizes that the timing and impacts of future changes in plant operations, such as ceasing enrichment, could impact the need for replacement systems. The 2006 Site Wide Remedy Review Team concluded that optimization of the interim pump-and-treat systems could increase contaminant mass removal and save operational costs. In 2006, the combined annual operational and maintenance (O&M) cost for the Northwest and Northeast systems exceeded \$1.5 million. Future annual costs under a revised contract will be approximately \$1 million. In 2001, EPA reported that the average annual cost of O&M of a EPA-funded pump-and-treat system (based on 79 systems analyzed) was \$570,000, with a median cost of \$350,000. The 2003 CERCLA Five-Year Review Report for PGDP states that the Northeast Plume treatment system removed a total of 160 gallons of TCE at a cost of about \$7,000 per gallon since it began operation in February 1997. Similarly, the Northwest Plume treatment system removed a total of 1,623 gallons of TCE at a cost of about \$11,000 per gallon since operation began in August 1995. Of the estimated 250,000+ gallons of TCE present in the UCRS and RGA from the Building C 400 source area alone, 1,800 gallons has been removed via the extraction wells in 2003, at a cost exceeding \$18 million, or \$10,000 per gallon.

#### 1.6 Remediation System Evaluation Process

The USACE Hazardous, Toxic, and Radioactive Waste Center of Expertise (HTRW CX) developed the Remediation System Evaluation (RSE) process in the late 1990s. RSEs are meant to be low-cost, rapid assessments of available information and current conditions; not detailed engineering or technical studies. The RSEs consist of data and report review, interviews, a site visit, data analysis, and report generation.

There are several reasons to use the RSE process. This is a small effort, in cost and time, to potentially provide significant benefits to the project. The RSE process is intended to:

- Identify ways to save money on operations and maintenance
- Shorten the time to closure, through periodic optimization and consideration of new technologies
- Support periodic (e.g., Five-Year) reviews of the protectiveness and performance of the remedy
- Verify that there are clear goals and realistic closure criteria for the project
- Assure that Government-owned equipment is being adequately maintained

The US Environmental Protection Agency (EPA) has generally adopted the RSE process to assess performance and cost saving opportunities at its fund-financed sites.

#### **1.7 Positive Observations**

The Review Team found a very motivated and capable project team looking for ways to improve the existing remedies at the site. The Northwest Plume treatment plant was well maintained. The project team members, both from DOE and contractors, were very helpful during the Review Team's efforts. The Review Team greatly appreciates the assistance and hospitality from all involved.

#### **1.8** Integration of Groundwater Strategy with Facility Programmatic Strategy

The development of a credible risk-based end-state is underway at the PGDP (DOE, 2005). While developing consensus on such overarching strategic efforts is always challenging, the Review Team strongly supports continuing development and efforts toward integration. This recommendation is particularly pertinent to the plans to address the contaminants (primarily the solvents and <sup>99</sup>Tc) in groundwater, given that the current regulations governing the groundwater cleanup do not necessarily encourage, nor require, that the decisions and actions be integrated into an overall vision for the site and the surrounding area. In isolation, a legally acceptable approach to addressing the groundwater plumes can be developed. However, when coordinated with the overall facility programmatic strategy, the Review Team believes that a legally acceptable, but potentially more optimal, solution is achievable. The integrated model for groundwater strategy development will minimize the potential for a risk transfer cycle in which collateral impacts and lost environmental services are insufficiently considered or valued. The key objectives in the integration process are those that are already identified in the current PGDP End State Vision (DOE, 2005):

- Protect residential receptors
- Protect recreational users
- Protect industrial workers
- Protect environmental receptors

The PGDP groundwater contaminant plumes are large with widely varying contaminant concentrations and biogeochemical conditions. Central to the integration and optimization of the groundwater strategy at PGDP is a careful matching process in which the strengths of the response action are matched to site conditions and needs, while poorly matched technologies or incompatible technologies are avoided. This is depicted graphically in Figure 5. This figure depicts a continuum of technology classes applicable to soil and groundwater contamination with aggressive technologies (e.g., excavation, thermal treatment or chemical oxidation) on the left ranging to more passive technologies (e.g., monitored natural attenuation) on the right. The technologies are roughly overlaid on the general structure of a contaminant plume in the environment – with the various technology classes matched to the appropriate target portion of the contaminant plume and with specific example technologies within the class identified. Several idealized plume structures are presented, from top to bottom, depicting the expected changes through time as the plume undergoes remediation.

As depicted in Figure 5, selected technologies should match the target conditions throughout the plume and criteria should be developed up front for transitioning to less aggressive and less intrusive technologies at appropriate times – in this manner, adverse collateral impacts are minimized, energy use is optimized and the overall protection of the environment is encouraged. The recommended approach is one that is aware, and responsive to, the collateral impacts on the potential "risk receivers." For example, environmental technologies that use strong chemical reagents or large amounts of energy

reduce local contamination levels in a source zone, but could transfer risk to the broader environment through energy use and/or ecological damage – factors that may not be considered in either the technology selection process or the implementation and design. How does one account for and balance the benefits and damages from an environmental cleanup process? Where are the more aggressive technologies justified? What technologies are appropriate for sites where contamination levels are relatively low? In developing and optimizing the groundwater strategy for PGDP, the Review Team supports consideration of those factors listed above and the following factors: coupling groundwater decisions with the amount of source treatment needed (and addressing additional sources that are identified), land and energy use, natural attenuation rates and mechanisms, and the potential for enhancing such mechanisms either in the subsurface or in vicinity of the discharge zone.

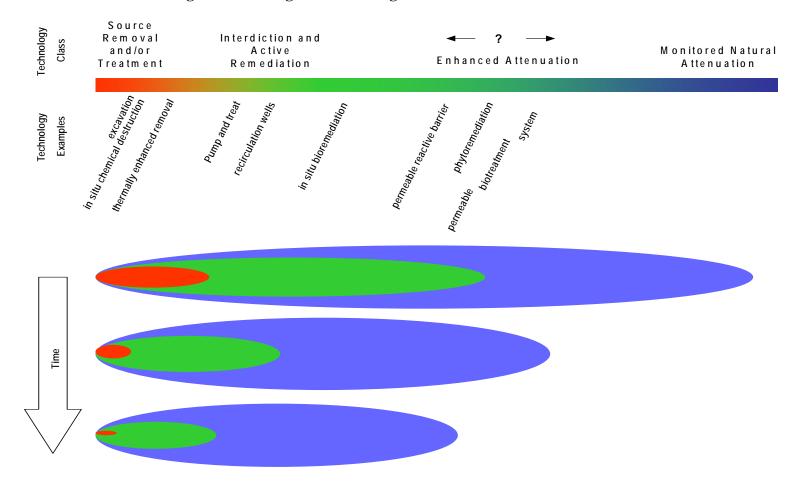


Figure 5. A Range Of Technologies Is Needed To Match Site Conditions.

12 Groundwater Remedial System Performance Optimization at DOE Paducah Gaseous Diffusion Plant, Paducah, Kentucky

#### 2.0 RECOMMENDATIONS

The Review Team has developed a number of recommendations that will improve performance, speed achievement of cleanup goals, and reduce annual and life-cycle costs. Recommendations address both the existing extraction and treatment systems and conditions affecting the longevity of those systems. Additional recommendations are made for control of other potential environmental exposures via groundwater transport of contaminants.

#### 2.1 Place Northeast Plume Extraction System on Stand-by and Develop Early-Warning Strategy

The intent of the Northeast Plume Extraction System as an interim remedial measure was to control the downgradient extent of a high-concentration (>1000  $\mu$ g/L) TCE plume through groundwater extraction and treatment. The extraction system is within the PGDP property boundary, but outside the plant boundary. The extraction well locations were reportedly chosen to control the TCE plume without significant mobilization of <sup>99</sup>Tc-contaminated groundwater that was found upgradient within the plant boundary. The extraction system was installed in 1997, and has generally operated continuously since then. Treatment is efficiently accomplished by mixing extracted water with recirculating water used in plant cooling towers. Any blow down is discharged to on-site lagoons.

