

# Evaluation of Background Aquifer Aqueous Geochemistry

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Technical Memorandum

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Date

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TableFormat

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**Aquifer Geochemistry****Adrian Brown****1. INTRODUCTION**

For most of 1996, monitoring wells at the Envirocare 11e.(2), located in Clive, Utah, have routinely registered exceedences with respect to arsenic and occasionally for other elements of concern (e.g. selenium). Previously, only one arsenic exceedence had been observed, for one specific well (GW-57 in January 1995). This communication focuses only on the issues related to arsenic, although similar efforts are being developed to address other constituents.

Over the period of time that the 11e.(2) facility has operated two distinct changes have occurred which may contribute to the observed arsenic exceedences.

- there has been a change in the contract laboratory that performs the analyses
- groundwater elevations at each of the monitoring wells has slowly increased

It is not clearly understood to what degree either, or both, of these changes has contributed to observed exceedences for arsenic, or if observations simply represent background conditions that may warrant a change in the established background concentration for each of the individual wells monitoring the facility.

The purpose of this Technical Memorandum is to provide an initial review of how operational and environmental factors may relate to observed exceedences. It intends, in part, to lay some of the fundamental groundwork for a continuing program of investigation to systematize understanding of geochemical changes at the site and the degree to which Envirocare may play a role in those processes.

**2. ESTABLISHED BACKGROUND AND RECENT EXCEEDENCES**

Experiencing regulatory exceedences for monitoring wells at the 11e.(2) facility is driven by two principle features

- the established a background concentration for arsenic in groundwater at the site that is a reference point for potential future exceedences
- observing, after initiation of facility operation, concentrations in monitoring wells that are greater than the previously established background concentration, defining an exceedence

This section reviews the activities related to establishing background concentrations and their reliability. Later sections speak to the issue of current observations, which are interpreted to be regulatory exceedences.

**2.1 Background Data Collection**

Each of the monitoring wells surrounding the 11e.(2) cell were sampled routinely prior to May, 1994. Some had sampling periods that began as far back as January 1991 and have as many as sixteen data points, others were not sampled for background until August of 1993 and have only four data points.

## 2.2 Analytical Procedures

Analyses of background groundwater samples were performed by American West Analytical Laboratories (AWAL) of Salt Lake City, Utah. All arsenic analyses were performed using Method 7060, which employs a graphite furnace atomic absorption (GFAA) technology.

Concentrations of arsenic in monitoring wells was observed to be very low, commonly greater than the detection limit (DL) of the analytical instrumentation. However, due to the high salinity of the groundwater samples which results in significant interference's, analytical results often fell below the Practical Quantitation Limit (PQL). Thus, the analytical results would be anticipated to have large uncertainties associated with them, on the order of twenty to twenty-five percent.

## 2.3 Evaluation of Established Background

After all background data had been collected, it was statistically analyzed to determine a regulatory limit for background concentrations of arsenic at the site. The procedure followed (by the Nuclear Regulatory Commission, NRC) for this determination generally included

- review of data for distribution characteristics (Gaussian or log normal)
- deletion of statistical outliers
- calculation of the statistical mean
- calculation of the associated standard deviation
- calculation of a representative background concentration for each well as the mean plus two standard deviations

The present review has confirmed that for samples collected and analyzed prior to May 1994

- normal Gaussian distributions are applicable
- outliers were correctly identified and discarded
- standard deviations and their addition to calculated means are consistent

Groundwater data collected for each well was determined to be statistically different from other site wells and background conditions for the site were established on an individual well basis. This observed wide variability could be attributable to either

- significant variability of site specific arsenic geochemistry in the playa lake sediments associated with the site
- significant analytical variability for analytical results due to high uncertainties and interference's resulting in analytical results that, being between the DL and PQL, may only be considered qualitative



**Aquifer Geochemistry****Adrian Brown****2.4 Current and Future Activity**

Although regulatory background concentrations for wells at the 11e.(2) cell were calculated in a procedurally and statistically correct fashion, there may be a need to revisit the issue. As discussed below, there is a strong potential that perceived exceedences in recent times may actually be attributed to background processes. Therefore, it may prove necessary to recalculate background concentrations for each monitoring well on site to reflect new data that will produce higher background regulatory limits.

**3. EFFECTS OF CONTRACT LABORATORY**

Although AWAL performed all analyses that established background and initial phases of operational monitoring through January 1996, they are not responsible for analytical results collected for most of 1996.

