

*Draft Technical Report*

**CONSIDERATIONS RELATED TO POST-CLOSURE MONITORING OF  
URANIUM IN-SITU LEACH/IN-SITU RECOVERY (ISL/ISR) SITES**

**Radiation Protection Division  
Office of Air and Radiation  
U.S. Environmental Protection Agency**

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This report provides background information to assist the SAB in performing its advisory review. To do that, the information in this report is grouped into nine sections, split between two parts. Part 1 details a draft overall approach; Part 2 discusses specific issues and case studies associated with the draft overall approach. Additional detailed information is provided in five attachments. EPA believes it is important to provide the SAB with the context so that the SAB may relate the technical questions to the complex physical situations in which they might be applied. We also believe it is important for the SAB to understand the statutory basis governing our regulatory approach, *i.e.*, EPA's standards must be consistent with RCRA requirements, but those standards are implemented and enforced by NRC or its Agreement States through its licensing requirements. It should therefore be understood that while EPA is requesting advice on the technical aspects to be considered in a rulemaking that will establish standards applicable to ISL/ISR facilities, EPA is not requesting advice on either the form or content of those standards. EPA's regulatory proposal will be informed, in part, by the technical advice of the SAB, and will be developed in a manner that is consistent with EPA's UMTRCA standard-setting authority while taking into account the Agency's broader groundwater protection and risk management policies.

In its charge to the SAB, EPA requested that the SAB address the following with respect to ISL/ISR extraction processes:

- (1) Comment on the technical areas described in this report and their relative importance for designing and implementing a monitoring network. Identify any technical considerations that have been omitted or mischaracterized.
- (2) Comment on the proposed approaches for characterizing baseline groundwater chemical conditions in the pre-mining phase and proposed approaches for determining the duration of such monitoring to establish baseline conditions.
- (3) Comment on the approaches considered for monitoring in the post-mining/restoration phase and the approaches considered for determining when groundwater chemistry has reached a "stable" level.
- (4) Comment on statistical techniques about which you are aware that have been used in other applications, as well as the subsequent data requirements for their use relative to ISL mining applications (particularly for the areas in items 2 and 3 above).

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- Attachment B: Post-Restoration Stability Monitoring Case Histories
- Attachment C: Aquifer Restoration (Extracted from NRC 2009, Section 2.11.5)
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## ACRONYMS AND ABBREVIATIONS

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BPT	Best Practicable Technology
C vs. D	concentration vs. distance
C vs. T	concentration vs. time
CBR	Crow Butte Resources
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CFR	<i>Code of Federal Regulations</i>
COGEMA	Cogema Mining, Inc.
DBS&A	Daniel B. Stephens and Associates, Inc.
DENR	Department of Environment and Natural Resources (South Dakota)
DEQ	Department of Environmental Quality
DQO	data quality objective
EDTA	Ethylenediaminetetraacetic Acid
Eh	oxidation-reduction potential
EPA	Environmental Protection Agency (U.S.)
GCGCD	Goliad County Groundwater Conservation District
gpm	gallons per minute
GWS	groundwater sweep
IAEA	International Atomic Energy Agency
ISL	in-situ leach
ISR	in-situ recovery
$K_d$	partition or distribution coefficient
LQD	Low-Q Diffractometer
MARSSIM	Multi-Agency Radiation Survey and Site Investigation Manual
MCL	maximum contaminant level
MDD	minimum detectable difference
mg/L	milligram per liter
MNA	monitored natural attenuation
MU	Mine Unit
NDEQ	Nebraska Department of Environmental Quality

NEM	non-electrostatic surface complexation model
NRC	Nuclear Regulatory Commission (U.S.)
OSWER	Office of Solid Waste and Emergency Response
PAA	Production Authorization Area or Proposed Action Area
pH	measure of acidity of a solution
pCi/L	picocurie per liter
ppm	parts per million
PQL	practical quantitation limit
PRI	Power Resources, Inc.
QA	quality assurance
RAI	Request for Additional Information
RCRA	Resource Conservation Recovery Act
RO	reverse osmosis
SAB	Science Advisory Board
SI	saturation index
SRB	sulfate-reducing bacteria
TCEQ	Texas Commission on Environmental Quality
TDS	Total Dissolved Solids
TENORM	Technologically Enhanced Naturally Occurring Radioactive Material
UIC	Underground Injection Control
UMTRCA	Uranium Mill Tailings Radiation Control Act
USGS	U.S. Geological Survey
UST	underground storage tank
WDEQ	Wyoming Department of Environmental Quality
WQD	Water Quality Division
WRS	Wilcoxon Rank Sum

# OVERVIEW

## Background

In accordance with the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) section 206, the U.S. Environmental Protection Agency (EPA) is authorized to develop standards for the protection of public health, safety, and the environment from radiological and non-radiological hazards associated with residual radioactive materials at inactive uranium mill tailings sites and with the processing, possession, transfer, and disposal of byproduct material (tailings or wastes) at sites where ores are processed primarily for their uranium content or used for disposal of byproduct material. UMTRCA requires EPA to develop health and environmental standards for both Title I inactive mill sites administered by the U.S. Department of Energy (DOE) and Title II (present and future) operations licensed by the U.S. Nuclear Regulatory Commission (NRC) or its Agreement States.

In 1983, EPA promulgated regulations at *40 CFR Part 192 – Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings* in response to the statutory requirements of UMTRCA. When the Agency promulgated 40 CFR Part 192, uranium recovery from ore was based almost exclusively on the conventional milling process, where a few pounds of uranium were recovered for each ton of ore mined and processed. The residues from the milling process (the tailings or byproduct material) accumulated in large piles on the surface at the mill site. Concern that these tailings piles would be a continuing source of radiation exposure unless properly reclaimed was the driving force behind the passage of UMTRCA. Because the major environmental risk at that time was perceived to come from the conventional uranium mill tailings, other uranium recovery operations, such as heap leaching and in-situ leaching (ISL), received little attention.

The EPA last revised its regulations for uranium and thorium milling in 1995, and currently is reviewing them to determine if revisions are necessary to bring them up-to-date. Since 40 CFR Part 192 was promulgated, there has been a shift in uranium recovery from conventional milling to ISL where, in a sense, a portion of the milling process is conducted underground. Where the ore body is amenable to use of the ISL technology, uranium can be recovered economically without extensive surface facilities, large waste volumes, or expectations of long-term site maintenance associated with conventional milling. In the ISL process, also referred to as in-situ recovery (ISR), chemical solutions are pumped underground through an array of wells into the ore body, where the uranium is dissolved in place. The uranium-rich solutions are pumped to the surface, where the uranium is extracted. The solutions are then chemically reformed and pumped back into the ore body to recover additional uranium.

EPA's standards must address non-radiological, as well as radiological, constituents. Therefore, for Title I sites, UMTRCA states that the standards shall, "... to the maximum extent practicable, be consistent with the requirements of the Solid Waste Disposal Act, as amended," now known as the Resource Conservation and Recovery Act (RCRA). For Title II sites, the non-radiological standards shall be "... consistent with the standards required under subtitle C of the Solid Waste Disposal Act, as amended, which are applicable to such hazards."

EPA's current standards in 40 CFR Part 192 incorporate the RCRA groundwater monitoring requirements for hazardous waste units specified in 40 CFR Part 264, including statistical techniques applicable to determining when monitoring requirements have been achieved. A key question in amending 40 CFR Part 192 is whether, and to what extent, it is appropriate to apply these technical approaches, developed to address releases to groundwater from engineered units such as landfills, impoundments, and tanks, to ISL/ISR facilities, where the regulated "unit" is a defined portion of an aquifer.

## **Draft Technical Report Contents Overview**

With ISL/ISR operations expected to be the most common type of new uranium extraction facility in the U.S., and the potential for these facilities to affect groundwater, EPA is considering how to address groundwater monitoring as a component of the regulatory standards specifically applicable to these facilities in its revision of 40 CFR Part 192. To support a request for technical advice from the Agency's Science Advisory Board (SAB), EPA has prepared this draft Technical Report, *Considerations Related to Post-Closure Monitoring of Uranium In-Situ Leach/In-Situ Recovery (ISL/ISR) Sites*, to address considerations involved in establishing groundwater monitoring systems around uranium ISL/ISR operations (e.g., sampling protocols, time frames, statistical tools and techniques).

There are several objectives for monitoring an ISL/ISR uranium extraction operation, specifically: to establish baseline (pre-operational) groundwater chemical compositions; to detect excursions of the injected and mobilized components beyond the well field; and to determine when the post-operational/restoration phase groundwater chemistry has "stabilized," i.e., reached concentration levels that are expected to remain constant over time.

EPA's regulatory effort will focus on establishing requirements applicable to ISL/ISR facilities. Because the "milling" of uranium ore is performed within the aquifer by injection of mobilizing agents, ISL/ISR facilities present challenges for groundwater protection that are distinct from those posed by conventional mills. Further, the intent of ISL/ISR operators is to release the site after additional processing of ore is no longer economically viable, making it available for other uses. Given the disruption of the aquifer inherent in ISL/ISR technology and the foreseeable desire for a relatively short period of post-operational institutional control, groundwater protection will be of central importance in amendments to 40 CFR Part 192.

As noted above, one purpose of monitoring is to demonstrate that the aquifer conditions (i.e., contaminant concentrations or geochemical characteristics) established at the end of restoration are sustainable, or stable, over time. Currently, the duration of stability monitoring is a site-specific period of time established in the license(s) required by the NRC or the appropriate Agreement State. In the past, the license-established restoration period frequently has been about six months. More recently, the trend has been to increase the monitoring period established in the license to at least one year. In practice, the actual period necessary for contaminant concentrations to stabilize may be several years, based on iterative analyses of additional samples required by the regulators.



The draft Technical Report is intended to support the SAB's technical consideration of issues associated with establishing the groundwater baseline for new facilities, demonstrating that the restored groundwater has reached steady state, and post-restoration stability monitoring to ensure that the groundwater quality is not deteriorating over time after restoration.

Organizationally, the draft Technical Report addresses two main topic areas. The report initially focuses on the process and considerations associated with the overall approach. Specifically, the first section of the report provides an outline of the technical requirements associated with monitoring of ISL/ISRs and includes: a summary of UMTRCA; a summary of relevant components of RCRA; background information on the ISL/ISR process; a discussion of the purposes of a groundwater monitoring system; factors affecting the timeframe and ability to restore an ISL/ISR wellfield to baseline conditions; and discussion of various statistical techniques and approaches to measure achievement of post-operational restoration goals. Second, the report focuses on specific issues associated with ISL/ISR facilities and groundwater monitoring. This latter discussion provides case studies, identifies key issues associated with post-closure monitoring, and summarizes performance issues regarding groundwater monitoring at ISL/ISR facilities.

# PART 1

## 1.0 INTRODUCTION

In 1983, the U.S. Environmental Protection Agency (EPA) promulgated regulations at *40 CFR Part 192 – Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings* in response to the statutory requirements of the Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978. UMTRCA amended AEA by directing EPA to set generally applicable health and environmental standards to govern the stabilization, restoration, disposal, and control of effluents and emissions at both active and inactive mill tailings sites.

Title I of the Act covers inactive uranium mill tailing sites, depository sites, and vicinity properties. In addition to EPA's standard-setting responsibilities, Title I designated the U.S. Department of Energy (DOE) as the agency responsible for implementing EPA's standards for the tailings piles (residual radioactive material) and vicinity properties and for providing long-term stewardship of some properties. In addition, the U.S. Nuclear Regulatory Commission (NRC) was designated to review completed site cleanups for compliance with EPA standards and to license sites to the state or DOE for long-term stewardship, as necessary.

Title II of the Act covers operating uranium processing sites licensed by the NRC. EPA was directed to promulgate standards for the processing, possession, transfer, and disposal of uranium mill tailings (byproduct material). NRC, or its Agreement States, was required to implement and enforce these standards at Title II sites.

40 CFR Part 192 thus establishes standards for active and closed mill sites, including groundwater, soil, and building clean-up requirements. These standards are applicable to uranium and thorium extraction facility licensing, operations, sites, and wastes and are implemented and enforced by the NRC and its Agreement States, and DOE. Part 192 applies to residual radioactive material and byproduct material from conventional mills, in situ leach/recovery (ISL/ISR) facilities, and heap leach facilities, but not conventional mines (open pit or underground).

Since 40 CFR Part 192 was promulgated, there has been a shift in emphasis in uranium recovery methods from conventional milling to ISL/ISR, which is considered to be "underground milling."<sup>1</sup> In the ISL/ISR process, chemical solutions (*i.e.*, lixiviants) are pumped underground through an array of wells into the ore body, where the uranium is dissolved. The lixiviants are then pumped to the surface, where the uranium is extracted.

In response to this shift in production technology, EPA announced on May 27, 2010, that they planned to review 40 CFR Part 192. In support of the review, EPA is requesting guidance from the Science Advisory Board (SAB) on selected issues related to explicitly incorporating

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<sup>1</sup> Like conventional mills, ISL/ISR operations are regulated by NRC as a form of uranium processing. However, the injection-extraction technology is also applied to the recovery of other minerals, where it is broadly known as "solution mining." Where this draft Technical Report uses the term "mining," which may be more familiar to the general public, it is referring to the ISL/ISR extraction method.

standards for in-situ leaching facilities into 40 CFR Part 192. These issues center on groundwater monitoring and stability, which are the subject of this draft Technical Report.

Groundwater monitoring within and in the vicinity of an ISL site serves vital functions that are necessary for efficient uranium recovery with minimal adverse environmental impacts. Proper monitor well placement and data collection from these wells assures that the aquifer constituents are detected, and then restored, to pre-mining levels. Without adequate monitoring well placement and proper data collection, including consideration of sample frequency and sampling timeframe, mine operators and regulators (1) may not detect excursions of lixiviant outside the mining area during operations, and (2) may not be able to confidently determine whether the impacted aquifer needs further restoration or has been restored to its pre-mining state or another suitable condition that satisfies regulatory requirements.

EPA's standards in 40 CFR Part 192 are required by statute to address non-radiological, as well as radiological, constituents, and to provide for the "protection of human health and the environment consistent with the standards required under Subtitle C of the Solid Waste Disposal Act..." (UMTRCA sec. 206(b)(2)). In particular, for Title I sites, UMTRCA states that the standards shall, "... to the maximum extent practicable, be consistent with the requirements of the Solid Waste Disposal Act, as amended," now known as the Resource Conservation and Recovery Act (RCRA). For Title II and future NRC licensed sites, the standards shall be "... consistent with the standards required under subtitle C of the Solid Waste Disposal Act, as amended, which are applicable to such hazards."

The existing standards incorporate groundwater protection requirements applicable to hazardous waste management units. These requirements are specified in 40 CFR Part 264, Subpart F (Releases from Solid Waste Management Units). These requirements also provide a reasonable basis for a proposal to address post-operational groundwater monitoring and restoration at ISL/ISR facilities, while also providing the flexibility for site-specific, performance-based implementation by the regulatory authority (NRC or Agreement State).

## **2.0 RESOURCE CONSERVATION AND RECOVERY ACT**

### **42 U.S.C. §6901 et seq. (1976)**

The purpose of this section is to provide an overview of the Resource Conservation and Recovery Act (RCRA) program. Provisions specifically relevant to ISL/ISR facility licensing/oversight are discussed in detail. These include: Subtitle C facilities; groundwater monitoring requirements; and Treatment Storage and Disposal Facilities.

### **2.1 Summary**

The Resource Conservation and Recovery Act (RCRA) was passed in 1976, as an amendment to the Solid Waste Disposal Act of 1965, to ensure that solid wastes are managed in an environmentally sound manner. RCRA gives EPA the authority to control hazardous waste from the "cradle-to-grave." This includes the generation, transportation, treatment, storage, and disposal of hazardous waste (Subtitle C). RCRA also set forth a framework for the management of non-hazardous solid wastes (Subtitle D). RCRA has been further amended to extend its application; for example, the 1986 amendments to RCRA enabled EPA to address environmental problems that could result from underground tanks storing petroleum and other hazardous substances.

RCRA is a key component of EPA's UMTRCA standards in 40 CFR Part 192. As noted in Chapter 1, Congress specified that EPA's standards were to address non-radiological, as well as radiological, constituents. Therefore, for Title I sites, UMTRCA states that the standards shall, "... to the maximum extent practicable, be consistent with the requirements of the Solid Waste Disposal Act, as amended," now known as RCRA. For Title II and future NRC licensed sites, the standards shall be "... consistent with the standards required under subtitle C of the Solid Waste Disposal Act, as amended, which are applicable to such hazards." UMTRCA Section 206(a)

EPA's current standards in 40 CFR Part 192 incorporate the RCRA groundwater monitoring requirements for hazardous waste units specified in 40 CFR Part 264, including statistical techniques applicable for determining when standards have been achieved. A key question in this advisory is whether, and to what extent, it is appropriate to apply these techniques, which were developed to address releases to ground water from engineered hazardous waste units such as landfills, impoundments, and tanks, to in situ leach uranium recovery facilities, where the regulated "unit" is a defined portion of an aquifer.

The RCRA approach to protecting groundwater represents a reasonable starting point for developing criteria and standards specific to ISL/ISR facilities. The remainder of this chapter provides additional detail on the RCRA requirements and discusses technical challenges in applying those requirements to ISL/ISR facilities. Part 2 of this document describes technical approaches for consideration by the SAB, including potential modifications, extensions, and additions to the RCRA requirements.

## **2.2 Groundwater Monitoring Requirements for Treatment, Storage, and Disposal Facilities (TSDFs)**

### **2.2.1 Overview**

The groundwater monitoring requirements for hazardous waste treatment, storage, and disposal facilities (TSDFs) are an important aspect of the RCRA hazardous waste management strategy for protecting human health and the environment from accidental releases of hazardous constituents. While land disposal restrictions and unit specific standards seek to reduce the toxicity of waste and prevent releases, respectively, the groundwater monitoring requirements represent the last line of defense by ensuring that any releases are detected and remediated in a timely manner.

TSDFs that manage hazardous waste in landfills, surface impoundments, land treatment units, and some waste piles (referred to as “regulated units” in the regulations) are required to implement a groundwater monitoring program to detect the release of hazardous constituents to the underlying ground water. The regulations for permitted facilities are found at 40 CFR Part 264, “Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities.” Specifically, Subpart F addresses “Releases from Solid Waste Management Units” and includes elements of a monitoring program such as:

- Groundwater protection standard;
- Hazardous constituents;
- Concentration limits;
- Point of compliance;
- Compliance period;
- General monitoring requirements;
- Detection monitoring;
- Compliance monitoring; and
- Corrective action.

The overall goal of these requirements is to protect the ground water in the uppermost aquifer from contamination by the hazardous constituents managed at the TSDF.

### **2.2.2 Permitted Facilities**

For permitted TSDFs, a groundwater monitoring program consists of three phases: detection monitoring (§264.98), compliance monitoring (§264.99), and corrective action (§264.100). The phases are sequential, with a facility able to move back and forth between phases as certain criteria are met. The regulations are written as performance standards that require each facility’s groundwater monitoring program to have a sufficient number of wells installed at the appropriate locations and depths that can yield representative samples of background conditions and water quality at the point of compliance in the uppermost aquifer (defined as the geological formation nearest the natural surface that is capable of yielding significant quantities of ground water to wells or springs).

To meet these standards, each facility must design, install, and operate a groundwater monitoring program based upon the site's specific geology and hydrology, as well as the type of waste management unit and the characteristics of the waste being managed. The monitoring wells must be appropriately designed and installed and consistent sampling and analytical procedures must be implemented to ensure accurate and representative samples are taken. The specific sampling requirements and procedures (including frequency of sampling) are specified in the facility's hazardous waste permit.

### ***2.2.3 Detection Monitoring***

Detection monitoring is phase one of the groundwater monitoring program. Under this phase, facilities are monitoring to detect and characterize any releases of hazardous constituents into the uppermost aquifer. Samples are taken from the monitoring wells and analyzed for specific indicator parameters and any other waste constituents or reaction products that indicate that a release might have occurred. The facility's permit identifies the specific constituents and parameters to be monitored and establishes the frequency of sampling. At a minimum, four samples must be taken from each well semi-annually.

Samples taken from the point of compliance (*i.e.*, the wells downgradient of the waste management unit) are compared to the background samples taken from the upgradient well(s). These samples are analyzed to determine if a statistically significant increase (SSI) in the levels of any of the monitored constituents has occurred. When analyzing the samples, facility owner/operators may use one of the following five methods:

- Parametric analysis of variance.
- Nonparametric analysis of variance based on ranks.
- Tolerance or prediction interval procedure.
- A control chart approach.
- Another statistical test method approved by the EPA Regional Administrator.

If an SSI is detected, the facility must switch to a compliance monitoring program, unless the owner/operators can demonstrate that the SSI was due to a sampling, analysis, or statistical analysis error; or is due to natural variations in the groundwater chemistry. If unable to make this demonstration, the owner/operators must:

- Notify the EPA Regional Administrator of the SSI within 7 days.
- Immediately sample all wells for hazardous constituents listed in Part 264 Appendix IX.
- Determine which Part 264 Appendix IX constituents are present and at what levels.
- Submit a permit modification application within 90 days to begin a compliance monitoring program.
- Submit an engineering feasibility plan for a corrective action program within 180 days.

#### ***2.2.4 Compliance Monitoring***

The purpose of a compliance monitoring program is to ascertain whether the constituents released to the uppermost aquifer are exceeding acceptable concentration levels and threatening human health and the environment. The first step in this process is establishing a groundwater protection standard (GWPS). As stated above, a facility must submit a permit modification application to switch from detection monitoring to compliance monitoring when an SSI is detected. As part of this modified permit, the EPA Regional Administrator specifies the GWPS for the facility. The GWPS establishes:

- The list of hazardous constituents for which to monitor (from Part 261, Appendix VIII).
- The concentration limits for each of the listed constituents based either on background levels, Safe Drinking Water Act (SDWA) Maximum Contaminant Levels (MCLs), or alternate concentration levels (ACLs) determined by the EPA Regional Administrator.
- The point of compliance, which is the vertical surface at which the facility must monitor the uppermost aquifer to determine if the GWPS is being exceeded.
- The compliance period during which the GWPS applies and compliance monitoring must be continued.

During compliance monitoring, samples are taken at each well located at the point of compliance (four samples from each well) and compared to the GWPS. The frequency of sampling is determined by the EPA Regional Administrator and specified in the modified facility permit. At a minimum, samples must be taken at least semi-annually. The facility must also analyze samples for Part 264 Appendix IX constituents at least annually. If any new constituents are found to have an SSI, then they also must be added to the GWPS list of constituents.

If the level of any of the constituents exceeds the GWPS, the owner/operators must notify the EPA Regional Administrator in writing within 7 days. The owner/operators also must submit a permit modification application to establish a corrective action program. Compliance monitoring must be continued during this period.

#### ***2.2.5 Corrective Action***

Once an exceedance of the groundwater protection standard (GWPS) has been detected, the facility must take action to bring the constituent concentration levels back into compliance with the GWPS. To achieve this, the owner/operator must either remove the hazardous constituents or treat them in place. The *EPA Regional Administrator* will approve the facility's selected corrective action method and specify the time frame in which it must take place. Any hazardous constituents that have migrated beyond the point of compliance also must be remediated. The facility must continue corrective action until the GWPS has not been exceeded for three consecutive years. At that point, the facility may return to compliance monitoring.

## 2.3 Application to ISL/ISR Facilities

While the application of the RCRA groundwater monitoring requirements to conventional mills and tailings impoundments is relatively straightforward, the ISL/ISR technology presents additional technical challenges for post-operational monitoring. First, the technology is applied within the aquifer by intentionally altering its chemical characteristics to facilitate transport of uranium. Thus, in the RCRA framework, contaminants have already been released into the environment and are no longer contained within the engineered hazardous waste unit (that is, a surface impoundment). This suggests that the situation could be viewed as a corrective action from the time operations cease.

The intent of the operator to release the site for unrestricted use presents the more significant challenge. Unlike conventional tailings impoundments, which are subject to long-term stewardship requirements, ISL/ISR facilities will leave no significant surface facilities or waste behind. Restoration of the groundwater will therefore need to be achieved throughout the well field, within which there may be significant heterogeneity. Further, from a corrective action standpoint, the “source” of contamination cannot necessarily be identified to a specific location within the affected area. It is therefore particularly important that an appropriate monitoring program be developed, including an appropriate number of wells in the right locations, to determine, with the appropriate level of confidence, that restoration and stability have been achieved. As discussed in this document, there may be technical approaches that can be used to modify or extend the RCRA requirements. Additionally, there may be better-suited technical approaches for these particular types of facilities.

This situation has been further complicated for operating ISL/ISR facilities by the fact that permits for lixiviant injection wells must be obtained from EPA’s Underground Injection Control (UIC) program developed pursuant to the SDWA (in some cases, authority to issue UIC permits has been delegated to states). In issuing the UIC permit, the regulatory authority must exempt the portion of the aquifer affected by the activity. The primary concern is that there be no transport of contaminants beyond the exempted portion of the aquifer (“excursion”) into an Underground Source of Drinking Water (USDW). Requirements for restoration of the exempted portion of the aquifer under the UIC program are limited compared to the requirements of 40 CFR Part 192. Failure to recognize the applicability of 40 CFR Part 192 to all groundwater at an ISL/ISR facility (*i.e.*, in the well field) has led to a situation in which operators at some ISL/ISR facilities have not been held to the more stringent standards in 40 CFR Part 192 (see case studies included in this document). Further, in some cases the appropriate baseline conditions may not have been recorded. Advice on handling these cases is also needed.



## 3.0 GROUNDWATER MONITORING AT ISL/ISR FACILITIES

### 3.1 Overview

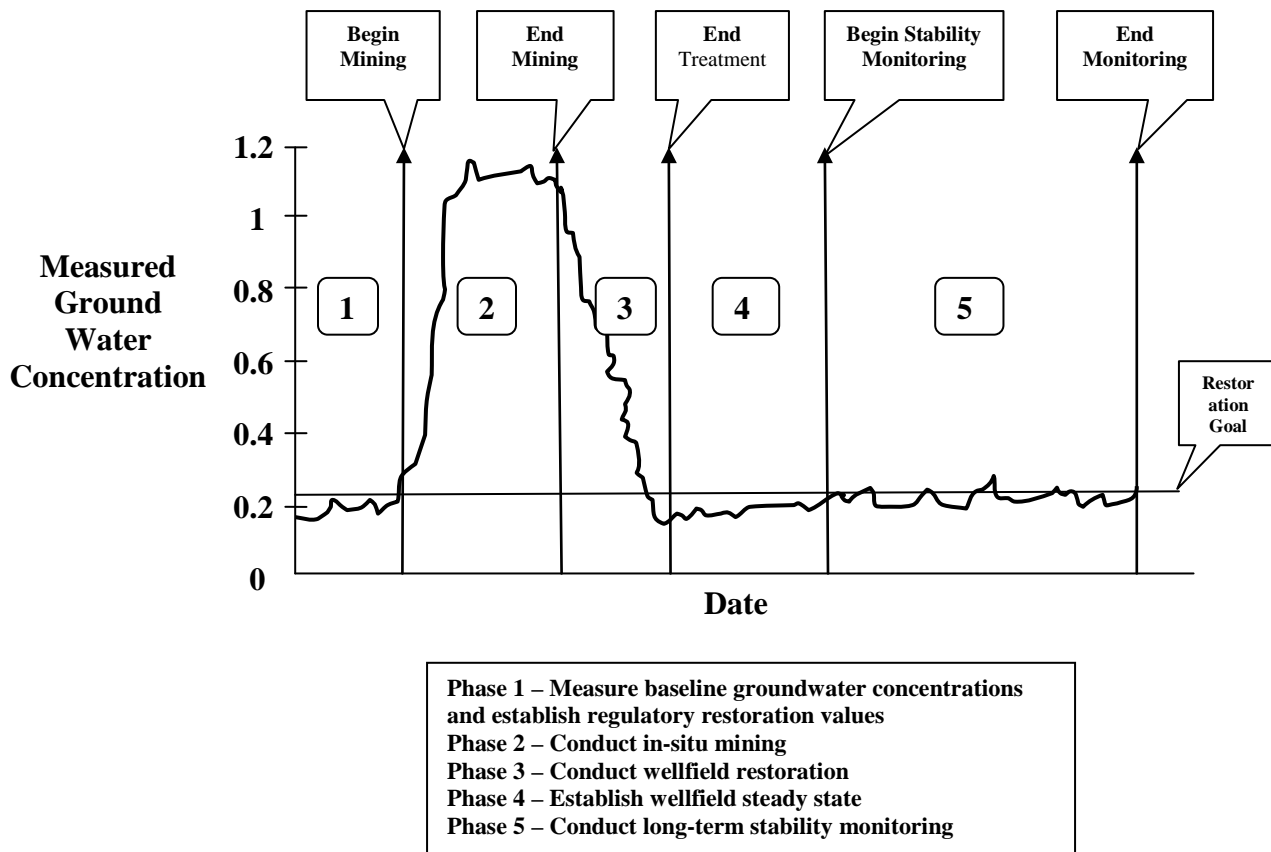
The lifecycle of an ISL/ISR facility includes the following:

- Exploration and development to establish that a commercially viable operation is possible
- Establishment of site baseline conditions for in-situ leaching (mining) of the ore body
- Recovery of uranium from the ore body
- Restoration of the groundwater to predetermined conditions
- Demonstration that restored groundwater has reached steady state
- Post-restoration stability monitoring of the groundwater
- Decommissioning of mined area and surface facilities

This draft Technical Report is most concerned with the pre- and post-operational aspects of groundwater monitoring, specifically establishment of the groundwater baseline, demonstration that the restored groundwater has reached steady state, and post-restoration stability monitoring to ensure that the groundwater quality is not deteriorating over time after restoration. Figure 3-1 is a graphic representing an evolution of a groundwater component of interest during the phases described below.

The five phases of groundwater monitoring during the life of the ISL/ISR facility are:

- Phase 1 – Measure baseline groundwater concentrations and establish regulatory approved restoration goals based on statistical procedures that embrace pre-mining temporal and spatial variability.
- Phase 2 – Conduct in-situ mining. Detect lixiviant excursions outside the mining area if they occur. Determine the groundwater chemistry at the end of ISL/ISR operations.
- Phase 3 – Conduct wellfield restoration. Monitor the progress of restoration through groundwater sampling.
- Phase 4 – Establish wellfield steady state. At the end of this phase, the groundwater potentiometric surface will have returned to baseline conditions (to the extent practicable) and statistical tests show that groundwater chemistry is stable.
- Phase 5 – Conduct long-term stability monitoring. At the end of this phase, use statistical tests to show that concentration of the monitored species is not increasing with time and that concentration is not statistically different from baseline conditions, or if baseline conditions are unachievable, that the concentration is not statistically different from approved restoration goals.



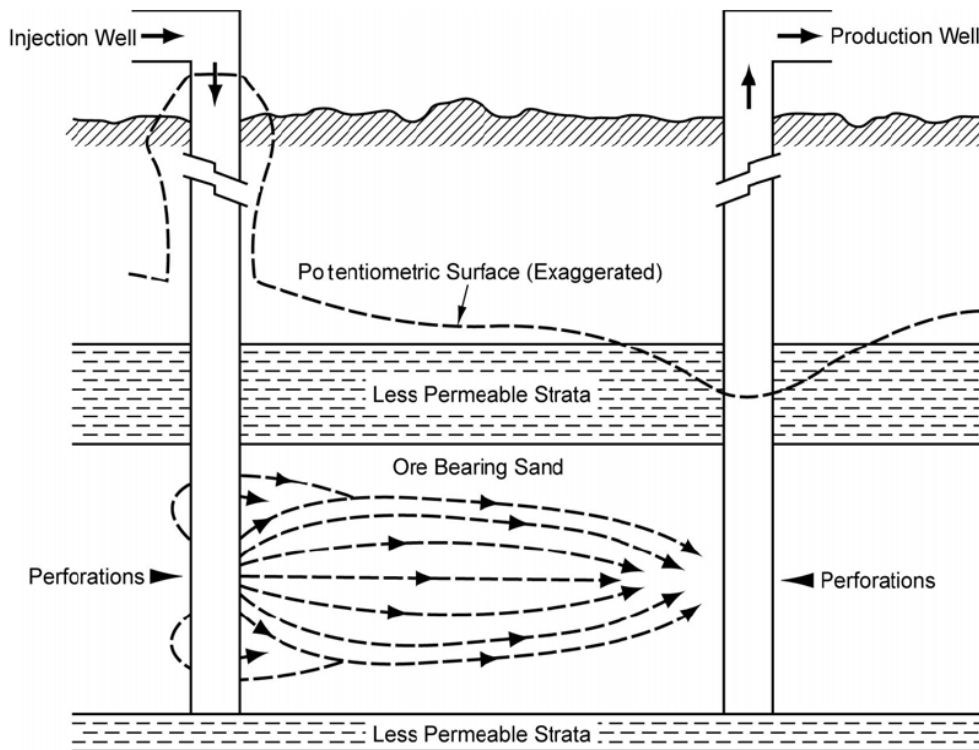
**Figure 3-1. Variation of Typical Groundwater Constituent Over Time**

### 3.2 Pre-Operational Monitoring (Phase 1)

The key to any baseline monitoring program is to adequately characterize groundwater temporal and spatial variations before mining begins. In order to provide the basis of comparison for assessing progress in restoring the wellfield after mining has been completed, the breadth of pre-operational groundwater monitoring needs to be sufficiently robust for adequate comparisons with post-operational monitoring.

### 3.3 The ISL/ISR Leaching Process (Phase 2)

During typical ISL/ISR operations, chemicals such as sodium carbonate/bicarbonate, gaseous oxygen, and hydrogen peroxide are added to the groundwater to produce a concentrated oxygen-rich leaching solution called the lixiviant. The lixiviant is injected into the production zone to create groundwater oxidizing conditions which mobilize the uranium from the uranium rich geologic zone. This mobilized uranium is pumped back to the surface for extraction at a processing plant (Figure 3-2).



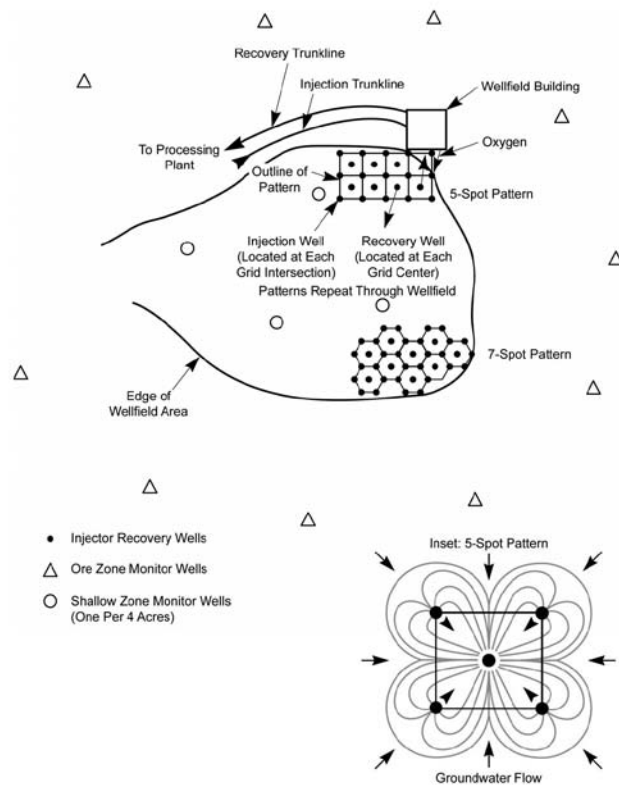
**Figure 3-2. Idealized Schematic Cross Section to Illustrate Ore-Zone Geology and Lixiviant Migration from an Injection Well to a Production Well (NRC 2009)**

The most common injection/pumping patterns are five- and seven-spot (NRC 2003). The shape of the mineralized ore body and surface topography, however, may give rise to other patterns (NRC 1997). A typical five-spot pattern contains four injection wells and one recovery well. The dimensions of the pattern vary depending on the mineralized zone, but the injection wells are generally between 40 to 150 feet apart. In order to effectively recover the uranium and also to complete the groundwater restoration, the wells are often completed so that they can be used as either injection or recovery wells. During mining operations, a slightly greater volume of water will be recovered from the mineralized zone aquifer than was injected, in order to create a cone of depression or a flow gradient towards the recovery wells. This practice is intended to minimize excursions of leachate outside the production area. Groundwater monitoring is necessary to detect any excursions of lixiviant outside the mining area during operations. A typical well arrangement using five- and seven-spot patterns is shown in Figure 3-3. Figure 3-4 illustrates a typical wellfield. Piping connecting the individuals to the header house is typically run underground.

Ore body size and geometry will also influence the number of wells in a wellfield. For example, at the Crow Butte ISL facilities in Dawes County, Nebraska, the number of injection and production wells varied from about 190 in the first wellfield (MU-1) to about 900 in later wellfields (MU-5 and MU-6) (NRC 1998).