TCE concentrations throughout the Northeast Plume are below 1000  $\mu$ g/L at extraction wells and monitoring wells. Concentrations of TCE over time at the extraction wells are presented in Figure 6. Figure 7 depicts a plot of TCE concentrations in MW292, located upgradient of the Northeast Plume extraction wells, from 1996 through 2004, and is representative of trends in other monitoring wells. It is inferred that concentrations are less than 1,000  $\mu$ g/L up gradient of the Northeast Plume Extraction system along likely groundwater flow paths. The interim goal of the Northeast Plume Extraction System to control migration of water contaminated by >1000  $\mu$ g/L TCE has been achieved.

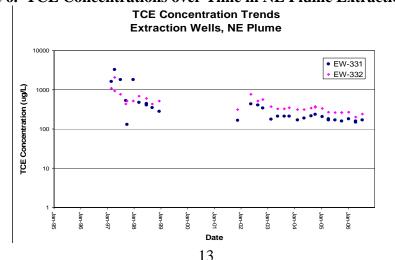
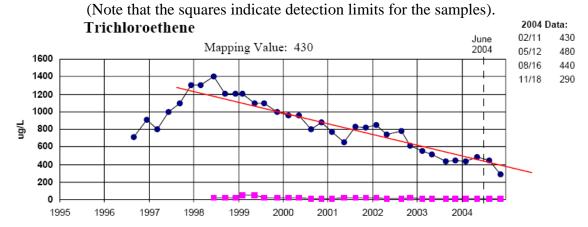


Figure 6. TCE Concentrations over Time in NE Plume Extraction Wells.



#### Figure 7. TCE Concentrations over Time in Northeast Plume Monitoring Well 292.

The Review Team recommends this system be placed in stand-by mode, with continued detection monitoring to assess the potential reappearance of TCE concentrations above  $1000 \ \mu g/L$ . Decision criteria will need to be developed that clarify under what conditions the extraction system will be restarted based on observed TCE in designated performance monitoring wells located upgradient of the extraction system. It is possible that new monitoring well locations and/or target depths may be required for this purpose.

The Review Team understands that an optimization review of the groundwater monitoring program will be performed in 2007. A key objective of this review should be to assess the adequacy of the existing monitoring program for continued detection and trend analysis of TCE and <sup>99</sup>Tc in the Northeast Plume. Specifically, the need for additional wells, monitoring at strategic depth locations within the UCRS and RGA, redundant locations, target analytes, and frequencies should be evaluated toward the overall goal.

Groundwater transport modeling is also recommended (see Section 2.6) to assess potential concentration increases downgradient of the current extraction wells, if this recommendation is implemented, to confirm that potential downgradient receptors will not be negatively impacted. Suggested decision logic is presented in the Appendix.

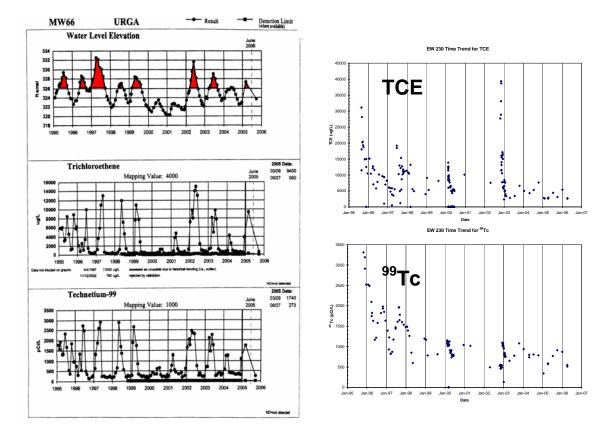
There may be capital costs if new monitoring wells are required, and there may be an increase in groundwater monitoring costs if additional monitoring wells are installed and/or groundwater monitoring frequency is increased at selected wells. However, implementation of this recommendation will eliminate labor associated with visiting the wells and maintaining the equipment. It will also reduce costs associated with process monitoring, electricity usage, and equipment replacement.

14

#### 2.2 Investigate Possible Source(s) Near SWMU 30 and 7

TCE concentrations at Extraction Well (EW) 230, shown on Figure 9, exhibit significant spiking with concentrations oscillating between a lower range of 3,000 to 5,000  $\mu$ g/L, and a higher range of 15,000 to 40,000  $\mu$ g/L. The activities of <sup>99</sup>Tc in this extraction well exhibited somewhat similar behavior, oscillating between a lower range of 500 to 1,000 pCi/L, and a higher range of 1,000 to 2,000 pCi/L. EW 230 is located in the "south wellfield area" of the Northwest Plume. Similar concentration spiking is observed in some of the nearby monitoring wells located upgradient of EW 230, including MW66 (Figure 8) and MW248.

# Figures 8 and 9. Water Levels and Concentrations over Time of TCE and <sup>99</sup>Tc in Monitoring Well 66. (Water levels in MW66 > 326 feet; mean sea level is in red.)



TCE and <sup>99</sup>Tc in Extraction Well 230, South Well Field, Northwest Plume.

The spiking behavior suggests <u>significant local contaminant source(s)</u> in the vicinity of the MW66 and 248: sources which release contaminant and/or change the plume structure in response to seasonal and climactic variations. This has important implications for the management of PGDP groundwater, in general, and for the remediation of the Northwest Plume, in particular. Specifically, the presence of

substantive TCE sources downgradient of the C 400 Building will potentially impact the design, modeling and interpretation of the effectiveness of the planned thermal treatment (source removal action) in the vicinity of C 400. In addition, contaminant loading from local source(s) and the resulting spiking behavior complicates interpretation of the more regional groundwater time trends, minimizing the power of statistics to discern whether concentrations in the wells are stable, decreasing, or increasing.

The presence of a continuing source of variable contaminant concentrations in the vicinity of the Northwest Plume extraction system will affect the operation of the treatment plant. Spikes will affect the treatment processes including the ability for the air stripping towers to meet discharge limits and the frequency of ion exchange resin and vapor-phase carbon change outs. The facility has procured a sixth tray for the air stripper in the event concentrations increase such that the existing five tray stripper is unable to treat the influent concentration. If VOC concentrations rise significantly, operations personnel will need to assess the capability of the existing tray stripper, even with the added tray and make an assessment of the best path forward concerning high VOC concentrations. The on-going source will also perpetuate the need for extraction and treatment in the Northwest Plume area.

The influence of local surface source(s) is further demonstrated by the strong correlation of concentration spikes to water level spikes in the upper and middle RGA, particularly at monitoring well MW66. MW66 is located approximately 600 ft upgradient of EW 230, and is completed in the upper portion of the RGA. As shown in Figure 8, the TCE concentrations in MW66 oscillate between a lower range of <500 µg/L, and a higher range of 8,000 to 14,000 µg/L. The activities of <sup>99</sup>Tc in this well oscillate between a lower range of <250 pCi/L, and a higher range of 2,000 to 3,000 pCi/L. The concentration and activity spikes in MW66 are triggered by seasonal factors and local high water levels above 326 ft msl. Recovery well EW 230 responses typically lag MW66 by a few months, consistent with groundwater travel time predictions.

There are several mechanisms for which increased precipitation and increased water levels release contaminant or change plume structure (e.g., episodic flooding/release of wastes, preferential paths, capillary and suction controls in the vadose zone, etc.). The observed contaminant concentration behavior in the upper RGA is likely associated with nearby facilities in the overlying UCRS, such as the waste disposal facilities in PGDP Solid Waste Management Units (SWMUs) 7 and 30. Major sources upgradient, such as Building C 400, are unlikely to be the cause of the local spiking behavior. Expression of contaminant loading from C 400 would (1) occur in the middle to lower RGA, (2) be observed more broadly in the monitoring well network, and (3) not respond as strongly to seasonal influences after flowing distances of several thousand feet.