**3.1 Change in Contract Laboratory**

In January of 1996, Envirocare terminated its contract with AWAL in favor of Mountain States Analytical Lab (MS). This change was driven by concerns on the part of Envirocare related to quality assurance issues of data produced by AWAL. Similar concerns were raised by the U.S. Environmental Protection Agency (EPA). After changing the service provider, the initial samples analyzed by MS indicated exceedences for arsenic while the previous quarter's results were below threshold concentrations.

In response, Envirocare initiated a program to submit splits of monitoring well samples for the remainder of 1996 to both MS and AWAL. This action was taken in support of an internal quality control/quality assurance (QA/QC) program to assess the consistency between laboratory performance to provide an evaluation of the comparison of AWAL background data and current MS performance.

**3.2 Contrast in Analytical Procedure**

Though the change in analytical laboratory services was driven by issues of quality control, it also resulted in a change of procedure. QA/QC efforts on the part of MS resulted in a change of analytical protocol and Method 7060 (GFAA) was discarded in favor of Method 7061, a hydride generation atomic absorption (HAA) technique. This change diminished interference's from the saline matrix associated with the groundwater at the 11e (2) cell ( $\geq 20,000$  ppm chloride). This provided better sensitivity and lower PQL's.

The split samples analyzed by both AWAL and MS contrast markedly. For a series of samples collected November 18-22, 1996, the Utah Department of Environmental Quality (UDEQ) also analyzed a split sample for several wells. UDEQ used an inductively coupled plasma emission (ICP) technique for analysis of arsenic. Figure 1 below illustrates the variability in the analytical results from each source.



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As Figure 1 indicates, MS reports analytical results that are consistently higher than AWAL, and AWAL's results are consistently below the background concentration for wells reported. This implies that a direct comparison of MS data for current conditions at the site might not be fairly compared to background concentrations established using AWAL data. As illustrated in Figure 2 below, there is a good correlation between the results reported by AWAL and those by MS, with the latter being about 1.5 times higher on average.

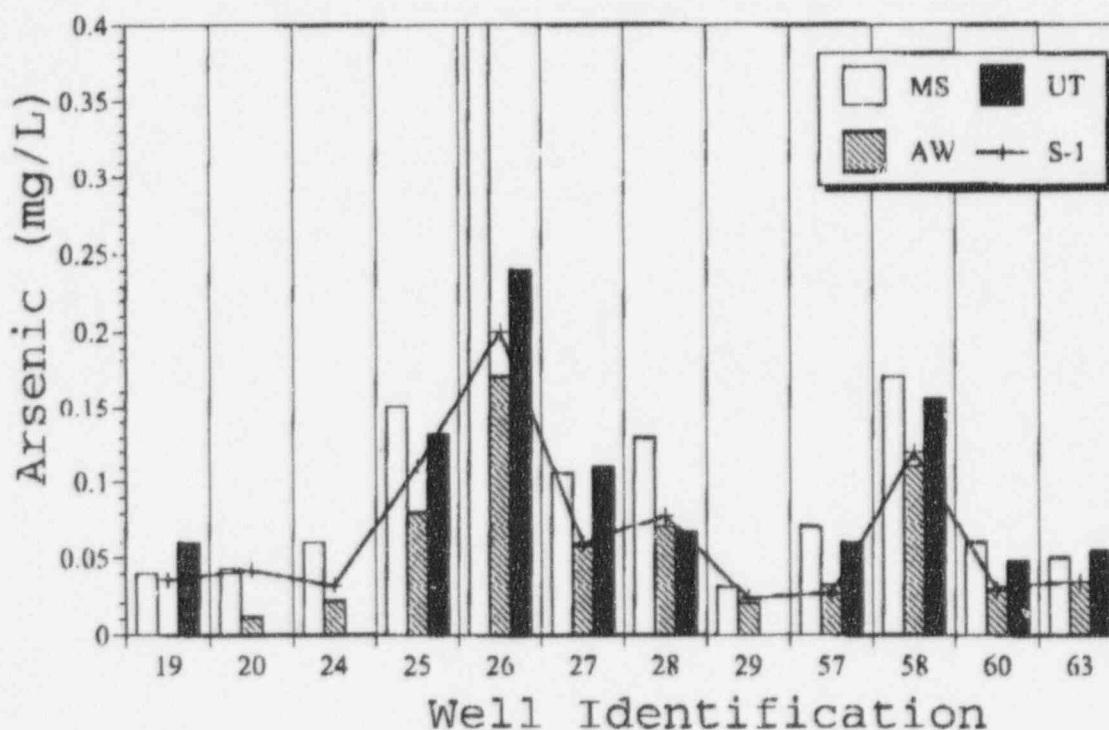


Figure 1. Comparison of lab split samples.