Three types of wells predominate at uranium ISL/ISR facilities during the operational (leaching) phase (see Figure 3-3):

- (1) Injection wells for introducing solutions into the uranium mineralization
- (2) Production wells for extracting uranium-enriched solutions
- (3) Perimeter monitoring wells for assessing containment of leachate within the wellfield (the ore zone monitor wells in Figure 3-3)



**Figure 3-3. Schematic Diagram of a Wellfield Showing Typical Injection/Production Well Patterns, Monitoring Wells, Manifold Buildings, and Pipelines (NRC 2009)**



**Figure 3-4. Wellheads and Header House, Smith Ranch, Converse County, Wyoming**  
(NRC 2009, Figure 2.1-4)

### **3.4 Post-Operational Monitoring (Phases 3 through 5)**

The intent of restoration efforts is to establish hydrologic and geochemical conditions in the mined areas that will maintain steady-state conditions in all potentially affected aquifers (*i.e.*, overlying, underlying, and adjacent aquifers) and assure no degradation of water quality from pre-mining conditions. During restoration, the operator monitors progress by periodic sampling of the groundwater constituents and analysis in an effort to determine when steady-state conditions are attained. Establishment of steady-state conditions requires that the groundwater potentiometric surface be restored, to the extent practicable, to its pre-leaching status, so that the flow regime is similar to that existing before mining. In addition, constituents in the groundwater must be returned to the predetermined restoration goal and remain at that level for a sufficient period to demonstrate that the results are not trending upwards to higher concentration levels.

Once the operator concludes that restoration has been completed and has obtained concurrence from the regulator(s) that a steady state has been established, post-restoration stability monitoring begins. The purpose of the stability monitoring is to demonstrate that the aquifer conditions established at the end of restoration are sustainable over time. Currently, the duration of the stability monitoring period is site-specific, with the period established in the license(s). In the past, the license-established restoration period typically has been about 6 months. More recently, the trend has been to increase the monitoring period established in the license. In practice, the actual period of stabilization may be several years, based on iterative analyses of additional samples requested by the regulators.

A key question associated with this issue is: Is the use of a confidence level an appropriate potential metric for determining when the aquifer can be considered stable?

## **4.0 TECHNICAL CONSIDERATIONS FOR ISL/ISR GROUNDWATER MONITORING**

Monitoring wells within an in-situ mining area and site vicinity serve vital functions necessary for efficient uranium recovery with minimal adverse environmental impacts. Proper monitor well placement and data collection from these wells assure that the aquifer constituents are detected and then restored to pre-mining levels. Without adequate monitoring well placement and proper data collection, which includes consideration of sample frequency and sampling timeframe, mine operators and regulators (1) may not detect excursions of lixiviant outside the mining area during operations; and (2) may not be able to confidently determine whether the impacted aquifer needs further restoration or has been restored to its pre-mining state or predetermined conditions specified by regulators.

This section focuses on technical considerations for groundwater monitoring through all phases of an ISL/ISR facility. Because the monitoring goals and practices are dependent on the characteristics of the ore body, this section begins with a discussion of geographic, geologic, and chemical characteristics typical of uranium deposits suitable for leaching.

### **4.1 Uranium Geology**

The principal regions of uranium recovery by ISL/ISR are the Wyoming basin, the Colorado Plateau and the Gulf Coastal Plain of Texas. The southern Black Hills in South Dakota and northeast Colorado/western Nebraska within the Great Plains region also contain sedimentary uranium deposits amenable to ISL/ISR.

Leachable uranium deposits are found in sandstones that have been deposited in intermontane basins, along mountain fronts, and in near-shore marine and deltaic environments. The deposited sediments were created as a complex and heterogeneous rock sequence that may be greater than 2,000 meters thick (Rojas 1989). This rock sequence can be made up of a number of water-bearing units separated by confining units. The water-bearing unit containing the ore body is separated (at least locally) from other water-bearing units above and below.

Zones of uranium mineralization follow a general trend of drainage channels. Individual ore bodies in sandstone lenses rarely exceed a few hundred yards in length (Rojas 1989). These are typically “roll-front” deposits that are formed when oxygenated water enters the sandstone aquifer by local recharge dissolving the uranium. Deeper into the aquifer, the oxygen becomes depleted and typically a convex curved redox interface is formed, with reducing conditions on the downgradient side and oxidizing conditions on the upgradient side. Reducing conditions can be caused by contact with carbonaceous material and pyrite.

Freshly precipitated uranium along with uranium in the arkosic sandstone minerals is continuously dissolved by oxygenated groundwater and displaced further downgradient (Rojas 1989). As the uranium comes in contact with the reducing conditions downgradient, an economically recoverable deposit of uranium may eventually be formed. The term “roll front” is used because over time, the redox interface rolls downgradient as more oxygen is transported into the aquifer. The inner contact of ore and altered sandstone are generally sharp, whereas the uranium concentration on the reduced side of the interface is gradational.

## 4.2 Establishing Baseline Conditions

Prior to initiating the ISL/ISR activities, knowledge of the aquifer baseline characteristics is needed to help determine restoration goals for the post-mining phase. Pre-mining monitoring and testing wells are installed to collect data that define the groundwater flow regime through the extraction zone and surrounding areas and determine the chemical characteristics of the groundwater. Monitoring wells should be installed at well locations upgradient, downgradient, and tangential to the proposed ISL/ISR field, as well as within the “ore-zone.” Well placement should be designed to measure all potential “escape” pathways for introduced constituents and mobilized metals, as well as to provide data to determine the choice and effectiveness of aquifer restoration actions. The design of the monitoring network is largely a site-specific decision predicated on a thorough knowledge of the groundwater flow regime and the effects of the injection and withdrawal rates on the flow system behavior. A system of wells should be emplaced to monitor the horizontal and vertical groundwater velocity and flow paths, groundwater chemical conditions, and the potential for hazardous constituents to migrate beyond the ISL/ISR mine field, both within the mined aquifer and through transmission of contamination to overlying and underlying aquifers. These areas beyond the ISL/ISR may experience contamination from the mined area beneath them.

The following components and parameters need to be considered in establishing baseline site characteristics (more details can be found in Part 2):

- (1) Hydro-geochemical Conditions – Eh (including redox sensitive couples), dissolved oxygen, pH, major ions, total dissolved solids (TDS), carbonate alkalinity, pCO<sub>2</sub>, radioactive constituents, colloids, organic constituents, hydrogen sulfide, trace elements (to be compared against post-restoration measurements).
- (2) Concentrations of those constituents listed in 40 CFR Part 192 – Arsenic, Barium, Cadmium, Chromium, Lead, Molybdenum, Nickel, Radium-226 and -228, Selenium, Silver, Thorium, Uranium, etc.
- (3) Uranium Ore Deposit Types and Oxidation States – The site-specific and varied diagenic processes that formed the uranium deposits will determine how baseline conditions will be affected by ISL/ISR operations and which restoration approach is likely to be most effective. Knowledge of these processes can be used as a framework in estimating the timeframe needed for the aquifer to reach baseline conditions once post-mining restoration and monitoring are initiated.
- (4) Hydro-geologic Setting – Pre-mining groundwater velocities (un-stressed), flow paths, and solute transport timeframes. A reliable and defensible characterization survey of the ISL/ISR site requires thorough core and water sampling from all monitoring wells and exploration boreholes. Sufficient data must be collected before the mining activity to understand when baseline levels have been reached after mining. Aquifer pump/stress tests and core sample analysis will determine aquifer characteristics within and surrounding the ore body and be used to determine:
  - a. Host rock and ore zone permeability, porosity, storativity, thickness

- b. Whether more monitoring wells are needed for post-closure activities and to assess the timeframe of post-closure monitoring
- c. Timeframe estimates after mining has ceased, in order for the system to reach pre-ISL/ISR conditions
- d. Recharge/discharge points
- e. Impermeable layers above and below ore zone
- f. Proximity to groundwater barriers
- g. Proximity to surface water bodies – natural or manmade

Sampling the groundwater may require special sample collection techniques, depending on the chemical constituents of concern. For major ions and some other chemical species, sampling may be relatively simple, in that these species are not susceptible to change upon exposure to atmospheric conditions. For species that are susceptible to re-equilibration in response to atmospheric conditions, particularly redox-sensitive species and the carbonate-bicarbonate system, water sampling may require that the sampled interval be “packed off” within the well and water samples taken in containers, which were placed within the sealed intervals prior to the “packing-off” and left to equilibrate in the flowing groundwater for a period of time prior to removal. Redox-sensitive couples typically examined include ferrous (II)/ferric (III) iron, and the arsenic (III) /arsenic (V) couple. In addition to dissolved oxygen levels, these couples can produce important characterization of the redox conditions in the production zone prior to, during, and after the leaching process, and can also be important in determining the effectiveness of various aquifer restoration processes.

In addition, uranium speciation is strongly affected by pH and carbonate concentrations in the groundwater, which, in turn, are a function of the  $p\text{CO}_2$  in the groundwater. Exposure of the groundwater sample to the atmosphere can result in the escape of  $\text{CO}_2$  and re-equilibration of the uranium-carbonate system due to the out-gassing. The uranium concentrations in the re-equilibrated water would not reflect the actual speciation in-situ, and, consequently, could result in misleading calculations of uranium speciation and solubility constraints in the subsurface waters. Because of these effects and their relative importance to characterizing the in-situ groundwater chemistry, monitoring water chemistry in and around the “ore body” may well require differing sampling methods.

### **4.3 Extraction Operations Phase**

During the ISL/ISR mining operations phase, wells are placed in the active ISL/ISR-treatment zone, fringe zone (wells at the ISL/ISR-mine boundary), and outside the impacted areas. The functions of a monitoring system during the extraction phase include:

- (1) Monitoring the extraction process to determine uranium recovery rates within the mining zone
- (2) Assessing the mass-balance of the lixiviant fluids



- (3) Monitoring excursions beyond the ore zone (both within the ore-bearing aquifer and in overlying and underlying aquifers)
- (4) Monitoring groundwater chemical composition in wells surrounding and downgradient of the extraction field
- (5) Monitoring the chemical composition of groundwater upgradient of the extraction field to determine if these waters are chemically stable over the course of the extraction effort

#### 4.4 Post-Extraction Phase

The post-extraction monitoring system should be designed to assess the effectiveness of the remediation process, assess when final remediation objectives have been met, and assure that the impacted aquifer is at steady state and the site is ready for decommissioning. A system of wells located in the active treatment zone, as well as outside the boundary of the impacted area, is required to monitor the horizontal and vertical groundwater velocity and flow paths within and around the vicinity of the ISL/ISR site. The functions of a post-mining monitoring system include:

- (1) Measuring downgradient groundwater chemical constituents to determine if and/or when the groundwater chemistry has returned to pre-ISL/ISR compositions (baseline)
- (2) Determining if additional chemical components have been added to the groundwater as a product of the extraction process (*e.g.*, metals mobilized with the uranium)
- (3) Demonstrating when the groundwater chemistry has reached “stable” levels (*i.e.*, statistically equivalent compositions over an extended time period)
- (4) Determining if post-mining restoration levels for groundwater constituents have been met

#### 4.5 Factors Affecting Post-Mining Timeframes and Wellfield Stability

Post-restoration monitoring must be of sufficient duration to assure that once groundwater chemistry appears to have reached acceptable restoration levels, these levels are at steady state and the groundwater system is at equilibrium. Steady-state restoration levels are not just for uranium, but include other hazardous constituents that may have been mobilized by ISL/ISR operations, such as radium, manganese, and selenium. Chemical speciation and solubility, as well as natural attenuation processes, must be understood to determine when the impacted aquifer has reached a steady-state condition.

Aquifer restoration is complex and results can be influenced by a number of site-specific hydrological and geochemical characteristics. In some cases, such as at Bison Basin and Reno Creek, the aquifer was restored in a relatively short time. In other cases, restoration required much more time and treatment than was initially estimated (*e.g.*, the A- and C-Wellfields at the Highland ISL facility).

The environmental chemistry of uranium is largely dictated by its oxidation state, with the solubility, and therefore mobility, of uranium the greatest when it is in the U(VI) state. Because different chemicals may be used during the restoration process than were used during ISL/ISR operation, the chemical form of uranium or other hazardous constituents may differ during restoration. Since most of the available computer codes do not have a method of calculating reaction rates, these reactions may be unexpected, and the duration of the monitoring program must be long enough to accommodate such unexpected conditions.

Natural attenuation processes include a variety of physical, chemical, and biological processes that can act to reduce the mass, mobility, volume, or concentration of contaminants in groundwater. Attenuation processes important at ISL/ISR sites include pH buffering and acid neutralization, adsorption at the mineral-water interface, mineral precipitation, dilution, and biological processes.

Another factor affecting the post-monitoring timeframe and wellfield stability is the form of remediation utilized. Pump and treat and geochemically-based techniques are commonly applied remediation approaches. Monitored natural attenuation is another response action that may be effective in certain situations.

#### *Pump and Treat*

Alternative approaches included in pump and treat remediation are:

- Groundwater Transfer – This involves transferring groundwater between the wellfield starting restoration and another where uranium leach operations are beginning. No liquid effluents are generated as water is transferred between one wellfield and another.
- Groundwater Sweep – Injection of lixiviant is stopped and the contaminated liquid is pumped from the leaching zone via all the injection and production wells. Fresh groundwater flows into the leaching zone from the outside, which displaces lixiviant in the pore spaces. Typically, an ion-exchange system is used to process the sweep water, which is disposed of either in evaporation ponds or via deep well injection in accordance with the site permit. The pumping rates are site specific, and the duration and volume of water removed depends on the aquifer affected by the ISL/ISR. Due to heterogeneities in the aquifers, groundwater sweep alone is insufficient and uneconomical for complete restoration. In addition, groundwater sweep may cause oxic conditions from upgradient waters to enter the ore zone, making it more difficult to re-establish chemically reducing conditions.
- Reverse Osmosis (RO) – To return groundwater to baseline conditions, it is usually necessary to remove contamination from the mined zone water while minimizing disposal of waste liquids. Reverse osmosis, which involves passing the water being restored through pressurized, semi-permeable membranes, is a common way of treating groundwater. The RO treatment results in clean water or permeate that can be re-injected into the aquifer and brine that is water with concentrated ions. The brine is usually sent to an evaporation pond, injected into deep disposal wells, or dried (using an evaporator) for disposal at a licensed facility.

- Permeate Injection – Many aquifers are characterized by porosity where groundwater with decreased mobility resides in regions of moderate to low permeability. It is very difficult to remove all of the lexiviant and associated contamination from this portion of the groundwater, which will act as a source of contaminants, even after long periods of pumping and treating. Chemicals may be added to injection water in the latter stages of restoration to assist in re-establishing baseline conditions. This includes reducing the mobility of many of the metal species that make up contaminants of concern, including uranium, selenium, molybdenum, and arsenic.

### *Geochemically-Based Techniques*

Another component of aquifer restoration is accomplished by establishing a chemical environment that alters the solubility of dissolved constituents, such as uranium, arsenic, and selenium. These methods typically invoke chemical reactions in which the valence state of elements are either oxidized to a higher valence state or reduced to a lower valence state.

### *Monitored Natural Attenuation*

Monitored natural attenuation (MNA) refers to the reliance on natural processes to achieve site-specific remediation objectives within a reasonable timeframe. These processes include biodegradation, dispersion, dilution, sorption, and volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants. The overall impact of MNA at a given site can be assessed by evaluating the rate at which contaminant concentrations are decreasing either spatially or temporally. EPA has prepared a technical resource document (EPA 2007a and 2007b) that presents a four-tiered assessment of MNA as a viable response action for selected metal, metalloid, and radionuclide contaminants encountered in groundwater and involves the following: (1) demonstrating contaminant sequestration mechanisms; (2) estimating attenuation rates; (3) estimating attenuation capacity of aquifer solids; and (4) evaluating potential reversibility issues. Additional details on MNA can be found in Part 2, section 7.4.

## **4.6 Modeling**

Groundwater fate and transport modeling is often utilized to reduce the uncertainty regarding the spatial and temporal behavior of the contaminant plume(s). For example, groundwater modeling is commonly implemented at ISL/ISR facilities to assist in meeting the following objectives:

- Optimize the monitoring well spacing to detect injection fluid excursions into non-mined aquifer zone(s)
- Estimate the number of pore volumes needed during site remediation activities to adequately reduce contaminant concentrations
- Establish a specific period of monitoring for ISL/ISR facilities once uranium extraction operations are completed

A conceptual model that summarizes the theoretical understanding of the primary conditions that affect groundwater flow and chemical transport and fate is first developed. Then, to solve the general model, a computer code is used. Computer codes frequently used to meet the modeling objectives at ISL/ISR facilities include three types: (1) groundwater flow, (2) particle tracking; and (3) transport codes.

## 5.0 STATISTICAL ANALYSES TO COMPARE PRE- AND POST-ISL/ISR CONDITIONS

Although statistical analyses are used in all phases of the ISL/ISR process described above, statistical hypothesis tests are specifically used to establish baseline monitoring requirements (Phase 1), to determine when restoration is complete (Phase 4), and when long-term stability has been demonstrated (Phase 5). Hypothesis testing is a statistical tool for deciding when the groundwater has reached steady state, and for the comparison of post-restoration conditions with predetermined restoration goals.

The statistical tests are based on measurements of baseline and post-restoration water quality conditions at the site. These measurements include a wide variety of water quality parameters. Usually, the measured parameter is a concentration of a possible contaminant in a specific well at a given time, although other water quality parameters may also be analyzed using the methods in this section.

Both linear regression and the nonparametric Mann-Kendall trend test are recommended as viable alternatives in EPA 2006 and EPA 2009. Linear regression relies on a variety of assumptions, for example, normality which needs to be tested. The Mann-Kendall trend test may be used with any series of four or more independent samples to test for trends in well parameters. The test can be employed in Phase 1 to check for unexpected trends in baseline samples, in Phase 4 to determine when steady state is reached, and particularly in Phase 5 to establish long-term stability. The Wilcoxon Rank Sum test (also known as the Mann-Whitney or Wilcoxon-Mann-Whitney test) can be applied in Phase 5 to compare post-restoration well parameters with baseline parameters, assuming that both datasets are stationary. The Wilcoxon Rank Sum (WRS) test is recommended for comparing baseline and post-remedial wells in EPA 2006.

It is essential that sufficient data be collected to support a statistical comparison of baseline and post-restoration conditions. Under ideal conditions, the dataset would include a complete time series of measurements systematically collected at each well at equally spaced times using the same measurement device with a very low limit of detection. In reality, such datasets exist only in textbook examples.

In summary, the preferred statistical approaches for each phase are:

### ***Phase 1 Baseline Sampling***

- Estimate required number of samples
- Adjust measured data for seasonality, if required
- Use Mann-Kendall test to check for unexpected trends

### ***Phase 4 Determination of Steady State***

- Adjust measured individual well data for seasonality, if required.
- Use Mann-Kendall test for individual well trends.

- If a trend is detected, use linear regression or Theil-Sen test<sup>2</sup> to assess trend magnitude.
- If trends not detected, use WRS test to compare baseline to steady-state measurements for statistical differences for a single well. Repeat for all wells.
- For multiple wells, when trends are not detected, first test wells for homogeneity. If test results confirm homogeneity, then test to confirm compliance of all wells with restoration goals.
- If steady-state data are from different wells than the baseline data and trends are not detected, use WRS test to compare baseline to steady-state measurements for statistical differences for the pooled data of all wells combined, which are treated as a single well.

### ***Phase 5 Long-term Stability Monitoring***

- Adjust measured data for each well for seasonality, if required.
- Use Mann-Kendall test for trends for each well.
- If trend is detected, use linear regression or Theil-Sen test to assess trend magnitude.
- If trends not detected, use WRS test to compare baseline to stability monitoring results for a single well. Repeat for each well.
- If the before/after comparison is made between multiple wells, first test all wells for homogeneity using chi-squared approach, then test to confirm compliance of all wells with restoration goals.
- If post-restoration data are from different wells than baseline data and trends are not detected, use WRS test to compare baseline to stability monitoring results for the pooled data of all wells combined.

Statistical tests for trends are recommended for demonstrating stability of the site after restoration. Statistical tests are also recommended for comparing post-restoration conditions with baseline conditions after stability has been reached. Several EPA sources were used as the bases for the statistical tests. Although these sources do not recommend procedures for ISL/ISR sites in particular, the sources are either general in nature or address related issues. These sources include guidance for applying the Data Quality Objectives (DQOs) at remediated CERCLA sites (EPA 2002a), guidance for conducting the statistical tests in the *Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM)* (EPA 2000), guidance for statistical analysis of groundwater monitoring data at RCRA facilities (EPA 2009), and general guidance for the application of nonparametric statistical tests found in *Data Quality Assessment: Statistical Methods for Practitioners*, EPA QA/G-9S (EPA 2006). Many of the procedures for conducting the tests discussed above, in section 8, and explained in detail in Attachment D were adapted from the EPA QA/G9S document.

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<sup>2</sup> Theil-Sen test is a nonparametric alternative to linear regression and is often used when constructing trends on data sets containing non-detects. The Theil-Sen line estimates the change in *median* concentration over time and not the *mean* as in linear regression.

## PART 2

### Overview to Part 2

Part 1 of this document provided basic background and context to frame issues related to groundwater monitoring at ISL/ISR sites. Part 2 provides additional technical detail specific to the questions of establishing baseline conditions, post-operational stability monitoring, and statistical approaches that can be applied to determine that the restoration performance objectives have been achieved.

EPA believes it is important to provide the SAB with the context so that the SAB may relate the technical questions to the complex physical situations in which they might be applied. We also believe it is important for the SAB to understand the statutory basis governing our regulatory approach, *i.e.*, EPA's standards must be consistent with RCRA requirements, but those standards are implemented and enforced by NRC or its Agreement States through its licensing requirements. It should therefore be understood that while EPA is requesting advice on the technical aspects to be considered in a rulemaking that will establish standards applicable to ISL/ISR facilities, EPA is not requesting advice on either the form or content of those standards. EPA's regulatory proposal will be informed, in part, by the technical advice of the SAB, and will be developed in a manner that is consistent with EPA's UMTRCA standard-setting authority while taking into account the Agency's broader groundwater protection and risk management policies.

EPA recognizes that setting standards involves both policy and technical elements and that it can be difficult to clearly separate the two. For example, defining technical criteria that would indicate stability of post-restoration conditions naturally raises the question of how long such monitoring should be conducted. As a technical matter, EPA is requesting advice from the SAB to account for influences such as the size of the well field and seasonal variation. As a policy matter, EPA will determine whether a monitoring period should be specified and, if so, what that period should be.

Similarly, this document addresses statistical approaches such as confidence levels and specific tests that can be applied to determine restoration goals and whether those goals have been achieved. EPA is requesting advice from the SAB regarding the validity of these approaches, whether other approaches might be equally valid or more suitable for the situation, and what factors may affect their application (*e.g.*, the amount of data required). EPA will determine how to incorporate these considerations into our standards, which will be developed through notice-and-comment rulemaking.

### 6.0 ACTIVE/EXISTING ISL/ISR FACILITIES: MONITORING ISSUES

Many of the standards in 40 CFR 192.32 refer to RCRA 40 CFR 264 Part, Subpart F, which describe EPA's regulatory approach for releases to groundwater from waste management units that store, treat, and dispose of hazardous waste. Although §264.97 is not specifically cited in §192.32, it provides some useful guidance regarding general requirements that could be considered for establishing a suitable groundwater baseline:

*(g) In detection monitoring or where appropriate in compliance monitoring, data on each hazardous constituent specified in the permit will be collected from background wells and wells at the compliance point(s). The number and kinds of samples collected to establish background shall be appropriate for the form of statistical test employed, following generally accepted statistical principles. The sample size shall be as large as necessary to ensure with reasonable confidence that a contaminant release to ground water from a facility will be detected. The owner or operator will determine an appropriate sampling procedure and interval for each hazardous constituent listed in the facility permit which shall be specified in the unit permit upon approval by the Regional Administrator. This sampling procedure shall be:*

- (1) A sequence of at least four samples, taken at an interval that assures, to the greatest extent technically feasible, that an independent sample is obtained, by reference to the uppermost aquifer's effective porosity, hydraulic conductivity, and hydraulic gradient, and the fate and transport characteristics of the potential contaminants, or*
- (2) An alternate sampling procedure proposed by the owner or operator and approved by the Regional Administrator.*

Issue: In practice, the procedures for establishing the groundwater baseline are site-specific and are included in the facility license issued by the NRC or Agreement State.

## **6.1 Groundwater Baseline: Case Studies**

There is some variation among states in the requirements for baseline monitoring. An example of the development of the groundwater baseline for the proposed Dewey-Burdock ISL/ISR operation in South Dakota is included in Attachment A. In Texas, 26 chemical constituents are measured before mining to establish a baseline, as shown in Table 6-1. This is example data from Production Authorization Area (PAA) No. 1 at the Zamzow ISL/ISR facility. Baseline values shown in the table represent the highest average concentration from either the production or mine area, which are commonly selected as initial restoration goals (Hall 2009).

In its license application for the Moore Ranch Uranium Project in Campbell County, Wyoming, Energy Metals Corporation proposed that the wellfield baseline would be established by sampling production zone wells 4 times, with a minimum of 2 weeks between samplings (NRC 2010, Section 6.3.1.1) Energy Metals also proposed that the number of wells sampled would be 1 well for each 3 acres of mine unit. Data for each sampled parameter are to be averaged and used to calculate restoration goals. The average and range of baseline values in the production zone are then used to assess the effectiveness of subsequent groundwater restoration.



**Table 6-1. Baseline Water Quality Data for Zamzow PAA-1**

	Parameter	Unit	Production Zone					
			Mine Area**			Production Area		
			Low	Average	High	Low	Average	High
1	Cadmium	mg/l	122	317	552	195	269	390
2	Magnesium	mg/l	15	38.4	84.2	3.0	21.1	40
3	Sodium	mg/l	239	387	750	235	383	466
4	Potassium	mg/l	19	30.3	49	18.9	26.7	90
5	Carbonate	mg/l	0	0	0	0	0	0
6	Bicarbonate	mg/l	128	297	400	157	269	346
7	Sulfate	mg/l	454	793	1,520	441	601	940
8	Chloride	mg/l	350	503	936	394	538	662
9	Fluoride	mg/l	0.16	0.54	1.19	0.01	0.36	0.50
10	Nitrate - N	mg/l	<0.01	0.16	0.9	<0.01	0.14	0.49
11	Silica	mg/l	31	51.6	85	11	43.9	74
12	pH	Std. units	6.6	7.0	7.66	6.68	7.0	7.45
13	TDS	mg/l	1,697	2,289	3,220	1,810	2,037	2,360
14	Conductivity	µmhos	2,720	3,204	4,300	2,680	3,049	3,430
15	Alkalinity	Std. units	105	275	400	206	238	204
16	Arsenic	mg/l	<0.001	0.009	0.03	<0.001	0.006	0.044
17	Cadmium	mg/l	<0.0001	0.001	0.007	<0.0004	0.001	0.0013
18	Iron	mg/l	0.01	0.915	8.0	0.03	0.075	0.26
19	Lead	mg/l	<0.001	0.001	0.006	<0.001	0.004	0.02
20	Manganese	mg/l	0.009	0.224	0.82	0.01	0.118	0.19
21	Mercury	mg/l	<0.0001	0.0004	0.0018	0.0001	0.0006	0.001
22	Selenium	mg/l	<0.001	0.01	0.01	<0.001	0.004	0.01
23	Ammonia	mg/l	<0.01	0.374	1.4	<0.01	0.298	0.78
24	Uranium	mg/l	<0.001	0.171	1.7	<0.001	0.039	0.432
25	Molybdenum	mg/l	<0.001	0.03	0.95	<0.001	0.226	2.1
26	Radium-226	pCi/l	1.5	155	959	6.5	152	744

\*\* - Monitor wells

Source: Hall 2009

In another example, Mine Unit 4 of the Christensen Ranch Project located in Wyoming, the wellfield covered about 12 acres and, consequently, 12 injection or production wells were used to establish baseline groundwater conditions within the ore zone, which in turn set the restoration goals (Cogema 1994).

Commercial-scale uranium ISL/ISR facilities usually have more than one wellfield. For example, the Crow Butte facility in Dawes County, Nebraska, has constructed 10 wellfields since 1991 (Crow Butte 2007). The locations and boundaries for each wellfield are adjusted as more detailed data on the subsurface stratigraphy and uranium mineralization distribution are collected during wellfield construction.

## 6.2 Wellfield Restoration

Wellfield restoration is defined as those actions taken to assure that the quality of the groundwater adjacent to the ISL/ISR wellfields will not be adversely affected by the uranium extraction process (NRC 2001). This requires returning the wellfield water quality parameters to

meet the restoration goals included in the facility license by NRC or the Agreement State. Based on pre-mining monitoring, the operator establishes baseline values for the groundwater quality. The regulator then uses these baseline values to set restoration goals in the wellfield license.

It should be noted that the portion of the aquifer undergoing uranium extraction is exempt from EPA regulatory protection under the Safe Drinking Water Act (specifically the UIC Program at 40 CFR Part 144). However, groundwater adjacent to the exempted portion of the aquifer must still be protected, and groundwater protection provisions for this water are in effect. Similar to the NRC Agreement State provisions,<sup>3</sup> the EPA Primacy State may impose more stringent requirements for groundwater restoration than the federal program (NRC 2003). Groundwater restoration requirements may vary from state to state. Of particular importance is underground injection and point source discharge into surface waters. Currently, UIC programs are administered (as authorized by EPA) in Wyoming, Nebraska, and New Mexico. South Dakota administers the program jointly with EPA.

### **6.3 Wellfield Restoration: Case Study**

Restoration results from 22 PAAs in Texas are summarized in Table 6-2 (Hall 2009). It is apparent that for all of the PAAs, post-restoration analyses exceeded the baseline for some of the parameters tested. Similar information on restoration of sites in other states was extracted from NRC 2009 and is included as Attachment C.

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<sup>3</sup> Texas, Colorado, and Utah operate as Agreement States under NRC regulations in establishing state-specific ISL regulations, while Wyoming, New Mexico, and South Dakota are directly regulated by NRC. Nebraska is also an Agreement State, but since it does not have specific ISL regulations, these facilities are regulated by the NRC.

**Table 6-2. Groundwater Chemistry of Texas In-Situ Uranium Production Authorization Areas (PAAs)**

Analyte	EPA and TCEQ Drinking Water Standards (mg/l)	Baseline Range	Post-Restoration Range	PAAs with Baseline Above MCL or Recommended Standards	PAAs with Post-Restoration Water Above MCL or Recommended Standards	PAAs Where Post-Restoration Analyses Exceed Baseline	PAAs Where Post-Restoration Analyses are Below Baseline
EPA and TCEQ Primary Maximum Contaminant Levels (MCLs):							
Arsenic	0.01	.004–0.23	.002–.323	77%	55%	18%	82%
Cadmium	0.005	0.0001–0.0126	0.0001–0.01	45%	23%	27%	73%
Fluoride	4	0.21–1.8	0.29–1.6	0%	0%	31%	69%
Lead	0.02	0.003–1.97	0.001–0.05	81%	18%	9%	91%
Mercury	0.002	0.0001–0.445	0.0001–0.01	9%	0%	22%	64%
Nitrate	10	0.031–10.0	0.001–2.8	0%	0%	4%	96%
Selenium	0.05	0.001–0.049	0.001–0.102	18%	4%	54%	45%
Radium (226 & 228 Ra: pCi/l)	5 pCi/l	9.36–429.8	5.2–149	100%	100%	4%	96%
Uranium	0.03	0.025–2.0	0.013–3.02	95%	86%	68%	32%
TCEQ Secondary Recommended Standards:							
Sulfate	300	15.8–250	78–3881	0%	18%	86%	14%
Chloride	300	196.9–3505	138–3326	86%	86%	22%	78%
Total Dissolved Solids	1000	785.7–6349	706.3–6155	81%	77%	31%	55%
Iron	0.3	0.04–5.49	0.01–2.7	54%	9%	4%	96%
Manganese	0.05	0.01–0.41	0.01–0.84	77%	50%	40%	60%
No Established MCL or Secondary Standards							
Calcium	–	4.13–241	14.7–191			77%	23%
Magnesium	–	0.477–125	2.27–53			72%	28%
Sodium	–	200–2356	169–2247			31%	65%
Potassium	–	6.38–101	6.1–70			14%	86%
Carbonate	–	0.1–17.9	0–14.6			50%	30%
Bicarbonate	–	160–500	160–500			66%	25%
Silica	–	16.3–76	13.4–77.6			19%	81%
Conductivity (µmhos/cm)	–	1310–11160	1429–3697			76%	24%
Alkalinity (as CaCO <sub>3</sub> )	–	134–349	145–408			81%	10%
Molybdenum	–	0.01–0.2	0.0001–3.38			42%	54%
Ammonia-N	–	0.01–7.49	0.04–120			76%	24%

Baseline and post-restoration date was available for all 22 PAAs with the exception of Ra, Mo, K, Si, Bicarbonate, Ammonia (21), Conductivity (14), Alkalinity (11), & Carbonate (10)

## 7.0 ISSUES ASSOCIATED WITH ESTABLISHMENT OF POST-RESTORATION STEADY STATE

During restoration, the operator monitors progress by periodic sampling of the groundwater constituents until steady-state conditions are attained. Establishment of steady state requires that the groundwater potentiometric surface be restored, to the extent practicable, to its pre-leaching status, so that the flow regime is similar to that existing before mining. In addition, constituents in the groundwater must be in compliance with restoration goals and remain at those levels for a sufficient period to demonstrate that the results are not trending upwards to higher concentration levels. EPA defines a “steady state,” which is characterized by the following relevant components (EPA 1992, Chapter 7):

- (1) After treatment, the water levels and water flow, and the corresponding variability associated with these parameters (*e.g.*, seasonal patterns), should be essentially the same as for those from comparable periods of time prior to the remediation effort.
- (2) The pollutant levels should have statistical characteristics (*e.g.*, a mean and standard deviation), which will be similar to those of future periods.

The first of these components provides the general behavior and characteristics of the groundwater at the site. The second is more judgmental and projects future contamination, based on available current information. These projections cannot be made with certainty; however, there are various criteria that can be used in determining whether a steady state has been reached. Statistical tests for measuring attainment of steady state are discussed in Sections 8.3 and 8.4. When the regulator is satisfied that steady state has been achieved, the operator is authorized to undertake long-term post-restoration stability monitoring.

### 7.1 Post-Restoration Stability Monitoring

Once the operator concludes that restoration has been completed and has obtained concurrence from the regulator(s) that a steady state has been established, post-restoration stability monitoring begins. The purpose of the stability monitoring is to demonstrate that the aquifer conditions established at the end of restoration are sustainable over time. Currently, the duration of stability monitoring is a site-specific period of time established in the license(s). In the past, the license-established restoration period typically has been about 6 months (see case histories in Attachment B). More recently, the trend has been to increase the monitoring period established in the license. In practice, the actual period of stabilization may be several years, based on iterative analyses of additional samples requested by the regulators. If the sandstone in the aquifer is heterogeneous, extended restoration times may be required to insure that groundwater in slow pathways is addressed.

#### 7.1.1 ISL/ISR Extraction Phase

During the ISL/ISR mining phase (Phase 2, Figure 3-1, wells are placed in the active ISL/ISR-treatment zone, fringe zone (wells at the ISL/ISR-mine boundary), and outside the impacted areas (see Figure 2-4). Parameters that need to be measured are site-specific. Basic

measurements include Eh, pH, major ions, TDS, carbonate species, radioactive constituents, colloids, organic constituents, and trace elements compared with pre-ISL/ISR measurements. The measurement frequency for each monitoring well is dependent on ISL/ISR injection-extraction cycle and groundwater flow and transport times moving across ISL/ISR field. This report is not concerned with the detection and correction of excursions during the leaching operations. However, monitoring wells used to detect excursions during operation may also be used to collect data for post-mining groundwater evaluation.

## 7.2 Factors that Affect Post-Mining Monitoring Timeframes

A number of factors must be understood to determine when the impacted aquifer has reached a steady-state condition. This section summarizes these factors.

### 7.2.1 Fate and Transport Process

The monitored timeframe is dependent on mass balance estimates of how much extraction fluid remains in the aquifer. A mass balance of the total volume of lixiviant injected into the system and the volume withdrawn needs to be determined by the monitoring during operations. The lixiviant used to extract the uranium can mask baseline constituents and affect reaction kinetics. Knowing how much lixiviant remains in the aquifer will aid in understanding whether some reactants are still in the system, if some have migrated outside the monitored area, been temporarily sequestered in low permeability zones, or are undergoing incomplete or slow reaction kinetics that may release constituents later on.