In summary, the contaminant trends in EW 230 and upgradient monitoring wells in the upper (MW66) and middle (MW248) portions of the RGA suggest local contaminant sources in this area of the Northwest Plume. Consistent with this conceptual model, the Review Team recommends the following:

- Evaluate groundwater monitoring trends to more comprehensively identify 0 sources in the Northwest, Northeast, and Southwest Plumes. Examine the temporal data from all monitoring wells at the PGDP to identify episodic concentration spikes and other unusual features. For wells identified as exhibiting such behaviors, a follow-up assessment is recommended to determine the potential for, and significance of, local sources. This follow-up should consider any relevant historical data, the horizontal and vertical position of the well screen, the local geology, the location of the wells relative to known or suspect contamination sources, the correlation of observed spikes with factors such as weather patterns, rainfall and seasons, contaminant profiles (fingerprints) and any internal tracers associated with particular waste units, and similar information. In particular, for the data near EW 230 and MW66, the follow-up should include relevant historical waste site data for SWMUs 7 and 30 and other nearby facilities), relevant vadose characterization data, and past geology/contaminant cross sections and conceptual models (Claussen et al., 1993). Finally, the PGDP technical team should examine the results of the above actions and identify data gaps and develop cost-effective strategies to fill such gaps to support consensus on the nature and significance of any local sources. The recommendations regarding the identification and evaluation of sources (e.g., SWMUs 7 and 30) should be incorporated, as appropriate, into the Burial Ground Operable Unit (BGOU) RI/FS process.
- Assess the influence of newly-identified sources on the overall groundwater 0 remediation strategy at PGDP, current predictions of contaminant transport, as well as environmental and human health risk assessment. The impact of new contaminant sources on the overall groundwater PGDP groundwater remediation strategy should be assessed to address the following types of questions: Is this source accounted for in groundwater transport models, and how does the identified source impact any determination of mass balance related to natural attenuation and plume stability? How does such a source influence the predicted effectiveness of aggressive remediation technologies applied to upgradient sources such as the C 400 Building? How much remediation of the local source is necessary and what type(s) of cost-effective remediation options are available? A wide range of options (e.g., vapor extraction in the waste disposal zone, barometric controls, partitioning barriers, and other concepts) should be considered if local remediation is deemed desirable – this would maximize the potential for long term success.

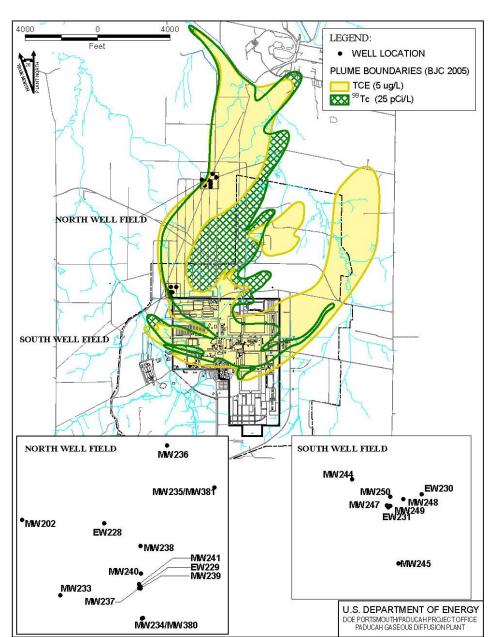
#### 2.3 Modify Northwest Plume Extraction System

The Northwest Plume extraction system currently operates with two northern and two southern extraction wells, illustrated on Figure 10. The system operates at a total extraction rate of approximately 200 gallons per minute (gpm). System operators indicated that a total of approximately 80 gpm is extracted from the two northern wells,

EW 228 and EW 229, and a total of approximately 120 gpm is extracted from the two southern wells, EW 230 and EW 231. System operators also indicated to the Review Team that capacity of the treatment plant for the combined Northwest Plume system is approximately 225 gpm, and the recommended minimum plant flow rate is 160 gpm.

Figure 11 illustrates the TCE concentration reductions over time at the northern extraction wells. TCE concentrations at the two northern extraction wells have declined and are currently in the range of 10 to 50  $\mu$ g/L.

A potential explanation for the concentration reductions at the northern extraction wells is the mass reduction provided by the southern extraction wells. Another potential explanation is a shift in the core of the TCE plume over time such that the northern extraction wells are no longer in the zone of highest concentration.





Plant,

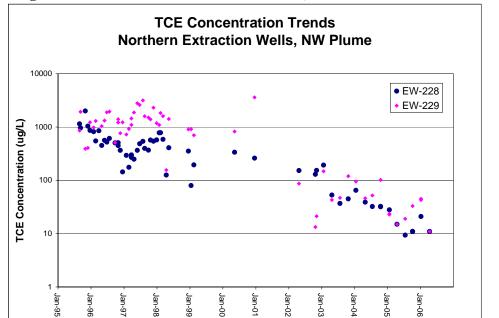


Figure 11. TCE Concentrations over Time, Northern Extraction Wells.

The southern extraction wells are currently extracting higher TCE concentrations than the northern extraction wells, as illustrated by comparing Figure 12 to Figure 11. In particular, EW 230 continues to extract TCE concentrations greater than 1,000  $\mu$ g/L, and at times concentrations have spiked to more than 10,000  $\mu$ g/L. Concentration reductions observed at EW 231 over time may represent a shift in the location of the plume core to the east, which could be caused by reductions in net recharge over time in the region between the Northwest Plume and the Northeast Plume. Such reductions in net recharge in that area could be due to changes over time in the use of lagoons and ditches over time, and/or due changes over time in the amount of water passed through pipes that might potentially leak.

Date

The Review Team recommends terminating the extraction at the two northern extraction wells, and increasing total extraction in the vicinity of the southern extraction wells by a similar amount (about 80 gpm). At this point, there is no reason to permanently dismantle these wells, the recommendation is only to terminate pumping from those wells. This design modification will increase contaminant mass removal and enhance capture near the southern extraction wells, which are closer to the contaminant sources. In turn, contaminant concentrations in groundwater should decrease downgradient, including discharges to Little Bayou Creek. The TCE concentrations in the northern portion of the plume have decreased significantly: from greater than 1000  $\mu$ g/L to a few hundred  $\mu$ g/L, or less. <sup>99</sup>Tc activities have also declined significantly; all monitoring wells in the northern portion of the plume are well below 900 pCi/L. This design modification does not require an increase in the capacity of the existing treatment plant.

Implementing this recommendation will also preclude the need for system operators to visit or maintain the northern extraction wells in the future.

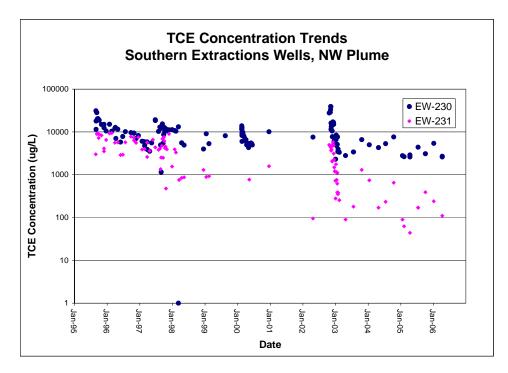


Figure 12. TCE Concentrations over Time, Southern Extraction Wells.