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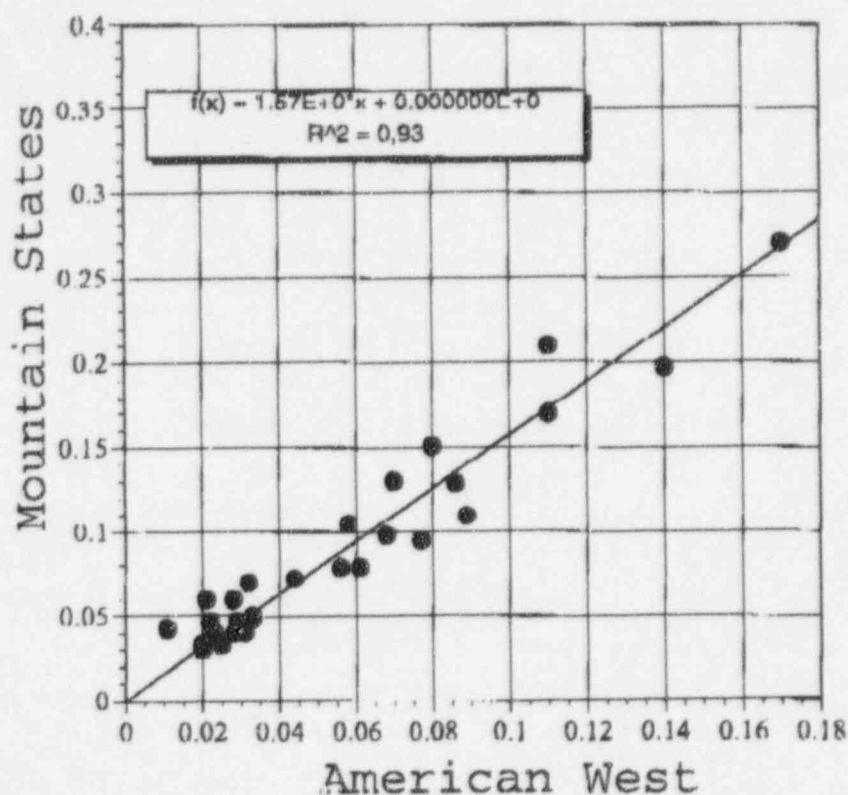


Figure 2. The correlation between analytical labs.

Increasing background concentrations determined by AWAL by twenty five percent (the estimated uncertainty in the background data collected), will make up the fifty percent increase required to reconcile the data from the two labs.

### 3.3 Implications for Established Background

Figure 2 suggests that background concentrations, to be compared directly to the current MS data may require revision and may be principally due to the differences in analytical methodologies. The least squares regression of the relationship between the two labs can be used to produce alternative background concentrations for monitoring wells that may be more representative of the concentrations that would have been observed had MS been performing the analytical work from the beginning. Table 1 reports the results of that exercise and shows the current background concentration for each well and the revised value based on the best fit equation of Figure 2. Values reported in italics in Table 1 for corrected background exceed maximum contaminant levels for arsenic of 0.05 mg/L.

Using the corrected background concentrations for arsenic in each of the monitoring wells excludes most exceedences. However, data for GW-57 still appear to be exceedences with the corrected background

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figures. This suggests that there may be geochemical reasons for these observations related to specific background processes, as distinct from analytical processes.

*Table 1. Present and corrected background concentrations.*

WELL IDENTIFICATION	TABLE S-1 BACKGROUND	CORRECTED BACKGROUND
19A	0.036	0.057
20	0.042	0.066
24	0.032	0.050
25	0.11	0.17
26	0.2	0.31
27	0.059	0.093
28	0.076	0.12
29	0.023	0.036
57	0.026	0.041
58	0.12	0.19
60	0.029	0.046
61	0.034	0.053

#### 4. CURRENT CONDITIONS

Whether or not present background concentrations for arsenic in monitoring wells are corrected for analytical differences between the present contract lab (MS) and the lab which collected background data (AWAT), it appears as though several site-specific conditions may argue against the 11e.(2) cell being the source of currently observed arsenic in groundwater. Thus, it is arguable that current observations may indeed be attributable to background and could be factored into a recalculation of the background concentrations at the site for each well.