#### 7.2.1.1 Speciation

The environmental chemistry of uranium is largely dictated by its oxidation state (*e.g.*, Fanghänel and Neck 2002). Under ambient oxidizing conditions, the predominant uranium oxidation state is U(VI). Where oxygen is limited, U(IV) may dominate. The metallic form, U(0), does not occur naturally, and is readily oxidized to U(IV), and eventually U(VI), upon exposure to oxidizing conditions. The mechanisms for the oxidation of U(0) and U(IV) to U(VI) are well established (*e.g.*, NRC 2007). It is rare to find other oxidation states of uranium [*e.g.*, U(V) and U(III)] under natural conditions, due to their instability.

In general, the solubility and therefore the mobility of uranium is greatest when it is in the U(VI) state. Complexation of U(VI) by inorganic anions, such as carbonate, fluoride, and phosphate, may enhance the solubility and mobility of this species. When reducing conditions are present, U(IV) is generally immobile and found either as an insoluble oxide (uraninite) or a silicate (coffinite). Under oxidizing conditions and near neutral pHs, U(VI) species dominate aqueous uranium concentrations. These highly soluble species are generally either hydroxy or carbonate complexes of the uranyl ( $\text{UO}_2^{2+}$ ) cation, although elevated concentrations of potential inorganic ligands near the ISL/ISR target zone may exert greater influence on U(VI) speciation (*e.g.*, phosphate).

Calcium (or other alkaline earth metals, such as magnesium) and inorganic carbon in groundwater tend to dominate the aqueous speciation of U(VI) under near neutral pH conditions.

The presence of these species is common in many natural groundwater systems (Hem 1985) and, as noted below, these speciation characteristics also influence the degree to which U(VI) will adsorb onto aquifer solids. Under reducing conditions, U(IV) species, primarily the uranyl cation and its complexes, predominate, but due to the very low solubility of U(IV) minerals, reach maximum concentrations on the order of 10 nM (2.4 µg U/L). For all practical purposes, therefore, only U(VI) aqueous species are at sufficient concentrations to be of environmental concern. Under oxidizing conditions and neutral pHs, U(VI) species dominate aqueous uranium concentrations.

Chemical reaction kinetic equations or equilibrium thermodynamic equations can be used to describe chemical interactions among dissolved chemical species, the dissolution of immobile solid phases, or the formation and precipitation of new, immobile solid phases.

Geochemical modeling is often performed at ISL/ISR facilities to gain a better understanding of thermodynamically controlled processes that include mineral dissolution/precipitation, oxidation/reduction and adsorption/desorption.

Most of the available computer codes assume thermodynamic equilibrium and do not have a method of calculating reaction rates (*i.e.*, kinetics). If a mineral forms or dissolves slowly in a system, the model developed from these codes will not account for these kinetic effects. This is not a major limitation for most aquifer systems, where residence times are measured in years; however, kinetic effects can become more important in modeling reactions anticipated to occur during applied remediation methods, such as the injection of reactants into an aquifer.

#### 7.2.1.2 Speciation: Case Study

Illustrative of speciation problems is experience with iron at the Crow Butte ISL/ISR facility. Crow Butte Resources (CBR) experienced difficulty in restoring desired iron levels during wellfield restoration. During the initial stabilization monitoring period in 1999, the iron concentration averaged 0.089 mg/L. Subsequent testing in the summer of 2002 showed an average iron content of 0.278 mg/L. The operator attributed this to speciation initiated by the original injection of lixiviant, with subsequent transitory solubility increases resulting from the selected restoration method. As stated in Crow Butte 2002:

*CBR believes that the elevated iron concentrations are due to the restoration process and will ultimately decrease to concentrations well below the restoration standard. During the in situ mining process, when the groundwater is oxygenated and the Eh is positive, the iron contained in pyrites is oxidized to ferric iron and forms ferric oxyhydroxides. The ferric oxyhydroxides are extremely insoluble, which explains the very low concentrations of iron in solution during mining, indicated by the end of mining values which, with the exception of one restoration well (PR-19), were below the detection limit of 0.05 mg/L. During the active restoration process, however, sodium sulfide is used as a reductant to decrease the Eh of the groundwater. As the Eh drops, the stable solid iron phase is reduced from ferric iron to ferrous iron, which is more soluble. During the transition from ferric to ferrous iron, the iron concentration in the groundwater*

*increases significantly. This increase in the iron concentration is transitory and, as the Eh continues to decrease, iron sulfide minerals will be the dominant iron phase. Because of the relative insolubility of these iron sulfide minerals, this will cause a significant decrease in the iron concentration in solution. Based on these mechanisms, CBR expects that the elevated concentrations of iron at the current time will ultimately decrease.*

### 7.2.1.3 Solubility

In most natural conditions, the thermodynamically stable uranium solid phases will be either U(VI) or U(IV) compounds. The most stable U(VI) compounds are the phosphates and vanadates, but their formation is often limited by the relatively low concentrations of these two anions, and thus more soluble U(VI) oxides, such as schoepite, which is bright yellow in color, are often seen if any U(VI) solid phases are present. A significant fraction of the solid-phase U(VI) will be adsorbed to iron (hydr)oxide surfaces, the edges of clay minerals, and to organic matter, rather than precipitated as discrete U phases. Maximum solubility of uranium is seen in oxidizing, phosphate-free, carbonate-rich solutions, and consequently, carbonates (or bicarbonates) and oxygen or hydrogen peroxide are the principal reagents used for ISL/ISR mining.

Under reducing conditions, the stable U(IV) solid phases are uraninite and, if high amounts of dissolved silica are present, coffinite. Organic complexes of U(IV) associated with humic material may also retain U(IV) in the solid phase. The solubility of the U(IV) phases is extremely low, and thus the presence of reducing conditions effectively halts or slows the movement of uranium in soils and sediments, provided that colloidal-sized phases are not formed and transported. The most common uranium ore-forming process involves reductive precipitation of U(IV) phases as a result of microbiological activity to form a roll-front deposit (Langmuir 1997). The stability fields for U(VI) and U(IV) as a function of pH and Eh for various water compositions suggest that a wide variety of uranium-bearing precipitates are possible, especially in complex groundwater systems that invariably contain silica, carbonate/bicarbonate, calcium/magnesium, sodium, and sometimes phosphate. Furthermore, it may be difficult to predict associations of uranium in the solid phase based upon analysis of aqueous chemical data and solubility predictions from thermodynamic chemical data. In the absence of confirmatory solid phase characterization data, equilibrium model projections only indicate the possible formation of specific uranium-bearing precipitates.

### 7.2.2 Natural Attenuation Processes

Natural attenuation processes include a variety of physical, chemical, and biological processes that can act to reduce the mass, mobility, volume, or concentration of contaminants in groundwater. Attenuation processes important at ISL/ISR sites include pH buffering and acid neutralization, adsorption at the mineral-water interface, mineral precipitation, and dilution/dispersion.

### 7.2.2.1 Adsorption

Adsorption of uranium typically involves inner-sphere complexation of uranyl (*i.e.*, those containing  $\text{UO}_2^{2+}$ ) species by oxygen ligands at the surfaces of iron oxyhydroxides, phosphates, and layered silicates. Uranyl species exhibit a high affinity for iron oxyhydroxide surfaces and for both basal and edge sites on layered aluminosilicates, such as the clays smectite and vermiculite. Adsorption of U(VI) to the aluminosilicate mineral, muscovite, has been observed in aquifer sediments at the Hanford Site in Richland, Washington (McKinley et al. 2007). Complexation of U(VI) by organic ligands in solid humic materials (primarily carboxylic-acid and phenolic groups) may also serve to remove uranium in shallow groundwater systems (Sowder et al. 2003).

A compilation of published  $K_d$  values for U(VI) sorption onto soils/sediments is documented in EPA 1999. However, as recognized by the authors of that compilation, there are significant limitations to the application of published  $K_d$ s for site-specific applications where either the groundwater chemistry or the aquifer matrix differs significantly from the conditions under which a  $K_d$  was determined (Ochs et al. 2006). Davis et al. (2004) document an alternative approach, whereby a site-specific  $K_d$  value is modeled through the use of a non-electrostatic surface complexation model (NEM) developed as a function of site geochemistry for aquifer sediments. This approach incorporates the important influence of uranium solution speciation, while avoiding the need to model the influence of individual mineral components (and their respective surface charging behavior). While this approach still requires site-specific data, it provides a means for projecting the influence of changes in groundwater chemistry on uranium sorption. The chemistry of groundwater may be influenced by reaction with aquifer solids and/or external recharge/infiltration from atmospheric precipitation or surface water. As previously noted, alkalinity influences the aqueous speciation of U(VI), and it also influences the degree of sorption of U(VI) onto iron oxyhydroxides and aquifer solids in which these minerals control uranium partitioning (*e.g.*, Um et al. 2007). It has been demonstrated that changes in groundwater chemistry influence the transport of U(VI) through an aquifer (Yabusaki et al. 2008). Alternatively, transition from oxidizing to reducing conditions along the transport pathway may be accompanied by a shift from adsorption of U(VI) species to precipitation of U(IV)-bearing solids (Davis et al. 2006). Reactive transport models used to project subsurface uranium mobility directly incorporate the influence of major ion chemistry and redox conditions on the chemical speciation of uranium.

There is field evidence that adsorption of uranium to mineral surfaces within an aquifer may be an intermediate step to the formation of uranium-bearing precipitates. Murakami et al. (2005) have observed the association of nanoparticulate U(VI)-phosphate precipitates with iron oxyhydroxides in the weathering zone downgradient from a uranium ore deposit. The U(VI) mineral was identified as metatorbernite, which was present in groundwater that was under-saturated with respect to precipitation of this mineral. Characterization of the textural associations between the nanocrystalline metatorbernite and iron oxyhydroxides present as fissure fillings, clay coatings, and nodules, along with compositional relationships between copper, phosphorous, and uranium (Sato et al. 1997), indicated that the formation of uranium precipitates was a secondary step following initial adsorption of these constituents onto iron oxyhydroxide mineral surfaces (Murakami et al. 2005). As summarized by Payne and Airey (2006), the observations in this subsurface system provide a point of reference for designing site



characterization strategies, and developing both conceptual and analytical models for interpreting and projecting uranium mobility in groundwater.

### 7.2.2.2 Role of Secondary Minerals

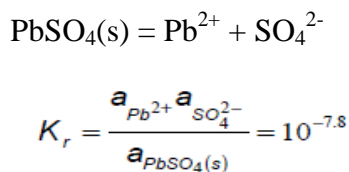
The oxidation of iron sulfides in the host rock results in the release of iron, sulfate, acidity, and metals to solution. High aluminum and silica concentrations are also commonly encountered in mine effluents and are the result of weathering of aluminosilicate minerals at low pH. Oxidation and hydrolysis reactions can subsequently lead to the precipitation of a wide array of hydroxide, sulfate, and/or hydroxysulfate minerals, depending on geochemical and biogeochemical conditions (Nordstrom and Alpers 1999). These secondary minerals play important roles in attenuating contaminants in the groundwater.

Secondary precipitates can remove contaminants from impacted waters through adsorption and/or coprecipitation reactions. Adsorption processes are typically categorized by the relative “strength” of the interaction between the adsorbate (species in solution) and the surface or adsorbent. If water molecules are positioned between the cation or anion and the surface, the adsorption complex is referred to as outer sphere and is considered to be weak. Conversely, if upon adsorption, the adsorbate loses waters of hydration such that there are no water molecules positioned between the cation or anion and the surface, the adsorption complex is referred to as inner sphere and is considered to be strong. The extent to which dissolved contaminants will sorb onto secondary precipitates as outer sphere or inner sphere complexes will vary as a function of the contaminant species, the secondary precipitate, pH, particle size and surface area, and the presence of other sorbing species that may compete for adsorption sites.

Inorganic contaminants may be removed from solution due to precipitation of an insoluble phase in which the contaminant represents a major or minor component within the solid. Examples of secondary precipitates that form in impacted sites include oxyhydroxides [*e.g.*, FeOOH(s)], hydroxysulfates [*e.g.*, Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)(s)], sulfates [*e.g.*, PbSO<sub>4</sub>(s)], and sulfides [*e.g.*, ZnS(s)]. For each of these minerals, there will be a limited compositional range of groundwater chemistry over which precipitation could occur and formation of these precipitates may compete with other removal processes, such as adsorption.

The potential for contaminant precipitation can be estimated by evaluating the saturation state of the groundwater with respect to possible precipitate phases using a saturation-state modeling approach. In order to evaluate whether a groundwater is oversaturated, undersaturated, or at equilibrium with a particular phase, computer geochemical speciation models are of practical use. As an example, consider the solubility expression for lead sulfate (anglesite):

The mass-action expression that applies to the equilibrium is:



A natural water may or may not be at saturation with respect to anglesite, depending on whether the phase is actually present, available surface area, residence time of water, and kinetic factors that may impede dissolution and/or precipitation. If equilibrium is assumed between water and anglesite, then the ion activity product,  $Q$ , should be the same as the equilibrium constant,  $K_r$ :

$$Q = a_{\text{Pb}^{2+}} a_{\text{SO}_4^{2-}} = K_r = 10^{-7.8}$$

where the activity ( $a$ ) of  $\text{PbSO}_4(\text{s})$  is taken to be 1. Because ion activity products may vary by orders of magnitude, it is often more convenient to take the logarithm of the ratio, that is, to compute the saturation index,  $SI$ :

$$SI = \log \frac{Q}{K_r} = 0$$

where  $SI = 0$  at equilibrium. If a water is oversaturated in a particular phase, then the  $SI$  is positive and there is a thermodynamic driving force for precipitation to occur. If the water is undersaturated, then the  $SI$  is negative, and the mineral, if present, will tend to dissolve:

$$SI > 0 \text{ if oversaturated}$$

and

$$SI < 0 \text{ if undersaturated}$$

As previously indicated, the stability of a precipitate will be dictated by the groundwater chemistry. Contaminant remobilization will occur as a result of dissolution of the precipitate phase, for example, when  $\log Q/K_r < 0$ . Precipitate dissolution may occur due to groundwater acidification, oxidation/reduction of precipitate components, dilution, or complexation of the precipitate component(s) with dissolved species that form more stable compounds. A key point is that attenuation processes involving inorganic contaminants are reversible (*e.g.*, Gault et al. 2005; Moncur et al. 2005). Metals taken up at the mineral-water interface can be released back into solution. Geochemical modeling of mineral stability and contaminant adsorption/desorption behavior can provide insight into contaminant remobilization potential due to future changes in geochemical conditions. However, it must be noted that thermodynamic databases are often incomplete, and thermodynamic constants for specific compounds may vary from database to database. Thus, results from geochemical models must be carefully reviewed. In addition, the method outlined above assumes equilibrium conditions and ignores rates (*i.e.*, kinetics) of mineral dissolution and precipitation. Data, however, are often lacking on the kinetics of biogeochemical processes responsible for contaminant uptake and remobilization, especially data that can be applied in field systems to predict the long-term behavior of contaminants.

With respect to predicting geochemical interactions at ISL/ISR facilities, the potential impacts from these types of limitations are illustrated by several concerns raised by a reviewer of the geochemical modeling of an ISL/ISR facility and presented in NUREG-6820 (NRC 2007). The reviewer noted that since the applied model is a non-kinetic model, any bacterial influences from naturally occurring *Desulfovibria* and *Thiobacillus* are eliminated from consideration. The comment further noted that these influences may be as (or more) important to long-term stability

than the addition of reductant during restoration. In addition, the role of pyrite during both restoration and stabilization was also a concern, and the reviewer noted that a kinetic approach might result in simulations that more closely compared with observed conditions.

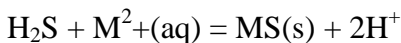
### 7.2.2.3 Role of Biological Processes

Microbial processes can play a role in both mobilizing and attenuating inorganic contaminants at ISL/ISR sites. For example, Macur et al. (2001) showed that microbial reduction of arsenate [As(V)] to arsenite [As(III)] occurred over relatively short time scales and resulted in enhanced arsenic mobilization in mine tailings pore water. In addition, iron-reducing bacteria may cause contaminant dissociation from aquifer solids as a consequence of iron oxide dissolution. Metals and metalloid species associated with secondary iron-bearing precipitates may be released via the activity of bacteria under certain conditions (Herbel and Fendorf 2006).

Sulfate-reducing bacteria (SRB), however, have the ability to attenuate the movement of metals through the precipitation of sulfide minerals (*e.g.*, Gammons et al. 2005), and by raising the pH of the water. This process is recognized in the restoration of ISL/ISR sites and also occurs in the natural environment (Church et al. 2007). The overall sulfate-reduction process can be described by the reaction:



where  $\text{CH}_2\text{O}$  represents organic matter, either in the solid or aqueous phase. The resulting dissolved hydrogen sulfide can precipitate with divalent metals in, for example ( $\text{M} = \text{Cd}, \text{Cu}, \text{Fe}, \text{Ni}, \text{Pb}, \text{or Zn}$ ):



The mass concentration of reactants involved in sulfate reduction is usually much larger than the mass concentration of metals involved in secondary precipitation reactions; hence, these combined reactions can lead to an increase in alkalinity and the pH of the water, while simultaneously attenuating divalent metals. Alkalinity produced during the sulfate reduction process can also drive the precipitation of carbonate minerals, such as calcite and siderite (Paktunc and Davé 2002), and can help neutralize acidity in the groundwater.

The purpose of the stabilization phase of aquifer restoration is to establish a chemical environment that reduces the solubility of dissolved constituents, such as uranium, arsenic, and selenium. An important part of stabilization during aquifer restoration is metals reduction (NRC 2007). During uranium recovery, if the oxidized (more soluble) state is allowed to persist after uranium recovery is complete, metals and other constituents such as arsenic, selenium, molybdenum, uranium, and vanadium may continue to leach and remain at elevated levels. To stabilize metals concentrations, the pre-operational oxidation state in the ore production zone should be re-established to the extent possible. This is achieved by adding an oxygen scavenger or reducing agent, such as hydrogen sulfide ( $\text{H}_2\text{S}$ ), or a biodegradable organic compound (such as ethanol) into the uranium production zone during the later stages of recirculation (NRC 2007).

### 7.2.2.4 Case Study

Table 7-1 presents projections of monitoring periods for a few facilities seeking licenses. The monitoring periods were taken from their respective Environmental Impact Statements. It is evident that restoration may take a period of a few years, while post-restoration usually is estimated for 1 year.

**Table7-1. Post Restoration and Stability Monitoring Periods**

Facility Name	State	Projected or Estimated Restoration Period	Projected or Estimated Post Restoration Monitoring Period	Comment/Reference
Moore Ranch Wellfield 1	Campbell County, Wyoming	3.5 years	1 year (quarterly)	NUREG 1910 Supplement 1
Moore Ranch Wellfield 2	Campbell County, Wyoming	5.25 years	1 year (quarterly)	NUREG 1910 Supplement 1
Nichols Ranch	Campbell & Johnson Counties, Wyoming	1 to 5 years	1 year (quarterly)	NUREG 1910 Supplement 2
Lost Creek	Sweetwater, Wyoming	2 years	6 months (monthly)	NUREG 1910 Supplement 3
Ruth Test Site	Johnson, Wyoming	12 months	12 months	Schmidt 1989

### 7.3 Geochemically-Based Restoration Techniques

Another component of aquifer restoration is accomplished by establishing a chemical environment that alters the solubility of dissolved constituents, such as uranium, arsenic, and selenium. These methods typically invoke chemical reactions in which the valence state of elements are either oxidized to a higher valence state or reduced to a lower valence state.

During uranium recovery, if the oxidized (more soluble) state is allowed to persist after uranium recovery is complete, metals and other constituents such as arsenic, selenium, molybdenum, uranium, and vanadium may continue to leach and remain at elevated levels. For example, if arsenic concentrations in mildly oxidizing water downgradient from an ISL/ISR facility must be lowered, then either increasing the redox potential to precipitate a less soluble arsenic oxide or reducing the redox potential and adding sulfide to form a less soluble sulfide mineral might be considered. Some of the issues to consider in the applied redox approach are the type and amount of reactant, means of emplacement, reaction kinetics, unwanted byproducts, solubility of contaminant-containing minerals, and geochemical stability of the imposed barrier environment.

Another method used to stabilize metals by the re-establishment of their pre-operational oxidation states is to add an oxygen scavenger or reducing agent [such as hydrogen sulfide (H<sub>2</sub>S)] or a biodegradable organic compound (such as ethanol) into the uranium production zone during the later stages of recirculation (NRC 2007).

As described in the case studies summarized in NRC (2007), sampling at some sites after H<sub>2</sub>S injection indicated that although reducing conditions were apparently achieved, they were not

maintained over the longer term. For example, as a field test of groundwater stabilization during aquifer restoration, hydrogen sulfide gas was injected as a reductant into the Ruth ISL/ISR research and development facility in Campbell County, Wyoming. After 6 weeks of hydrogen sulfide injection, the pH dropped relatively quickly from 8.6 to 6.3, and the sulfate concentration increased from 28 ppm to 91 ppm, indicating that the sulfide reductant was being consumed (NRC 2007). Concentrations of dissolved uranium, selenium, arsenic, and vanadium decreased by at least one order of magnitude. After 1 year of monitoring, however, reducing conditions were not maintained, and uranium, arsenic, and radium concentrations began to increase, suggesting that the amount of hydrogen sulfide injected was not sufficient to fully reduce all the material oxidized during the mining phase.

Based on the available field data from aquifer restoration, NRC (2007) concluded that aquifer restoration is complex and results could be influenced by a number of site-specific hydrological and geochemical characteristics, such as pre-operational baseline water quality, lixiviant chemistry, aquitard thickness and continuity, aquifer mineralogy, porosity, and permeability. In some cases, such as at Bison Basin and Reno Creek, the aquifer was restored in a relatively short time. In other cases, restoration required much more time and treatment than was initially estimated (*e.g.*, the A- and C-Wellfields at the Highland ISL/ISR facility).

#### 7.4 Monitored Natural Attenuation

Monitored natural attenuation (MNA) refers to the reliance on natural attenuation processes to achieve site-specific remediation objectives within a reasonable timeframe. Natural attenuation processes include a variety of physical, chemical, and/or biological processes that act without human intervention to reduce the mass or concentration of contaminants in soil and groundwater. These in-situ processes include biodegradation, dispersion, dilution, sorption, and volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants (EPA 1999).

The overall impact of natural attenuation processes at a given site can be assessed by evaluating the rate at which contaminant concentrations are decreasing either spatially or temporally. Guidelines included in OSWER Directive 9200.4-17P (EPA 1999) and by the American Society for Testing and Materials (ASTM 1998a) have endorsed the use of site-specific attenuation rate constants for evaluating natural attenuation processes in groundwater. The EPA directive on the use of Monitored Natural Attenuation (MNA) at Superfund, RCRA, and UST sites (EPA 1999) includes several references to the application of attenuation rates:

*Once site characterization data have been collected and a conceptual model developed, the next step is to evaluate the potential efficacy of MNA as a remedial alternative. This involves collection of site-specific data sufficient to estimate with an acceptable level of confidence both the rate of attenuation processes and the anticipated time required to achieve remediation objectives. At a minimum, the monitoring program should be sufficient to enable a determination of the rate(s) of attenuation and how that rate is changing with time.*

Site characterization (and monitoring) data are typically used for estimating attenuation rates. The *ASTM Standard Guide for Remediation of Groundwater by Natural Attenuation at Petroleum Release Sites* (ASTM 1998a) also identifies site-specific attenuation rates as a secondary line of evidence of the occurrence and rate of natural attenuation.

The 1999 OSWER Directive also provides some general guidelines for use of MNA as a remedial approach for inorganic contaminants. The key policy concerns are that the specific mechanisms responsible for attenuation of inorganic contaminants should be known at a particular site, and the stability of the process should be evaluated and shown to be irreversible. The specific policy language is as follows:

*MNA may, under certain conditions (e.g., through sorption or oxidation-reduction reactions), effectively reduce the dissolved concentrations and/or toxic forms of inorganic contaminants in groundwater and soil. Both metals and non-metals (including radionuclides) may be attenuated by sorption reactions such as precipitation, adsorption on the surfaces of soil minerals, absorption into the matrix of soil minerals, or partitioning into organic matter. Oxidation-reduction (redox) reactions can transform the valence states of some inorganic contaminants to less soluble and thus less mobile forms (e.g., hexavalent uranium to tetravalent uranium) and/or to less toxic forms (e.g., hexavalent chromium to trivalent chromium). Sorption and redox reactions are the dominant mechanisms responsible for the reduction of mobility, toxicity, or bioavailability of inorganic contaminants. It is necessary to know what specific mechanism (type of sorption or redox reaction) is responsible for the attenuation of inorganics so that the stability of the mechanism can be evaluated. For example, precipitation reactions and absorption into a soil's solid structure (e.g., cesium into specific clay minerals) are generally stable, whereas surface adsorption (e.g., uranium on iron-oxide minerals) and organic partitioning (complexation reactions) are more reversible. Complexation of metals or radionuclides with carrier (chelating) agents (e.g., trivalent chromium with EDTA) may increase their concentrations in water and thus enhance their mobility. Changes in a contaminant's concentration, pH, redox potential, and chemical speciation may reduce a contaminant's stability at a site and release it into the environment. Determining the existence, and demonstrating the irreversibility, of these mechanisms is important to show that a MNA remedy is sufficiently protective.*

#### **7.4.1 Tiered Approach to Assessing Suitability of MNA**

EPA's Office of Research and Development has prepared a technical resource document for the application of MNA to inorganic contaminants in groundwater (Reisinger et al. 2005; EPA 2007a and 2007b). The technical resource document presents a four-tiered assessment of MNA as a viable response action for selected metal, metalloid, and radionuclide contaminants encountered in groundwater at a particular location. Components of the approach common to each tier include (1) demonstrating contaminant sequestration mechanisms, (2) estimating attenuation rates, (3) estimating attenuation capacity of aquifer solids, and (4) evaluating potential reversibility issues. EPA expects that users of this document will include EPA and State cleanup program managers and their contractors, especially those individuals responsible for

evaluating alternative cleanup methods for a given site or facility. A decision-making approach is provided for evaluating MNA as a possible response action for contaminated groundwater. Emphasis is placed on developing a more complete understanding of the site through development of a conceptual site model that includes an understanding of the attenuation mechanisms, the geochemical conditions governing these mechanisms, and indicators that can be used to monitor attenuation progress (EPA 2007a).

This tiered decision-making approach is judged by EPA to be an appropriate and cost-effective way to screen out sites unsuitable for MNA while collecting the most relevant data at sites that might be amenable to this approach. Conceptually, a tiered assessment of MNA seeks to progressively reduce site uncertainty as MNA-specific data are collected. MNA for inorganics and radionuclides is most effectively implemented through four tiers that require progressively greater information on which to assess the reasonableness of MNA:

- Tier I. The plume is not threatening public health, is stable, and some direct evidence of contaminant attenuation exists.
- Tier II. The attenuation capacity of the site exceeds the estimated mass of contaminant at the site.
- Tier III. There is strong evidence that attenuation mechanism(s) will prevail over long periods of time.
- Tier IV. A record of decision, including a long-term monitoring plan and other site closure considerations, is developed.

#### **7.4.2 First-Order Attenuation Rate Determination**

First-order attenuation rate constant calculations are an important consideration for evaluating natural attenuation processes at groundwater contamination sites. Specific applications identified in EPA guidelines (EPA 1999) include use in characterization of plume trends (shrinking, expanding, or showing relatively little change), as well as estimation of the time required for achieving remediation goals. As described by Newell et al. (2002), the use of the attenuation rate data for these purposes is complicated, as different types of first-order rate constants represent very different attenuation processes:

Concentration vs. Time Rate Constants are used for estimating how quickly remediation goals will be met at a site; and, in units of inverse time (*e.g.*, per day), are derived as the slope of the natural log concentration vs. time curve measured at a selected monitoring location.

Concentration vs. Distance Bulk Attenuation Rate Constants are used for estimating whether a plume is expanding, showing relatively little change, or shrinking due to the combined effects of dispersion, biodegradation, and other attenuation processes. The attenuation rate constant, in units of inverse time (*e.g.*, per day), is derived by plotting the natural log of the concentration vs. distance and (if determined to match a first-order pattern) calculating the rate as the product of the slope of the transformed data plot and the groundwater seepage velocity contaminant transport vs. transport of a tracer, or more commonly, calibration of solute transport model to field data.

To interpret the past behavior of plumes, and to predict their future behavior, it is necessary to describe the behavior of the plume in both space and time. Therefore, it is important to collect long-term monitoring data from wells that are distributed throughout the plume. Concentration vs. Time Rate Constants describes the behavior of the plume at one point in space; while Concentration vs. Distance Rate Constants describes the behavior of the entire plume at one point in time. Under appropriate conditions, each of these constants can assist in site-specific evaluation and quantification of natural attenuation processes. Each of these terms is identified as an “attenuation rate.” Because the rate constants differ in their purpose and relevance, it is important to understand their proper application, as summarized below:

***Concentration vs. Time Rate Constants:*** A rate constant derived from a concentration vs. time (C vs. T) plot at a single monitoring location provides information regarding the potential plume longevity at that location, but that information cannot be used to evaluate the distribution of contaminant mass within the groundwater system. The C vs. T rate constant at a location within the source zone represents the persistence in source strength over time and can be used to estimate the time required to reach a remediation goal at that particular location. To adequately assess an entire plume, monitoring wells must be available that adequately delineate the entire plume, and an adequate record of monitoring data must be available to calculate a C vs. T plot for each well. At most sites, the rate of attenuation in the source area is slower than the rate of attenuation of materials in groundwater, and plumes tend to shrink back towards the source over time. In this circumstance, the lifecycle of the plume is controlled by the rate of attenuation of the source, and can be predicted by the C vs. T plots in the most contaminated wells. At some sites, however, the rate of attenuation of the source is rapid compared to the rate of attenuation in groundwater. This pattern is most common when contaminants are readily soluble in groundwater and when contaminants are not biodegraded in groundwater. In this case, the rate of attenuation of the source as predicted by a C vs. T plot will underestimate the lifetime of the plume. This behavior would be expected at ISL/ISR sites, following the remediation of the source.

***Concentration vs. Distance Rate Constants:*** Attenuation rate constants derived from concentration vs. distance (C vs. D) plots serve to characterize the distribution of contaminant mass within *space* at a given point in time. A single C vs. D plot provides no information with regard to the variation of dissolved contaminant mass over *time* and, therefore, cannot be employed to estimate the time required for the dissolved plume concentrations to be reduced to a specified remediation goal. This rate constant incorporates all attenuation parameters (sorption, dispersion, biodegradation) for dissolved constituents after they leave the source. Use of the rate constant derived from a C vs. D plot (*i.e.*, characterization of contaminant mass over space) for this purpose (*i.e.*, to characterize contaminant mass over time) will provide erroneous results. The C vs. D-based rate constant indicates how quickly dissolved contaminants are attenuated once they leave the source, but provides no information on how quickly a residual source zone is being attenuated. Note that most sites will have some type of continuing residual source zone, even after active remediation, making the C vs. D rate constant inappropriate for estimating plume lifetimes for most sites.



## 7.5 Fate and Transport Modeling to Support ISL/ISR Compliance Activities

### 7.5.1 *Modeling Objectives*

Groundwater fate and transport modeling is often utilized to reduce the uncertainty regarding the spatial and temporal behavior of the contaminant plume(s). For example, groundwater modeling is commonly implemented at ISL/ISR facilities to assist in meeting the following objectives:

- Optimize the monitoring well spacing to detect injection fluid excursions into non-mined aquifer zone(s)
- Estimate the number of pore volumes needed during site remediation activities to adequately reduce contaminant concentrations
- Establish a specific period of monitoring for ISL/ISR facilities once uranium extraction operations are completed

### 7.5.2 *Development of the Conceptual Model*

Because computer codes are generic in nature and must be adapted to actual field conditions in order to be useful, a clear understanding of the existing physical system (a conceptual model) is required. The hydrogeologist develops a conceptual model of the hydrogeologic environment based on field experience and available literature. A conceptual model generally summarizes the theoretical understanding of the primary conditions that affect groundwater flow and chemical transport and fate.

As contaminant plumes move downgradient from the mined area, they tend to spread laterally and vertically, thereby lowering the average contaminant concentration as the plume expands. The shape taken by an individual plume varies, primarily depending on the nature of the geologic materials making up the aquifer, but also on the rate of groundwater flow. In fine-grained unconsolidated sediments, such as sands and silts, plumes tend to spread out laterally in a fan shape as they move downgradient. This process is called dispersion. Vertical flow also occurs and is controlled by the uniformity of the sediments, as well as the vertical hydraulic gradient. When all the aquifer materials are of essentially the same size and are well-rounded, vertical flow can easily take place assuming a vertical hydraulic gradient exists. Fine-grained layers of sediments such as clays and silts in an otherwise coarse-grained aquifer prevent or retard downward (or upward) vertical flow. Groundwater flowing at a moderate to fast rate tends to minimize both horizontal and vertical dispersion, while slower flow (normally in fine-grained materials) allows greater dispersion. All of these processes, however, will be complicated by the effects caused by the injection and withdrawal of water during the active and remedial phases of the ISL/ISR mining.

Contaminant plumes extend downgradient from the mined area over time until a steady-state condition is reached, based on the concentration of contaminants in the groundwater and the degree of chemical attenuation taking place within the aquifer. Contaminant concentrations decline as downgradient flow occurs, because processes such as dispersion, adsorption, and chemical transformation are constantly taking place in the aquifer. The length of a plume will

depend on (1) how rapidly these processes work, (2) the rate of groundwater flow, (3) the rate of chemical releases to the aquifer, and (4) other environmental factors, such as temperature and the basic chemistry of the groundwater. Ultimately, even with a constant source of contamination to the aquifer, any plume will reach a point beyond which it can no longer expand and will more or less stabilize. This stabilization, or steady-state condition, occurs when attenuation processes in the aquifer remove as much contaminant mass as is being released to the aquifer in the source area.

If the source of the contamination is cut off (for example, by pump and treat extraction wells), a reduction in chemical concentrations will occur downgradient of the mined area and will be especially noticeable along the axis of the plume. Over time, the reduction in plume concentrations will be propagated farther downgradient consistent with the hydraulic conductivity of the aquifer. Subsequently, the plume will begin to contract in extent.

### ***7.5.3 Basic Aspects of Fate and Transport Modeling***

The objectives related to assessing the potential impacts of ISL/ISR mining activities are frequently satisfied by completing the following steps during the modeling process:

1. Adopting a conceptual model to guide creation of model elements
2. Choosing an appropriate computer code for the analysis
3. Establishing the time period represented by the model and the duration of subdivisions of this period (time steps) required for modeling
4. Selecting a suitable model domain and determining the dimensional (horizontal and vertical) limits of the analysis
5. Establishing the model structure by determining the number of model layers and the grid spacing requirements for the flow analysis
6. Incorporating hydraulic boundaries and features, including the shape and characteristics of constant-head boundaries, rivers, precipitation/recharge, and pumping/injection
7. Assigning hydraulic parameters consisting of hydraulic conductivity, porosity, and specific storage (for transient analyses)
8. Specifying initial head values (groundwater surface elevation)
9. Selecting hydraulic calibration targets (*i.e.*, water levels)
10. Evaluating and assigning appropriate model computational characteristics (for example, solution method, iteration limits, and convergence criteria) to enhance model stability, computational efficiency, and solution accuracy
11. Running the model and adjusting assigned model parameters within predetermined limits to achieve the closest fit between model results (hydraulic heads) and calibration targets
12. Evaluating the sensitivity of model results to changes in model parameters

13. Placing particles within the model to determine groundwater flow directions and capture zone characteristics
14. Establishing the model structure, including determining the number of model layers and the grid spacing requirements for the transport analysis
15. Assigning the characteristics of chemical sources (*e.g.*, leaks, spills) consisting of dimensions, locations, concentrations, and time dependency
16. Assigning transport parameters, including the distribution coefficient (which defines contaminant adsorption to soil/rock and affects transport by retarding the rate of contaminant movement) and the decay coefficient (which relates to the rate of chemical decay or ‘half-life’ in the groundwater system)
17. Selecting chemical calibration targets
18. Running the model and adjusting assigned model parameters within predetermined limits to achieve the closest fit between model results and calibration targets
19. Conducting chemical transport scenarios

Completion of these steps is necessary to create a model representing anticipated field conditions as accurately as possible within the constraints of practicality and data availability.