Strategies for increasing extraction in the vicinity of the southern wells include the following:

- Increase extraction at existing wells EW 230 and EW 231. The advantage of this approach is that no new extraction wells and no new piping are required. The site team would establish the extent to which pumping at each well could be increased, based on specific capacity and available drawdown at each well. Pumping rate at each well would then be managed so that the well with the highest extracted concentrations would be pumped as much as possible, with the balance of the treatment plant capacity extracted from the other well. A disadvantage of this approach is that a total pumping rate approaching the treatment plant capacity may not be possible using just these two wells. Another disadvantage is that these wells may not be located in the core portion of the plume, either now or in the future.
- Add additional extraction locations near EW 230 and EW 231. The advantage of this approach is that it improves the potential for groundwater to be extracted from the core portion of the plume, which is expected to shift to the east over time due to reductions in anthropogenic net recharge to the east. This approach also

improves the likelihood that a total extraction rate approaching the treatment plant capacity will be achieved on a consistent basis, because more than two extraction wells will be available. In this approach, one or more additional extraction wells would likely be installed east of EW 230. Pumping rates would be dynamically managed over time so that extraction is maximized at wells with the highest concentrations. Capture could be further enhanced by placing one additional extraction well just to the north of this east-west line of extraction wells. Potential well configurations could be evaluated and optimized with groundwater flow modeling (refer to Section 2.6). The disadvantage of this approach is that additional cost is required for installing, and maintaining, one or more new extraction wells and associated piping. Given the proximity of the treatment plant, and available use of the existing header from the northern wells, piping costs would be minimal.

Influent concentrations of TCE and <sup>99</sup>Tc to the treatment plant will increase significantly if this recommendation is implemented, because the lower concentrations from the northern extractions wells will no longer blend with the higher concentrations from the southern extraction wells. With respect to TCE, the air stripper has historically treated influent TCE concentrations over 5,000 µg/L with limited excursions, although the system was designed for a maximum influent concentration of 3000 µg/L at a maximum flow rate of 250 gpm. It is possible that blended influent TCE concentrations would be at or near the limit for the stripper, and might exceed 10,000  $\mu$ g/L, at times, if the recommendation is implemented. The Review Team believes that the current air stripper will be unable to meet a 5  $\mu$ g/L treatment standard for TCE at those higher concentrations. Paducah has procured a sixth tray for the air stripper in the event concentrations increase such that the existing five tray stripper is unable to treat the influent concentration. If VOC concentrations rise significantly, operations personnel will need to assess the capability of the existing tray stripper. Should effluent monitoring determine that treatment of TCE is not sufficient, even with an added sixth tray, a granular activated carbon (GAC) polishing step at the end of the plant, or a second air stripper could be added. The current off-gas treatment system using 2-3500 pound GAC vessels should have adequate capacity to treat concentrations above the plant TCE influent design concentration of 2000 µg/L at 250 gpm (which differs from the maximum air stripper design parameters of 3000  $\mu/L$  at 250 gpm). The GAC change-out frequency will increase from the current 6 months to an approximate frequency of 2 to 3 months at a sustained average TCE plant influent concentration of 5000 µg/L.

With respect to <sup>99</sup>Tc, both of the southern extraction wells currently have influent <sup>99</sup>Tc concentrations below the groundwater cleanup goal of 900 pCi/L (see Figure 13). The current state permit does not have an effluent criterion to surface water for <sup>99</sup>Tc. The plant is likely to be subjected to higher concentrations of <sup>99</sup>Tc. It is unlikely those concentrations will exceed historic concentrations during early plant operations, or the ion exchange system design concentration of 2000 pCi/L that the plant was able to treat to the required 25 pCi/L treatment goal. Treatment of <sup>99</sup>Tc to the treatment goal should

Groundwater Remedial System Performance Optimization at DOE Paducah Gaseous Diffusion Plant, Paducah, Kentucky

not be a problem with the current resin treatment process, even if influent concentrations increase above 900 pCi/L as a result of implementing this recommendation.

#### 2.4 Consider Innovative Treatment Approach for Seeps Area along Little Bayou Creek

The Review Team understands that measurable levels of TCE, tens to hundreds of  $\mu g/L$ , are present in water discharging from various seeps along Little Bayou Creek. This represents a limited, but real exposure pathway for ecological receptors and a potential exposure for humans. The Review Team recommends that additional consideration be given to low-cost alternatives for reducing concentrations in groundwater, either in-situ or prior to discharge of the water to Little Bayou Creek. Preference should be given to techniques that would not require much maintenance or a power supply, and to techniques that would be effective throughout the year. The Review Team notes that biologically mediated techniques may be limited to the warmer times of the year, and techniques that enhance anaerobic reduction of the TCE may also mobilize iron, manganese, and arsenic, causing both aesthetic and toxicity issues in the surface water.

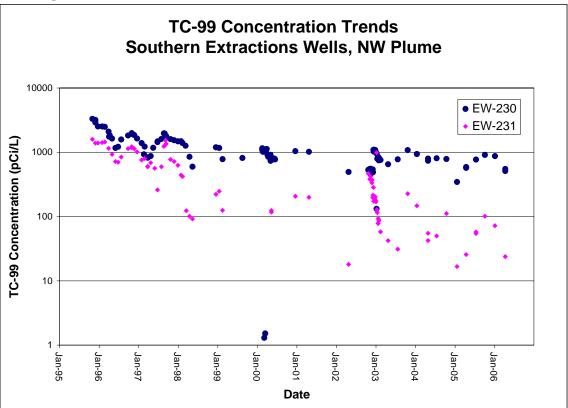


Figure 13. <sup>99</sup>Tc Concentrations over Time in Southern Extraction Wells.

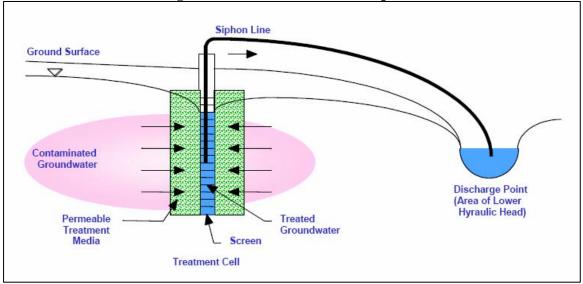
Groundwater Remedial System Performance Optimization at DOE Paducah Gaseous Diffusion Plant, Paducah, Kentucky

22

Given the low concentrations of the contaminants, a possible solution is to enhance volatilization by channeling seep discharge into a rock-lined channel prior to discharge to the creek, coupled with fencing to prevent direct exposure by humans to the contaminated water and limiting ecological impacts in Little Bayou Creek.

Another alternative is a geosiphon. A geosiphon is able to extract water from the subsurface without the use of a pump by allowing the extracted water to discharge at a lower water level than the water level at the extraction point. This may either be used to induce more concentrated flow to pass through in-ground treatment media (e.g., zero-valent iron) surrounding the extraction well (see the schematic in Figure 14), or to direct contaminated water to a treatment vessel located downhill nearer the extraction point. Such a system has been installed at the Savannah River Site (see http://www.rtdf.org/PUBLIC/permbarr/prbsumms/profile.cfm?mid=36). This could be used in conjunction with enhanced aeration to restore oxygen to the treated water prior to discharge into Little Bayou Creek. The long-term performance of such a siphon would need to be verified, particularly as water levels are drawn down near the seeps. Note that the use of zero-valent iron may result in concentration of <sup>99</sup>Tc in a near surface location.

Other alternatives include an engineered wetland, or other measures to enhance biodegradation of TCE. This may require the expansion of the area at or near the normal creek stage and the introduction of specific species and addition of nutrients. Such a wetland may accumulate <sup>99</sup>Tc. The effectiveness of wetlands treatment may be diminished in the winter months.





#### 2.5 Further Characterize Factors Affecting Migration of the Southwest Plume

The Southwest Plume contains various contaminants, including chlorinated organics and <sup>99</sup>Tc, and is believed to originate from several sources. In the RGA, the Southwest Plume is significantly shorter than the Northwest and Northeast plumes, as currently characterized. The reason for the discrepancy should be further investigated.