##### 4.1 Time of Travel

The regional hydrologic gradient is relatively low and advective transport of contaminants derived from the 11e.(2) is expected to be correspondingly slow. The site-wide hydrologic gradient is approximately 0.002, the hydraulic conductivity is on the order of  $5.3 \times 10^{-4}$  cm/s and the porosity is 0.29.

Correspondingly, the groundwater velocity is about 0.56 m/yr. This velocity appears to be inconsistent with the time of travel required to move arsenic from the location of the placed waste to GW-19A

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(farthest away showing an apparent exceedence). GW-19A is about 730 meters away from placed waste and it has been on the order of three years since the first waste was deposited in the cell. Thus, advective movement would have to be 243 m/yr to reach this monitoring well in the allocated time, 435 times greater than the site-wide hydrologic velocity.

Similarly, other monitoring wells report the appearance of arsenic in time frames that too short to attribute to the transport by groundwater. In addition, the noted appearance of arsenic in virtually all site wells at the same time would argue strongly against groundwater transport. Firstly, because there are different distances between wells and placed waste and, secondly, because some of the affected wells are upgradient from the 11e.(2) cell (albeit a slight gradient).

In addition to the inordinately high travel times required to travel from source to monitoring site, other energetic barriers exist. Due to the infiltration of relatively clean surface water into a previous surface excavation, a groundwater mound is present that lies directly in the path of travel from the 11e.(2) cell and monitoring locations. The presence of this groundwater mound requires that any contaminants that might be hypothetically be released from the cell travel locally *up hydrologic gradient* to reach most monitoring sites.

The unreasonableness of the travel times required for contaminant transport and that exceedences for arsenic have occurred almost simultaneously, despite generally having to travel against the hydrologic gradient is good reason to think that a more fundamental geochemical mechanism for arsenic appearance is operative (assuming no systematic influences of the analytical procedures described above).

#### **4.2 The Changing Groundwater Table**

Changes in the background arsenic concentration for wells could be produced if the groundwater table became elevated or if the local flow direction shifts. Elevating the groundwater table would cause groundwater to contact solids previously in the unsaturated vadose zone to potential release arsenic. The variability in arsenic concentration for wells site wide suggests that flow direction shifts which cause water to flow to a well from a somewhat different source area could lead to changes in concentration.

Over the past several years, there has been a gradual increase in the groundwater table elevation observed in monitoring wells site-wide. Figure 3 illustrates the rise in water table elevation for wells located on the western margin of the 11e.(2) cell. It is not clear, however, if these solids can act as a source of arsenic or not, although this has been suggested as a possible mechanism. For focus, Figure 4 illustrates the groundwater elevation rise in GW-57 and also plots the associated arsenic concentration.

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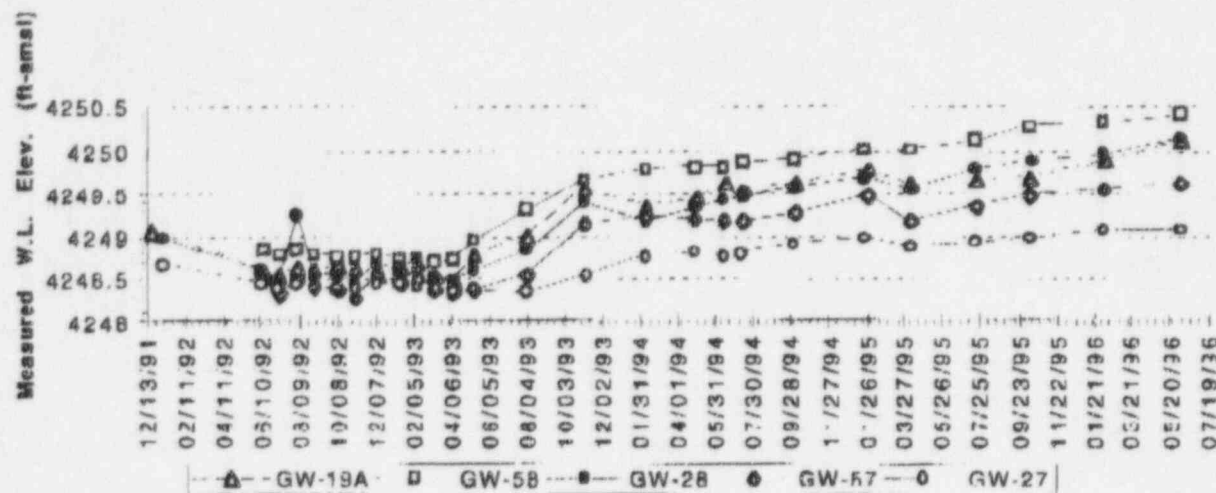


Figure 3. Groundwater elevation rise west of 11e.(2).