## 8.0 DETAILS ON STATISTICAL ANALYSES TO COMPARE PRE- AND POST ISL/ISR CONDITIONS

Although statistical analyses are used in all phases of the ISL/ISR process shown in Figure 3-1, three phases use procedures based on statistical hypothesis tests:

- Phase 1 – Measure baseline groundwater concentrations and establish restoration goals based on statistical procedures that embrace temporal and spatial variability.
- Phase 4 – Establish wellfield steady state. At the end of this phase, the groundwater potentiometric surface will have returned to baseline conditions, and statistical tests for significant trends are used to verify stability.
- Phase 5 – Conduct long-term stability monitoring. At the end of this phase, statistical tests for trends are again used to show that concentration of the monitored parameter is not increasing (or, in some cases, decreasing) with time. Other statistical tests for comparing post-restoration data with baseline conditions are used to determine when pre-ISL/ISR conditions are achieved. The trend test and comparison with baseline conditions first are conducted well-by-well. If the wells exhibit homogeneous dynamics, the well-by-well statistics may be combined for a wellfield analysis,

The statistical tests are based on measurements of baseline and post-restoration water quality conditions at the site. These measurements include a wide variety of water quality parameters. Usually, the measured parameter is a concentration of a possible contaminant in a specific well at a given time, although other water quality parameters may also be analyzed using the methods in this section.

Both linear regression and the nonparametric Mann-Kendall trend test are recommended as viable alternatives in EPA 2006 and EPA 2009. Linear regression relies on a variety of assumptions, for example, normality, which need to be tested. The Mann-Kendall trend test has been applied in groundwater monitoring at RCRA sites.<sup>4</sup> The Mann-Kendall trend test may be used with any series of four or more independent samples to test for trends in well parameters. The test is employed in Phase 1 to check for unexpected trends in baseline samples, in Phase 4 to determine when steady state is reached, and particularly in Phase 5 to establish long-term stability. The Wilcoxon Rank Sum test (WRS) (also known as the Mann-Whitney or Wilcoxon-Mann-Whitney test) is applied in Phase 5 to compare post-restoration well parameters with baseline parameters, assuming that both datasets are stationary. (EPA 2006)

It is necessary that sufficient data be collected to support a statistical comparison of baseline and post-restoration conditions. Under ideal conditions, the dataset would include a complete time series of 12 measurements per year systematically collected at each well at equally-spaced times using the same measurement device with a very low limit of detection compared to the level of the parameter under pre- and post-restoration conditions. In reality, such datasets exist only in textbook examples. Given an ideal dataset spanning 50 to 100 time periods, a multivariate time series analysis of the type described by Anderson (1994) and Box and Jenkins (2008) would be

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<sup>4</sup> See, for example, HydroGeoLogic, Inc. (2005). OU-1 Annual Groundwater Monitoring Report – Former Fort Ord, California, Appendix D: Mann Kendall Analysis.

appropriate. The multivariate nature of the problem extends over both wells and parameters, with many possible temporal and cross-correlations that would require attention in this type of analysis.

Post-restoration samples are expected to have a higher degree of variability and trend than found in baseline samples. Accordingly, periodic measurements for each contaminant [per 40 CFR 264.97(h)] should be taken from each well over the initial post-restoration period. It is anticipated that the sampling will be quarterly, with four samples per year at each well. Quarterly sampling permits analysis of the data for seasonal variations to determine if variations in measurements reflect normal seasonal variability and not an increase in contaminants.

## 8.1 Hypothesis Testing and Data Quality Objectives

Hypothesis testing is a statistical tool for deciding when the groundwater has reached steady state, and for the comparison of post-restoration conditions with baseline conditions. The hypothesis tests are conducted for individual wells and, when wells exhibit homogenous dynamics, for all wells combined.

The first step in developing a hypothesis test is to transform the problem into statistical terminology by formulating a null hypothesis and an alternative hypothesis. These hypotheses form the two alternative decisions that the hypothesis test will evaluate. When a well is compared with the baseline, the unknown parameter of interest ( $\delta$ ) is the amount by which the post-restoration distribution exceeds the baseline distribution. Delta ( $\delta$ ) is an unknown value, and statistical tests may be used to evaluate hypotheses relating to its possible values. A hypothesis test is designed to reject or not reject hypotheses about  $\delta$  based on test statistics computed from the sample data.

At its core, this is another example of the “How clean is clean?” problem. The action level for baseline comparisons is the largest difference in the two distributions that is acceptable to the decision maker. In this report, the action level for this difference is defined as a substantial difference ( $\Delta$ ), which may be zero or a positive value based on the risk assessment, an applicable regulation, a screening level, or guidance.

This document does not establish a specific value for a substantial difference  $\Delta$ , since the value will vary from parameter to parameter and from site to site. Therefore, specific values for  $\Delta$  should be considered on a case-by-case basis. In many cases, the minimum feasible value of  $\Delta$  is determined by the normal variability in that parameter during pre-ISL/ISR phase. The selection of a value for  $\Delta$  is discussed further in Appendix A of EPA 2002a. The determination of  $\Delta$  for each parameter of interest should be considered during the development of a Quality Assurance Project Plan as part of the planning process for the site evaluation.

Hypothesis testing is a quantitative method to determine whether a specific statement concerning the unknown difference  $\delta$  (a statement known as the *null hypothesis*) can be rejected based on the data at hand. Decisions concerning the true value of  $\delta$  (e. g., is  $\delta > 0$ ?) reduce to a choice between “Yes” or “No.” When viewed in this way, two types of incorrect decisions, or decision errors, may occur:

- Incorrectly deciding the answer is “Yes” when the true answer is “No”
- Incorrectly deciding the answer is “No” when the true answer is “Yes”

While the possibility of decision errors can never be totally eliminated, it can be controlled to acceptable levels. To control decision errors, it is necessary to control the uncertainty in the estimate of  $\delta$ . Uncertainty arises from three sources:

- Sampling error
- Measurement error
- Natural variability

The decision maker has some control over the first two sources of uncertainty. For example, a larger number of samples may lead to fewer decision errors because the probability of a decision error decreases as the number of samples increases. Use of more precise measurement techniques or duplicate measurements can reduce measurement error, thus minimizing the likelihood of a decision error. The third source of uncertainty is more difficult to control. Natural variability arises from the uneven distribution of chemical concentrations and conditions at the site.

Natural variability is measured by the true standard deviation ( $\sigma$ ) of the distribution. A large value of  $\sigma$  indicates that a large number of measurements will be needed to achieve a desired limit on decision errors. Since post-restoration variability is usually higher than in the baseline, post-restoration data collected on the site ideally would be used to estimate  $\sigma$ .

It is advisable to overestimate  $\sigma$  rather than underestimate the true variability. A very crude approximation for  $\sigma$  may be made by dividing the anticipated range (maximum–minimum) by 6 (EPA 2002a, Section 3.1). It is important that overly optimistic estimates for  $\sigma$  be avoided, because this may result in a sample size that fails to generate data with sufficient power for the decision.

The minimum detectable difference (MDD) for a statistical test indicates that differences smaller than the MDD cannot be detected reliably. If the test is used to decide if post-restoration concentrations exceed the baseline concentrations by more than  $\Delta$ , it is necessary to ensure that MDD for the test is less than  $\Delta$ . In the planning stage, this requirement is met by designing a sampling plan with sufficient power to detect differences as small as  $\Delta$  ( $MDD \leq \Delta$ ). If data were collected without the benefit of a sampling plan, retrospective calculation of the power of the test may be necessary before making a decision.

In the planning stage, the absolute size of the MDD is of less importance than the ratio of the MDD to the natural variability of the post-restoration concentrations. This ratio is termed the relative difference defined as  $MDD/\sigma$ , where  $\sigma$  is an estimate of the standard deviation of the post-restoration distribution. The relative difference expresses the power of resolution of the statistical test (MDD) in units of uncertainty ( $\sigma$ ). Relative differences much less than one standard deviation ( $MDD/\sigma \ll 1$ ) are more difficult to resolve unless a larger number of

measurements are available. Relative differences of more than three standard deviations ( $MDD/\sigma > 3$ ) are easier to resolve.

## 8.2 Decision Errors and Confidence Levels

A key step in developing a sampling and analysis plan is to establish the level of precision required of the data used for decision-making. These requirements will determine the required sample size. An increased number of samples generally increases the level of precision. Due to the uncertainties that result from sampling variation, decisions will be subject to errors. There are two ways to err when analyzing data (Table 8-1):

- *Type I Error:* Based on the observed data, the test may reject the null hypothesis when, in fact, the null hypothesis is true (a false positive). This is a Type I error. The probability of making a Type I error is  $\alpha$  (alpha).
- *Type II Error:* On the other hand, the test may fail to reject the null hypothesis when the null hypothesis is, in fact, false (a false negative). This is a Type II error. The probability of making a Type II error is  $\beta$  (beta).

The acceptable level of decision error associated with hypothesis testing is defined by two key parameters; confidence level and power (see Box 8-2). These parameters are closely related to the two error probabilities,  $\alpha$  and  $\beta$ .

- *Confidence level:*  $100(1-\alpha)\%$ . As the confidence level is lowered (or alternatively, as  $\alpha$  is increased), the likelihood of committing a Type I error increases.
- *Power:*  $100(1-\beta)\%$ . As the power is lowered (*i.e.*, as  $\beta$  is increased), the likelihood of committing a Type II error increases.

The selection of appropriate levels for decision errors and the resulting number of samples is a critical component of the data quality objectives (DQO) process that should concern all stakeholders.

Because there is an inherent tradeoff between the probability of committing a Type I or Type II error, a simultaneous reduction in both types can only occur by increasing the number of samples. If the probability of committing a false positive is reduced by increasing the level of confidence of the test (in other words, by decreasing  $\alpha$ ), the probability of committing a false negative is increased, because the power of the test is reduced (increasing  $\beta$ ).

When the site is sampled for a number of species, the selection of appropriate data quality objectives for each contaminant will be influenced by the relative health risks and costs of control for each species. If a single contaminant is the major focus of concern, the data quality objectives ( $\alpha$  and  $\beta$ ) may be based on this species. If more than one species is a matter of concern, then the Bonferroni correction<sup>5</sup> is a simple approach for addressing the problem. If the

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<sup>5</sup> Bonferroni correction is a statistical method used to address the problem of multiple comparisons. It helps control the probability of Type I errors (*i.e.*, false positives).

species are of equal concern, the nominal significance level for each test ( $\alpha$ ) is divided by the number of contaminants that are to be tested. Similarly, adjustments may be made when the species have different levels of concern using a different  $\alpha$  for each species. However, the sample size calculations (described below) show that this reduction in the significance level requires a significant increase in the amount of data to be collected. The issue of multiple comparisons is beyond the intended scope of this document. A complete discussion of Bonferroni confidence intervals and newer alternative approaches to the multiple-comparison problem is presented in Bickel and Doksum (2006).

A Type 1 error occurs if the null hypothesis is rejected when it is true. Since the null hypothesis states that the post-restoration values exceed the baseline by more than  $\Delta$ , a Type I error means that the site was incorrectly determined to be in compliance with restoration goals. A point to be made is that the null hypothesis depends on what the “working assumption” is for each monitoring phase, and, perhaps more generally, what has already occurred. For post-restoration, one “assumes” that values exceed the baseline by delta, and compliance can only be shown by rejection of the null hypothesis, *i.e.* “proving” the alternative. For this phase, a regulator would be primarily concerned with occurrence of Type I Errors (showing compliance when not justified). However, for showing that the site is stable, the null hypothesis would be a statement of no trend. For that phase of the process, one would be concerned with Type 2 errors, and the discussion of MDDs and minimum sample sizes would be relevant<sup>6</sup>.

A Type 2 error occurs if the null hypothesis is accepted when it is not true. A Type 2 error means that the site was incorrectly determined to require further restoration. From a human health perspective, a Type 1 error is more serious than Type 2 error. Hence, it is reasonable that the Type 1 error rate ( $\alpha$ ) should be smaller than the Type 2 error rate ( $\beta$ ). In almost all scientific studies,  $\alpha$  is selected to be either 0.05 or 0.10, limiting the chance of a Type 1 decision error to 5% or 10%, respectively. Once  $\alpha$  is selected, a higher value of  $\beta$  will reduce the required number of samples, but there will a greater likelihood that the site is incorrectly determined to be out of compliance. In this case, the site operator faces a trade-off and may select to reduce the value of  $\beta$  (at the expense of a greater number of samples) and increase the power of the test in order to avoid the possibility of a Type 2 error.

For the purposes of this report, minimum recommended performance measures are:

- **Confidence level at least 90% ( $\alpha \leq 0.10$ ) and power at least 80% ( $\beta \leq 0.20$ ).**  
[EPA 2002a, Section 3.2]

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<sup>6</sup> Documents such as EPA (2009) "Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities" describe processes involving several phases, and the null hypothesis depends on the phase of the process and/or what may have occurred previously. For some stages, the null hypothesis would be a statement that "all is well", *e.g.* there is no trend for a particular contaminant at a particular well monitoring location. For other stages, the null hypothesis is just the opposite, *e.g.* the site is out of compliance with respect to a particular contaminant. For the former, rejection of the null hypothesis in effect "proves" that the site is not stable, and regulators would be primarily concerned with the occurrence of what statisticians refer to as Type 2 Errors (we are unable to detect a worrisome trend when such trend exists). For the latter, the primary concern would be the occurrence of a Type I Error (falsely concluding the site is finally in compliance when it isn't).



These performance standards are described in more detail in Box 8-2.

**Table 8-1. Hypothesis Testing: Type I and Type II Errors**

Decision Based on Sample Data	Actual Site Condition	
	H <sub>0</sub> is True	H <sub>0</sub> is not True
H <sub>0</sub> is not rejected	Correct Decision: (1 - $\alpha$ )	Type II Error: False Negative ( $\beta$ )
H <sub>0</sub> is rejected	Type I Error: False Positive ( $\alpha$ )	Correct Decision: (1 - $\beta$ )

**Box 8-1. Definitions**

$\delta$  (*delta*): The true difference between the post-restoration distribution and the baseline distribution of parameter X. Delta is an unknown value that describes the true state of nature. Hypotheses about its value are evaluated using statistical hypothesis tests. In principle, we can select any specific value for  $\delta$  and then test if this difference is statistically significant or not with a given confidence and power.

$\Delta$  (*a substantial difference*): A difference between the two distributions that is sufficiently large to warrant additional interest based on health or ecological information.  $\Delta$  is the investigation level. If  $\delta$  exceeds  $\Delta$ , the difference in concentrations is judged to be sufficiently large to be of concern for the purpose of the analysis. A hypothesis test uses baseline and post-restoration measurements to determine if  $\delta$  exceeds  $\Delta$ .

*MDD (minimum detectable difference)*: The smallest difference that the statistical test can resolve. The MDD depends on sample-to-sample variability, the number of samples, and the power of the statistical test. The MDD is a property of the survey design.

**Box 8-2. Interpretation of the Statistical Measures**

*Confidence level = 90%*: On average, in 90 out of 100 cases, post-restoration concentrations are correctly identified as exceeding baseline concentrations by more than  $\Delta$ , while in 10 out of 100 cases, post-restoration concentrations will be incorrectly identified as not exceeding baseline concentrations by more than  $\Delta$  when, in fact, they do.

*Power = 80%*: On average, in 80 out of 100 cases, post-restoration concentrations will be correctly identified as not exceeding baseline concentrations by more than  $\Delta$ , while in 20 out of 100 cases, post-restoration concentrations will be incorrectly identified as exceeding baseline concentrations by more than  $\Delta$  when, in fact, they don't.

Adopting hypothesis tests and a DQO approach described in EPAQA/G9S (EPA 2006, Section 3.4) can help control the probability of making decision errors. However, incorrect use of hypothesis tests can lead to erratic decisions. Each type of hypothesis test is based on a set of assumptions that should be verified to confirm proper use of the test. Procedures for verifying the selection and proper use of parametric tests, such as the t-tests, are provided in EPA 2006 (Chapter 4). The tests recommended in this document for verifying stability and determining when the site has met the remedial goals are nonparametric tests. Nonparametric tests generally have fewer assumptions to verify.

The minimum sample size ( $N^*$ ) required in each phase for these tests may be obtained using the approximate formula:<sup>7</sup>

$$N^* = 1.16 \cdot [(0.25) z_{1-\alpha}^2 + 2 (z_{1-\alpha} + z_{1-\beta})^2 \sigma^2 / (\text{MDD})^2]$$

Here  $z_p$  is the  $(100 \cdot p)^{\text{th}}$  percentile of the standard normal distribution.<sup>8</sup> Power and sample size calculations tend to be much more difficult for nonparametric procedures than for parametric procedures. Nonparametric procedures usually have less statistical power than parametric tests when the data follow a known distribution. The sample size formula above includes an adjustment factor of 1.16 to account for the possible loss of efficiency when nonparametric procedures are used. In addition, MARRSIM (EPA 2000, Section 5.5.2.4) recommends increasing  $N^*$  by 20% to account for possible underestimation of  $\sigma$  and to prepare for unplanned events that result in missing or unusable data. With this added safety margin, the recommended sample size is  $n = m = 1.2 \cdot N^*$  (rounded up to the next integer). Values of  $m$  and  $n$  represent the number of baseline samples and the number of post-restoration samples, respectively.

The number of measurements required to achieve the desired decision error rates has a strong inverse relationship with  $\text{MDD}/\sigma$ . Smaller values of  $\alpha$  and  $\beta$  (leading to larger values for the  $z$  terms) magnify the strength of this inverse relationship. Hence, a tradeoff exists between cost (number of samples required) and benefit (better power of resolution of the test). The value of  $n$  is tabulated for a variety of  $\sigma$  values in Table 8-2 for hypothetical values of  $\alpha = \beta = 0.10$  and  $\text{MDD} = 50 \text{ mg/l}$ . Note the dramatic increase in the minimally sufficient sample size as  $\text{MDD}/\sigma$  is lowered from 1 to 0.25. This document does not recommend a specific sample size, since each site will have different variability ( $\sigma$ ) and DQO parameters ( $\alpha$  and  $\beta$ ).

Achievable levels of  $\alpha$  (and  $\beta$ ) for selected sample sizes of  $m$  in the baseline and  $n$  in the post-restoration period with  $m = n$  and a hypothetical value of  $\text{MDD}/\sigma = 1$  are shown in Table 8-3. A complete set of sample size estimates for  $m + n$  for  $\alpha = 0.01/0.025/0.05/0.10/0.20$  and for  $\beta = 0.01/0.025/0.05/0.10/0.20$  are tabulated for a range of the  $\text{MDD}/\sigma$  ratio in Table E-4 in Attachment E. The sample sizes in Tables 8.2, 8.3 and Attachment E include the added safety margin of 1.2.

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<sup>7</sup> See EPA QA/G-9S (EPA 2006, Section 3.3.2.1.1 and Box 3-32, Step 6 of that document) and EPA 2002a (Chapter 3).

<sup>8</sup> The value of  $z_p$  may be calculated in Excel using the spreadsheet function:  $z_p = \text{NORMSINV}(p)$ .

**Table 8-2. Required Sample Size for Selected Values of  $\sigma$**

( $\alpha = \beta = 0.10$  and MDD = 50 mg/l)

$\sigma$ (mg/l)	MDD/ $\sigma$	N*	n=m*
25	2	4.29	6
50	1	15.72	19
75	0.67	34.77	42
100	0.50	61.44	74
125	0.40	95.73	115
150	0.33	137.6	166
175	0.29	187.2	225
200	0.25	244.3	294

Note: \*m is the number of baseline samples and n is the number of post-restoration samples.

**Table 8-3. Achievable Values of  $\alpha = \beta$  for Selected Values of n=m with MDD/ $\sigma$  = 1**

n=m	N*	Z(1- $\alpha$ )	$\alpha=\beta$
10	8.3	0.933	0.175
11	9.2	0.979	0.164
12	10.0	1.022	0.153
13	10.8	1.064	0.144
14	11.7	1.104	0.135
15	12.5	1.143	0.127
16	13.3	1.180	0.119
17	14.2	1.217	0.112
18	15.0	1.252	0.105
19	15.8	1.286	0.099
20	16.7	1.320	0.093
22	18.3	1.384	0.083
24	20.0	1.446	0.074
26	21.7	1.505	0.066
28	23.3	1.561	0.059
30	25.0	1.616	0.053
35	29.2	1.746	0.040
40	33.3	1.866	0.031
45	37.5	1.980	0.024
52	43.3	2.128	0.017

Referring to Table 8.3, it can be seen that 38 samples (m + n) are required to have a 90% confidence limit (1- $\alpha$ ) and a 90% power of the test (1- $\beta$ ), if MDD/ $\sigma$ =1.

The information contained in Table E-4 may be used several ways. If values for  $\alpha$ ,  $\beta$ ,  $\Delta$ , MDD, and  $\sigma$  have been determined, then the table may be used to estimate the number of baseline and post-restoration samples required to achieve the targeted values. Alternatively, the table may be used to determine the maximum resolution that is obtainable with a fixed number of baseline and post-restoration samples for the selected DQO parameters  $\alpha$  and  $\beta$ .

For example, consider an ISL/ISR site with 10 wells and 8 baseline samples per well, collected 1 per quarter over a period of 2 years. For post-restoration sampling, it is proposed to collect 12 additional samples from the same wells, 1 per quarter over a 3-year period. In this example, a total of 200 samples are collected, 20 quarterly samples from each of 10 wells. If  $\alpha = 0.10$  and  $\beta = 0.10$ , then the corresponding column is selected from Table E-4. This column is reproduced

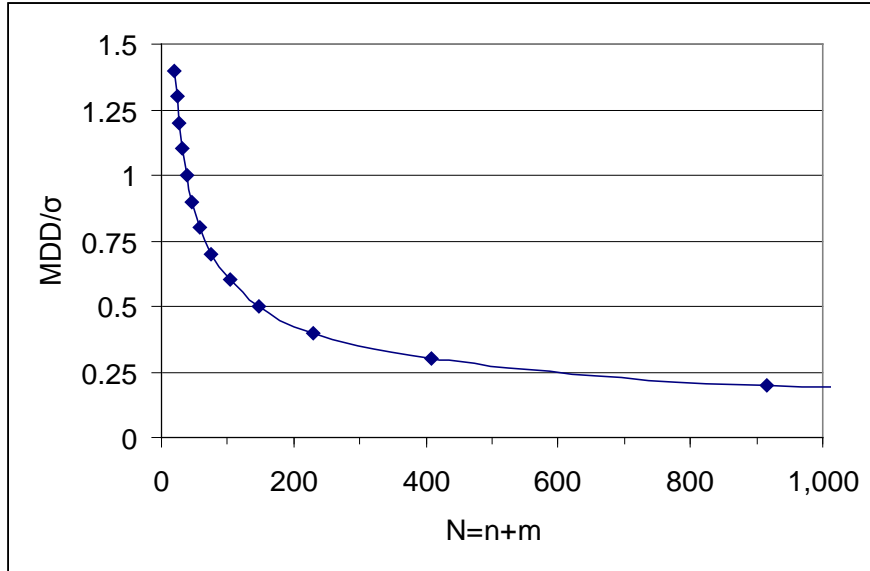
in Table 8-4. These values are plotted in Figure 8-1. Note that increases in sample size generate increasingly smaller increments of resolution for the site-wide post-restoration versus baseline comparison when the sample size is increased beyond 200. However, for individual wells with 20 samples per well, increases in the sample size will generate relatively larger increases in resolution, due to the steepness of the curve on the far left.

With the proposed site-wide sample size of 200 samples, resolutions ( $MDD/\sigma$ ) of approximately  $0.5\sigma$  are achievable. With this sample size, differences of  $\sigma/2$  or larger between overall baseline and post-restoration conditions at the site are resolvable with the desired level of confidence and power. There are 20 samples, 8 in the baseline plus 12 in the post-restoration period, for each well. For individual wells, differences of approximately  $1.4\sigma$  or larger between baseline and post-restoration conditions are resolvable at the desired level of confidence and power. If only 5 wells were sampled in each period, the resolution for each well would remain the same. However, the site-wide total sample size is now 100. This would reduce the resolution of the site-wide comparison to approximately  $0.7\sigma$  (a reduction in resolution of approximately 40%).

**Table 8-4. Minimum Sample Size for Selected Values of  $MDD/\sigma$  with  $\alpha = 0.10$  and  $\beta = 0.10$**

(Table shows values of  $m + n$ .)

	$\alpha = 0.10$
$MDD/\sigma$	$\beta = 0.10$
0.1	3,660
0.2	916
0.3	408
0.4	230
0.5	148
0.6	103
0.7	76
0.8	59
0.9	47
1	38
1.1	32
1.2	27
1.3	23
1.4	20
1.5	-



**Figure 8-1. Test Resolution (MDD/σ) versus Total Sample Size (N)**

### 8.3 Statistical Methods for Trends and Seasonality

The first step in analyzing measurements in one or more wells is to plot the data as a time series. Examples of such plots are shown in the example discussed in Attachment D. Plots of the data may reveal patterns such as seasonality and/or the existence of outliers or blunders in the data. Outliers are values that appear to be unusually high or low when compared to the other values. Outliers may be valid data or may arise from unusual circumstances unrelated to the process being measured. Blunders are outright errors made in recording the data, transcription, or calculations. A common blunder is a mistake in the units of measure. Plotting is used to detect these situations, but does not provide for an explanation or resolution for the unusual value. If a value is identified as erroneous, it should be removed from the dataset. In cases of doubt, the value should be retained. The nonparametric statistical tests discussed in this section were selected due to their robustness. The statistical term “robust” is loosely defined as resistant to the effects of outliers and blunders in the data.

#### *8.3.1 Adjusting for Seasonality*

Seasonality may occur in baseline samples in Phase 1, while the site is reaching steady state in Phase 4, and/or in Phase 5, where seasonality may affect decisions concerning long-term stability and whether target remediation values are attained.

Seasonality is a pattern that repeats periodically in a cycle. An annual seasonal pattern has a cycle which can span 12 months or 4 quarters. A seasonal index measures how far the average for a particular period is above (or below) the average for all periods. The unified RCRA Guidance (EPA 2009) provides the following recommendations concerning seasonality:

*Seasonal fluctuations in intrawell background can be treated in one of two ways. A seasonal Mann-Kendall trend test built to accommodate such fluctuations can be employed (Section 14.3.4). Otherwise, the seasonal pattern can be estimated and removed from the background data, leaving a set of seasonally-adjusted data to be analyzed with either a prediction limit or control chart. In this latter approach, the same seasonal pattern needs to be extrapolated beyond the current background to more recent measurements from the compliance well being tested. These later observations also need to be seasonally-adjusted prior to comparison against the adjusted background, even if there is not enough compliance data yet collected to observe the same seasonal cycles.*

However, the following caveat is added.

*Corrections for seasonality should be used cautiously, as they represent extrapolation into the future. There should be a good physical explanation for the seasonal fluctuation as well as good empirical evidence for seasonality before corrections are made. Higher than average rainfall for two or three Augusts in a row does not justify the belief that there will never be a drought in August, and this idea extends directly to groundwater quality. At least three complete cycles of the seasonal pattern should be observed on a time series plot before attempting the adjustment below. If seasonality is suspected but the pattern is complicated, the user should seek the help of a professional statistician.*

The seasonal Mann-Kendall test is a variation of the Mann-Kendall test for trends described below in Section 8.3.2. The test is described in detail in EPA 2009 in Section 14.3.4.

Seasonal adjustment procedures are commonly applied to ecological and economic data to account for seasonal patterns. The process of *deseasonalizing* the data removes these periodic seasonal variations to reveal the underlying longer-term pattern. The  $i^{\text{th}}$  seasonal component ( $Q_i$ ) is defined as the deviation of the seasonal mean ( $Y_i$ ) from the overall mean ( $Y_M$ ):  $Q_i = Y_i - Y_M$ . The deseasonalized time series ( $X$ ) is obtained by subtracting the seasonal means from the original data series:  $X_{t,i} = Y_{t,i} - Q_i$  (EPA 2009, Eq. 14.23). The deseasonalized data series has the short-term seasonal variations removed; longer-term trends remain in the data. Plots of the seasonally adjusted data series are useful for determining when suspected outliers in sample values reflect the normal variability of monitored parameters after adjusting for the seasonal variations.

When there are four quarterly measurements in each year, the data may be seasonally adjusted by the procedure described in Section D.1 in Attachment D. Appropriate modifications must be made for periodic variations based on other timeframes. Some parameters may require seasonal adjustment and others not. Formal tests for the presence of seasonality across several wells are based on an Analysis of Variance (ANOVA). This procedure is described in EPA 2002b (Sections 14.2.2 and 14.3.3).

The seasonal adjustment procedures are applicable to data that are approximately symmetric and normally distributed. For highly skewed lognormal data series, the calculations above would be applied to the logarithms of the measurements. This is equivalent to using the ratio of the

quarterly mean to the overall mean ( $Q_i^* = Y_i / Y_M$ ) as the seasonality index in place of the additive index above. If this index is 1.2, this means that on average the period (season) is 20% higher than average. In this case, the seasonally adjusted data series is obtained by dividing the original data series by the seasonal index:  $X_{t,i} = Y_{t,i} / Q_i^*$ .

We have assumed that there is a complete set of quarterly measurements for 3 years with no missing or “non-detect” values. If one or two non-detects occur in the data series, one should replace those values with the limit of detection. If there is at most one missing data value, these methods may be applied using the averages of the available data to compute the seasonal index. If more than one value is missing, the appropriateness of adjusting for seasonal variation should be discussed with a statistician familiar with environmental sampling.

***Unless otherwise noted, in the remaining sections of this chapter the term “data” refers to the seasonally adjusted data series  $X_{t,i}$ .***

### 8.3.2 Using Trend Tests to Determine Stability

Trend tests may be used with any series of four or more independent samples to test for trends in well parameters. The test is employed in Phase 1 to check for unexpected trends in baseline samples, in Phase 4 to determine when steady state is reached, and particularly in Phase 5 to affirm long-term stability.

The following text was excerpted from EPA QA/G-9S (EPA 2006):

#### *4.3.2.1 Estimating a Trend Using the Slope of the Regression Line*

*The classic procedures for assessing linear trends involve regression. Linear regression is a commonly used procedure in which calculations are performed on a data set containing pairs of observations ( $X_i, Y_i$ ), so as to obtain the slope and intercept of a line that best fits the data. For temporal data, the  $X_i$  values represent time and the  $Y_i$  values represent the observations. An estimate of the magnitude of trend can be obtained by performing a regression of the data versus time and using the slope of the regression line as the measure of the strength of the trend.*

*Regression procedures are easy to apply. All statistical software packages and spreadsheet programs will calculate the slope and intercept of the best fitting line, as well as the correlation coefficient  $r$  (see Section 2.2.4). However, regression entails several limitations and assumptions. First of all, simple linear regression (the most commonly used method) is designed to detect linear relationships between two variables; other types of regression models are generally needed to detect non-linear relationships such as cyclical or non-monotonic trends. Regression is very sensitive to outliers and presents difficulties in handling data below the detection limit, which are commonly encountered in environmental studies. Hypothesis testing for linear regression also relies on two key assumptions: normally distributed errors, and constant variance. It may be*

*difficult or burdensome to verify these assumptions in practice, so the accuracy of the slope estimate may be suspect. Moreover, the analyst must ensure that time plots of the data show no cyclical pattern; outlier tests show no extreme data values; and data validation reports indicate that nearly all the measurements were above detection limits. **Due to these drawbacks, linear regression is not recommended as a general tool for estimating and detecting trends**, although it may be useful as an informal and quick screening tool for identifying strong linear trends. [Emphasis added.]*

Due to the drawbacks of using regression to *detect* a trend, a nonparametric test (Mann-Kendall) for trends is used in this document to detect a trend. However, the Mann-Kendall test does not provide an estimate of the magnitude of the trend. Once a trend has been detected using the Mann-Kendall test, an estimate of the magnitude of the trend may be required. In this regard, linear regression may be used to *estimate* the trend, provided that the assumptions required for linear regression are met.<sup>9</sup>

The assumptions concerning outliers and non-detects may preclude the use of linear regression for estimating the magnitude of the trend. If there are outliers and/or non-detects in the dataset, a nonparametric method (the Theil-Sen trend line estimator<sup>10</sup>) may be used to estimate the magnitude of the trend.

#### *8.3.2.1 A Nonparametric Statistical Test for Detecting Trends*

The Mann-Kendall test is recommended to detect trends in the data series. The Mann-Kendall test is a nonparametric statistical test. One need not assume that the data are normally distributed, and the test accommodates outliers and values below the detection limit. The test is applied to the data series for each well. Test results for a set of wells may be combined to test for a common trend across all wells (see Section 8.3.3).

The Mann-Kendall test may be used with any series of four or more independent samples to test for trends. The test is employed in Phase 1 to check for unexpected trends in baseline samples, in Phase 4 to determine when steady state is reached, and particularly in Phase 5 to establish long-term stability.

As noted in EPA 2006:

#### ***4.3.4.1 One Observation per Time Period for One Sampling Location***

*The Mann-Kendall test involves computing a statistic  $S$ , which is the difference between the number of pairwise differences that are positive minus the number that are negative. If  $S$  is a large positive value, then there is evidence of an increasing trend in the data. If  $S$  is a large negative value, then there is evidence of a decreasing trend in the data. The null hypothesis or baseline condition for*

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<sup>9</sup> A complete discussion of linear regression techniques for assessing trends and projecting probable future levels is found in EPA 1992, Chapter 6.

<sup>10</sup> The Theil-Sen trend estimator is described in detail in EPA 2009 in Section 17.3.3. The Mann Kendall test (discussed in the next section) is also described in EPA 2009 in Section 17.3.2.



*this test is that there is no temporal trend in the data values. The alternative hypothesis is that of either an upward trend or a downward trend.*

The Mann-Kendall test is applied to the post-restoration data to verify stability, where stability is defined as the lack of a trend. Consider measurements  $y_k(t)$  of a single parameter in  $K$  wells ( $k=1, \dots, K$ ) at times  $t$  spanning two stationary time periods. There are  $m_k$  samples from well  $k$  ( $t = 1, \dots, m_k$ ) in the baseline period and  $n_k$  samples from well  $k$  in the post-restoration period ( $t = m_k+1, \dots, m_k+n_k$ ).

The Mann-Kendall statistic  $S_k$  is used in testing well  $k$  for trend in a single parameter in post-restoration period ( $t > m_k$ ):

$$S_k = \sum_{t=m_k+2}^{m_k+n_k} \sum_{i=1}^{t-1} \text{sign}[x_k(t) - x_k(t-i)]$$

If  $S_k$  is sufficiently large, the null hypothesis of no trend in well  $k$  is rejected in favor of the alternative and a trend has been detected. Detailed instructions for performing the Mann-Kendall test for a single well are shown in Attachment D in Boxes D-1, D-2 and D-3. For additional information on the Mann-Kendall test that is accessible to non-statisticians, see Gilbert 1987 (Chapter 16).

EPA 1992 suggests the following “rule-of-thumb:”

#### *7.4.2 A Test for Trends Based on Charts*

*The charts described here provide a simple way of identifying trends. If six consecutive data points are increasing (or decreasing) – sometimes stated as “5 consecutive intervals of data” so that it is understood that the first point in the string is to be counted – then there is evidence that the variable being monitored (e.g., water levels or flows, or contaminant concentrations) has changed (exhibits a trend).*

The Mann-Kendall statistic can also be used to detect short-term trends in the stabilization period following restoration. Critical values of the Mann-Kendall statistic  $S$  are tabulated in Table E-1 in Attachment E for values of  $n$  from 4 to 40 for  $\alpha = 0.01, 0.05$  and  $0.10$ .

#### *8.3.3 Testing Multiple Wells for Trends*

The Mann-Kendall test is useful for analyzing the trend in data from a single well. If the data were collected systematically across the site at approximately the same sampling times, the Mann-Kendall test statistics  $S_k$  for all wells may be combined to make an overall summary for the entire set of wells. In this approach, the statistics  $S_k$  are used as a summary measure of the trend in each well. There must be consistency in the data series across wells to make a determination of trend that is valid across all wells.

A single statement applicable to trends across all wells is valid if the wells exhibit approximately steady trends in the same direction (upward or downward), with roughly comparable slopes.

Formal statistical tests for the comparability of the data series across wells and for a common trend are described in EPA QA/G9S (EPA 2006) in the text below. Both tests are based on the chi squared distribution. The two tests are designed to be implemented sequentially, first testing for comparability of slopes, then for a significant common trend across wells.

The hypothesis tests described in EPA 2006 are:

**Comparability of stations.**  $H_0$ : Similar dynamics affect all  $K$  stations vs.  $H_A$ : At least two stations exhibit different dynamics.

**Testing for overall monotonic trend.**  $H_0^*$ : Contaminant levels do not change over time vs.  $H_A^*$ : There is an increasing (or decreasing) trend consistent across all stations.

*Therefore, the analyst must first test for homogeneity of stations, and then, if homogeneity is confirmed, test for an overall monotonic trend. Directions for the test are contained in Box 4-11 and ideally, the stations in Box 4-11 should have equal sample sizes. However, the numbers of observations at the stations can differ slightly, because of isolated missing values, but the overall time periods spanned must be similar. This guidance recommends that for less than 3 time periods, an equal number of observations (a balanced design) are required. For 4 or more time periods, up to 1 missing value per sampling location may be tolerated.*

Plots of the measurements from all wells using a different symbol for each well are examined to assess the consistency across wells. Examples of these plots are shown in Attachment D. Detailed instructions for performing the Mann-Kendall test for multiple wells are shown in Attachment D in Boxes D-4, D-5 and D-6.