The Review Team believes that a possible explanation is that the Southwest Plume is bounded by potential sources of recharge, including Bayou Creek, process water supply ponds, and various ditches that drain to Bayou Creek (e.g., the Outfall Ditch north of the Southwest Plume), in addition to the limit posed by the edge of the Porters Creek terrace. It is possible that these factors have provided hydraulic control that has effectively limited spreading of the Southwest Plume. The Review Team recommends that additional monitoring points for water levels and contaminant concentrations be considered, in conjunction with groundwater modeling, to confirm this hypothesis and/or refine the conceptual model with respect to fate and transport of the Southwest Plume. This will subsequently allow for improved prediction of the changes in the plumes as a result of altered operation of some of the features (e.g., the process water supply ponds) as the mission of the PGDP changes. This will be useful for assessing more robust remedial options under those conditions.

The Review Team also notes that the downgradient extent of the Southwest Plume is poorly constrained. Monitoring points in the program downgradient of MW354 are sparse. Additional permanent monitoring points, spanning the vertical extent of the RGA, in the vicinity of Bayou Creek are warranted, and would serve to validate and model predictions, as well as observations of the Review Team noted in this report. Note that if plant effluent discharge to the Outfall Ditch north of the Southwest Plume continues to diminish, the Southwest Plume may migrate on a more northerly heading and may merge with the Northwest Plume. (Refer to the following discussion regarding other potential plume changes, if operations at the facility substantially diminish.) There is evidence for such a shift towards the east already occurring. Monitoring wells 84, 86, and 87 display a significant increase in TCE concentrations since 2000, as shown in Figure 15. Middle RGA well MW84 first displayed this trend, followed by the colocated but deeper MW86 (lower RGA), and then by MW87 located farther east. Such trends should be tracked closely.

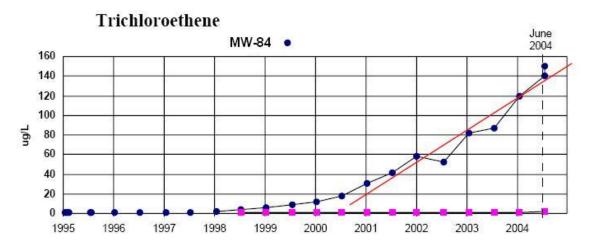


Figure 15. TCE Concentrations over Time in MW84. (Note that boxes are the detection limits for the analyses)

#### 2.6 Update Site Groundwater Model and Reassess Plume Migration

Groundwater flow and transport modeling is a valuable tool for evaluating historical changes, and predicting future changes, to the physical system. Examples include the following:

- Variations in anthropogenic net recharge. Enhanced net recharge includes the north lagoons (e.g., cooling tower blow-down water), the North-South Ditch, the Outfall Ditch, and the west lagoons (e.g., process water). For instance, the Review Team believes that groundwater mounding between the Northwest Plume and the Northeast Plume is responsible to some degree for the historical configuration of these plumes, and reduced net recharge between the Northwest Plume and the Northeast Plume in the future may cause the plume axes to shift towards the center. This might also cause a more northerly direction of contaminant migration from the Building C 400 source area in the future. Anthropogenic net recharge may also impact the fate and transport of the Southwest Plume. Groundwater modeling can be calibrated to historical water levels and plume configurations, and then used to predict future changes to groundwater flow directions that might result from changes to anthropogenic net recharge. These simulation results can then be used to guide remediation and monitoring strategies.
- *Changes in remediation pumping strategies.* Groundwater modeling can be used to predict changes in the extent of capture resulting from different extraction strategies, such as the increased pumping in the vicinity of the southern extraction wells for the Northwest Plume. Transport modeling can also be used to assess the

fate and transport of contaminants after terminating extraction at specific locations, such as the potential for TCE impacts to spread to residential areas if the Northeast Plume extraction system is terminated.

Source area remediation. Groundwater modeling can be used to simulate mass flux leaving one or more source areas, using ranges of potential source reduction associated with source area remedial action(s). This modeling can provide a basis for establishing the degree of source reduction needed to achieve acceptable concentrations at specified point-of-compliance (POC) locations (e.g., at the Plant boundary) that would in turn correspond to acceptable concentrations at downgradient point-of-exposure (POE) locations. For instance, if thermal treatment in the C 400 Area does not reduce concentrations leaving that area below some critical value determined by the modeling to be protective at POC and POE locations, application of additional source remediation technologies may be warranted.

The Review Team recommends construction and calibration of an updated groundwater flow and transport model by building on previous modeling efforts. The groundwater model used by the Project Team was last updated in 1999, and is described in "Transport Modeling Results for the Northeast Plume Interim Remedial Action and the Northwest Plume at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky, April 1999" prepared by the Jacobs EM Team. A newly updated model will incorporate information obtained since 1999, such as investigations of source areas and updated plume configurations. The Review Team recommends use of the MODFLOW and MT3DMS codes, because they are public domain codes that are technically appropriate and widely accepted.

The Review Team recommends evaluation and integration of information from recent modeling-related efforts by the USACE Engineer Research and Development Center (ERDC) and the Kentucky Research Consortium for Energy and the Environment (KRCEE) into the modeling update, to the extent possible. ERDC has reportedly integrated comprehensive geologic data into the GMS platform (completed in 2003). The Review Team is not suggesting that GMS should be the de facto platform for the groundwater modeling update, but rather is recommending that the information from the EDRC effort be evaluated and incorporated as appropriate into the modeling update. KRCEE has recently performed flow and transport modeling using the MODFLOW and MODFLOWT codes to assess scenarios such as modified extraction configurations, modified anthropogenic recharge, and variations in TCE half-life.

Additional suggestions for the modeling update include the following:

• Utilize the historical plume configuration as a primary calibration target in addition to matching water levels. This is particularly important at this site because the water levels in the RGA vary over a small range within the Plant boundary, such that subtle changes or errors in water levels can cause significant changes in groundwater flow directions. The resulting uncertainty is best

resolved by demonstrating that groundwater flow directions simulated by the model over time can reproduce the observed plume configuration, based on particle tracking and/or transport modeling in conjunction with locations of known groundwater source areas.

- Incorporate an aerobic degradation half-life for TCE. There does not appear to be significant anaerobic degradation of TCE at the site. However, as presented by Dr. Hope Lee during the Review Team site visit, aerobic degradation of TCE has been determined to be a degradation process at many other sites and would be expected to occur at this site. Incorporation of this degradation process in the transport modeling will provide for more realistic prediction of TCE concentrations at potential POEs. The modeling can utilize a range of aerobic degradation half life determined at other sites and reported in the literature, or preferably be based on site-specific data by comparing enhanced TCE degradation along a flow path versus a more conservative constituent such as <sup>99</sup>Tc. Aerobic degradation can also be confirmed in the field using activity-dependent enzyme probes.
- Identify potential locations of significant anthropogenic sources of net recharge to the subsurface over time. The Review Team believes that flow directions and plume shapes are sensitive to anthropogenic sources of net recharge. A quantitative water budget that provides sufficient detail for developing model input is not recommended, because the required effort would be too large and the results subject to considerable uncertainty. However, the Review Team does suggest that a qualitative review be performed that list specific locations where anthropogenic sources of net recharge such as lagoons, outfall ditches, leaky pipes, or injection wells may have been present, at different periods of time. This qualitative information can then be used to support or guide assignments of the net recharge parameter in the model to better match water levels and historical plume configuration.
- Generate plumes and incorporate continuing sources of groundwater contamination, rather than initializing plumes. The Review Team suggests that simulations of future contaminant fate and transport utilize initial plume configurations generated with the model, based on simulation of historical contaminant transport from identified (or presumed) sources. This is a superior approach compared to initializing contaminant plumes based on interpreted concentration contours, which assigns an initial plume configuration that is generally not in equilibrium with the governing equations of groundwater flow and solute transport. In the latter approach, the model must then establish conditions in equilibrium with governing equations of groundwater flow and solute transport, and that often masks the actual contaminant fate and transport that is of interest. Specification of continuing sources is also important for realistic prediction of future concentrations at POC or POE locations. For instance, it is not realistic to assume that thermal treatment at the Building C 400

area will eliminate all continuing sources of groundwater contamination, and simulation of some continuing source is appropriate. As discussed earlier, transport modeling can be used to establish an acceptable strength of a continuing source in that area, such that future concentrations at downgradient POC and POE locations are sufficiently low.