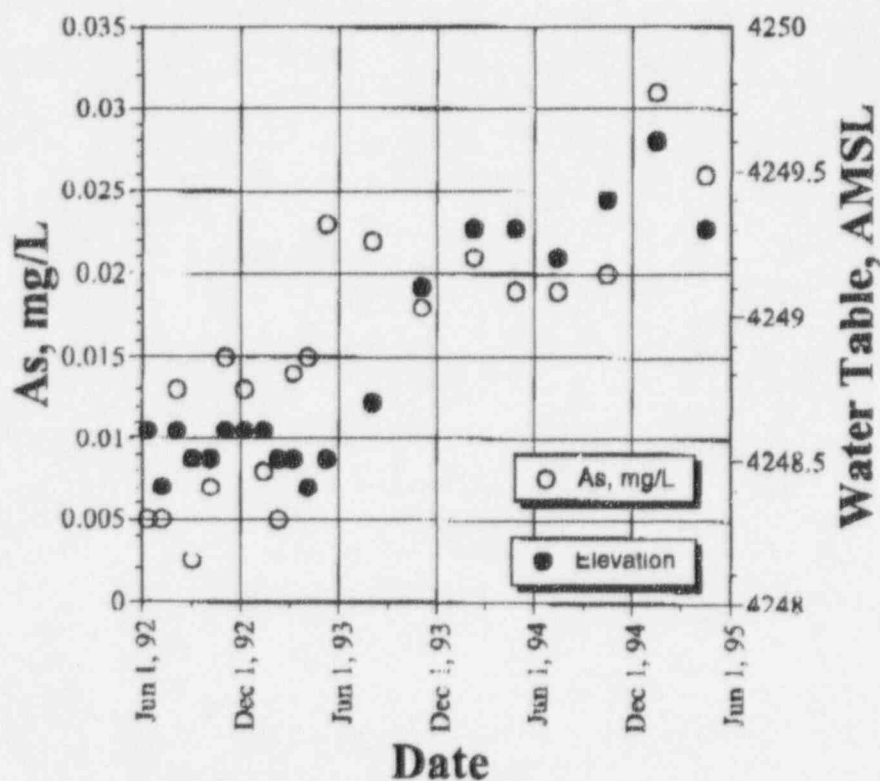


Figure 4. Arsenic concentrations and water level for GW-57.

From Figure 4 it would appear that groundwater elevation and arsenic concentration are fairly closely linked. However, this relationship does not appear to be as strong when directly graphing arsenic against the corresponding water level, as is shown in Figure 5.