#### 8.3.3.1 Multiple Observations per Time Period for Multiple Wells

If multiple measurements are taken at various times and stations, then the previous approaches are still applicable. However, the variance of the statistic  $S_k$  must be calculated using a different equation for calculating  $V(S)$ . Details of this calculation are provided in Sections 4.3.4.2 and 4.3.4.3 of EPA 2006.

### 8.4 Verify that Contaminants and Hazardous Constituent Concentrations are Below Required Restoration Levels

The hypothesis testing framework described in Section 8.1 is used to verify that contaminants and hazardous constituent concentrations are below required restoration levels. A hypothesis test is used to compare the post-restoration conditions to the baseline. The comparison may be based on a statistical parameter (e.g., a mean or median) of a probability distribution selected to best represent the population, or it may be a distribution-free comparison of the two populations. With small sample sizes, it is difficult to demonstrate conclusively that a particular distribution represents both populations adequately. Tests that do not assume a known family of probability distributions (e.g., normal or lognormal) to represent the populations are called distribution-free

or nonparametric tests. A nonparametric statistical test may be more useful for comparing two populations than one which assumes a specific distribution, because the nonparametric tests are less sensitive to deviations from the assumed distribution.

When the exact same sampling wells are used for baseline and post-restoration samples, then the two sets of samples are *paired* and not independent. In this case, the statistical test is applied to the differences in contaminant levels for each well. In the paired approach, contaminant levels in each well after restoration are compared to contaminant levels from the same well before treatment. The differences are then compared to a threshold value using a two-sample statistical test for differences.

The threshold value may be zero, in which case, the comparison is used to determine whether the post-restoration well values are less than baseline levels, or threshold value may be a positive number representing the maximum allowable difference between the two populations. This threshold  $\Delta$  is defined as a “substantial difference.” It is anticipated that  $\Delta$  will be different for each parameter.

When the baseline and post-restoration samples are not collected from the same wells, the test involves a comparison of two independent populations.

#### *8.4.1 Nonparametric Tests for Comparing Baseline and Post-Restoration Conditions*

A comparison of post-restoration with baseline samples is conducted in Phase 4 to assess steady-state conditions, and in Phase 5 to determine if post-restoration values have achieved targeted remediation levels. In these comparisons, the statistical approach adopted will depend on the type of data collected. If the baseline and post-restoration samples are from the same wells, then the paired nature of the data is used in the analysis and the wells are analyzed separately; then results are combined to conduct an analysis of the entire site. If the baseline and post-restoration samples are from the different wells, then the baseline and post-restoration data are pooled into two datasets (before and after) and the comparison method described for a single well is applied to conduct a site-wide analysis of the pooled data.

The statistical tests are designed to compare post-restoration parameter values with baseline well parameters, assuming that both datasets were collected under stable conditions. It is likely that the baseline well data will meet this condition, except for possible seasonal effects. Before proceeding with the test for comparing baseline samples with post-restoration samples, it is first necessary to conduct the test for homogeneity of trends and for existence of a monotonic trend as described in Section 8.3.3 and in Attachment D in Boxes D-4, D-5 and D-6. These prior steps are applied to the post-restoration data to affirm stability. If the test for homogeneity of trend across wells is not met, then the individual wells should be tested for trends as described in Section 8.3.2.1 and in Attachment D in Boxes D-1, D-2 and D-3. In this case, the following procedures for determining if remediation goals are met are applicable only to the set of wells with demonstrated stability.

#### 8.4.1.1 Comparing One Well to the Baseline

The comparison of baseline and post-restoration samples from stable wells is made using the Wilcoxon Rank Sum (WRS) test (also called the Mann-Whitney or Wilcoxon-Mann-Whitney test). The advantage of the nonparametric WRS test is that the data need not have a known distribution. Given the small sample sizes, it would be difficult to determine this distribution empirically. The WRS test also allows for non-detect measurements to be present in the baseline and/or post-restoration samples. As a general rule, the WRS test can be used with up to 40% “less than” measurements in either dataset. Two assumptions underlying this test are:

- (1) Samples from the baseline and post-restoration periods are independent, identically distributed random samples
- (2) Each measurement is independent of every other measurement, regardless of the set of samples from which it came

The null hypothesis is that the post-restoration data exceed the baseline by a substantial difference. The null hypothesis is formulated for the express purpose of being rejected if the data provide support for the alternative:

- The null hypothesis ( $H_0$ ): The post-restoration distribution exceeds the baseline by more than  $\Delta$ . Symbolically, the null hypothesis is written as  $H_0: \delta > \Delta$ .
- The alternative hypothesis ( $H_A$ ): The post-restoration distribution does not exceed the baseline by more than  $\Delta$  ( $H_A: \delta < \Delta$ ).

Here,  $\Delta$  is the investigation level. The investigation level is determined on a case-by-case basis.

The hypothesis test is structured so that the post-restoration data must provide evidence that the site is within acceptable limits. This test assumes that any difference between the baseline and post-restoration sample value distributions is due to a shift in the distribution of sample values to higher values in the post-restoration period. The hypotheses to be tested using the WRS test have the following definition.

*Null Hypothesis  $H_0$ : The post-restoration distribution exceeds the baseline distribution by more than a substantial difference delta ( $\Delta$ );*

versus the:

*Alternative Hypothesis  $H_A$ : The post-restoration distribution is lower than the baseline distribution or exceeds the baseline distribution by no more than  $\Delta$ .*

*The null hypothesis is assumed to be true unless the statistical test indicates that it should be rejected in favor of the alternative.*

A two-sample statistical is a test for differences between the distributions of two independent samples. The post-restoration samples from well k are compared with the baseline samples from the same well to determine if remediation goals have been met. The WRS test is a test based on

the relative rank of the post-restoration samples versus the baseline samples. The WRS statistic for well  $k$  is defined as:

$$W_k \equiv U_k + m(m + 1) / 2$$

Here,  $U_k$  is the Mann-Whitney statistic for well  $k$ .  $U_k$  is equal to the number of positive differences in the set of all  $n_k m_k$  possible differences between the (possibly augmented) baseline data and the post-restoration data for well  $k$ :

$$U_k = \sum_{j=1}^{n_k} \sum_{i=1}^{m_k} I[(x_k(i) + \Delta) - x_k(\tau + j)]$$

Here, the indicator function  $I[y]$  equals 1 if  $y > 0$  and equals 0 otherwise. Box D-7 in Attachment D has detailed instructions for calculating the statistics  $U_k$  and  $W_k$ . For additional information on the Wilcoxon-Mann-Whitney test that is useful to non-statisticians, see Conover 1998 (Chapter 5).

To determine if well  $k$  has met the remediation goal, the test statistic  $W_k$  is compared with the critical value for the WRS test for sample sizes  $m_k$  and  $n_k$  in Attachment E in Tables E-5, E-6, E-7, and E-8 for  $\alpha = 0.01, 0.025, 0.05, 0.10$ , respectively. If the test statistic exceeds the critical value from the table, the null hypothesis is rejected and we conclude that the parameter values in the post-restoration period are below the baseline or exceed the baseline by no more than  $\Delta$ .

#### 8.4.1.2 *Comparing Multiple Wells Testing for Homogeneity and Overall Compliance to the Baseline*

The WRS test described above is useful for analyzing the data from a single well. The WRS statistic  $W_k$  for all wells may be combined to make an overall summary for the entire set of wells. In this approach, the statistics  $W_k$  are used as a summary measure of compliance in each well. However, there must be consistency across wells in the relative levels of the baseline and post-restoration data to make a determination of compliance that is valid across all wells.

The procedures described in Section 8.3.3 for conducting an overall test for a trend using the summary Mann-Kendall statistics for each well may be modified to construct an overall test for determining when remediation goals are met. Two tests are used; first a test for homogeneity across wells and then a test for overall compliance. Again, both tests are based on the chi squared distribution. The two tests are designed to be implemented sequentially, testing first for homogeneity, then for compliance across wells as follows:

##### ***Step 1. Test for comparability of wells for compliance determination***

- $H_0$ : *Similar dynamics affect all  $K$  wells vs.*  
 $H_A$ : *At least two wells exhibit different dynamics*

## Step 2. Test for overall compliance

- $H_0^*$ : Baseline values are exceeded by more than a substantial difference  $\Delta$  at one or more wells vs.
- $H_A^*$ : Post-restoration values are lower than baseline values or exceed baseline values by no more than a substantial difference  $\Delta$ .

The expected value and variance of  $W_k$  under the null distribution are:

$$E_k = E(W_k) = m_k(n_k + m_k + 1)/2$$
$$V_k = Var(W_k) = n_k m_k (n_k + m_k + 1)/12$$

The standardized form of the test statistic  $W_k$  is  $z_k = (W_k - E_k)/\sqrt{V_k}$ . If  $z_k$  is sufficiently large, there is evidence that this well has met the remediation goal.

To perform the test for homogeneity (or comparability), first calculate the average of the standardized test statistics  $Z_M = \sum Z_k/K$ . The homogeneity chi-square statistic is  $\chi^2_h = (\sum Z_k^2) - KZ_M^2$ . Using the chi-squared table in Table E-3 of Attachment E, find the critical value for  $\chi^2$  with  $(K-1)$  degrees of freedom at significance level  $\alpha$ . For example, with a significance level of 5% and 5 degrees of freedom,  $\chi^2_{(5)} = 11.07$ , i.e., 11.07, is the cut point, which puts 5% of the probability in the upper tail of a chi-square variable with 5 degrees of freedom. If  $\chi^2_h \leq \chi^2_{(K-1)}$ , there are comparable test statistics across wells at significance level  $\alpha$ . If  $\chi^2_h > \chi^2_{(K-1)}$ , the wells are not homogeneous at the significance level  $\alpha$ . In this case, individual  $\alpha^*$ -level WRS tests should be conducted at each well using the methods presented in Box D-7.

If the hypothesis of homogeneity across wells is accepted in Step 1, use Step 2 to affirm the compliance of all wells with the remediation goals. The chi-squared table in Table E-3 of Attachment E is used to find the critical value for  $\chi^2$  with 1 degree of freedom at significance level  $\alpha^*$ . Calculate the overall compliance test statistic  $\chi^2_c = KZ_M^2$ . If  $\chi^2_c \geq \chi^2_{(1)}$ , reject  $H_0^*$  and conclude that the site appears to be below baseline conditions or no more than  $\Delta$  higher than baseline conditions. If  $\chi^2_c < \chi^2_{(1)}$ , there is not sufficient evidence (at the  $\alpha^*$  significance level) that all wells are in compliance with the remediation goals. In this case, additional remediation may be required.

## 8.5 Summary of Statistical Approaches

The preferred statistical approaches outlined in the previous sections are summarized here.

### Phase 1 Baseline Sampling

- Estimate required number of samples (Section 8.2, Tables 8.1 and 8.2; Attachment E, Table E-4)
- Adjust measured data for seasonality if required (Section 8.3.1 and Attachment D, Section D.1)

- Use Mann-Kendall test to check for unexpected trends (Section 8.3.2, 8.3.3 and Attachment D, Sections D.2 and D.3)

#### ***Phase 4 Determination of Steady State***

- Adjust measured individual well data for seasonality if required (Section 8.3.1 and Attachment D, Section D.1)
- Use Mann-Kendall test for individual well trends (Section 8.3.2, 8.3.3 and Attachment D, Sections D.2 and D.3)
- If a trend is detected, use linear regression or Theil-Sen test to assess trend magnitude (Section 8.3.2)
- If trends not detected, use WRS test to compare baseline to steady-state measurements for statistical differences for a single well. Repeat for all wells. (Section 8.4.1.1 and Attachment D, Section D.4)
- For multiple wells, when trends are not detected, first test wells for homogeneity. If test results confirm homogeneity, if hypothesis of homogeneity across all wells is accepted, then test to confirm compliance of all wells with restoration goals. (Section 8.4.1.2 and Attachment D, Section D.5)
- If steady-state data are from different wells than the baseline data and trends are not detected; use WRS test to compare baseline to steady-state measurements for statistical differences for the pooled data of all wells combined, which are treated as a single well. (Section 8.4.1.1 and Attachment D, Section D.4)

#### ***Phase 5 Long-term Stability Monitoring***

- Adjust measured data for each well for seasonality if required (Section 8.3.1 and Attachment D, Section D.1)
- Use Mann-Kendall test for trends for each well (Section 8.3.2, 8.3.3 and Attachment D, Sections D.2 and D.3)
- If trend is detected, use linear regression or Theil-Sen test to assess trend magnitude (Section 8.3.2)
- If trends not detected, use WRS test to compare baseline to stability monitoring results for a single well. Repeat for each well. (Section 8.4.1.1 and Attachment D, Section D.4)
- If the before/after comparison is made between multiple wells, first test all wells for homogeneity using chi-squared approach, then test to confirm compliance of all wells with restoration goals (Section 8.4.1.2 and Attachment D, Section D.5)
- If post-restoration data are from different wells than baseline data and trends are not detected, use WRS test to compare baseline to stability monitoring results for the pooled data of all wells combined (Section 8.4.1.1 and Attachment D, Section D.4)

Gilbert 1987 contains extensive discussions of the issues concerning use of statistics in environmental and groundwater monitoring. For a detailed discussion of the tests mentioned in

this chapter, as well as step-by-step guidance on calculations for the various types of comparisons, see also EPA 2000 and EPA 2006.



## 9.0 SUMMARY OF POST-CLOSURE PERFORMANCE ISSUES

This section provides a synopsis of the topics discussed in the previous sections that are important to designing a monitoring network and demonstrating acceptable post-closure performance of an in-situ mining operation.

### 9.1 Designing the Monitoring Program to Allow Reliable Baseline Conditions to be Established Prior to Active Mining

A meaningful interpretation of post-closure monitoring results relies on the accurate characterization of baseline groundwater conditions before active mining (leaching) begins. The baseline monitoring program must capture both temporal and spatial variability in groundwater chemistry. Considerations for this performance issue include:

- Placement of monitoring wells (both within and beyond the influence of the injection-withdrawal field) and well construction (*e.g.*, screened intervals)
- Chemical constituents to be monitored, including sampling techniques, and frequencies
- Duration of sampling to determine natural variations in pre-mining groundwater chemistry
- Statistical methods for assessing variations in data and confidence measures for these data and subsequent decisions about baseline conditions (*e.g.*, temporal variations in “background” levels and how much data are sufficient for decision-making)

The placement and number of monitoring wells in and around an in-situ mining operation is strongly, if not totally, dependent on the site-specific hydrogeologic setting. The flow characteristics of the ore bearing aquifer, the injection and withdrawal rates and spacing of these wells will dictate the placement of monitoring wells to not only assess baseline conditions in the aquifer, but to enable the detection of excursions of the treated groundwaters beyond the withdrawal wells.

Extensive experience in collecting and analyzing groundwater chemical components exists within the technical community concerned with fate and transport of pollutants. In addition, there is a reasonable experience base from previous investigations and restoration efforts at in-situ mining operations. Sampling protocols are reasonably well developed and can be reliably adapted to the in-situ mining application. The mining and post-mining restoration efforts involve actively altering the chemical environment. Although reaction kinetics ultimately dictate how and over what timeframes the groundwater chemistry will respond, the uncertainties introduced by the heterogeneities in the ore-bearing zone are too complex and locally variable to allow reliable predictive modeling of the system response. Statistical assessments of groundwater chemistry in monitoring well samples are still the best tools for assessing the achievement of steady-state conditions.

Constituents to be monitored should be established on a site-specific basis. Currently, 40 CFR Part 192 requires that molybdenum and uranium be added to the list of hazardous constituents in

40 CFR 264.93,<sup>11</sup> and Ra-226+Ra-228 (5 pCi/L) and gross alpha (15 pCi/L) are added to the concentration limits provided in 40 CFR 264.94. These, together with several additional parameters, are listed by NRC in its guidance for ISL/ISR license review (Standard Review Plan).

To insure that temporal variability is captured, monitoring should be conducted over a period sufficient to capture seasonal variations. Both the EPA and NRC have recommended that at least four quarterly sets of samples be taken (NRC 2003 and 40 CFR 264.97) to establish the baseline. Since this approach only covers one set of seasons, a larger number of samples may be required to obtain adequate statistics if seasonal variations are anticipated. If significant seasonal variations are anticipated, longer timeframes for collecting samples sufficient to cover a number of seasonal cycles would be appropriate to establish confidence in the baseline characterization.

Monitoring for spatial variability within the permit area for mining should include wells upgradient, downgradient, laterally adjacent to, and within the proposed leach area, sufficient to identify high and low permeability zones. Monitoring should also include overlying and underlying aquifers, which could become contaminated from leaching activities. Offsite wells in the vicinity, such as drinking water wells and stock water wells, should also be monitored. In its Standard Review Plan for ISL/ISRs, NRC defines an acceptable set of samples as including all wellfield perimeter monitor wells, all upper and lower aquifer monitor wells, and at least one production/injection well per acre in each wellfield, except that the requirement of one production well per acre can be reduced for very large wellfields. It is difficult to define minimum well spacing without detailed characterization of the flow system and injection/withdrawal rates and configuration of the mining wellfield.

## 9.2 Determining that the Groundwater Chemistry has Reached Steady State and Restoration Processes Can be Discontinued

Sufficient information must be provided to the regulator so that a determination can be made that restoration is complete and steady-state conditions have been achieved prior to initiating post-restoration stability monitoring, or to indicate that additional restoration efforts are necessary.

As noted in EPA 1992 (Section 7.5):

*Finding that the ground water has returned to a steady state after terminating remediation efforts is an essential step in the establishment of a meaningful test of whether or not the cleanup standards have been attained. There are uncertainties in the process, and to some extent it is judgmental. However, if an adequate amount of data are carefully gathered prior to beginning remediation and after ceasing remediation, reasonable decisions can be made as to whether or not the ground water can be considered to have reached a state of stability.*

*The decision on whether the ground water has reached steady state will be based on a combination of statistical calculations, plots of data, ground water modeling,*

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<sup>11</sup> 40 CFR 264.93 lists the following inorganic species: Ag, As, Ba, Cd, Cr, Hg, Pb, and Se.

*use of predictive models, and expert advice from hydrogeologists familiar with the site.*

In addition to groundwater chemistry, attention must also be directed to site hydrology to establish that the potentiometric surface has returned to baseline conditions.

It is anticipated that restoration will take several years (see Table 7-1). During this time, groundwater sampling will be used to follow the progress of the restoration process.

Considerations for this performance issue include:

- Placement of monitoring wells in and surrounding the injection-extraction field (proximity to the extraction field), sampling frequency, and sampling techniques (particularly if they differ from the pre-mining techniques)
- Chemical constituents to be examined (mobilized species) and constituents that may have been added to the groundwater in attempts to restore pre-mining conditions (*e.g.*, chemical reducing agents or other chemicals to sequester or inhibit movement of mobilized metals)
- Statistical tools necessary to determine when steady-state post-mining conditions are established (data demands and consequent uncertainty levels)

The statistical tools for assessing “steady-state” conditions have a well-established record of application in other contaminant remediation efforts and are easily adapted to the in-situ leaching application. Care must be exercised in the application of these tools to assure that the database for the site is detailed enough to allow clear application and interpretation of the results. Statistical tools required to determine steady-state conditions using the Mann-Kendall test (*i.e.*, absence of trends) are described in Section 8.3.2 and 8.3.3. Statistical tools that can be used to compare the restored groundwater to the baseline using the WRS test are discussed for single wells and multiple wells in Sections 8.4.1.1 and 8.4.1.2, respectively. If the monitoring period is too short, divergent data reflecting slower flow paths through the ore zone, and still active chemical processes, could be missed and an incorrect assessment of the aquifer’s chemical state could result.

### 9.3 Post-Restoration Stability Monitoring

After the regulators have judged that the restoration process is complete, the period of long-term stability monitoring begins. In the past, the stability monitoring period has been set as a license condition at about 6 months, but more recently, this has been increased to a minimum of 1 year (Table 7-1). Field experience suggests that 1 year may not be adequate. In some cases, the actual stability monitoring period has extended over several years to insure that stability has been achieved (see Attachment B). Uranium in-situ leaching locations are typically in fluvial sandstone deposits, which characteristically exhibit lithologic heterogeneities reflecting the original depositional environments of the deposits. The formation of the uranium deposits in these sediments also introduces changes in the porosity and permeability of the ore zone in contrast to the surrounding aquifer. The mining and post-mining restoration activities would further alter the local flow regime in the ore body. In such systems, groundwater flow paths

through the ore-body would be anticipated to differ significantly from the surrounding media, strongly suggesting that post-mining monitoring timeframes should be longer than sometimes applied, in order to capture the effects of locally variable flow fields.

Considerations for this performance issue include:

- Chemical constituents in pre- and post-mining waters are examined to determine if aquifer water quality has been degraded by the leaching operations
- Statistical measures needed to insure that the groundwater remains stable over several years (*i.e.*, concentrations are not trending upward)
- Statistical measures needed to make decisions on whether the aquifer has achieved restoration goals

The same statistical tools can be used for post-restoration stability monitoring as described in Section 9.2. As mentioned above, quantitative prediction of the groundwater system's chemical evolution is extremely difficult, and statistical measures to assess "steady-state" attainment remain the primary tool for evaluating the success of post-mining restoration efforts.

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## **ATTACHMENT A: DEVELOPMENT OF GROUNDWATER BASELINE FOR DEWEY-BURDOCK ISL SITE IN SOUTH DAKOTA**

Powertech (USA) Inc., is seeking an NRC source material license to operate an ISL facility in South Dakota (the Dewey-Burdock site) (Powertech 2009). The license application was resubmitted to the NRC in October 2009 and technical review is ongoing.<sup>12</sup> The Proposed Action Area (PAA) encompasses about 10,520 acres. Startup of the Dewey and Burdock operations will commence upon completion of construction and will continue for approximately 7 to 20 years or more, during which time additional wellfields will be completed along the roll-fronts at both Dewey and Burdock sites. It is planned that groundwater restoration can be accomplished within NRC requirements for timeliness in decommissioning (10 CFR § 40.42); however, in the event restoration cannot be accomplished within this timeframe, Powertech (USA) will seek NRC approval for an alternate schedule (Powertech 2009).

Baseline groundwater sampling was conducted in general accordance with NRC Regulatory Guide 4.14 as appropriate to ISL operations (NRC 1980). For the baseline study for the NRC permit application, 19 groundwater wells (14 existing and 5 newly drilled) were selected in response to an NRC direction to characterize point of contact water quality and water within overlying, production, and underlying aquifers. The existing wells selected for sampling include eight domestic wells and six stock watering wells. The subset includes wells within the Fall River Formation (4), Lakota Formation (7), Inyan Kara Group (Fall River or Lakota) (2), Sundance Formation (1), and alluvium (5). Initial baseline sampling of these wells was conducted quarterly from July 2007 through June 2008.

As required by the South Dakota Department of Environment and Natural Resources (DENR), an additional 12 wells were sampled monthly beginning in March 2008 and continuing through February 2009. Of these 12 wells, 6 wells are in the Dewey area and 6 wells are near Burdock. At Dewey, a set of Fall River and Lakota wells were sampled at three places; upgradient, within, and downgradient of the proposed operations. Near the Burdock area, the same well arrangement applies with two wells each upgradient, within, and downgradient of the proposed operations. In addition, one water quality sample was collected from each of the monitor wells used during the May 2008 aquifer pump tests.

A groundwater quality constituent list was developed based on NUREG-1569 (NRC 2003) groundwater parameters, NRC Regulatory Guide 4.14 parameters (NRC 1980), and added parameters based on a constituent list review with South Dakota DENR. Table A-1 lists constituents analyzed for in groundwater samples, the number of samples analyzed for each constituent, the analytical method, and the Practical Quantitation Limit (PQL).

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<sup>12</sup> See <http://www.nrc.gov/materials/uranium-recovery/license-apps/ur-projects-list-public.pdf>.

**Table A-1. Dewey-Burdock Site - Number of Groundwater Samples Collected, Analytical Method, and PQL by Constituent**

Constituent, Unit	Number of Samples Analyzed	Analytical Method	PQL <sup>1</sup>
<b>Major Cations and Anions</b>			
<b>Anions (meq/L)</b>	140	A1030 E	
Bicarbonate as HCO <sub>3</sub> (mg/L)	140	A2320 B	5
Carbonate as CO <sub>3</sub> (mg/L)	140	A2320 B	5
Sulfate (mg/L)	140	E300.0	36
Chloride (mg/L)	140	E300.0	1
Fluoride (mg/L)	140	E300.0	0.1
Nitrogen, Nitrite as N (mg/L)	140	E300.0	0.1
Nitrogen, Nitrate as N (mg/L)	140	E300.0	0.1
<b>Cations (meq/L)</b>	140	A1030 E	
Ammonia (mg/L)	140	A4500-NH <sub>3</sub> G	1
Sodium-Dissolved (mg/L)	140	E200.7	0.8
Calcium-Dissolved (mg/L)	140	E200.7	0.5
Magnesium-Dissolved (mg/L)	140	E200.7	0.5
Potassium-Dissolved (mg/L)	140	E200.7	0.5
Silica-Dissolved (mg/L)	140	E200.7	0.5
<b>General Water Quality Indicators</b>			
Alkalinity-Total as CaCO <sub>3</sub> (mg/L)	140	A2320 B	5
Anion/Cation Balance (± 5) (%)	280	A1030 E	
Conductivity @ 25 C (µmhos/cm)	140	A2310 B	5
Oxidation-Reduction Potential (mV)	118	A2580 B	
pH	140	A4500-H B	0.01
Sodium Adsorption Ratio (meq/L)	120	Calculation	0.1
Solids-Total Dissolved TDS (mg/L)	140	A2540 C	5
Solids-Total Dissolved , Calc. (mg/L)	140	Calculation	5
TDS Balance (0.80 – 1.20) (dec.%)	140	A1030 E	
<b>Methods, Dissolved</b>			
Aluminum-Dissolved (mg/L)	140	E200.8	0.1
Arsenic-Dissolved (mg/L)	140	E200.8	0.001
Barium-Dissolved (mg/L)	140	E200.8	0.1
Boron-Dissolved (mg/L)	140	E200.7	0.1
Cadmium-Dissolved (mg/L)	140	E200.8	0.005
Chromium-Dissolved (mg/L)	140	E200.8	0.05
Cooper-Dissolved (mg/L)	140	E200.8	0.01
Iron-Dissolved (mg/L)	140	E200.7	0.03
Lead-Dissolved (mg/L)	140	E200.8	0.001
Manganese-Dissolved (mg/L)	140	E200.8	0.01
Mercury-Dissolved (mg/L)	140	E200.8	0.001
Molybdenum-Dissolved (mg/L)	140	E200.8	0.1
Nickel-Dissolved (mg/L)	140	E200.8	0.05
Selenium-Dissolved (mg/L)	140	A3114 B	0.001
Selenium-IV-Dissolved (mg/L)	118	A3114 B	0.001
Selenium-VI-Dissolved (mg/L)	118	A3114 B	0.001
Silver-Dissolved (mg/L)	140	E200.8	0.005
Thorium 232-Dissolved (mg/L)	140	E200.8	0.005
Uranium-Dissolved (mg/L)	140	E200.8	0.003
Vanadium-Dissolved (mg/L)	140	E200.8	0.1
Zinc-Dissolved (mg/L)	140	E200.8	0.01

**Table A-1. Dewey-Burdock Site - Number of Groundwater Samples Collected, Analytical Method, and PQL by Constituent**

Constituent, Unit	Number of Samples Analyzed	Analytical Method	PQL <sup>1</sup>
<b>Metals, Suspended</b>			
Uranium-Suspended (mg/L)	138	E200.8	0.0003
<b>Metals, Total</b>			
Antimony-Total (mg/L)	95	E200.8	0.003
Arsenic-Total (mg/L)	95	E200.8	0.001
Barium-Total (mg/L)	95	E200.8	0.1
Beryllium-Total (mg/L)	95	E200.8	0.001
Boron-Total (mg/L)	95	E200.7	0.2
Cadmium-Total (mg/L)	95	E200.8	0.005
Chromium-Total (mg/L)	95	E200.8	0.05
Cooper-Total (mg/L)	95	E200.8	0.01
Iron-Total (mg/L)	95	E200.7	0.03
Lead-Total (mg/L)	95	E200.8	0.001
Manganese-Total (mg/L)	95	E200.8	0.01
Mercury-Total (mg/L)	163	E200.8	0.001
Molybdenum-Total (mg/L)	95	E200.8	0.1
Nickel-Total (mg/L)	95	E200.8	0.05
Selenium-Total (mg/L)	95	E200.8	0.002
Silver-Total (mg/L)	95	E200.8	0.005
Strontium-Total (mg/L)	95	E200.8	0.1
Thallium-Total (mg/L)	95	E200.8	0.001
Uranium-Total (mg/L)	99	E200.8	0.0003
Zinc-Total (mg/L)	95	E200.8	0.01
<b>Radionuclides</b>			
Gross Alpha-Dissolved (pCi/L)	140	E900.0	1
Gross Beta-Dissolved (pCi/L)	140	E900.0	2
Gross Gamma-Dissolved (pCi/L)	140	E901.1	20
Lead-210-Dissolved (pCi/L)	140	E909.0M	1
Lead-210-Suspended (pCi/L)	138	E909.0M	1
Lead-210-Total (pCi/L)	20	E909.0M	1
Polonium 210-Dissolved (pCi/L)	140	RMO-3008	1
Polonium 210-Suspended (pCi/L)	138	RMO-3008	1
Polonium 210-Total (pCi/L)	20	RMO-3008	1
Radium 226-Dissolved (pCi/L)	134	E903.0	0.2
Radium 226-Suspended (pCi/L)	133	E903.0	0.2
Radium 226-Total (pCi/L)	90	E903.0	0.2
Radon 222-Total (pCi/L)	120	D5072-92	100
Thorium 230-Dissolved (pCi/L)	140	E907.0	0.2
Thorium 230-Suspended (pCi/L)	138	E907.0	0.2
Thorium 230-Total (pCi/L)	20	E907.0	0.2

<sup>1</sup> PQL = Practical Quantitation Limit. The concentration that can be reliably measured within specified limits during routine laboratory operating conditions, below which results are reported as “less than reporting limit.” The contracting laboratory uses the PQL as the reporting limit.

Source: Powertech 2009, Table 2.7-30

Table A-2 lists current National Primary and Secondary Drinking Water Standards as regulated by EPA, together with the number of samples analyzed for each constituent, the total number of detections above the reporting limit, and the total number of detections equal to or above the Maximum Contaminant Level (MCL) for each constituent. These standards or MCLs are enforced by the EPA on public drinking water systems, but only serve as a guide for private water systems. Private water systems, as defined by the EPA, serve less than 25 people and have less than 15 service connections; all other systems are defined as public water systems. All drinking water wells within the Production Authorization Area (PAA) are private water systems.

**Table A-2. Dewey-Burdock Baseline Water Quality Sampling Statistics with Water Quality Regulatory Limits for Public Drinking Water Supply Systems**

Test Analyte/Parameter	Units	EPA Maximum Contaminant Level (MCL)	Number of Samples Analyzed*	Number of Detections	Number of Detections Equal to or Above MCL
<b>BULK PROPERTIES</b>					
pH	pH Units	6.5–8.5 [1]	141	141	6
Total Dissolved Solids (TDS)	mg/L	500 [1]	141	141	141
<b>CATIONS/ANIONS</b>					
Sodium, Na	mg/L	200 [1]	141	141	63
Chloride, Cl	mg/L	250 [1]	141	141	4
Fluoride, F	mg/L	4; 2 [1]	141	136	0
Sulfate, SO <sub>4</sub>	mg/L	250 [1]	141	141	141
Nitrate (as Nitrogen)	mg/L	10	141	29	0
Nitrite (as Nitrogen)	mg/L	1	141	0	0
Nitrate and Nitrite (Combined)	mg/L	10	141	29	0
<b>TRACE METALS (total)</b>					
Antimony, Sb	mg/L	0.006	98	0	0
Aluminum, Al	mg/L	0.05–0.2 [1]	141	0	0
Arsenic, As	mg/L	0.01	98	80	11
Barium, Ba	mg/L	2	98	6	0
Beryllium, Be	mg/L	0.004	98	2	0
Boron, B	mg/L	1.4 [2]	98	29	3
Cadmium, Cd	mg/L	0.005	98	0	0
Chromium, Cr	mg/L	0.1	98	1	0
Copper, Cu	mg/L	1.0 [1]; 1.3 [3]	98	5	0
Iron, Fe	mg/L	0.3 [1]; 5 [4]	98	95	2 [1]; 1 [4]
Mercury, Hg	mg/L	0.002	170	1	0
Manganese, Mn	mg/L	0.05 [1]; 0.8 [4]	98	98	89 [1]; 19 [4]
Molybdenum, Mo	mg/L	0.04 [2]	98	8	2
Nickel, Ni	mg/L	0.1 [2]	98	1	1
Lead, Pb	mg/L	0.015 [3]	98	18	8
Selenium, Se	mg/L	0.05	98	26	0
Silver, Ag	mg/L	0.1 [1], [2]	98	0	0
Strontium, Sr	mg/L	4 [2]	98	97	37
Thallium, Tl	mg/L	0.002	98	0	0
Uranium, U	mg/L	0.030	102	77	18
Zinc, Zn	mg/L	5 [1]; 2 [2]	98	35	0

**Table A-2. Dewey-Burdock Baseline Water Quality Sampling Statistics with Water Quality Regulatory Limits for Public Drinking Water Supply Systems**

Test Analyte/Parameter	Units	EPA Maximum Contaminant Level (MCL)	Number of Samples Analyzed*	Number of Detections	Number of Detections Equal to or Above MCL
<b>RADIONUCLIDES</b>					
Beta Particles and Photons (Combined)	mRem/Year	4	141	137	N/A
Radium 226 and 228 (Combined)	pCi/L	5	135	119	59
Radon-222 (total)	pCi/L	300 [5]	121	121	105

Notes:

[1] Secondary guideline value above which use of water may give complaints by consumers.

[2] Health Advisory – Lifetime

[3] Action level which if exceeded triggers treatment.

[4] Region 8 Permit Limit

[5] Proposed MCL

N/A – Not available

\* - Number of samples includes results for only those wells that were sampled quarterly or monthly as part of the baseline sampling plan

Source: Powertech 2009, Table 2.7-35

### Attachment A References

NRC (U.S. Nuclear Regulatory Commission) 1980. *Radiological Effluent and Environmental Monitoring at Uranium Mills*. Regulatory Guide 4.14, Revision 1.

NRC (U.S. Nuclear Regulatory Commission) 2003. *Standard Review Plan for In-Situ Leach Uranium Extraction License Applications—Final Report*. NUREG-1569. Washington, DC. June 2003.

Powertech 2009. *Dewey-Burdock Project Application for NRC Uranium Recovery License, Fall River and Custer Counties, South Dakota Technical Report*. February 2009. ML092870295.

## ATTACHMENT B: POST-RESTORATION STABILITY MONITORING CASE HISTORIES

### **Power Resources Inc. (PRI), Smith Ranch - Highland Uranium Project: A-Wellfield**

Most of the following information was extracted from Power Resources 2004. The A-Wellfield was mined from January 1988 through July 1991 using a lixiviant formed by adding gaseous carbon dioxide and oxygen to the natural groundwater. Restoration began in July 1991 and was completed in October 1998. The Wyoming Department of Environmental Quality (WDEQ) mine permit and the NRC license required that post-restoration stability monitoring be conducted over a period of 6 months. However, PRI initially collected stability data from February 1999 through April 2000 (14 months). Additional stability data on a limited suite of parameters (chloride, bicarbonate, conductivity, and uranium) were collected through November 2003. In November 2003, the WDEQ concluded that stability had been demonstrated, but decommissioning could not begin until an additional monitoring plan related to natural attenuation was approved.

During restoration, PRI applied Best Practicable Technology (BPT) and returned the groundwater to a quality of use equal to, and consistent with, uses for which the water was suitable prior to in-situ leaching. Restoration involved groundwater sweep, reverse osmosis treatment, and use of a chemical reductant. All of the groundwater parameters except iron, manganese, selenium, and radium were restored to baseline or to a condition within the WDEQ/WQD Class I classification (Domestic Use Suitability). The baseline for radium was 100 times the WDEQ/WQD upper limit for domestic or agricultural use and 30 times higher than the EPA treatability limit.<sup>13</sup> The only acceptable use for the water was WDEQ/WQD Class V – Commercial – Mineral (*e.g.*, uranium mining).