#### 2.7 Recommendations for Other Potentially Applicable Technologies

A number of potentially applicable technologies for groundwater treatment in lieu of groundwater extraction and treatment have been suggested to the Paducah team in the past six years. These technologies include: C-Sparge<sup>TM</sup>, zero-valent iron barriers, and biobarriers. To this list, the Review Team added and evaluated the use of groundwater recirculation wells.

The Team recommends against the use of the C-Sparge<sup>TM</sup> technology that uses an ozone amendment to an air sparging system, reportedly to increase chemical oxidation of compounds such as TCE. There are many uncertainties in the application of such a technology, including the longevity of the ozone and contact with the contaminants before the ozone breaks down to dissolved oxygen. C-Sparge would not treat <sup>99</sup>Tc and would have to be used in conjunction with another technology for that purpose.

The Team also recommends against the use of zero-valent iron barriers at the site due to the difficulty in placing the iron to the depths necessary, the challenges to adequate and persistent treatment of contaminants in such a high permeability and aerobic unit as the RGA, and the difficulty in adjusting the treatment location in the event of changes in the location of the plume.

A biobarrier would include the placement of organic materials (e.g., mulch, vegetable oil) into the paths of the plumes. The intent would be to promote reducing conditions that would degrade the chlorinated organics, and possibly sorb the <sup>99</sup>Tc as well as the TCE. The biobarriers would have the advantage of low cost, and with the vegetable oil, a reasonably easy placement technique (injection). The disadvantages would be the need for periodic replenishment of the organic substrate, the potential for incomplete reduction of the TCE and accumulation of dichloroethene and vinyl chloride, and the accumulation of <sup>99</sup>Tc. In addition, the barrier location would not be easily modified to address future shifts in the plume locations. This technology may be worth considering in conjunction with existing remedial components. For instance, if thermal treatment in the Building C 400 area does not mitigate concentrations to levels determined to be protective based on fate and transport modeling, then additional biological treatment as described above could subsequently be attempted.

Finally, the Team considered the applicability of groundwater recirculation wells. These wells create convection in the aquifer through the intake of water through one of two screened intervals (i.e., within the RGA), in-well treatment through aeration, and discharge of the partially treated water through the other of the two screened intervals.

Water is theoretically cycled through the well multiple times before exiting the convection system in the regional gradient. This technology, when applied as multiple wells, can significantly reduce concentrations of volatile organics either in hot spots or along a plume path. It may be an alternative for treating higher concentrations of dissolved TCE. Treatment of water with mechanisms other than aeration (e.g., ultraviolet light, carbon) has extended the applicability of the technology to other contaminants. The technology may be hard pressed to treat <sup>99</sup>Tc, however. There is also a risk of spreading the plume through unexpected permeability distributions. The team does not recommend the application of the technology at this time, but it may have a role for one or more specific locations in conjunction with other remedy components.

#### 2.8 Re-evaluate Basis for Change-Out of Resins and Carbon

#### 2.8.1 Ion Exchange Resin

The current ion exchange system design consists of two parallel trains with two units in series, with each vessel containing 62.5 cubic feet of Purolite A-520E resin. The system was designed for a maximum <sup>99</sup>Tc influent concentration of 2000 pCi/L, effluent of 25 pCi/L, and a flow rate of 250 gpm. The current concentration of <sup>99</sup>Tc in the plant influent is less than 250 pCi/L, a value well below the 900 pCi/L groundwater cleanup goal. The current system has effectively met the 25 pCi/L effluent design standards over the life of the plant. As stated in Section 2.3, eliminating the two north extraction wells and increasing the extraction rate from the two southern wells (or adding a well adjacent to the other two southern wells) will likely increase the <sup>99</sup>Tc concentration in the influent above the groundwater cleanup goal. If this occurs, the current ion exchange configuration should still be adequate to meet the 25 pCi/L design standard.

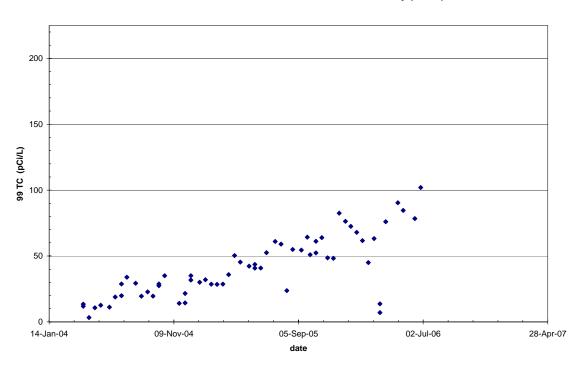
The current protocol requires the resin be changed when the concentration in the effluent stream from the lead column reaches 50% of the plant influent concentration. This result is a variable concentration at which the column resin is changed out, as well as the variable activity present in the resin disposed. It appears that this protocol results in wasted resin exchange capacity. The PDGP technical team should re-evaluate whether treatment is needed for influent <sup>99</sup>Tc levels below the treatment goal. If the decision is made to continue treatment, then the appropriate effluent quality should be assessed. If an effluent activity level above the current 25 pCi/L is endorsed, then other options such as split <sup>99</sup>Tc treatment can be evaluated (i.e., treat only enough water to meet the effluent standard, bypassing the rest), or allowing the resin to operate until the lead exchange column is fully exhausted.

A plot of the effluent concentration over time, as shown in Figure 16, indicates the current resin exchanges the <sup>99</sup>Tc over a long period of time and does not break through abruptly. This is indicative of a resin that has significant exchange capacity remaining when the resin is changed out at a concentration corresponding to 50% of the influent concentration. The facility should implement a plan to monitor the lead column to extend its operation cycle to correspond to 90 – 100% breakthrough. Given the low

concentration of <sup>99</sup>Tc in the influent relative to the groundwater cleanup goal, the exchange capacity present in the down stream columns will likely meet the 25 pCi/L effluent design criteria, and if that level is exceeded, the effluent concentration will still be well below the groundwater cleanup goal. The Review Team notes that extending the use of the lead column until it is fully exhausted will cause the <sup>99</sup>Tc activity level in the resin to increase, which could impact future disposal options. A discussion of disposal options is included below.

The current resin Purolite A 520E, is somewhat nonselective, and indiscriminately sorbs a number of anions such as nitrate, bicarbonate, sulfate and chlorine generally present in concentrations well above <sup>99</sup>Tc. Purolite has developed a new resin (A 530E) in cooperation with Oak Ridge National Lab that selectively removes <sup>99</sup>Tc. Tests conducted at Paducah using this new resin in 1999 (DOE, 2002), revealed the <sup>99</sup>Tc exchange capacity was approximately 3 times that of the A 520E resin. PGDP should assess the potential future use of the Purolite A 530E resin. An analysis of resin cost, an increase in activity level in the spent resin, and impacts related to the disposal cost should all be assessed when evaluating the use of the A 530E resin.

#### Figure 16. Effluent <sup>99</sup>Tc Concentrations over Time from Lead Ion-Exchange Vessel.



Time Trend for Lead Resin Column Effluent <sup>99</sup>Tc Activity (IHV23)

#### 2.8.2 Modify Carbon Change-out Basis

The current vapor-phase (VP) GAC system design consists of two units in series each with 3,500 pounds of activated carbon. The system was designed for a maximum TCE influent concentration of 2000  $\mu$ g/L, and a 250 gpm flow rate, resulting in a VP mass flow rate to the carbon of 0.25 pounds of TCE per hour. Typical VP carbon adsorption rates for TCE based on vendor literature indicate that GAC has an adsorption capacity of 20 to 35 percent by weight.