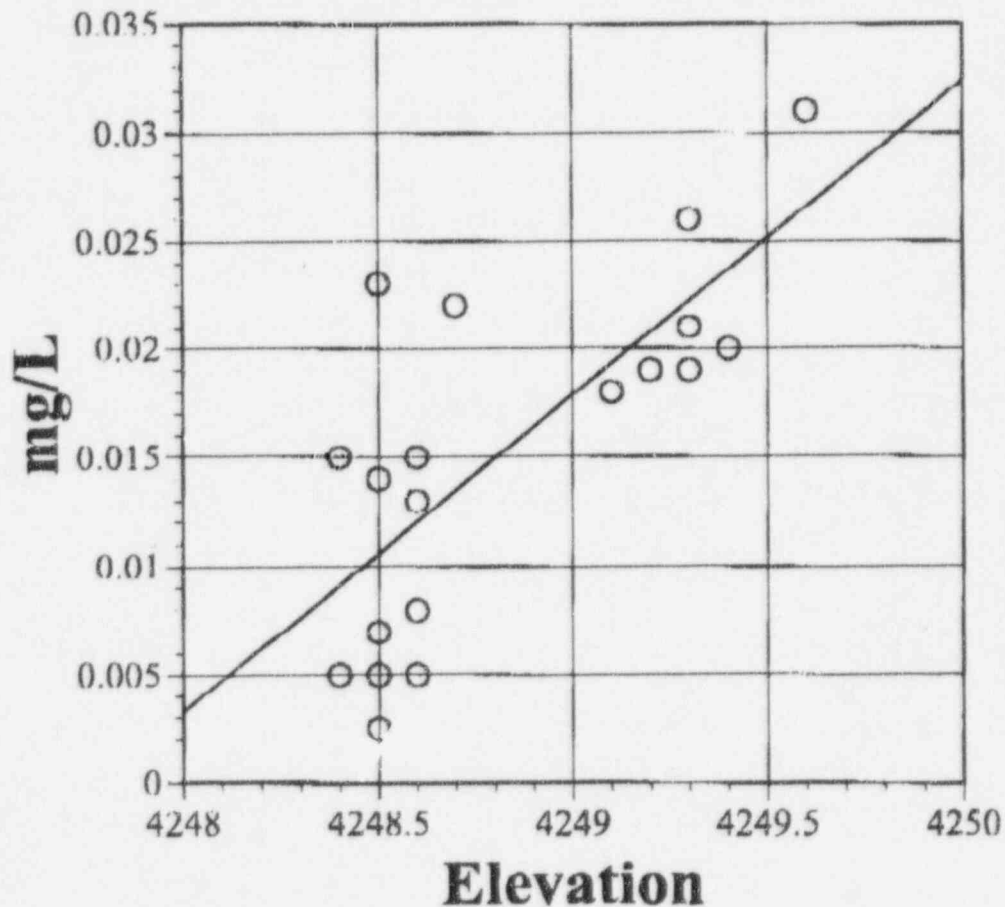


Figure 5. Direct correlation of arsenic and elevation for GW-57.

As can be seen, the correlation is not overly strong. Ignoring the data representing the highest groundwater elevation and highest arsenic concentration, it would appear that there is only a minor correlation. However, with the uncertainties associated with analytical procedures, the trend, or lack thereof for arsenic is not as well constrained as it could be.

### 4.3 Arsenic in Placed Waste

The mass of waste placed in the 11e.(2) cell and its associated arsenic concentration were reviewed to determine if sufficient arsenic occurs in the waste to account for monitor well observations. Most waste has had arsenic concentrations that were below the limits of detection. Several allotments had as much as



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5 mg/kg. Typical average concentrations of arsenic in soils can range from 0.1 to 40 mg/kg worldwide. Therefore, the material placed in the 11e.(2) cell to date does not represent a material that is unusually rich in arsenic. It does appear, however, that sufficient arsenic occurs in the placed waste to account for the total amount of arsenic that appears to be present in the local groundwater to a depth of about 10 feet.

**4.4 Present and Future Activity**

The correlations presented here for GW-57 will continue to be extended to other wells proximal to the 11e.(2) cell. More thorough evaluations of the relationship between groundwater elevation and the observed arsenic concentration need to be completed before any conclusive statements can be made as to the influence of this process. Particularly, the availability of arsenic in the local solids will be quantified.

**5. CONCLUSIONS**

This preliminary evaluation of apparent exceedences for arsenic leads to several conclusions and suggests several routes of investigation for future activities. All the activities are focused on providing a scientific basis for understanding the occurrence and movement of arsenic proximal to the 11e.(2) cell.

- The data produced by AWAL is inconsistent with that produced by MS, with the latter routinely fifty percent higher than the former. This means that the data collected by MS cannot be directly compared to AWAL data collected for background. Submission of split samples to a laboratory that specializes in the analysis of high salinity solutions may do much to take steps toward resolving the discrepancies.
- The local groundwater linear velocities are simply not great enough to conduct dissolved constituents from the location of the placed waste to the point of observation at monitoring wells.
- The change in local groundwater elevation may have contributed to arsenic loading at the well locations from solids previously located in the vadose zone. However, data will need to be collected to demonstrate that sufficient arsenic occurs in these solids and that leaching characteristics are consistent with fluxes required to produce observed groundwater concentrations.
- Groundwater mounding proximal to the 11e.(2) cell may have caused local changes in groundwater flow direction that bring higher arsenic solution to well locations that previously had lower concentrations. An analysis of the change in arsenic concentration for all wells will be necessary to evaluate this hypothesis.