Baseline values were established via five monitoring wells. Table B-1 shows the average baseline values for the 35 monitored parameters (WDEQ Guideline 8 parameters) together with values at the end of mining, during restoration prior to the introduction of H<sub>2</sub>S as a reductant, and at the end of restoration. The final column lists WDEQ standards for Class I water. PRI noted that the post-mining values of pH and HCO<sub>3</sub><sup>-</sup> were based on laboratory measurements, where degassing of the samples inevitably occurs. In-situ values were expected to be about 6.0 for pH and 1,200 mg/L for HCO<sub>3</sub>.

Initial stability period sampling involved measuring the 35 parameters from five baseline monitor wells on February 23, 1999; August 18, 1999, and October 20, 1999. In addition, conductivity, water level elevation, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and U<sub>nat</sub> were sampled more frequently (up to 9 samples during the 8-month period). On the basis of the monitoring results, PRI concluded that wellfield stability had been achieved (March 31, 2000). Presumably WDEQ did not concur, since PRI subsequently measured the 35 parameters on April 26, 2000. As noted above, sampling of the five baseline wells for conductivity, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and U<sub>nat</sub> continued through November 2003.

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<sup>13</sup> According to the EPA, existing technology for the safe treatment of potable water containing more than 20 pCi/L is impractical for populations of less than 10,000 people.



On May 5, 2003, the WDEQ requested that additional samples be provided on uranium and selenium from three mining zone wells. The requested data, together with data from five monitor wells and five production wells that had been collected since March 31, 2000 (the date PRI stated that stability had been achieved), were submitted to WDEQ on May 23, 2003.

PRI subsequently conducted fate and transport modeling to show that natural attenuation would prevent endangerment of adjacent groundwater. (Details of these calculations are not available electronically.) On November 25, 2003, the Wyoming Land Quality Division determined that, even though for some elements the groundwater had not been returned to baseline quality, the A-Wellfield met statutory and regulatory requirements. Nevertheless, the WDEQ requested that additional monitoring be conducted to support the modeling calculations (November 25, 2003). NRC concurred with WDEQ that restoration had been completed, but that additional long-term monitoring should be conducted to demonstrate that natural attenuation is effective (NRC 2004).

Based on an April 26, 2011, telephone conversation with Steve Ingle (307-777-7064) at the WDEQ, the attenuation modeling involved both groundwater flow modeling with MODFLOW and PHREEQC geochemical modeling. The calculations showed that a maximum of 15 years would be required to achieve the full benefits of natural attenuation. To support the modeling results, the operator was required perform semi-annual monitoring of four wells (a “hot spot” well with elevated levels of U and Se, an upgradient well, a downgradient well, and a lateral well) beginning in 2004. According to Ingle, the results are stable, but not declining as would be expected from natural attenuation. He also noted that the WDEQ is moving toward a minimum of 1 year for stability monitoring, with sufficient sampling to statistically characterize trends.

**Table B-1. A-Wellfield, Average Water Quality at Wells MP-1 through MP-5**

(All values in mg/L, except pH, conductivity in  $\mu\text{mhos/cm}$ , and Ra in pCi/L)

	<b>BASELINE (Aug. 1987)</b>	<b>END MINING (July 1991)</b>	<b>PRE-H<sub>2</sub>S (May 1995)</b>	<b>END REST (Feb. 1999)</b>	<b>CLASS 1 (*see below)</b>
Ca	44.1	313.4	68.6	73.4	
Mg	9.0	59.5	12.4	13.5	
Na	55.0	80.8	37.4	42.2	
K	8.0	13.4	4.7	4.4	
CO <sub>3</sub>	0.0	0.0	0.0	0.0	
HCO <sub>3</sub>	215.0	720.2	242.2	256.6	
SO <sub>4</sub>	91.0	380.6	83.9	127.2	250.0
Cl	4.7	212.6	14.4	18.0	250.0
NH <sub>4</sub>	0.1	0.7	0.2	0.29	
NO <sub>2</sub>	0.0	0.1	0.1	0.1	
NO <sub>3</sub>	0.0	0.2	0.1	0.1	
F	0.2	0.2	0.1	0.15	
SiO <sub>2</sub>	16.0	20.5	12.6	11.9	
TDS	330	1507	342	410	
COND	525	2390	579	647	
ALK	177	591	199	211	
pH	8.00	6.78	7.25	7.31	
Al	0.1	0.1	0.1	0.1	
As	0.001	0.001	0.010	0.030	0.050
Ba	0.1	0.1	0.1	0.1	
B	0.1	0.1	0.1	0.1	
Cd	0.01	0.03	0.005	0.005	
Cr	0.05	0.05	0.05	0.05	
Cu	0.01	0.02	0.03	0.01	
Fe	0.05	0.05	1.32	1.30	0.30
Pb	0.05	0.05	0.05	0.05	
Mn	0.03	0.66	0.41	0.49	0.05
Hg	0.001	0.001	0.001	0.001	
Mo	0.10	0.10	0.10	0.10	
Ni	0.05	0.08	0.05	0.05	
Se	0.001	0.990	0.160	0.070	
V	0.10	0.19	0.10	0.10	
Zn	0.01	0.04	0.01	0.01	
U	0.05	40.19	3.00	3.53	5.00
Ra	675	3286	1056	1153	5

\* Class 1 Domestic Use Suitability Standard, Chapter VIII of the WDEQ, Water Quality Division Rules and Regulations.

### Highland A-Wellfield References

Power Resources 2004. Letter to Gary Janosko, NRC, from W.F. Kearney, Power Resources, Inc., dated January 15, 2004. Subject: Smith Ranch – Highland Uranium Project, Docket 40-8964, SUA-1548, A-Wellfield Groundwater Restoration Information. (ML040300369).

NRC 2004. Letter to W.F. Kearney, Power Resources, Inc., from Gary Janosko, NRC, dated June 29, 2004. Subject: Review Of Power Resources, Inc.'s A-Wellfield Ground Water Restoration Report for the Smith Ranch-Highland Uranium Project. (ML041840470).

**Crow Butte Mine Unit 1**

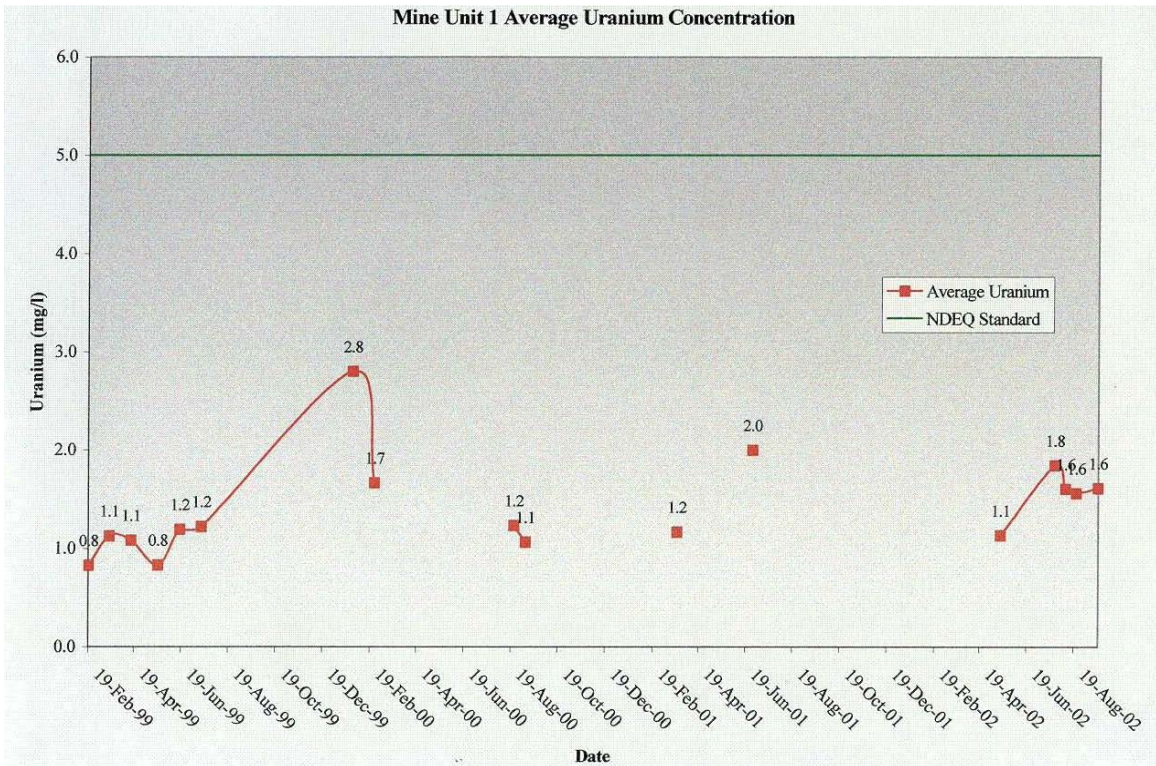
On September 3, 1999, Crow Butte Resources (CBR) submitted Mine Unit 1 Restoration Report to the Nebraska Department of Environmental Quality (NDEQ) for approval. On November 18, 1999, NDEQ accepted restoration of Mine Unit 1 as completed. Then on January 10, 2000, CBR submitted Mine Unit 1 Restoration Report to NRC requesting approval of groundwater restoration by the Commission (Crow Butte 2000). The report covered both restoration activities and post-restoration stability monitoring results over a 6-month period. On June 26, 2001, NRC requested additional information on efforts made to achieve primary restoration goals, efforts made to ensure restoration of wellfield flare, and additional data on stability monitoring. CBR provided the requested information on August 24, 2001. On March 29, 2002, NRC denied approval of restoration based on concerns about the stability of six groundwater parameters, which NRC felt showed increasing trends—ammonium, Se, TDS, U, Fe, and Ra-226. CBR was directed by NRC to resume stability monitoring.

The proposed supplemental monitoring plan submitted by CBR to NRC involved measuring the 6 groundwater parameters in 6 wells with a minimum of 3 samples for each parameter collected over a 3-month period. The additional monitoring results were supplied to the NRC on October 11, 2002 (Crow Butte 2002). A comparison of results from the 1999 and 2002 stability monitoring results is presented in Table B-2.

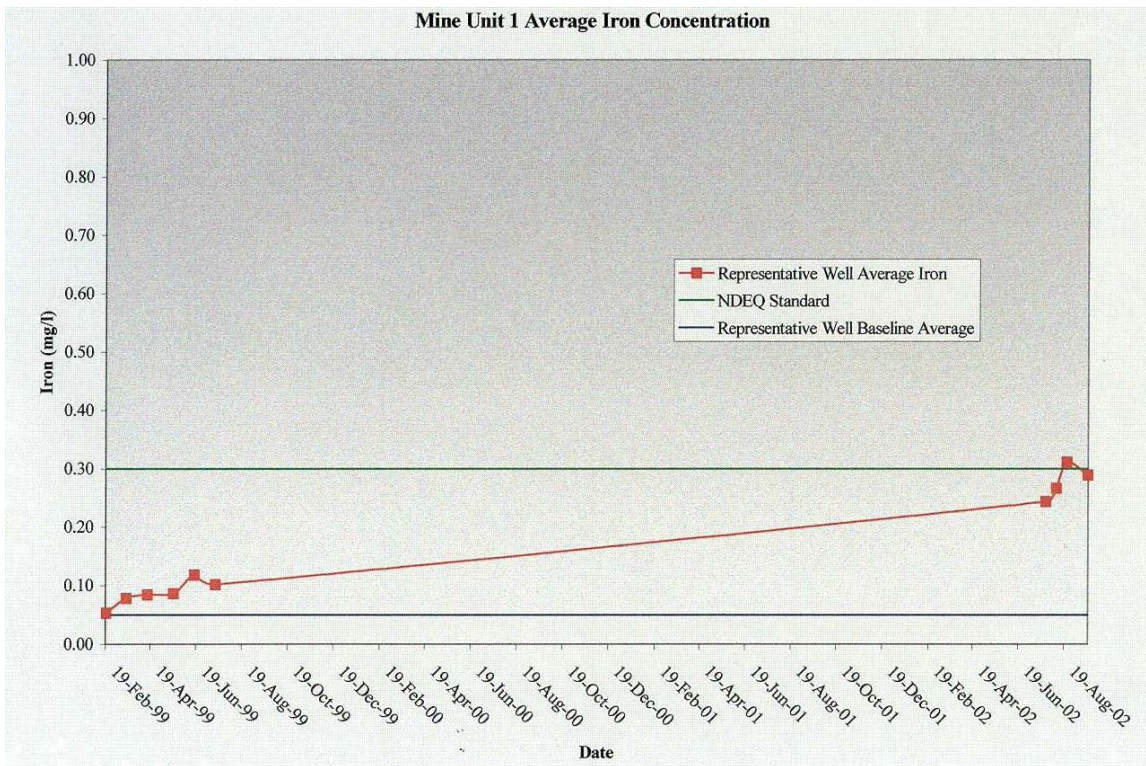
**Table B-2. Comparison of Stability Monitoring Results for 1999 and 2002 at Crow Butte Mine Unit 1**

Species	1999		2002		NDEQ Restoration Standard	Baseline
	Range	Average	Range	Average		
Uranium (mg/L)	1.09–2.33	1.73	1.6–1.8	1.66	5	N/A
Radium-226 (pCi/L)	216–385	303	298–330	314	584	230
Ammonium (mg/L)	0.07–0.18	0.12	0.05–0.06	0.05	10	0.37
Selenium (mg/L)	0.001–0.003	0.002	0.0013–0.002	0.0016	0.05	0.003
Iron (mg/L)	0.049–0.127	0.089	0.24–0.31	0.278	0.3	0.44
TDS (mg/L)	1026–1153	1094	1078–1089	1084	1218	1170

Figures B-1 and B-2 show trend lines for uranium and iron.



**Figure B-1. Uranium Stability Monitoring at Crow Butte Mine Unit 1**



**Figure B-2. Iron Stability Monitoring at Crow Butte Mine Unit 1**

Comparison of the 1999 and 2002 stability monitoring in Table B-2 shows that, with the exception of iron, stability was realized. In the case of iron, as stated in Crow Butte 2002:

*CBR believes that the elevated iron concentrations are due to the restoration process and will ultimately decrease to concentrations well below the restoration standard. During the in situ mining process, when the groundwater is oxygenated and the Eh is positive, the iron contained in pyrites is oxidized to ferric iron and forms ferric oxyhydroxides. The ferric oxyhydroxides are extremely insoluble, which explains the very low concentrations of iron in solution during mining, indicated by the end of mining values which, with the exception of one restoration well (PR-19), were below the detection limit of 0.05 mg/L. During the active restoration process, however, sodium sulfide is used as a reductant to decrease the Eh of the groundwater. As the Eh drops, the stable solid iron phase is reduced from ferric iron to ferrous iron, which is more soluble. During the transition from ferric to ferrous iron, the iron concentration in the groundwater increases significantly. This increase in the iron concentration is transitory and, as the Eh continues to decrease, iron sulfide minerals will be the dominant iron phase. Because of the relative insolubility of these iron sulfide minerals, this will cause a significant decrease in the iron concentration in solution. Based on these mechanisms, CBR expects that the elevated concentrations of iron at the current time will ultimately decrease.*

No discussion was provided on the expected timeframe for the postulated decrease.

Restoration of Mine Unit 1 was approved by NRC on February 12, 2003 (NRC 2003).

#### Crow Butte References

Crow Butte 2000. *Mine Unit 1 Restoration Report, Crow Butte Uranium Project*. Submitted to NRC January 10, 2000. (ML003677938).

Crow Butte 2002. *Mine Unit 1 Groundwater Stability Data, Source Materials License SUA-1534, Docket Number 40-8943*. Letter from Michael Griffin, Crow Butte Resources, Inc., to Daniel Griffen, NRC, dated October 11, 2002. ML022980095. This reference includes a report entitled “Additional Stability Monitoring Data for Mine Unit 1 Groundwater Restoration.”

NRC 2003. Letter from Daniel M Gillen, NRC, to Michael L Griffin, dated February 12, 2003. License Amendment 15, Crow Butte Resources In Situ Leach Facility License No. SUA-1534, Wellfield #1 Restoration Acceptance (TAC No. L52491).

#### Christensen Ranch

The Christensen Ranch uranium in-situ leach project is located in Johnson and Campbell Counties, Wyoming. Wellfield restoration operations were initiated at Mine Units 2, 3, and 4 (MU2, MU3, and M4, respectively) in 1997, and in Mine Units 5 and 6 (MU5 and MU6) in 2000. Restoration of all MUs, including stability monitoring, was completed by 2006. An average of 10.1 pore volumes of water were treated for the five Christensen Ranch MUs during

restoration activities. Groundwater within the production zone has been restored to the pre-mining class of use, using Best Practicable Technology (BPT), as required by the WDEQ (Cogema 2008).

Table B-3 indicates parameters that were not restored to desired values.

**Table B-3. Parameters Exceeding Remediation Goals and WDEQ or EPA Standards**

Mine Unit	TDS	Fe	Mn	Se	U	Ra
MU2		X	X			X
MU3			X			
MU4	X	X	X	X	X	X
MU5			X	X	X	
MU6			X	X	X	

X – Parameter exceeds remediation goals and WDEQ Class 1 drinking water use or EPA maximum concentration limit.

Baseline water quality was determined for each MU prior to commencement of production. Baseline water quality was measured within the production zone of the MU, on the perimeter of the production zone, and in the overlying and underlying aquifers. Ore zone baseline water quality was established by sampling designated restoration wells 4 times, separated by a minimum of 2 weeks. The restoration well density was one well per acre of wellfield.

Consider stability monitoring of MU2 for illustrative purposes. Post-restoration stability monitoring involved sampling each of the 25 restoration monitoring wells 4 times over a 9-month period. Summary results based on wellfield averages are included in Table B-4, together with results at various points in the restoration process (after mining, after groundwater sweep [GWS], after remote osmosis treatment [RO], and after reductant[H<sub>2</sub>S] addition).

**Table B-4. Restoration and Stability Monitoring Water Quality Results, Mine Unit 2, Christensen Ranch, Wyoming**

	Active Restoration Monitoring				Stability Monitoring			
	Post Mining	Post GWS	Post RO	Post Reductant	Round 1	Round 2	Round 3	Round 4
<b>Major Ions mg/l:</b>								
Ca	285.8	160.0	36.4	32.3	52.6	64.6	65.7	63.3
Mg	53.1	33.7	6.7	3.9	5.7	7.5	8.0	7.9
Na	696.4	522.6	140.7	65.2	88.7	105.5	106.4	109.2
K	9.4	6.5	2.0	1.2	1.2	1.4	1.4	1.5
CO <sub>3</sub>	1.0	1.0	1.0	1.0	1.2	1.2	1.0	1.0
HCO <sub>3</sub>	1898.8	1376.0	365.3	172.4	210.1	237.5	260.5	273.0
SO <sub>4</sub>	784.1	504.9	108.8	78.4	155.6	194.2	191.8	175.7
Cl	122.9	77.1	15.0	7.4	7.8	8.5	8.5	8.6
NH <sub>4</sub>	0.52	0.35	0.08	0.17	0.14	0.10	0.10	0.10
NO <sub>2</sub> (N)	0.12	0.10	0.11	0.10	0.10	0.10	0.10	0.10
NO <sub>3</sub> (N)	0.22	0.39	0.10	0.10	0.10	0.31	0.10	0.10
F	0.10	0.12	0.12	0.10	0.10	0.10	0.10	0.10
SiO <sub>2</sub>	12.6	7.8	6.2	7.4	4.8	10.8	10.5	10.8
TDS	3054.6	2143.6	509.4	297.5	435.4	542.4	569.2	548.4
Cond. (µmho/cm)	4007.8	3032.2	806.8	464.4	627.8	796.9	786.0	792.6
Alk. (as CaCO <sub>3</sub> )	1484.9	1128.4	302.0	143.8	170.9	195.0	213.7	224.2

**Table B-4. Restoration and Stability Monitoring Water Quality Results, Mine Unit 2, Christensen Ranch, Wyoming**

	Active Restoration Monitoring				Stability Monitoring			
	Post Mining	Post GWS	Post RO	Post Reductant	Round 1	Round 2	Round 3	Round 4
pH (units)	7.51	7.90	7.85	7.69	7.51	7.77	7.82	7.76
<b>Trace Metals mg/l:</b>								
Al	0.10	0.10	0.13	0.18	0.10	0.10	0.10	0.10
As	0.12	0.09	0.01	0.02	0.01	0.01	0.01	0.01
Ba	0.10	0.10	0.12	0.37	0.49	0.50	0.50	0.50
B	0.10	0.11	0.10	0.07	0.06	0.04	0.06	0.06
Cd	0.010	0.005	0.005	0.003	0.002	0.002	0.002	0.002
Cr	0.05	0.05	0.05	0.02	0.01	0.01	0.01	0.01
Cu	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.14	0.40	0.14	0.43	1.19	1.06	0.66	0.57
Pb	0.05	0.05	0.05	0.03	0.02	0.02	0.02	0.02
Mn	0.66	0.37	0.17	0.27	0.38	0.41	0.39	0.34
Hg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Mo	0.10	0.11	0.10	0.05	0.02	0.02	0.02	0.02
Ni	0.12	0.05	0.05	0.03	0.01	0.01	0.01	0.01
Se	6.33	2.40	1.29	0.01	0.01	0.01	0.01	0.01
V	0.24	0.10	0.10	0.10	0.10	0.10	0.09	0.10
Zn	0.05	0.02	0.01	0.01	0.01	0.01	0.01	0.01
<b>Radiometric:</b>								
U (mg/l)	11.75	12.58	3.33	0.76	0.28	0.26	0.27	0.36
Ra 226 (pCi/l)	257.7	191.4	161.2	219.6	228.2	351.3	295.3	223.9

Numeric values represent the mean of all designated restoration wells for the specified phase of restoration.

On April 8, 2008, Cogema requested that NRC approve restoration of MU2 through MU6 (Hargrove 2008). On February 19, 2009, the NRC stated that (Linton 2009):

*By letter to the U.S. Nuclear Regulatory Commission (NRC) dated April 8, 2008, (ADAMS Accession Package No. ML081060155), COGEMA Mining, Inc. (COGEMA) submitted a Wellfield Restoration Report for mine units 2 through 6 at its Christensen Ranch facility. NRC conditionally accepted the application for review in a letter to COGEMA dated May 13, 2008 (ADAMS Accession No. ML081330021) requesting that COGEMA confirm groundwater class of use designation from the Wyoming Department of Environmental Quality (WDEQ). COGEMA confirmed the groundwater class of use with the WDEQ and forwarded its response to the NRC in a letter dated July 28, 2008. NRC staff has completed a safety review of COGEMA’s Wellfield Restoration Report. NRC staff requires additional information from COGEMA in order to complete its assessment of the license renewal application.*

The NRC raised a large number of questions about the Wellfield Restoration Report. A recurring theme was concerns about establishment of reducing conditions and the role of natural attenuation:

*Section 8 of the Report states, “The reestablishment of long-term reducing conditions in the restored aquifer is an important factor that can serve to limit the*

*migration of constituents affected by ISR mining because reducing conditions have a major effect on the mobility of many constituents associated with uranium roll front deposits, including U, Se, As, Mo, S.” In Section 9 the Report states, “significant attenuation of uranium will occur as groundwater from the wellfields moves into the down gradient reducing portions of the aquifer.” Demonstrate the basis for these comments by providing information that reducing conditions have been reestablished within the wellfields or exist at monitoring well ring wells down gradient of the wellfields such that reducing conditions would likely limit the movement of monitored constituents.*

Cogema provided responses on December 31, 2009 (Hargrove 2009). On June 8, 2010, the NRC advised the operator (now Uranium One Americas, Inc.) as follows (Linton 2010):

*While the Wellfield Restoration Report review is not complete at this time, NRC’s preliminary review of the RAI responses indicates that monitoring well 5MW66 upper control limit concentrations have continued to increase and uranium concentrations are reported as several times higher than background. Cogema, and now Uranium One, has been sampling 5MW66, as per Cogema’s proposed recommendations to the Wyoming Department of Environmental Quality, dated December 9, 2004, and agreed to by the NRC. However, with the current excursion status of this well, the increasing trends in all upper control limit concentrations and confirmation of uranium several times above background, NRC has determined that corrective action is required consistent with NRC License SUA-1341, License Condition 11.2.*

Although the excursion status on well 5MW66 was resolved on April 19, 2011 (Arbogast 2011), NRC has not made a determination regarding restoration of MU2 through MU6.

#### Christensen Ranch References

Arbogast 2011. Letter from Larry Arbogast, Uranium One Americas, Inc., to Document Control Desk (Keith McConnell), NRC, dated April 19, 2011. Subject: Termination of the excursion status of monitor well 5MW 66. ML11116A144.

Cogema 2008. *Wellfield Restoration Report Christensen Ranch Project, Wyoming*. March 5, 2008, Cogema Mining, Inc, and Petrotek Engineering Corp. (ML081060131). <http://www.wise-uranium.org/udusail.html#CHRISTENS>

Hargrove 2008. Letter from Tom Hargrove, Cogema Mining Inc., to Ron Linton, NRC, dated April 8, 2008. Ref: Docket No 040-08502, Source Material License SUA-1341, Wellfield Restoration Report, Christensen Ranch Project. ML081060129.

Hargrove 2009. Letter from Tom Hargrove, Cogema Mining Inc. to Document Control Desk, NRC, dated December 30, 2009, Ref: Docket No 040-08502, License No. SUA-1341, Request for Additional Information. Wellfield Restoration Report, Christensen Ranch Project. ML100131020.



Linton 2009. Letter from Ron Linton, NRC, to Tom Hardgrove, Cogema Mining Inc., dated February 19, 2009. Subject: Request for Additional Information, Wellfield Restoration Report, Christensen Ranch Project, Cogema Mining Inc., Irigaray and Christensen Ranch In Situ Uranium Recovery Project, Source Materials License SUA-1341 (TAC J00563). ML090360478.

Linton 2010. Letter from Ron Linton, NRC, to Jon Winter, Uranium One Americas Inc., dated June 8, 2010. Subject: Uranium One Exploration U.S.A., Inc., (Cogema Mining Inc.) Irigaray and Christensen Ranch Project, Campbell and Johnson Counties, Wyoming, Source Materials License SUA-1341, Groundwater Restoration Report Review, Christensen Ranch MU2-6 (TAC J00563). ML101580441.

**ATTACHMENT C: AQUIFER RESTORATION (EXTRACTED FROM NRC 2009,  
SECTION 2.11.5)**

Operational history at NRC-licensed ISL facilities is available to examine aquifer restoration at the wellfield scale. Table 2.11-4 shows a summary of restoration data for a 12-ha [30-acre] area covered by Production Units 1–9 at the commercial-scale Cogema Irigaray ISL facility (Cogema 2006a and 2006b). A comparison of the baseline and post-restoration stability monitoring groundwater analytical data determined that for the water quality in the production zone, the individual restoration and stabilization data fell within the baseline ranges for all constituents except for calcium, magnesium, sodium, carbonate, chlorine, ammonium, total dissolved solids, conductivity, alkalinity, lead, barium, manganese, and radium-226. These data showed that, when comparing pre-mining baseline ranges to post-mining stabilization ranges, several constituents did not meet the pre-mining baseline concentration levels. Additionally, post-mining mean concentrations for nearly half of the constituents exceeded the pre-mining baseline mean concentrations for the same constituents in Production Units 1–9 (Cogema 2006a and 2006b).

**Table 2.11-4. Irigaray Water Quality Summary for Designated Aquifer  
Restoration Wells\***

Constituents	Mine Units 1–9 Baseline			Mine Units 1–9 Round Four Restoration Results			Samples Exceeding Baseline Range
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	
<b>Major Ions (mg/L)</b>							
Calcium	1.6	27.1	7.8	11.6	65	28.8	17
Magnesium	0.02	9	0.9	2.8	13	7.0	7
Sodium	95	248	125	107	275	185.6	2
Potassium	0.92	17.5	2.4	1.1	4.9	2.9	0
Carbonate	0	98	13.2	<1.0	<1.0	0.8	0
Bicarbonate	5	144	88.3	5.1	631	409	31
Sulfate	136	504	188.1	62.8	237	132.0	0
Chloride	5.3	15.1	11.3	0.1	117	39.4	32
Ammonia	0.05	1.88	0.3	0.05	36.1	8.5	13
Nitrogen Dioxide	<0.1	1	<0.4	<0.1	<0.1	<0.1	0
Nitrate	0.2	1	0.9	<0.1	0.12	0.1	0
Fluoride	0.11	0.68	0.29	0.1	0.22	0.12	0
Silica Dioxide	3.2	17.2	8.3	2.5	7.3	4.99	0
Total Dissolved Solids	308	784	404	343	968	626	5
Specific Conductivity	535	1,343	658	604	1,970	1094	5
Alkalinity	67.8	232	104	127	518	345	30
pH	6.6	11.0	9.00	7.07	8.40	7.76	0
<b>Trace Metals (mg/L)</b>							
Aluminum	0.05	4.25	0.160	<0.1	0.140	0.102	0
Arsenic	<0.001	0.105	0.007	<0.001	0.029	0.005	0
Barium	<0.01	0.12	0.060	0.03	0.200	0.095	1
Boron	<0.01	0.225	0.110	<0.05	0.100	0.088	0
Cadmium	<0.002	0.013	0.005	<0.002	0.005	0.004	0
Chromium	<0.002	0.063	0.020	<0.005	0.050	0.039	0

**Table 2.11-4. Irigaray Water Quality Summary for Designated Aquifer Restoration Wells\***

Constituents	Mine Units 1–9 Baseline			Mine Units 1–9 Round Four Restoration Results			Samples Exceeding Baseline Range
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	
Copper	<0.002	0.04	0.011	<0.01	0.020	0.010	0
Iron	0.019	11.8	0.477	<0.03	0.500	0.113	0
Lead	<0.002	0.05	0.020	<0.001	0.090	0.039	1
Manganese	<0.005	0.19	0.014	0.060	0.950	0.215	13
Mercury	<0.0002	0.001	0.0004	<0.0002	<0.001	<0.001	0
Molybdenum	<0.02	0.1	0.060	<0.01	<0.1	0.069	0
Nickel	<0.01	0.2	0.100	<0.05	<0.05	<0.05	0
Selenium	<0.001	0.416	0.013	<0.001	0.086	0.019	0
Vanadium	<0.05	0.55	0.070	<0.05	<0.1	0.088	0
Zinc	0.009	0.07	0.016	<0.01	<0.01	<0.01	0
<b>Radiometric (pCi/L)</b>							
Uranium	0.0003	18.60	0.52	0.08	6.03	1.83	0
Radium-226	0	247.7	39.6	23.50	521.0	130.7	3

\*Wichers, D.L. “Re: Request: Summary Table Irigaray Mine Unit Restoration RAI Response.” E-mail to R. Linton (August 11), NRC. Mills, Wyoming: Cogema Mining, Inc. 2006.

Catchpole et al. (1992a and 1992b) provide an early discussion of small-scale restoration efforts for research and development of ISL uranium recovery facilities in Wyoming. These include the Bison Basin facility in Fremont County (described in NRC 1981), the Reno Creek project in Campbell County, and the Leuenberger Project in Converse County. Restoration activities required treatment of water from nine pore volumes at Bison Basin and five pore volumes at Reno Creek. In all cases, most water quality parameters were returned to within a statistical range of baseline values with the exception of uranium (Bison Basin and Reno Creek) and radium-226 (Leuenberger). For these parameters, Catchpole et al. (1992a and 1992b) report that water in the well field was returned to the same class of use.

NRC (2007) detailed available information on aquifer restoration at ISL uranium recovery facilities. These include a pilot scale study by Rio Algom for the Smith Ranch facility in Converse County, Wyoming (Rio Algom Mining Corporation 2001); the proposed Crownpoint ISL facility near Crownpoint, New Mexico (NRC 1997); the commercial-scale A-Well Field at the Highland Uranium Project in Converse County, Wyoming (Power Resources, Inc. 2004); and the commercial-scale Crow Butte Mine Unit No. 1 in Dawes County, Nebraska (NRC 2002, 2003). Rock core laboratory studies that Hydro Resources Inc. conducted for the Crownpoint facility (NRC 1997) also provide useful insights to water quality parameters that may present challenges for aquifer restorations.

NRC (2007) generally concluded that for the sites and data they examined, aquifer restoration took longer and required more pore volumes than originally planned. For example, at the A-Well Field at the Highland Uranium Project, the licensee’s original plan anticipated that restoration would last from four to seven years and require treating 5–7 pore volumes of groundwater. When uranium recovery in the well field ended in 1991, the baseline and class of use were not restored in the well field until 2004 (Table 2.11-5), and more than 15 pore volumes of water were involved (NRC 2006, 2004). Similarly, WDEQ has noted that the C-Well field at

the Smith Ranch-Highland Uranium Project has been undergoing restoration for 10 years (WDEQ 2008). At the Crow Butte Mine Unit No. 1, more than 9.85 pore volumes of groundwater were used in all the stages of aquifer restoration over approximately 5 years, as compared to the 8 pore volumes estimated before restoration (NRC 2002, 2003). Crow Butte Resources extracted uranium from an additional 26 pore volumes using ion exchange, without lixiviant injection, prior to active restoration.

**Table 2.11-5. Baseline Groundwater Conditions, Aquifer Restoration Goals, and Actual Final Restoration Values the U.S. Nuclear Regulatory Commission Approved for the Q-Sand Pilot Well Field, Smith Ranch, Wyoming\*†**

Parameter (units)	Range	Mean	Restoration Goal	Actual Restoration
Arsenic (mg/L) ‡	0.001–0.013	0.004	0.05	0.008
Boron (mg/L)	0.002–0.70	0.15	0.54	0.14
Calcium (mg/L)	24–171	72	120	78
Iron (mg/L)	0.01–0.27	0.025	0.3	0.24
Magnesium (mg/L)	3–22	16	0.092	0.06
Manganese (mg/L)	0.01–0.077	0.023	Not applicable	0.1
Selenium (mg/L)	0.001–0.024	0.004	0.029	0.003
Uranium (mg/L)	0.001–3.1	0.28	3.7	1.45
Chloride (mg/L)	4–65	18	250	15
Bicarbonate (HCO <sub>3</sub> ) (mg/L)	129–245	199	294	254
Carbonate (CO <sub>3</sub> ) (mg/L)	Nondetectible–75	18	15	Nondetectible
Nitrate (mg/L)	0.1–1.0	0.4	Not applicable	0.13
Potassium (mg/L)	7–34	12	23	8
Sodium (mg/L)	19–87	28	41	38
Sulfate (mg/L)	100–200	124	250	128
Total dissolved solids (mg/L)	155–673	388	571	443
Specific conductivity (µmhos/cm)	518–689	582	827	642
pH (standard units)	7.5–9.4	8.0	6.5–8.6	7.0
Radium-226 (pCi/l)	6–1132	340	923	477
Thorium-230 (pCi/l)	0.027–4.65	1.03	5.62	3.4

\*NRC. “Environmental Assessment for the Addition of the Reynolds Ranch Mining Area to Power Resources, Inc.’s Smith Ranch/Highlands Uranium Project Converse County, Wyoming.” Source Material License No. SUA–1548. Docket No. 40-8964. Washington, DC: NRC. 2006.

†Sequoyah Fuels Corporation. “Re: License Application, Smith Ranch Project, Converse County, Wyoming.” ML8805160068. Glenrock, Wyoming: Sequoyah Fuels Corporation. 1988.

‡1 mg/L = 1 ppm

As a field test of groundwater stabilization during aquifer restoration, hydrogen sulfide gas was injected as a reductant into the Ruth ISL research and development facility in Campbell County, Wyoming. After 6 weeks of hydrogen sulfide injection, pH dropped relatively quickly from 8.6 to 6.3, and sulfate concentration increased from 28 ppm to 91 ppm, indicating a more reducing environment (Schmidt 1989; NRC 2007). Concentrations of dissolved uranium, selenium, arsenic, and vanadium decreased by at least one order of magnitude. After 1 year of monitoring, however, reducing conditions were not maintained, and uranium, arsenic, and radium concentrations began to increase.

Based on the available field data from aquifer restoration, NRC (2007) concluded that aquifer restoration is complex and results could be influenced by a number of site-specific hydrological and geochemical characteristics, such as preoperational baseline water quality, lixiviant chemistry, aquitard thickness and continuity, aquifer mineralogy, porosity, and permeability. In some cases, such as at Bison Basin and Reno Creek, the aquifer was restored in a relatively short time. In other cases, restoration required much more time and treatment than was initially estimated (*e.g.*, the A- and C- Well Fields at the Highland ISL facility).

### Attachment C References

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Power Resources, Inc. 2004. “Smith Ranch–Highland Uranium Project, A-Well Field Groundwater Restoration Information.” ML040300369. Glenrock, Wyoming: Power Resources, Inc.

Rio Algom Mining Corporation 2001. “Amendment 1 to Source Material License SUA–1548.” ML020220040. Washington, DC: NRC.

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WDEQ 2008. “*In-Situ* Uranium Permits 603 and 633, Notice of Violation, Docket No. 4231-08.” Cheyenne, Wyoming: WDEQ, Land Quality Division. March 10, 2008.