Change out for this system is typically done on a 6-month interval regardless of the flow or the TCE influent concentration. Using the maximum design flow rate of 250 gpm and 2000  $\mu$ g/L of TCE, the resulting loading to the GAC over a 6-month period would be nearly 1,100 pounds. Using a conservative adsorption rate of 20% by weight, the GAC contained in both vessels would become exhausted in nearly 8 months, and under initial loading conditions (3000 pounds GAC/unit) both vessels would be exhausted in about 6.5 months. Conversely, using an average adsorption capacity of 25%, the estimated carbon life would be extended by 25%.

The present loading to the GAC is approximately 50% of the maximum design criteria (200 gpm versus 250 gpm, and 1200  $\mu$ g/L versus 2000  $\mu$ g/L). If the current operating conditions were to continue (2 northern and 2 southern extraction wells), the change-out frequency could likely be changed to annually with no resulting TCE emissions.

Should the modified extraction scenario recommended in Section 2.3 be implemented, changes to the GAC change-out frequency would likely be needed. The mass of TCE contained in the air stripper off gas would greatly exceed the design parameters of the air stripping system as well as the carbon system, necessitating the need to revise the change-out frequency from the present 6-month interval to every 3 or 4 months (TCE 5,000  $\mu$ g/L, 250 gpm). If the influent TCE concentration increased to 10,000  $\mu$ g/L at 250 gpm, assuming continued use of the present air stripping system, the carbon vessels would require replacement every 1.5 to 2 months.

#### 2.8.3 Reconsider Disposal Approach for Spent Resin

Currently, 10 ST-90 boxes and 30 to 50 55-gallon drums of resin waste are staged at the site. The resin waste is contaminated with <sup>99</sup>Tc at up to 180,000 pCi/g. The containers of resin waste have standing water in them. The waste will require dewatering prior to disposal. DOE has determined that it will be more cost effective for a commercial facility, EnergySolutions, to perform dewatering than for the government to do so inhouse.

DOE will access its contract with EnergySolutions (ES) which has fixed rates for treatment and disposal of soil-like low-level mixed waste (LLMW). According to ES, the effort required to dewater the resins will be very similar to the effort that would be

required to stabilize a LLMW. Therefore, ES intends to charge DOE the same rate to treat and dispose the resins as they would charge to treat and dispose a mixed waste.

However, disposal of waste in ES's mixed waste cell is more expensive than disposal of waste in ES's Class A low-level waste cell. If the resins are NOT mixed waste (that is, if no RCRA listed or characteristic constituents are present), the dewatered resins could be disposed in the less expensive Class A cell. DOE could negotiate a fee for dewatering and pay this, plus the unit disposal rate per cubic foot for disposal in the Class A cell per the DOE contract. It is recommended that DOE discuss this disposal option with ES.

#### 2.9 Reduce Frequency of Process Monitoring and Remote Well and Equipment Checks

Process monitoring discussions for the Northwest and Northeast Treatment Plant are based on information provided by PRS Operations Staff. The *process monitoring* sampling program, which excludes *groundwater monitoring*, is intended to monitor key parameters to assess how effectively each plant removes TCE and <sup>99</sup>Tc. Data from PRS "projected cost estimate backup information" identifies TCE related yearly monitoring through the plant consists of 289 daily samples (assumed to be 5 daily samples per week of plan effluent plus appropriate quality assurance samples) and 424 other TCE samples for process monitoring from other sampling ports. In addition to these samples, a gas chromatograph (GC) on line 24/7 analyzes a treatment plant effluent sample every 2 hours. The original GC was replaced with a new unit during the last year at a cost of approximately \$60,000. Similarly, 289 <sup>99</sup>Tc daily effluent samples plus 232 other <sup>99</sup>Tc samples from other sampling ports are analyzed yearly.

#### 2.9.1 Reduce Frequency of TCE Monitoring and Increase Lab Turnaround Time

The duplication of daily TCE lab analysis and on line GC operation should be discontinued. Since the GC was replaced within the last year and the plant staff is familiar with its operation, the Review Team recommends continuing its use to monitor the TCE concentration in the plant effluent. The sampling frequency for laboratory analysis should be revised from daily to a maximum of one sample per week, to correspond to TCE sampling requirements in the existing discharge permit (KY0004049). Implementing this recommendation could cut total TCE analytical costs by a minimum of 30 percent. The PRS Operations Staff should periodically assess the reliability of the on line GC by comparing GC-generated data with weekly lab analytical results. The specific sampling points and frequencies for the other TCE samples were not identified but the Review Team recommends evaluating the location, number, and frequency of those samples and how they fulfill a specific data need. It is likely the 424 other samples identified could be reduced as well, resulting in even greater savings. The staff should also reassess if a 14-day turn-around time for analytical results (effluent or other samples) is necessary, or if a 30-day turn around would be adequate. This would further reduce the analytical cost per sample by approximately one third.

# 2.9.2 Reduce Frequency of <sup>99</sup>Tc Monitoring and Increase Lab Turnaround Time

The Review Team recommends the <sup>99</sup>Tc effluent sampling frequency at the Northwest Treatment Plant should be revised to a maximum of weekly to correspond with the sampling efforts outlined for TCE above. The current influent concentration of <sup>99</sup>Tc is below the groundwater cleanup criteria of 900 pCi/L, and the need for treatment is unclear under the current operations scenario. Should the revisions identified in Section 2.3 be adopted, the <sup>99</sup>Tc influent concentration will likely exceed the identified 900 pCi/L groundwater cleanup goal,. As stated earlier, the existing system is designed to reduce influent <sup>99</sup>Tc concentration of 2000 pCi/L to approximately 25 pCi/L after treatment. As discussed with respect to the TCE sampling, reducing the sampling frequency from daily to a maximum of one effluent sample per week will reduce the total <sup>99</sup>Tc analytical cost by approximately one third. In addition, if the turn around time could be increased from 14 to 30 days, the analytical cost per sample could also be reduced by approximately one third. All sampling points and frequencies for the other <sup>99</sup>Tc samples were not identified, but the Review Team recommends evaluating the location, number, and frequency of those samples and how they fulfill a specific data need. For example, the two lead ion exchange columns are sampled for <sup>99</sup>Tc every 2 weeks. Based on past operational history, the lead ion exchange columns have a resin replacement frequency of approximately 3 to 5 years. This translates into 160–260 samples over the life of the resin. The sampling frequency should be evaluated based on the capacity of the resin and the expected time needed to reach >90 percent of that capacity. Typically, less frequent sampling would be appropriate during initial operations for a new bed, with an increase in frequency as the resin capacity is reached.

#### 2.9.3 Reduce Frequency of Remote Well and Equipment Checks

The well system provides minimal information to a central monitoring point immediately accessible to operations personnel. The primary indicator of a well malfunction is a significant reduction in flow at the corresponding treatment plant. The current standard operational procedure (PRS-ENR-0017) requires the maintenance staff visit each extraction well in the Northeast and Northwest Remediation System daily to verify each well is functioning properly by noting the flow and pressure reading. Similar data is collected at the Northeast Plume equalization/pump station. This data collection activity normally takes an operator several hours to complete. Given the inherent reliability designed into these systems, and a long monitoring history which reinforces this reliability, one could reasonably expect the frequency that a site operator needs to visit these locations could be significantly reduced. This revised frequency might be limited to periodic sampling events or situations when a well or equipment malfunction is otherwise identified. This procedure more closely corresponds to typical processes used in the private sector and will free up significant operations personnel time for other more vital activities. Reallocation of personnel from the extraction and treatment plant operations to other functions at the Paducah facility should be considered. Note that the current visits to the Northwest Plume North Well Field will not be required, if the recommendation to eliminate extraction at those wells (see Section 2.3) is implemented.

#### 2.10 Re-evaluate Approach to Extraction Well Rehabilitation

The Paducah team has been using best practices in evaluating extraction well performance and conducting extraction well rehabilitation when necessary to overcome fouling of well screens to maintain system performance. Well rehabilitation has reportedly included the use of blended heat and chemical treatment under the auspices of noted expert George Alford. The costs for the well rehabilitation, however, have been over \$100,000 per well. Given the depth and diameter of these wells, these costs appear to be excessive, especially given the availability of groundwater treatment on-site. Paducah personnel responsible for maintenance of monitoring wells indicated to the Review Team that the monitoring wells undergo similar rehabilitation when necessary at a cost of less than \$5,000 each.

The Review Team recommends the procedures for rehabilitation as well as the contracting process be reviewed to assure that costs are reasonable. Coordination with the team managing the monitoring network, possibly using a common subcontractor, is highly recommended. The use of the heat in addition to chemical treatment for the rehabilitation may not be necessary. Chemical treatment alone using a product such as Baroid's AquaClear products or comparable mixtures may offer adequate maintenance of well specific capacity. Additional guidance on well maintenance is available in the USACE Engineer Pamphlet "Operation and Maintenance of Extraction and Injection Wells at HTRW Sites" and can be accessed at

<u>http://www.usace.army.mil/publications/eng-pamphlets/ep1110-1-27/toc.htm</u>. There is also draft USACE guidance on well rehabilitation that can be provided to the Paducah team, if desired, provided it is not widely distributed.

### 3.0 SUMMARY

Т

The Review Team has reviewed the conditions and remedial operations at both the Northeast and Northwest Plumes and has developed a number of recommendations for the PGDP staff. These recommendations are summarized in Table 1

	Table 1 Summary of Recommendations
Paragraph	Recommendation
2.1	Place Northeast Plume extraction system on stand-by and develop an early warning system to restart extraction if there is evidence of plume migration offsite
2.2	Investigate possible source(s) near SWMUs 30 and 7 based on observed spiking in TCE and <sup>99</sup> Tc concentrations in monitoring wells.
2.3	Modify Northwest Plume extraction system to eliminate extraction in the northern portion of the plume and increasing extraction in the southern portion of the plume.
2.4	Consider innovative treatment approach for seeps area along the Little Bayou Creek, including enhancing volatilization of TCE by diverting seep discharge into a rock-lined channel, or the use of a geosiphon with treatment of the recovered water
2.5	Further characterize factors affecting migration of the Southwest Plume using installation of additional monitoring points and groundwater modeling. Additional tracking of increasing concentrations of TCE is recommended to assess an eastward shift in the plume.
2.6	Update site groundwater model and reassess plume migration by building on past modeling efforts. This would involve creation of a MODFLOW/MT3D model, calibration of the model with historical information regarding plume configuration, incorporation of an aerobic degradation half-life of TCE, and further resolution of the locations of significant anthropogenic recharge.
2.7	Consideration of groundwater recirculation wells and rejection of ozone sparging and iron-filing walls as candidate technologies at PGDP.
2.8	Re-evaluate basis for change-out of ion-exchange resins and carbon, and reconsider disposal approach for spent ion-exchange resins.
2.9	Reduce frequency of process monitoring and remote extraction well and equipment checks.
2.10	Re-evaluate approach to extraction well rehabilitation to reduce costs

#### 4. REFERENCES

Clausen J. L., J. Zutman, and N. Farrow. 1993. Characterization of the Northwest Plume Using a Driven Depth Discrete Sampling System. KY/ER-22. U. S. Department of Energy, Lexington, Kentucky.

DOE. 2005. 2005 End State Vision Annual Update for PGDP. DOE/OR/07-2119&D2/R. U. S. Department of Energy, Lexington, Kentucky.

DOE. 2003. CERCLA Five-Year Review for the U.S. Department of Energy Paducah Gaseous Diffusion Plant, Paducah, Kentucky. DOE/OR/07-2067&D2. U.S. Department of Energy, Lexington, Kentucky.

Interstate Technology & Regulatory Council. 2004. Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation. RPO-1. Washington D.C.: Interstate Technology & Regulatory Council, Remediation Process Optimization Team. http://www.itrc.org.

Jacobs EM Team. 1999. Transport Modeling Results for the Northeast Plume Interim Remedial Action and the Northwest Plume at the Paducah Gaseous Diffusion Plant. Paducah, Kentucky.

Kentucky Department for Environmental Protection. August 24, 2006. Permit to Discharge Treated Wastewater into Waters of the Commonwealth of Kentucky: KPDES No KY0004049.

Paducah Remediation Services. 2006. Projected Costs to Operate the NWPGS and NEPCS for 42 Months (April 24, 2006 to September 30, 2009).

Paducah Remediation Services. 2006. Northwest/Northeast Plume Daily Operational Data Collection and Maintenance: PRS-ENR-0017.

#### Appendix. Potential Contingent Strategy for Northeast Plume Extraction System Restart

The Northeast Plume extraction system has apparently achieved its goal of control of the portion of the trichloroethene (TCE) plume that exceeds 1000  $\mu$ g/L. Concentrations have declined in the monitoring wells near and upgradient of the extraction system to levels below 600  $\mu$ g/L. The Review Team recommends terminating extraction at the Northeast Plume extraction wells, but given the uncertainty in the future plume behavior, recommends maintaining the system in stand-by status with the contingency of restarting the system if evidence is found that contamination above 1000  $\mu$ g/L is once again migrating toward the property boundary. Stand-by status would include periodic inspection of the system (e.g., once per month or once per quarter), including verification that the pumps in the wells are functional and protective systems are properly maintained. The Review Team also recommends that extraction wells EW331 and 332 be added to the monitoring program while on stand-by status.

There are two conditions that could trigger restart of the system. First, the plume may increase in TCE concentrations along its former axis. Second, the plume may once again expand, but along a different axis due to changes in external influences, such as anthropogenic recharge and climactic variability. Monitoring will be required to assess both potential conditions. Though the strategy for restarting the system will ultimately be developed by the Paducah project team, an example strategy is presented here for consideration.

Upgradient (to the extraction system) monitoring wells MW292, 145, and 283 are critical indicators of potential renewed plume expansion (Figure A-1). As of 2004, these wells had approximate TCE concentrations of 300, 50, and 130  $\mu$ g/L, respectively. It is suggested that monitoring frequency in these wells and monitoring wells near the extraction system be quarterly, if not currently monitored at that frequency, if TCE results from two consecutive sampling events exceed 800  $\mu$ g/L in any of these three wells. Some rebound of concentrations may be possible once the extraction system is shut down, and 800  $\mu$ g/L is a value that recognizes that potential yet is below the 1000  $\mu$ g/L goal.

The plume may once again strengthen along its previous axis. If monitoring well MW 292 exceeds 1000  $\mu$ g/L TCE, or if any of the extraction wells (EW331 and EW332) or monitoring wells near the extraction wells (MW124, -126, -284, -288, -291, -293A, or -294A) exceed a threshold such as 800  $\mu$ g/L, those results should be confirmed with an additional sampling round (either scheduled or a special event). If confirmed, the extraction system should be restarted to provide a degree of plume capture consistent with current conditions. Given that there may be a portion of the plume above 800  $\mu$ g/L not sampled via the existing well network, setting the threshold for taking action at a level less than 1000  $\mu$ g/L is prudent.

If the plume appears to be moving on a more northerly course, increases in TCE concentrations in monitoring wells MW145 and MW283 would be expected. If the TCE concentrations in these wells increase above 800  $\mu$ g/L, further evaluation of the likely plume path would be recommended at that time considering concentration and piezometric data. This might require additional monitoring points to the north of these wells. Subsequent restart of the existing extraction system to control the plume would be required if TCE concentrations in MW145 and MW283 or any new monitoring points exceed 1000  $\mu$ g/L. Additional extraction wells may ultimately be required west of the existing extraction wells to fully control the plume. Any new extraction system. Well locations and pumping rates would be based on modeling or other analysis and would be chosen to assure efficient capture of the plume.