## ATTACHMENT D: INSTRUCTIONS AND EXAMPLES FOR STATISTICAL CALCULATIONS

This section demonstrates the application of the statistical methods discussed in Section 5. The tests are designed to show whether data are stable or trending upward, and for comparing post-restoration data with baseline conditions to determine when pre-ISL conditions are achieved. Three topics are addressed in this section:

- (1) Seasonal adjustment
- (2) Mann-Kendall test for trends
- (3) Wilcoxon Rank Sum (WRS) test for comparisons with baseline

The three types of analyses are meant to be applied sequentially, first adjusting for seasonality, then testing the post-restoration data from each well for trends using the Mann-Kendall test. If the trend tests indicate that the wells have reached stability, then the WRS test is used for comparing the post-restoration samples with baseline samples in each well. If (and only if) the well-specific summary statistics for the Mann-Kendall and WRS tests indicate that the wells exhibit homogenous dynamics, the summary statistics may be combined into a wellfield assessment for each parameter.

### D.1 Instructions for Seasonal Adjustment

Let  $Y_{t,i}$  represent the measured concentration in year  $t$  and season  $i$ . An array of values for 3 years and 4 seasons are shown in Table A-1. Also shown are the quarterly averages  $Y_{0,i}$  at the bottom of the table, the annual averages  $Y_{1,0}$  at the right, and the overall average (mean) denoted by  $Y_M$ . The time series is plotted in Figure D-1. It has peaks at quarters 2, 6, and 10, and valleys at quarters 4, 8, and 12. This pattern of regularly spaced peaks and valleys indicates there is a strong seasonal component in the time series.

The seasonal component in each quarter ( $Q_i$ ) is defined as the deviation of the seasonal mean from the overall mean:  $Q_i = Y_{0,i} - Y_M$ . The plot of the seasonal component in Figure D-2 shows the repeated pattern of seasonal component of the time series.

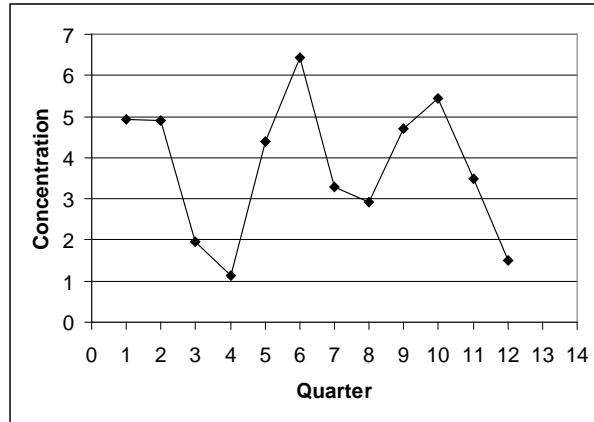
The “deseasonalized” time series ( $X$ ) is obtained by subtracting the seasonal means from the original data:  $X_{t,i} = Y_{t,i} - Q_i$ . The two series are compared in Figure D-3. The seasonally adjusted series has the same mean, but a lower variance. If the time series contains only a small seasonal component, the  $Q_i$  values will be small relative to the original data, and the seasonal adjustment procedure will not significantly affect the data. A formal statistical test for the existence of a significant seasonal component in the time series is based on an Analysis of Variance (ANOVA).<sup>14</sup>

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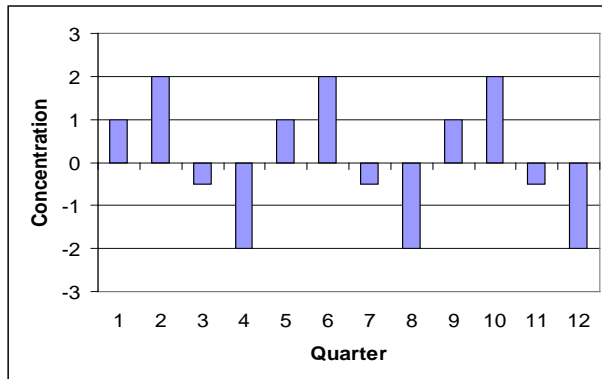
<sup>14</sup> This procedure is described in EPA 2002, Sections 14.2.2 and 14.3.3.

**Table D-1. Array Used for Seasonal Adjustments**

Year	Quarter				Annual Averages
	1	2	3	4	
1	$Y_{1,1}$	$Y_{1,2}$	$Y_{1,3}$	$Y_{1,4}$	$Y_{1,0}$
2	$Y_{2,1}$	$Y_{2,2}$	$Y_{2,3}$	$Y_{2,4}$	$Y_{2,0}$
3	$Y_{3,1}$	$Y_{3,2}$	$Y_{3,3}$	$Y_{3,4}$	$Y_{3,0}$
Quarterly Averages	$Y_{0,1}$	$Y_{0,2}$	$Y_{0,3}$	$Y_{0,4}$	$Y_M$

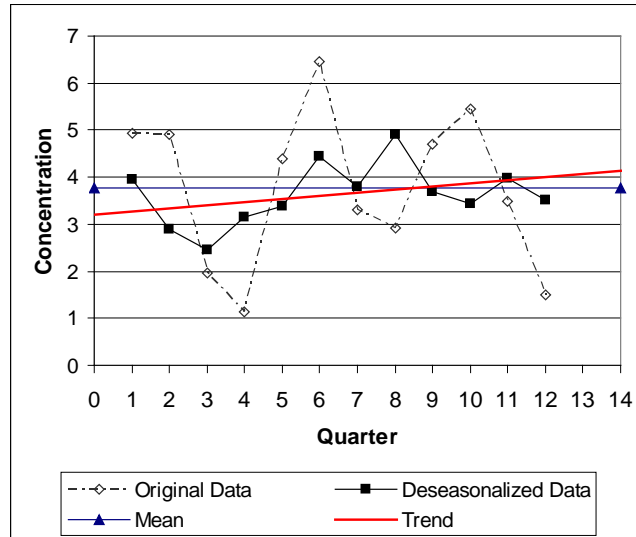


**Figure D-1. Data Series Showing Seasonal Variation**



**Figure D-2. Seasonal Components ( $Q_i$ )**





**Figure D-3. Comparison of the Original and Seasonally Adjusted Data Series**

## D.2 Performing the Mann-Kendall Trend Test

The Mann-Kendall test is applied to test the post-restoration data from each well for trends. This test is applied after seasonal adjustment of the data and before post-restoration conditions are compared with baseline conditions. Before wells are combined for a summary analysis of the wellfield, the post-restoration samples are analyzed for trends well by well.

If the summary statistics for the trend test on each well show no unusual trends and indicate that the wells exhibit similar dynamics, the summary statistics from each well may be combined into a wellfield assessment. If the trend tests indicate that the wells have reached stability, then the WRS test discussed in Section D.4 is used for comparing the post-restoration samples with baseline samples in each well.

Instructions for performing the Mann-Kendall test are shown in Boxes D-1 and D-2. The test is performed by calculating the sample value of  $S$  and comparing this value to the critical value for the test (for a series with 40 or fewer measurements) found in Table E-1 in Attachment E. If the post-restoration sample size ( $n$ ) exceeds 40, then the normal approximation shown in Box D-3 may be used. If all measurements in a series have the same limit of detection, non-detect values are assigned a common value equal to the limit of detection or one-half the limit of detection. (Both choices will result in the same test statistic.) If there are two or more detection limits for the parameter in question, use the highest detection limit for all non-detects.

<b>Box D-1. Triangular Array of Differences</b>						
		<b>t</b>				
<b>t-1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
<b>1</b>	$X_2-X_1$	$X_3-X_1$	$X_4-X_1$	$X_5-X_1$	$X_6-X_1$	$X_7-X_1$
<b>2</b>		$X_3-X_2$	$X_4-X_2$	$X_5-X_2$	$X_6-X_2$	$X_7-X_2$
<b>3</b>			$X_4-X_3$	$X_5-X_3$	$X_6-X_3$	$X_7-X_3$
<b>4</b>				$X_5-X_4$	$X_6-X_4$	$X_7-X_4$
<b>5</b>					$X_6-X_5$	$X_7-X_5$
<b>6</b>						$X_7-X_6$
<b>Signs of Differences</b>						
		<b>t</b>				
<b>t-1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
<b>1</b>	+	+	+	+	+	+
<b>2</b>		+	-	+	+	+
<b>3</b>			-	+	-	+
<b>4</b>				+	-	+
<b>5</b>					-	+
<b>6</b>						+
<b>Scoring of Differences</b>						
		<b>t</b>				
<b>t-1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>
<b>1</b>	1	1	1	1	1	1
<b>2</b>		1	-1	1	1	1
<b>3</b>			-1	1	-1	1
<b>4</b>				1	-1	1
<b>5</b>					-1	1
<b>6</b>						1
$S = 11$						

### Box D-2. Directions for the Mann-Kendall Trend Test

STEP 1: List the data in the order collected over time:  $X_1, X_2, \dots, X_n$ , where  $X_t$  is the datum at time  $t$ . Assign a value of  $DL/2$  to values reported as below the detection limit (DL). Construct a "Data Matrix" similar to that at the top of Box D-1.

STEP 2: Compute the sign of all possible differences as shown in the middle and bottom portion of Box D-1.

STEP 3: Compute the Mann-Kendall statistic  $S$ , which is the number of positive signs minus the number of negative signs in the triangular table:  $S = (\text{number of + signs}) - (\text{number of - signs})$ .

The absolute value of the Mann Kendall test statistic  $S$  is compared with the critical values in Table E-1 of Attachment E to determine if there is a significant trend. The critical values in Table E-1 are used to determine whether the time-series data is increasing, decreasing, or stable. For example, if  $n = 7$ , the critical values of  $S$  are  $S^* = 13$  for a test with significance  $\alpha = 0.05$  and  $S^* = 11$  for a test with significance  $\alpha = 0.10$ . Under the null hypothesis assumption of No Trend, the absolute value of the test statistic  $|S|$  would equal or exceed critical value of  $S^* = 11$  in less than 10% of repeated trials, and would exceed  $S^* = 13$  in less than 5% of the trials. If the test statistic does exceed the critical value, the null hypothesis is rejected.

Values of  $|S|$  greater than or equal to  $S^*$  will occur at a rate less than or equal to  $\alpha$  when the true trend is 0. To test the null hypothesis of no trend against  $H_1$  (upward trend), reject  $H_0$  if  $S > 0$  and if  $|S| \geq S^*$ . For testing the null hypothesis of no trend against  $H_2$  (downward trend), reject  $H_0$  if  $S < 0$  and  $|S| \geq S^*$ . In the example in Box D-1, the sum  $S$  is 11. Thus, the null hypothesis of No Trend can be rejected at the  $\alpha = 0.10$  significance level, but not at the  $\alpha = 0.05$  significance level. Referring to the more detailed Table A.21 in Hollander and Wolfe (1999), the exact probability under the null distribution that  $S \geq 11$  when  $n = 7$  is 0.068. Thus, there is borderline evidence of a positive trend in this well.

If the sample size is more than 40, a normal approximation to the Mann-Kendall procedure may be used to test for a significant trend. In this approach, the value of  $S$  calculated from the data series is standardized using the expected value and variance of the sampling distribution of  $S$  under the null hypothesis. The standardized value of  $S$  is used as the test statistic in the normal approximation as described in Box D-3.

**Box D-3. Directions for the Mann-Kendall Procedure Using Normal Approximation**

STEP 1: Complete steps 1, 2, and 3 of Box D-2.

STEP 2: Calculate the variance of  $S$ :  $V(S) = n(n-1)(2n+5)/18$ .

If ties occur, let  $g$  represent the number of tied groups and  $w_p$  represent the number of data points in the  $p^{\text{th}}$  group. The variance of  $S$  is:

$$V(S) = [n(n-1)(2n+5) - \sum_p w_p (w_p-1)(2w_p+5)]/18$$

STEP 3: Calculate  $Z = (S-1) / [V(S)]^{1/2}$  if  $S > 0$ ,  $Z = 0$  if  $S = 0$ , or  $Z = (S+1) / [V(S)]^{1/2}$  if  $S < 0$ .

STEP 4: Use Table E-2 of Attachment E to find the critical value  $z_{1-\alpha}$  such that  $100(1-\alpha)\%$  of the normal distribution is below  $z_{1-\alpha}$ . For example, if  $\alpha = 0.05$  then  $z_{1-\alpha} = 1.645$ .

STEP 5: For testing the hypothesis,  $H_0$  (no trend) against

- (1)  $H_1$  (an upward trend) – reject  $H_0$  if  $Z$  is greater than  $z_{1-\alpha}$ , or
- (2)  $H_2$  (a downward trend) – reject  $H_0$  if  $Z < 0$  and the absolute value of  $Z$  is greater than  $z_{1-\alpha}$ .

**D.3 Instructions for Performing the Mann-Kendall Trend Test for Multiple Wells**

When one measurement is taken for each time period for each well, a generalization of the Mann-Kendall statistic is used to test for a trend across all wells. This procedure is described in Box D-4.

**Box D-4. Data for Multiple Times and Multiple Wells**

Let  $i = 1, 2, \dots, n$  represent time,  $k = 1, 2, \dots, K$  represent wells, and  $X_{ik}$  represent the post-restoration measurements at time  $i$  from well  $k$ . This data can be summarized in matrix form, as shown in Box D-5, where  $S_k =$  Mann-Kendall statistic for well  $k$  (see STEP 3, Box D-2),  $V(S_k) =$  variance for  $S$  statistic for well  $k$  (see STEP 2, Box D-3), and  $Z_k = S_k / \text{VAR}(S_k)$ .

**Box D-5. Array for Multiple Wells**

Time	Wells			
	1	2	3	4
1	X <sub>1,1</sub>	X <sub>1,2</sub>	X <sub>1,3</sub>	X <sub>1,4</sub>
2	X <sub>2,1</sub>	X <sub>2,2</sub>	X <sub>2,3</sub>	X <sub>2,4</sub>
3	X <sub>3,1</sub>	X <sub>3,2</sub>	X <sub>3,3</sub>	X <sub>3,4</sub>
4	X <sub>4,1</sub>	X <sub>4,2</sub>	X <sub>4,3</sub>	X <sub>4,4</sub>
5	X <sub>5,1</sub>	X <sub>5,2</sub>	X <sub>5,3</sub>	X <sub>5,4</sub>
6	X <sub>6,1</sub>	X <sub>6,2</sub>	X <sub>6,3</sub>	X <sub>6,4</sub>
S <sub>k</sub>	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>
Var(S <sub>k</sub> )	Var(S <sub>1</sub> )	Var(S <sub>2</sub> )	Var(S <sub>3</sub> )	Var(S <sub>4</sub> )
Z <sub>k</sub>	Z <sub>1</sub>	Z <sub>2</sub>	Z <sub>3</sub>	Z <sub>4</sub>

**Box D-6. Testing for Comparability of Wells and an Overall Monotonic Trend**

Let  $i = 1, 2, \dots, n$  represent time,  $k = 1, 2, \dots, K$  represent sampling wells, and  $X_{ik}$  represent the measurement at time  $i$  from well  $k$ . Let  $\alpha$  represent the significance level for testing homogeneity and  $\alpha^*$  represent the significance level for testing for an overall trend.

STEP 1: Calculate the Mann-Kendall statistic  $S_k$  and its variance  $V(S_k)$  for each of the  $K$  wells using the method in Box D-4.

STEP 2: For each of the  $K$  wells, calculate  $Z_k = S_k / [V(S_k)]^{1/2}$

STEP 3: Calculate the average  $Z_M = \sum Z_k / K$

STEP 4: Calculate the homogeneity chi-square statistic  $\chi^2_h = (\sum Z_k^2) - K Z_M^2$

STEP 5: Using a chi-squared table (Table E-3 of Attachment E), find the critical value for  $\chi^2$  with  $(K-1)$  degrees of freedom at significance level  $\alpha$ . For example, for a significance level of 5% and 5 degrees of freedom,  $\chi^2_{(5)} = 11.07$ , *i.e.*, 11.07, is the cut point, which puts 5% of the probability in the upper tail of a chi-square variable with 5 degrees of freedom.

STEP 6: If  $\chi^2_h \leq \chi^2_{(K-1)}$ , there are comparable dynamics across wells at significance level  $\alpha$ . Go to Step 7.

If  $\chi^2_h > \chi^2_{(K-1)}$ , the wells are not homogeneous (*i.e.*, different dynamics at different wells) at the significance level  $\alpha$ . Therefore, individual  $\alpha^*$ -level Mann-Kendall tests should be conducted at each well using the methods presented in Box D-2.

STEP 7: Using a chi-squared table (Table E-3 of Attachment E), find the critical value for  $\chi^2$  with 1 degree of freedom at significance level  $\alpha$ . If  $KZ_M^2 > \chi^2_{(1)}$ , reject  $H_0^*$  and conclude that there is a significant (upward or downward) monotonic trend across all wells at significance level  $\alpha^*$ . The signs of the  $S_k$  indicate whether increasing or decreasing trends are present. If  $KZ_M^2 \leq \chi^2_{(1)}$ , there is not significant evidence of a monotonic trend across all wells. That is, the wells appear approximately stable over time.

**D.4 Performing the Wilcoxon Rank Sum Test**

Comparison of post-restoration with baseline samples is required in Phase 4 to assess steady-state conditions, and in Phase 5 to determine if post-restoration values have achieved targeted remediation levels. In these comparisons, the statistical approach adopted will depend on the type of data collected. Before a comparison is attempted, the post-restoration samples are

examined for trends using the procedures in Section D.2 to demonstrate that the wells have reached a stable condition.

If the baseline and post-restoration samples are paired (*i.e.*, from the same well), then the paired nature of the data is used in the analysis and the wells are analyzed separately. If (and only if) all individual wells exhibit similar dynamics, the results of tests on individual wells are then combined to conduct an analysis of the entire wellfield. Before wells are combined for a summary analysis of the wellfield, the post-restoration samples are compared well-for-well with the baseline samples using WRS test.

If some or all of the baseline and post-restoration samples are from unmatched wells, then the paired wells are treated individually using the procedure described above and the baseline and post-restoration data for the unpaired wells are pooled into two datasets (before and after), and the WRS comparison method described for a single well is applied to the set of unmatched wells.

Instructions for conducting the WRS test are outlined in the five steps shown in Box A-7 and the calculations for a single well are illustrated in Box A-8a. In this example, a value of  $\Delta = 3$  was selected, approximately 10% of the baseline average. The hypothetical baseline and post-restoration data in Box D-8a for Well 1 are plotted in Figure D-4. The values of the baseline plus  $\Delta$  are also plotted in this figure. For a test with a significance level of  $\alpha = 0.10$ , the critical value given in Table B-8 of Appendix B for  $n = 6$  and  $m = 4$  is 28. Since  $W_1 = 29$  is greater than the critical value for the test, we reject the null hypothesis that the post-restoration distribution exceeds the baseline distribution by more than a substantial difference  $\Delta$ . It appears that the post-restoration conditions in this well are below or no more than  $\Delta$  above baseline conditions.

#### **Box D-7. Test for a Substantial Difference between Baseline and Post-Restoration Conditions**

STEP 1: Create an array with the (seasonally adjusted) baseline values  $X_i$  across the top and the post-restoration values down the left side as shown in Box D-8a.

STEP 2: Obtain the  $m$  adjusted baseline measurements  $Z_i$  by adding the substantial difference  $\Delta$  to each baseline measurement:  $Z_i = X_i + \Delta$ .

STEP 3: Fill the matrix of all possible comparisons by assigning a value of +1 when the adjusted baseline measurement exceeds post-restoration measurement; otherwise assign a value of 0.

STEP 4: Calculate the sum of the sum of the matrix entries. This sum is the Mann-Whitney form of the test statistic. Add the quantity  $m(m+1)/2$  to the array sum. This is the WRS statistic for well  $k$  ( $W_k$ ).

STEP 5: Compare  $W_k$  with the critical value given in Attachment E in Table E-5 ( $\alpha=0.01$ ), Table E-6 ( $\alpha=0.025$ ), Table E-7 ( $\alpha=0.05$ ) or Table E-8 ( $\alpha=0.10$ ) for the appropriate values of  $n$ ,  $m$ . If  $W_k$  is greater than the tabulated value, reject the hypothesis that the post-restoration distribution exceeds the baseline distribution by more than a substantial difference  $\Delta$ . If the null hypothesis is rejected, it appears that the post-restoration conditions in this well are not significantly different from baseline conditions.

**Box D-8a. Calculating the WRS Statistic for Well 1**

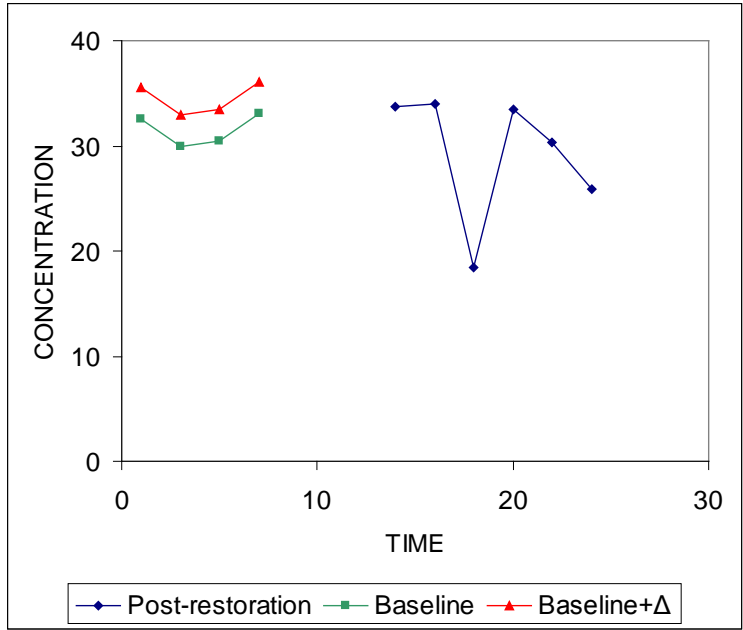
Delta= 3.0		Baseline Samples (m=4)			
Post-Remedial Samples	x	1	2	3	4
	x+Δ	32.6	30.0	30.5	33.1
1	33.7	1	0	0	1
2	34.0	1	0	0	1
3	18.4	1	1	1	1
4	33.4	1	0	1	1
5	30.4	1	1	1	1
6	25.8	1	1	1	1
<b>Sum</b>					19
<b>m(m+1)/2</b>					10
<b>W<sub>1</sub></b>					29

**Box D-8b. Calculating the WRS Statistic for Well 2**

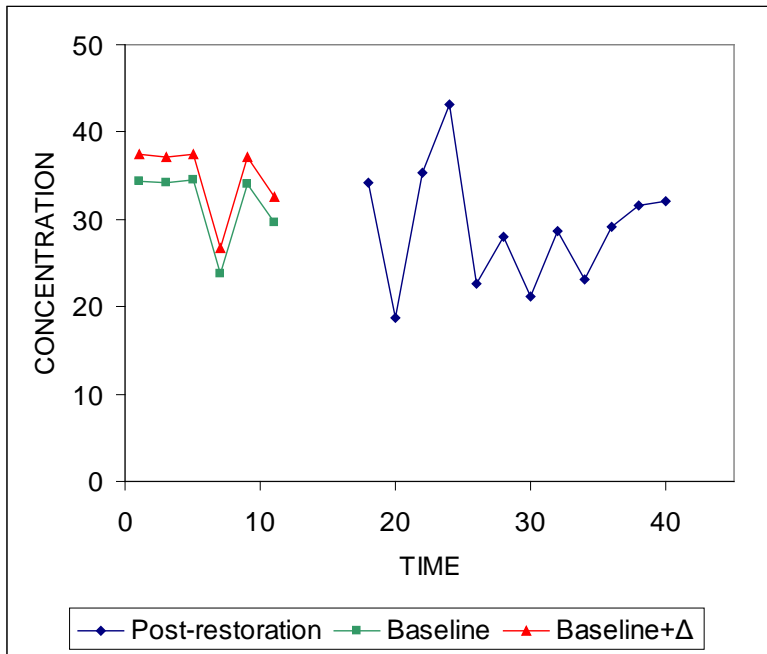
Delta= 3.0		Baseline Samples (m=6)					
Post-Remedial Samples	x	1	2	3	4	5	6
	x+Δ	34.4	34.1	34.5	23.7	34.1	29.6
1	34.2	1	1	1	0	1	0
2	18.8	1	1	1	1	1	1
3	35.4	1	1	1	0	1	0
4	43.2	0	0	0	0	0	0
5	22.6	1	1	1	1	1	1
6	28.0	1	1	1	0	1	1
7	21.1	1	1	1	1	1	1
8	28.7	1	1	1	0	1	1
9	23.1	1	1	1	1	1	1
10	29.2	1	1	1	0	1	1
11	31.5	1	1	1	0	1	1
12	32.0	1	1	1	0	1	1
<b>Sum</b>							57
<b>m(m+1)/2</b>							21
<b>W<sub>2</sub></b>							78

**Box D-8c. Calculating the WRS Statistic for Well 3**

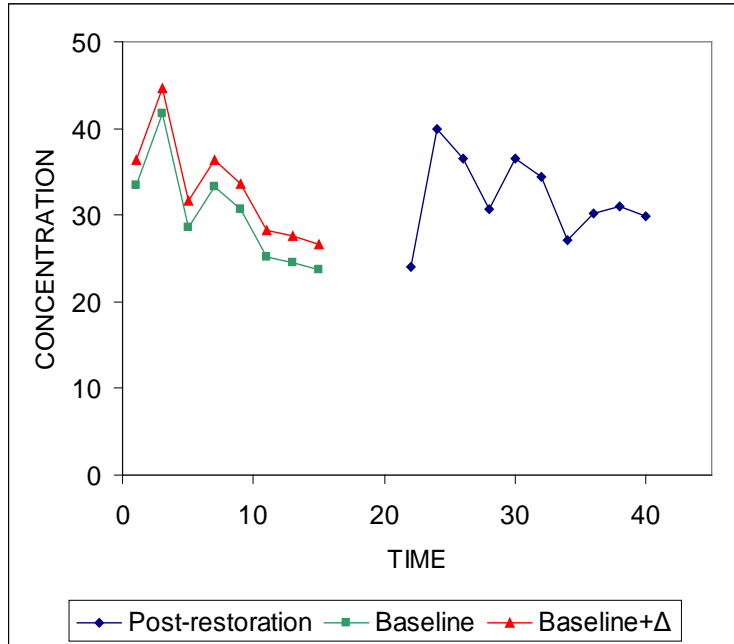
Delta= 3.0		Baseline Samples (m=8)							
Post-Remedial Samples	x	1	2	3	4	5	6	7	8
	x+Δ	33.4	41.7	28.6	33.3	30.7	25.2	24.6	23.6
1	24.0	1	1	1	1	1	1	1	1
2	40.0	0	1	0	0	0	0	0	0
3	36.6	0	1	0	0	0	0	0	0
4	30.7	1	1	1	1	1	0	0	0
5	36.6	0	1	0	0	0	0	0	0
6	34.4	1	1	0	1	0	0	0	0
7	27.2	1	1	1	1	1	1	1	0
8	30.2	1	1	1	1	1	0	0	0
9	31.1	1	1	1	1	1	0	0	0
10	29.9	1	1	1	1	1	0	0	0
<b>Sum</b>									41
<b>m(m+1)/2</b>									36
<b>W<sub>3</sub></b>									77



**Figure D-4. Hypothetical Baseline and Post-restoration Data for Well 1**



**Figure D-5. Hypothetical Baseline and Post-restoration Data for Well 2**



**Figure D-6. Hypothetical Baseline and Post-restoration Data for Well 3**

### D.5 Instructions for Performing the Wilcoxon Rank Sum Test for Multiple Wells

The comparison for multiple wells is based on the WRS statistics  $W_k$  for each well calculated using the instructions in Box D-7. Tables for calculating  $W_k$  for three wells are shown in Boxes D-8a, D-8b and D-8c.

To test for multiple wells, first compute the mean and variance of  $W_k$  under the null distribution as shown in Box D-9. The standardized form of the test statistic  $W_k$  is  $z_k = (W_k - E_k) / \sqrt{V_k}$ . Instructions for conducting the comparability test and the test for overall compliance with remediation goals are shown in Box D-9. The calculations for the three wells in Boxes D-8a, D-8b, and D-8c are illustrated in Box D-10. The hypothetical baseline and post-restoration data for Wells 1, 2 and 3 are plotted in Figures D-4, D-5 and D-6. The values of the baseline plus  $\Delta$  are also plotted in these figures.

#### Box D-9. Testing for Comparability of Wells and Overall Compliance with Remedial Goals

Let  $k = 1, 2, \dots, K$  represent sampling wells, and  $X_{ik}$  represent the measurement at time  $i$  from well  $k$ . Let  $\alpha$  represent the significance level for testing homogeneity and  $\alpha^*$  represent the significance level for testing for an overall compliance.

STEP 1: For each of the  $K$  wells, calculate the WRS statistic  $W_k$  using the instructions in Box D-7, and its expected value  $E(W_k)$  and variance  $V(W_k)$  using the equations below.

$$E_k = E(W_k) = m_k(n_k + m_k + 1) / 2$$

$$V_k = Var(W_k) = n_k m_k (n_k + m_k + 1) / 12$$



STEP 2: For each of the K wells, calculate the standardized test statistic

$$z_k = (W_k - E_k) / \sqrt{V_k}$$

STEP 3: Calculate the average  $Z_M = \sum Z_k / K$

STEP 4: Calculate the homogeneity chi-square statistic  $\chi^2_h = (\sum Z_k^2) - K Z_M^2$

STEP 5: Using a chi-squared table (Table E-3 of Attachment E), find the critical value for  $\chi^2$  with (K-1) degrees of freedom at significance level  $\alpha$ . For a significance level of 5% and 5 degrees of freedom,  $\chi^2_{(5)} = 11.07$ , *i.e.*, 11.07, is the cut point, which puts 5% of the probability in the upper tail of a chi-square variable with 5 degrees of freedom.

STEP 6: If  $\chi^2_h \leq \chi^2_{(K-1)}$ , there are comparable dynamics across wells at significance level  $\alpha$ . Go to Step 7.

If  $\chi^2_h > \chi^2_{(K-1)}$ , the wells are not homogeneous (*i.e.*, different dynamics at different wells) at the significance level  $\alpha$ . Therefore, individual  $\alpha^*$ -level WRS tests should be conducted at each well using the methods presented in Box D-7.

STEP 7: Using a chi-squared table (Table E-3 of Attachment E), find the critical value for  $\chi^2$  with 1 degree of freedom at significance level  $\alpha^*$ . If  $\chi^2_c = K Z_M^2 > \chi^2_{(1)}$ , reject  $H_0^*$  and conclude the site appears to be below baseline conditions or no more than  $\Delta$  higher than baseline conditions. If  $K Z_M^2 \leq \chi^2_{(1)}$ , there is not significant evidence at the  $\alpha^*$  level that all wells are in compliance with the remediation goals.

#### Box D-10. Tests for Homogeneity and Overall Compliance

k	$m_k$	$n_k$	$W_k$	$E_k$	$V_k$	$z_k$	$(z_k)^2$	
1	4	6	29	22	22.0	1.492	2.227	
2	6	12	78	57	114.0	1.967	3.868	
3	8	10	77	76	126.7	0.089	0.008	
						$Z_M$	1.183	6.104
						$\chi^2_h$	1.907	
						$\chi^2_c$	4.196	

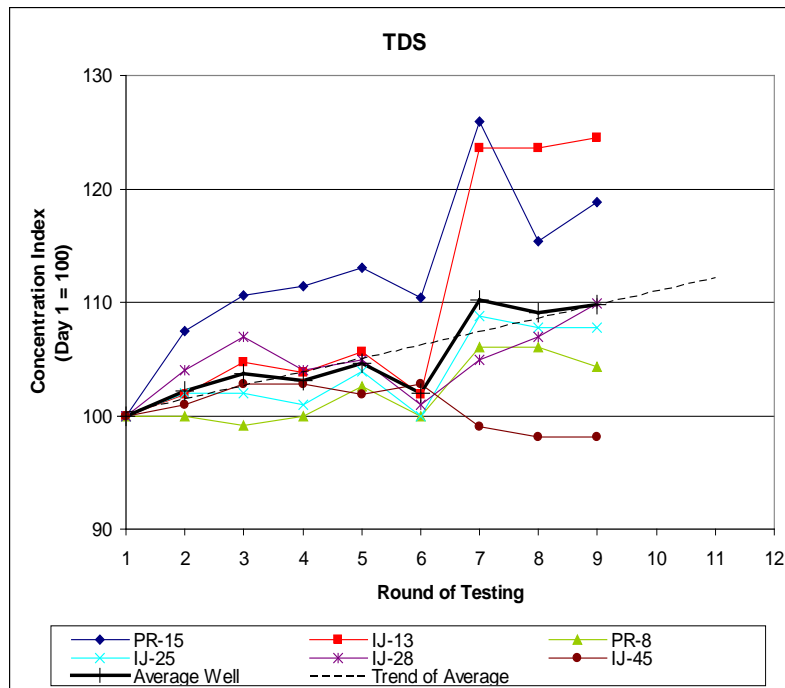
Comparing the value of  $\chi^2_h$  (1.907) in Box D-10 to the critical value from Table E-3 ( $\alpha=0.05$ , DF=2) of 5.991, we conclude that there are comparable dynamics across the wells (see Box D-9, Step 6). Similarly, comparing  $\chi^2_c = 4.196$  with the critical value from Table E-3 ( $\alpha=0.05$ , DF=1) of 3.841, we conclude that, since  $\chi^2_c > \chi^2_{(1)}$ , the restoration values are no more than  $\Delta$  higher than the baseline (Box D-9, Step 7).

#### D.6 A Real-life Example

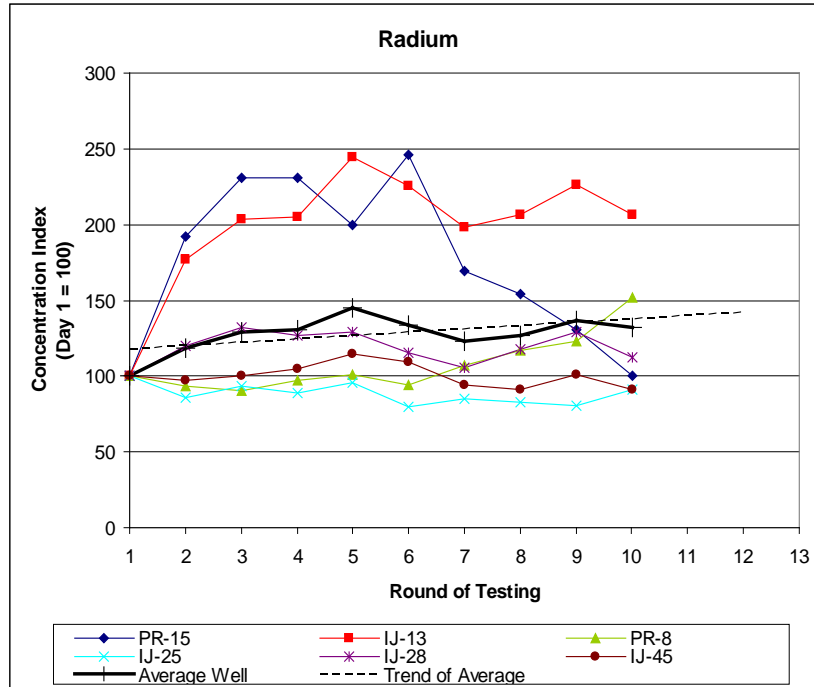
Figures D-7 through D-12 show plots of the post-restoration measurements of six groundwater parameters taken in six wells at the Crow Butte ISL site in Nebraska (see Attachment E for details.). The six parameters evaluated are total dissolved solids (TDS), radium, selenium, iron, ammonium, and uranium. A separate analysis was done for a time series consisting of the across-well average in each period. Values below the limit of detection have been replaced with a value equal to the limit of detection. The data were analyzed for trends in individual wells (Section 5.3.2 and Section D-2 of this attachment) and for a common trend across all wells (Section 5.3.3 and Section D-3 of this attachment). Separate analyses were conducted for each parameter. An error rate of  $\alpha=0.10$  was used for all tests.

Results of the analysis are shown in Table D-2. The table shows the value of the Mann-Kendall test statistic, number of data points, standard deviation and standardized test statistic for each parameter in each well. The test for homogeneity of trend across wells shows that the trend is not homogeneous for two parameters: TSD and radium. The test for monotonic trend across all wells is reported for the remaining four parameters. (The test results for TDS and radium are darkened, because the test for homogeneity of trend indicates these are not meaningful.) The test for a monotonic trend indicates that selenium and ammonium show no trend, while iron and uranium do show significant upward trends at the 0.10 level of confidence.

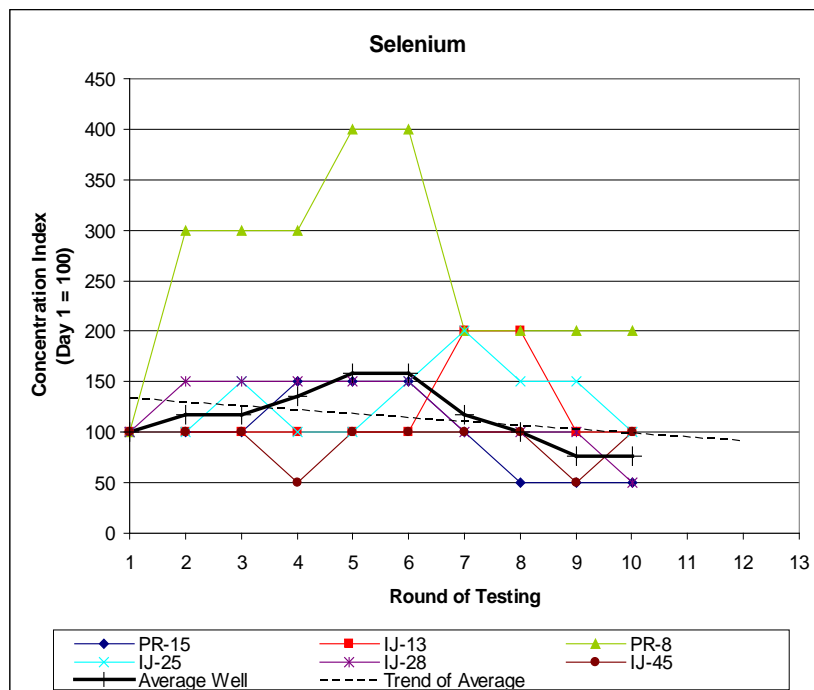
A summary of trend test results by well is shown at the bottom of Table D-2 for TDS and radium, which showed no homogeneity of trend across wells, and for iron and uranium, which showed significant upward trends. Individual wells generally have upward trends for TDS, iron, and uranium, while results are mixed for radium. All four parameters show upward trends for the average well at the 0.10 significance level. From an implementation perspective, the results for radium and TDS suggest that continued restoration and monitoring would be advisable to determine if these parameters attain steady-state values over an extended time period. TDS is typically considered an indicator of active changes in the geochemical state, *i.e.*, solutes are being actively introduced into or removed from the groundwater by some mechanism(s). Radium concentrations may be controlled by solubility constraints that may also still be evolving in the system, as suggested by the TDS behavior.



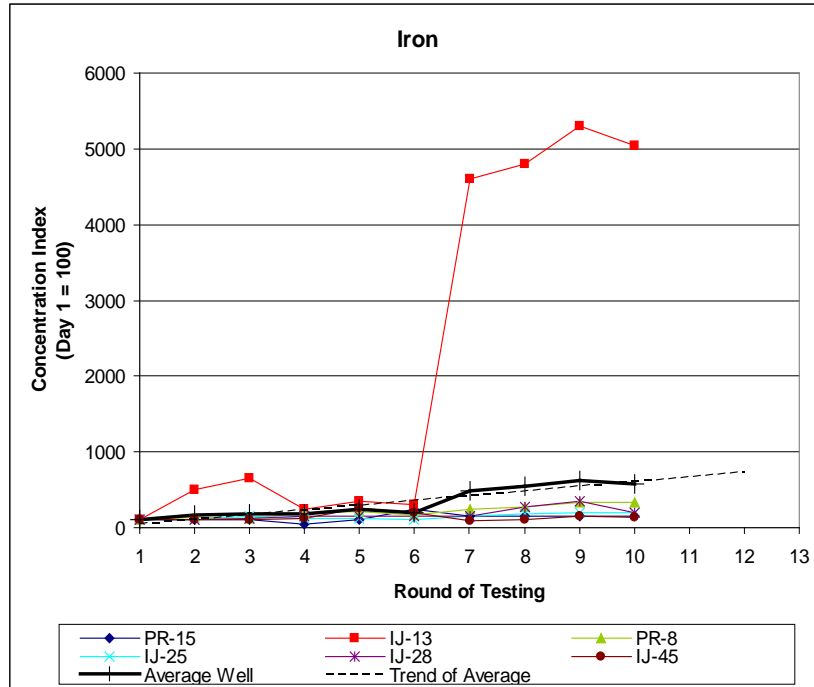
**Figure D-7. Total Dissolved Solids (TSD)**



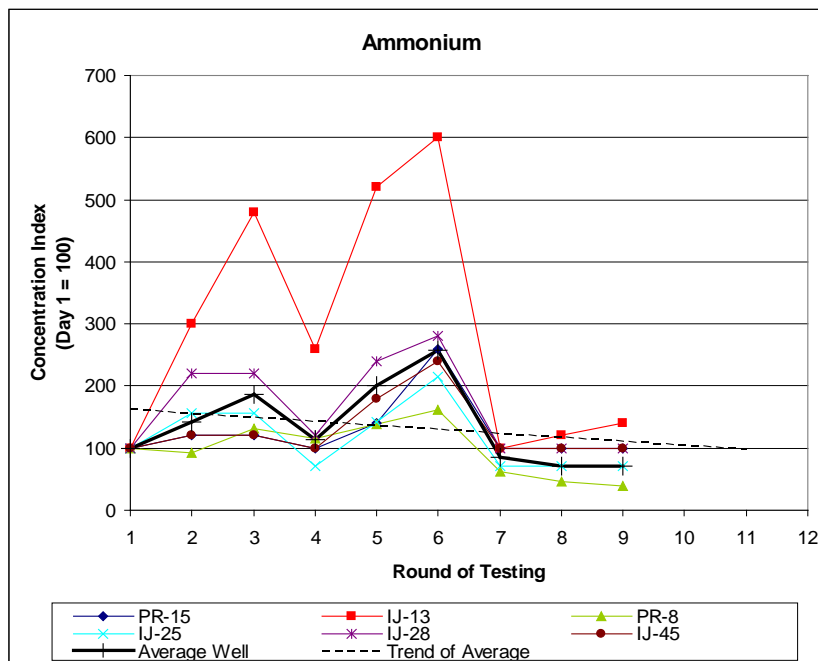
**Figure D-8. Total Dissolved Solids (TSD)**



**Figure D-9. Selenium**



**Figure D-10. Iron**



**Figure D-11. Ammonium**

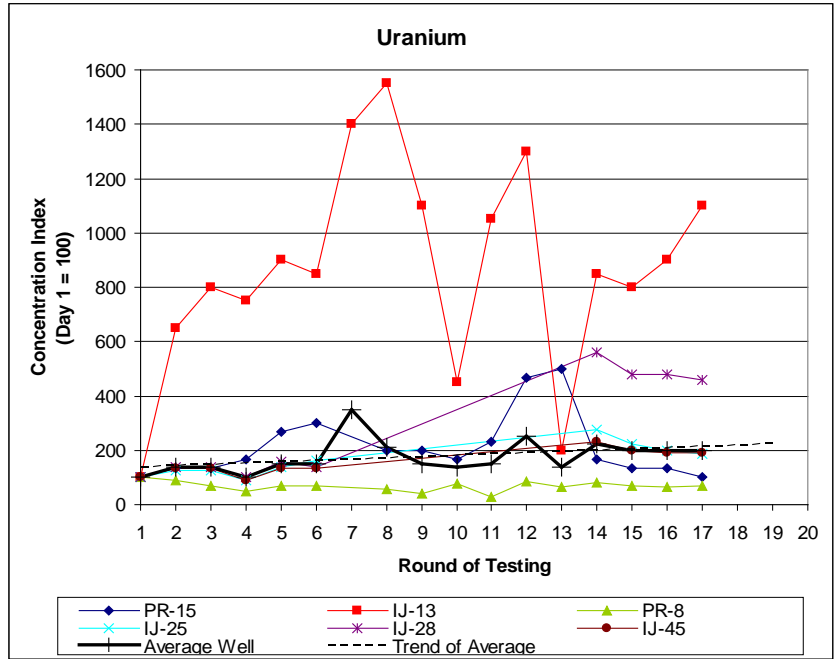


Figure D-12. Uranium

**Table D-2. Analysis for Trends of Six Parameters in Six Wells**

**S = Count**

Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	26	-13	-15	19	-3	7
IJ-13	26	22	8	29	1	32
PR-8	19	31	-5	38	-10	-19
IJ-25	17	-17	11	29	-11	26
IJ-28	19	-1	-19	34	-5	24
IJ-45	-12	-7	-4	12	-3	22
Average Well	22	19	-11	40	-9	52

**N = Sample Size**

Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	9	10	10	10	9	16
IJ-13	9	10	10	10	9	17
PR-8	9	10	10	10	9	16
IJ-25	9	10	10	10	9	10
IJ-28	9	10	10	10	9	10
IJ-45	9	10	10	10	9	10
Average Well	9	10	10	10	9	17

**SD(S) = Standard Deviation of S**

Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	9.59	11.18	11.18	11.18	9.59	22.21
IJ-13	9.59	11.18	11.18	11.18	9.59	24.28
PR-8	9.59	11.18	11.18	11.18	9.59	22.21
IJ-25	9.59	11.18	11.18	11.18	9.59	11.18
IJ-28	9.59	11.18	11.18	11.18	9.59	11.18
IJ-45	9.59	11.18	11.18	11.18	9.59	11.18
Average Well	9.59	11.18	11.18	11.18	9.59	24.28

**z(S) = Normal Score for S**

Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	2.61	-1.07	-1.25	1.61	-0.21	0.27
IJ-13	2.61	1.88	0.63	2.50	0.00	1.28
PR-8	1.88	2.68	-0.36	3.31	-0.94	-0.81
IJ-25	1.67	-1.43	0.89	2.50	-1.04	2.24
IJ-28	1.88	0.00	-1.61	2.95	-0.42	2.06
IJ-45	-1.15	-0.54	-0.27	0.98	-0.21	1.88
Average Well	2.19	1.61	-0.89	3.49	-0.83	2.10

**p(S) = Probability{Z>|z(S)|}**

Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	0.005	0.142	0.105	0.054	0.417	0.394
IJ-13	0.005	0.030	0.266	0.006	0.500	0.101
PR-8	0.030	0.004	0.360	0.001	0.174	0.209
IJ-25	0.048	0.076	0.186	0.006	0.149	0.013
IJ-28	0.030	0.500	0.054	0.002	0.338	0.020
IJ-45	0.126	0.296	0.394	0.163	0.417	0.030
Average Well	0.014	0.054	0.186	0.000	0.202	0.018

**Table D-2. Analysis for Trends of Six Parameters in Six Wells**

<b>Summary</b>						
Statistic	TDS	Radium	Selenium	Iron	Ammonium	Uranium
Mean(z)	1.58	0.25	-0.33	2.31	-0.47	1.15
Range(z)	3.75	4.11	2.5	2.33	1.04	3.05
<b>Test for Homogeneity of Trend Across Wells</b>						
Statistic	TDS	Radium	Selenium	Iron	Ammonium	Uranium
$\chi^2_h$	9.73	13.83	4.91	3.73	0.91	7.17
Result	Fail	Fail	Pass	Pass	Pass	Pass
<b>Test for Monotonic Trend Across All Wells</b>						
Statistic	TDS	Radium	Selenium	Iron	Ammonium	Uranium
$\chi^2_1$	15	0.39	0.65	32.03	1.32	7.95
Result	Up	Flat	Flat	Up	Flat	Up
<b>Significant Trends (<math>p(S) &lt; 0.10</math>)</b>						
Well	TDS	Radium	Selenium	Iron	Ammonium	Uranium
PR-15	UP	-	-	UP	-	-
IJ-13	UP	UP	-	UP	-	-
PR-8	UP	UP	-	UP	-	-
IJ-25	UP	DOWN	-	UP	-	UP
IJ-28	UP	-	DOWN	UP	-	UP
IJ-45	-	-	-	-	-	UP
Average Well	UP	UP	-	UP	-	UP

The two highlighted entries in the under the row titled “Test for Homogeneity of Trend Across Wells” indicate that the wells cannot be lumped together for TDS and radium. The entries in the “Test for Monotonic Trend Across All Wells” rows are darkened because the test is not appropriate for these parameters. The summary of individual well results at the bottom of the table indicates that almost all wells show up-trends for TDS and two wells show up-trends for radium.

The remaining four parameters pass the test for homogeneity of trend. The results of the test for a monotonic trend are only meaningful for these four parameters. Of the four, uranium and iron show monotonic up-trends across all wells. This is confirmed by the summary of individual well results at the bottom of the table.

Only two parameters demonstrate stability in the post-restoration period; selenium and ammonium.

## ATTACHMENT E: STATISTICAL TABLES

**Table E-1. Critical Values of S in Mann-Kendall Trend Test for a Series of Size N**

N	Alpha			N	Alpha		
	0.01	0.05	0.10		0.01	0.05	0.10
<b>4</b>	-	6	6	<b>23</b>	89	65	51
<b>5</b>	10	8	8	<b>24</b>	94	68	54
<b>6</b>	13	11	9	<b>25</b>	102	72	58
<b>7</b>	17	13	11	<b>26</b>	105	77	61
<b>8</b>	20	16	12	<b>27</b>	111	81	63
<b>9</b>	24	18	14	<b>28</b>	118	86	68
<b>10</b>	27	21	17	<b>29</b>	124	90	70
<b>11</b>	31	23	19	<b>30</b>	131	95	75
<b>12</b>	36	26	20	<b>31</b>	137	99	77
<b>13</b>	40	28	24	<b>32</b>	144	104	82
<b>14</b>	45	31	25	<b>33</b>	150	108	86
<b>15</b>	49	35	29	<b>34</b>	157	113	89
<b>16</b>	54	38	30	<b>35</b>	165	119	93
<b>17</b>	58	42	34	<b>36</b>	172	124	96
<b>18</b>	63	45	37	<b>37</b>	178	128	100
<b>19</b>	69	49	39	<b>38</b>	185	133	105
<b>20</b>	72	52	42	<b>39</b>	193	139	109
<b>21</b>	78	56	44	<b>40</b>	200	142	112
<b>22</b>	83	61	47				

Source: Adapted from Hollander and Wolfe 1999, Table A.21



## Tables E-2. Normal Distribution Table

(Cumulative probabilities for positive z-values are shown in table)

<b>z</b>	<b>0.00</b>	<b>0.01</b>	<b>0.02</b>	<b>0.03</b>	<b>0.04</b>	<b>0.05</b>	<b>0.06</b>	<b>0.07</b>	<b>0.08</b>	<b>0.09</b>
<b>0.0</b>	0.5000	0.5040	0.5080	0.5120	0.5160	0.5199	0.5239	0.5279	0.5319	0.5359
<b>0.1</b>	0.5398	0.5438	0.5478	0.5517	0.5557	0.5596	0.5636	0.5675	0.5714	0.5753
<b>0.2</b>	0.5793	0.5832	0.5871	0.5910	0.5948	0.5987	0.6026	0.6064	0.6103	0.6141
<b>0.3</b>	0.6179	0.6217	0.6255	0.6293	0.6331	0.6368	0.6406	0.6443	0.6480	0.6517
<b>0.4</b>	0.6554	0.6591	0.6628	0.6664	0.6700	0.6736	0.6772	0.6808	0.6844	0.6879
<b>0.5</b>	0.6915	0.6950	0.6985	0.7019	0.7054	0.7088	0.7123	0.7157	0.7190	0.7224
<b>0.6</b>	0.7257	0.7291	0.7324	0.7357	0.7389	0.7422	0.7454	0.7486	0.7517	0.7549
<b>0.7</b>	0.7580	0.7611	0.7642	0.7673	0.7704	0.7734	0.7764	0.7794	0.7823	0.7852
<b>0.8</b>	0.7881	0.7910	0.7939	0.7967	0.7995	0.8023	0.8051	0.8078	0.8106	0.8133
<b>0.9</b>	0.8159	0.8186	0.8212	0.8238	0.8264	0.8289	0.8315	0.8340	0.8365	0.8389
<b>1.0</b>	0.8413	0.8438	0.8461	0.8485	0.8508	0.8531	0.8554	0.8577	0.8599	0.8621
<b>1.1</b>	0.8643	0.8665	0.8686	0.8708	0.8729	0.8749	0.8770	0.8790	0.8810	0.8830
<b>1.2</b>	0.8849	0.8869	0.8888	0.8907	0.8925	0.8944	0.8962	0.8980	0.8997	0.9015
<b>1.3</b>	0.9032	0.9049	0.9066	0.9082	0.9099	0.9115	0.9131	0.9147	0.9162	0.9177
<b>1.4</b>	0.9192	0.9207	0.9222	0.9236	0.9251	0.9265	0.9279	0.9292	0.9306	0.9319
<b>1.5</b>	0.9332	0.9345	0.9357	0.9370	0.9382	0.9394	0.9406	0.9418	0.9429	0.9441
<b>1.6</b>	0.9452	0.9463	0.9474	0.9484	0.9495	0.9505	0.9515	0.9525	0.9535	0.9545
<b>1.7</b>	0.9554	0.9564	0.9573	0.9582	0.9591	0.9599	0.9608	0.9616	0.9625	0.9633
<b>1.8</b>	0.9641	0.9649	0.9656	0.9664	0.9671	0.9678	0.9686	0.9693	0.9699	0.9706
<b>1.9</b>	0.9713	0.9719	0.9726	0.9732	0.9738	0.9744	0.9750	0.9756	0.9761	0.9767
<b>2.0</b>	0.9772	0.9778	0.9783	0.9788	0.9793	0.9798	0.9803	0.9808	0.9812	0.9817
<b>2.1</b>	0.9821	0.9826	0.9830	0.9834	0.9838	0.9842	0.9846	0.9850	0.9854	0.9857
<b>2.2</b>	0.9861	0.9864	0.9868	0.9871	0.9875	0.9878	0.9881	0.9884	0.9887	0.9890
<b>2.3</b>	0.9893	0.9896	0.9898	0.9901	0.9904	0.9906	0.9909	0.9911	0.9913	0.9916
<b>2.4</b>	0.9918	0.9920	0.9922	0.9925	0.9927	0.9929	0.9931	0.9932	0.9934	0.9936
<b>2.5</b>	0.9938	0.9940	0.9941	0.9943	0.9945	0.9946	0.9948	0.9949	0.9951	0.9952
<b>2.6</b>	0.9953	0.9955	0.9956	0.9957	0.9959	0.9960	0.9961	0.9962	0.9963	0.9964
<b>2.7</b>	0.9965	0.9966	0.9967	0.9968	0.9969	0.9970	0.9971	0.9972	0.9973	0.9974
<b>2.8</b>	0.9974	0.9975	0.9976	0.9977	0.9977	0.9978	0.9979	0.9979	0.9980	0.9981
<b>2.9</b>	0.9981	0.9982	0.9982	0.9983	0.9984	0.9984	0.9985	0.9985	0.9986	0.9986
<b>3.0</b>	0.9987	0.9987	0.9987	0.9988	0.9988	0.9989	0.9989	0.9989	0.9990	0.9990
<b>3.1</b>	0.9990	0.9991	0.9991	0.9991	0.9992	0.9992	0.9992	0.9992	0.9993	0.9993
<b>3.2</b>	0.9993	0.9993	0.9994	0.9994	0.9994	0.9994	0.9994	0.9995	0.9995	0.9995
<b>3.3</b>	0.9995	0.9995	0.9995	0.9996	0.9996	0.9996	0.9996	0.9996	0.9996	0.9997
<b>3.4</b>	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9997	0.9998

**Table E-3. Chi Squared Distribution Table**

(Table shows values of x where probability  $\{\chi^2 > x\} = \alpha$ )

DF	$\alpha$								
	0.2	0.1	0.05	0.025	0.02	0.01	0.005	0.002	0.001
1	1.642	2.706	3.841	5.024	5.412	6.635	7.879	9.550	10.828
2	3.219	4.605	5.991	7.378	7.824	9.210	10.597	12.429	13.816
3	4.642	6.251	7.815	9.348	9.837	11.345	12.838	14.796	16.266
4	5.989	7.779	9.488	11.143	11.668	13.277	14.860	16.924	18.467
5	7.289	9.236	11.070	12.833	13.388	15.086	16.750	18.907	20.515
6	8.558	10.645	12.592	14.449	15.033	16.812	18.548	20.791	22.458
7	9.803	12.017	14.067	16.013	16.622	18.475	20.278	22.601	24.322
8	11.030	13.362	15.507	17.535	18.168	20.090	21.955	24.352	26.124
9	12.242	14.684	16.919	19.023	19.679	21.666	23.589	26.056	27.877
10	13.442	15.987	18.307	20.483	21.161	23.209	25.188	27.722	29.588
11	14.631	17.275	19.675	21.920	22.618	24.725	26.757	29.354	31.264
12	15.812	18.549	21.026	23.337	24.054	26.217	28.300	30.957	32.909
13	16.985	19.812	22.362	24.736	25.472	27.688	29.819	32.535	34.528
14	18.151	21.064	23.685	26.119	26.873	29.141	31.319	34.091	36.123
15	19.311	22.307	24.996	27.488	28.259	30.578	32.801	35.628	37.697
16	20.465	23.542	26.296	28.845	29.633	32.000	34.267	37.146	39.252
17	21.615	24.769	27.587	30.191	30.995	33.409	35.718	38.648	40.790
18	22.760	25.989	28.869	31.526	32.346	34.805	37.156	40.136	42.312
19	23.900	27.204	30.144	32.852	33.687	36.191	38.582	41.610	43.820
20	25.038	28.412	31.410	34.170	35.020	37.566	39.997	43.072	45.315
21	26.171	29.615	32.671	35.479	36.343	38.932	41.401	44.522	46.797
22	27.301	30.813	33.924	36.781	37.659	40.289	42.796	45.962	48.268
23	28.429	32.007	35.172	38.076	38.968	41.638	44.181	47.391	49.728
24	29.553	33.196	36.415	39.364	40.270	42.980	45.559	48.812	51.179
25	30.675	34.382	37.652	40.646	41.566	44.314	46.928	50.223	52.620
26	31.795	35.563	38.885	41.923	42.856	45.642	48.290	51.627	54.052
27	32.912	36.741	40.113	43.195	44.140	46.963	49.645	53.023	55.476
28	34.027	37.916	41.337	44.461	45.419	48.278	50.993	54.411	56.892
29	35.139	39.087	42.557	45.722	46.693	49.588	52.336	55.792	58.301
30	36.250	40.256	43.773	46.979	47.962	50.892	53.672	57.167	59.703
31	37.359	41.422	44.985	48.232	49.226	52.191	55.003	58.536	61.098
32	38.466	42.585	46.194	49.480	50.487	53.486	56.328	59.899	62.487
33	39.572	43.745	47.400	50.725	51.743	54.776	57.648	61.256	63.870
34	40.676	44.903	48.602	51.966	52.995	56.061	58.964	62.608	65.247
35	41.778	46.059	49.802	53.203	54.244	57.342	60.275	63.955	66.619
36	42.879	47.212	50.998	54.437	55.489	58.619	61.581	65.296	67.985
37	43.978	48.363	52.192	55.668	56.730	59.893	62.883	66.633	69.346
38	45.076	49.513	53.384	56.896	57.969	61.162	64.181	67.966	70.703
39	46.173	50.660	54.572	58.120	59.204	62.428	65.476	69.294	72.055
40	47.269	51.805	55.758	59.342	60.436	63.691	66.766	70.618	73.402
41	48.363	52.949	56.942	60.561	61.665	64.950	68.053	71.938	74.745
42	49.456	54.090	58.124	61.777	62.892	66.206	69.336	73.254	76.084
43	50.548	55.230	59.304	62.990	64.116	67.459	70.616	74.566	77.419
44	51.639	56.369	60.481	64.201	65.337	68.710	71.893	75.874	78.750
45	52.729	57.505	61.656	65.410	66.555	69.957	73.166	77.179	80.077
46	53.818	58.641	62.830	66.617	67.771	71.201	74.437	78.481	81.400
47	54.906	59.774	64.001	67.821	68.985	72.443	75.704	79.780	82.720
48	55.993	60.907	65.171	69.023	70.197	73.683	76.969	81.075	84.037
49	57.079	62.038	66.339	70.222	71.406	74.919	78.231	82.367	85.351
50	58.164	63.167	67.505	71.420	72.613	76.154	79.490	83.657	86.661

Source: <http://www.medcalc.org/manual/chi-square-table.php>

**Table E-4. Sample Sizes for the Wilcoxon Rank Sum Test**

(Table shows values of m + n)

MDD/ $\sigma$	$\alpha=0.01$					$\alpha=0.025$					$\alpha=0.05$					$\alpha=0.10$					$\alpha=0.20$				
	$\beta=0.01$	$\beta=0.025$	$\beta=0.05$	$\beta=0.10$	$\beta=0.20$	$\beta=0.01$	$\beta=0.025$	$\beta=0.05$	$\beta=0.10$	$\beta=0.20$	$\beta=0.01$	$\beta=0.025$	$\beta=0.05$	$\beta=0.10$	$\beta=0.20$	$\beta=0.01$	$\beta=0.025$	$\beta=0.05$	$\beta=0.10$	$\beta=0.20$	$\beta=0.01$	$\beta=0.025$	$\beta=0.05$	$\beta=0.10$	$\beta=0.20$
0.1	12058	10234	8785	7252	5592	10233	8559	7239	5854	4373	8783	7238	6028	4771	3445	7249	5852	4770	3660	2512	5589	4371	3443	2511	1579
0.2	3018	2562	2200	1816	1401	2561	2142	1812	1466	1096	2198	1811	1509	1194	863	1814	1464	1194	916	629	1398	1094	862	628	395
0.3	1344	1141	980	810	625	1140	954	807	653	489	978	806	672	532	385	807	652	531	408	281	622	487	383	280	176
0.4	758	644	553	457	354	643	538	455	369	276	551	455	379	300	218	455	367	300	230	159	350	274	216	158	100
0.5	486	413	356	294	228	412	345	293	237	178	354	292	243	193	140	292	236	192	148	102	225	176	139	101	64
0.6	339	288	248	206	159	287	241	204	166	125	246	203	170	135	98	203	164	134	103	71	156	122	97	71	45
0.7	250	213	183	152	118	212	178	151	123	92	182	150	125	100	73	150	121	99	76	53	115	90	71	52	33
0.8	193	164	141	118	92	163	137	116	95	71	140	115	97	77	56	115	93	76	59	41	88	69	55	40	26
0.9	153	131	113	94	73	129	109	93	75	57	111	92	77	61	45	91	74	61	47	33	70	55	43	32	20
1	125	107	92	77	60	105	89	76	62	47	90	75	63	50	37	74	60	49	38	27	57	45	35	26	-
1.1	104	89	77	64	50	88	74	63	52	39	75	62	52	42	31	62	50	41	32	22	47	37	29	22	-
1.2	88	75	65	55	43	74	63	53	44	34	63	53	44	35	26	52	42	35	27	-	40	31	25	-	-
1.3	76	65	56	47	37	64	54	46	38	29	54	45	38	31	23	45	36	30	23	-	34	27	21	-	-
1.4	66	56	49	41	33	55	47	40	33	25	47	39	33	27	20	39	31	26	20	-	30	23	-	-	-
1.5	58	50	43	36	29	49	41	35	29	23	41	35	29	24	-	34	28	23	-	-	26	20	-	-	-
1.6	51	44	39	33	26	43	37	31	26	20	37	31	26	21	-	30	24	20	-	-	23	-	-	-	-
1.8	41	36	31	27	22	35	30	26	21	-	29	25	21	-	-	24	20	-	-	-	-	-	-	-	-
2	34	30	26	22	-	29	25	21	-	-	24	20	-	-	-	20	-	-	-	-	-	-	-	-	-
2.25	28	24	22	-	-	23	20	-	-	-	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2.5	24	21	-	-	-	20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Notes: Shaded region shows resolutions (MDD/ $\sigma$ ) obtainable with a combined sample size of 144 = (6)(3)(4)(2): 6 wells with 3 years of quarterly measurements per well in baseline and post-remedial periods.

The upper highlighted entry for  $\alpha=0.05$  and  $\beta=0.05$  indicates that differences smaller than  $0.7\sigma$  are not resolvable with a sample size of 144 at this level of confidence, but larger differences are resolvable.

In individual wells (with 24 observations) differences of  $1.8\sigma$  are resolvable, but smaller differences are not (lower highlight)

- Sample size estimates based on normal approximation are not reliable if m or n is less than 10.

**Table E-5. Critical Value for WRS Test for  $\alpha=0.01$**

		n																		
		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
m	2	7	9	11	13	15	17	19	21	23	25	27	28	30	32	34	36	38	39	41
	3	12	15	18	21	24	26	29	31	34	37	39	42	45	47	50	52	55	58	60
	4	18	22	26	29	32	36	39	42	46	49	52	56	59	62	66	69	72	76	79
	5	25	30	34	38	42	46	50	54	58	62	66	70	74	78	82	86	90	94	98
	6	33	39	43	48	53	58	62	67	72	77	81	86	91	95	100	104	109	114	118
	7	42	48	54	59	65	70	76	81	86	92	97	102	108	113	118	123	129	134	139
	8	52	59	65	71	77	84	90	96	102	108	114	120	125	131	137	143	149	155	161
	9	63	70	77	84	91	98	105	111	118	125	131	138	144	151	157	164	170	177	184
	10	75	83	91	98	106	113	121	128	135	142	150	157	164	171	178	186	193	200	207
	11	88	97	105	113	122	130	138	146	153	161	169	177	185	193	200	208	216	224	232
	12	102	111	120	129	138	147	156	164	173	181	190	198	207	215	223	232	240	249	257
	13	116	127	137	146	156	165	174	184	193	202	211	220	229	238	247	256	265	274	283
	14	132	144	154	164	175	185	194	204	214	224	234	243	253	263	272	282	291	301	311
	15	149	161	172	183	194	205	215	226	236	247	257	267	278	288	298	308	319	329	339
	16	167	180	192	203	215	226	237	248	259	270	281	292	303	314	325	336	347	357	368
	17	186	199	212	224	236	248	260	272	284	295	307	318	330	341	353	364	376	387	399
	18	206	220	233	246	259	272	284	296	309	321	333	345	357	370	382	394	406	418	430
	19	226	242	256	269	283	296	309	322	335	348	361	373	386	399	411	424	437	449	462
	20	248	264	279	293	307	321	335	349	362	376	389	402	416	429	442	456	469	482	495

Note: m is the number of baseline samples and n is the number of post-restoration samples.  
 Source: MARSSIM, Appendix I (EPA 2000).

**Table E-6. Critical Value for WRS Test for  $\alpha=0.025$**

		n																		
		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
m	2	7	9	11	13	15	17	18	20	22	23	25	27	29	31	33	34	36	38	40
	3	12	15	18	20	22	25	27	30	32	35	37	40	42	45	47	50	52	55	57
	4	18	22	25	28	31	34	37	41	44	47	50	53	56	59	62	66	69	72	75
	5	25	29	33	37	41	44	48	52	56	60	63	67	71	75	79	82	86	90	94
	6	33	37	42	47	51	56	60	64	69	73	78	82	87	91	95	100	104	109	113
	7	42	47	52	57	63	68	73	78	83	88	93	98	103	108	113	118	123	128	133
	8	51	57	63	69	75	81	86	92	98	104	109	115	121	126	132	137	143	149	154
	9	62	69	76	82	88	95	101	108	114	120	126	133	139	145	151	158	164	170	176
	10	74	81	89	96	103	110	117	124	131	138	145	151	158	165	172	179	186	192	199
	11	87	95	103	111	118	126	134	141	149	156	164	171	179	186	194	201	208	216	223
	12	100	109	118	126	135	143	151	159	168	176	184	192	200	208	216	224	232	240	248
	13	115	125	134	143	152	161	170	179	187	196	205	214	222	231	239	248	257	265	274
	14	131	141	151	161	171	180	190	199	208	218	227	236	245	255	264	273	282	292	301
	15	148	159	169	180	190	200	210	220	230	240	250	260	270	280	289	299	309	319	329
	16	166	177	188	200	210	221	232	242	253	264	274	284	295	305	316	326	337	347	357
	17	184	197	209	220	232	243	254	266	277	288	299	310	321	332	343	354	365	376	387
	18	204	217	230	242	254	266	278	290	302	313	325	337	348	360	372	383	395	406	418
	19	225	239	252	265	278	290	303	315	327	340	352	364	377	389	401	413	425	437	450
	20	247	261	275	289	302	315	329	341	354	367	380	393	406	419	431	444	457	470	482

Note: m is the number of baseline samples and n is the number of post-restoration samples.

Source: MARSSIM, Appendix I (EPA 2000).

**Table E-7. Critical Value for WRS Test for  $\alpha=0.05$**

		n																		
		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
m	2	7	9	11	12	14	16	17	19	21	23	24	26	27	29	31	33	34	36	38
	3	12	14	17	19	21	24	26	28	31	33	36	38	40	43	45	47	50	52	54
	4	18	21	24	27	30	33	36	39	42	45	48	51	54	57	59	62	65	68	71
	5	24	28	32	35	39	43	46	50	53	57	61	64	68	71	75	79	82	86	89
	6	32	36	41	45	49	54	58	62	66	70	75	79	83	87	91	96	100	104	108
	7	41	46	51	56	61	65	70	75	80	85	90	94	99	104	109	113	118	123	128
	8	50	56	62	67	73	78	84	89	95	100	105	111	116	122	127	132	138	143	148
	9	61	67	74	80	86	92	98	104	110	116	122	128	134	140	146	152	158	164	170
	10	73	80	87	93	100	107	114	120	127	133	140	147	153	160	166	173	179	186	192
	11	86	93	101	108	115	123	130	137	144	152	159	166	173	180	187	195	202	209	216
	12	99	108	116	124	132	140	147	155	165	171	179	186	194	202	209	217	225	233	240
	13	114	123	132	140	149	157	166	174	183	191	199	208	216	224	233	241	249	257	266
	14	129	139	149	158	167	176	185	194	203	212	221	230	239	248	257	265	274	283	292
	15	146	157	167	176	186	196	206	215	225	234	244	253	263	272	282	291	301	310	319
	16	164	175	185	196	206	217	227	237	247	257	267	278	288	298	308	318	328	338	348
	17	183	194	205	217	228	238	249	260	271	282	292	303	313	324	335	345	356	366	377
	18	202	215	226	238	250	261	273	284	295	307	318	329	340	352	363	374	385	396	407
	19	223	236	248	261	273	285	297	309	321	333	345	356	368	380	392	403	415	427	439
	20	245	258	271	284	297	310	322	335	347	360	372	385	397	409	422	434	446	459	471

Note: m is the number of baseline samples and n is the number of post-restoration samples.

Source: MARSSIM, Appendix I (EPA 2000).

**Table E-8. Critical Value for WRS Test for  $\alpha=0.10$**

		n																		
		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
m	2	7	8	10	11	13	15	16	18	19	21	22	24	26	27	29	30	32	33	35
	3	11	13	16	18	20	22	24	27	29	31	33	35	37	40	42	44	46	48	50
	4	17	20	22	25	28	31	34	36	39	42	45	48	50	53	56	59	61	64	67
	5	23	27	30	34	37	41	44	47	51	54	57	61	64	67	71	74	77	81	84
	6	31	35	39	43	47	51	55	59	63	67	71	75	79	83	87	91	94	98	102
	7	40	44	49	54	58	63	67	72	76	81	85	90	94	99	103	108	112	117	121
	8	49	54	60	65	70	75	80	85	91	96	101	106	111	116	121	126	131	136	141
	9	60	66	71	77	83	89	94	100	106	112	117	123	129	134	140	145	151	157	162
	10	71	78	84	91	97	103	110	116	122	128	135	141	147	153	160	166	172	178	184
	11	84	91	98	105	112	119	126	133	139	146	153	160	167	173	180	187	194	201	207
	12	97	105	113	120	128	135	143	150	158	165	172	180	187	194	202	209	216	224	231
	13	112	120	129	137	145	153	161	169	177	185	193	201	209	217	224	232	240	248	256
	14	128	136	145	154	163	171	180	189	197	206	214	223	231	240	248	257	265	273	282
	15	144	154	163	172	182	191	200	209	218	227	236	246	255	264	273	282	291	300	309
	16	162	172	182	192	202	211	221	231	241	250	260	269	279	289	298	308	317	327	336
	17	180	191	202	212	223	233	243	253	264	274	284	294	305	315	325	335	345	355	365
	18	200	211	222	233	244	255	266	277	288	299	309	320	331	342	352	363	374	384	395
	19	220	232	244	256	267	279	290	302	313	325	336	347	358	370	381	392	403	415	426
	20	242	254	267	279	291	303	315	327	339	351	363	375	387	399	410	422	434	446	458

Note: m is the number of baseline samples and n is the number of post-restoration samples.

Source: MARSSIM, Appendix I (EPA 2000).