Department of Energy
Office of Legacy Management

March 10, 2008

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Dear Mr. Fischer and Mr. Schneider:

SUBJECT: **Evaluation of Aqueous Ions in the Monitoring Systems of the On-Site Disposal Facility (OSDF)**

Enclosed please find the subject report. Issue of this report fulfills an agreement that was made between the Department of Energy, U.S. Environmental Protection Agency (EPA), and Ohio EPA at the March 8, 2005 TIE meeting, to conduct a common ion study within the Leachate Collection System (LCS), Leak Detection System (LDS), and Horizontal Till Wells (HTW) of the OSDF. Monitoring to support the study was initiated in May 2005 and completed last year. The objective of the study was to determine which ions could be used as useful indicators of leachate leaking from the LCS to the LDS, or from the LDS to the HTW.

The report concludes that no one ion can serve as a leak indicator for all cells of the disposal facility, but useful indicator ions for specific target horizons of each cell are identified. For the indicator ions identified, baseline data are sufficient to establish control charts.

Fluid volume appears to be the key monitoring parameter to indicate the potential for leachate migration from the OSDF, and the sampling of and analysis for indicator ions are useful only if the hydraulic conditions permit leachate to migrate.

We look forward to discussing the report with you as part of our efforts to refine the OSDF post-closure monitoring program. If you have any questions or require any additional information, please call me at (513) 648-3148.

Sincerely,

Jane Powell

Jane Powell
Fernald Site Manager
DOE-LM-20.1

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DOE–LM/1591–2008

Fernald Site

Evaluation of Aqueous Ions in the Monitoring Systems of the On-site Disposal Facility

March 2008

U.S. Department of Energy

Office of Legacy Management

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Fernald Site

Evaluation of Aqueous Ions in the Monitoring Systems of the On-site Disposal Facility

March 2008

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for the U.S. Department of Energy Office of Legacy Management, Grand Junction, Colorado

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Executive Summary

A comprehensive geochemical and statistical evaluation was performed on the reported concentrations of 50 aqueous ions in fluid samples collected from the on-site disposal facility (OSDF) leachate collection system (LCS), leak detection system (LDS), and underlying horizontal till wells (HTW). Samples were collected quarterly (between May 2005 and March 2007) from each of the three horizons in the eight cells that constitute the OSDF, if sufficient fluid was available to obtain a sample. The fluid yield to the Cell 2 LDS was negligible after the initial sample was collected in May 2005, and this single sample represents the available data set for this location.

Mineral solubility plays a significant role in controlling the range of values observed for some major ions (i.e., ions with the highest concentrations). Calcite, dolomite, and gypsum are present in the glacial till and in the crushed carbonate gravel that lines the LCS and LDS horizons. When rainwater contacts these minerals, dissolution occurs, and calcium, magnesium, carbonate, and sulfate ions are released into the fluid phase. Additionally, salts (e.g., calcium chloride and sodium chloride) that are spread to deice road surfaces dissolve and release calcium, sodium, and chloride ions into the fluids. A geochemical analysis of trends on ion variation diagrams (e.g., calcium vs. carbonate) will reveal the role of mineral solubility on the fluid composition, and ions may be dismissed as useful indicator ions for leachate migration when the controlling mineral phase is present in all three monitoring horizons.

For an ion to serve as a useful indicator ion of leachate leaking from the LCS to the LDS, or from the LDS to the HTW, it must be present at a much higher concentration in the source horizon (LCS or LDS), relative to the target horizon (LDS or HTW, respectively). This is due to the very small volume of source fluid that migrates to the target horizon (relative to the volume of fluid in the target horizon) and the mathematics behind calculating an ion concentration in a mixture of two fluids. In this evaluation, a conservatively high source-volume/target-volume ratio (1 gal LCS/10 gal LDS) was used to evaluate the ion concentrations, and this ratio indicates that the ion concentration in the source must be at least 4 times greater than that in the target horizon if the ion is to be used as an indicator ion. This analysis is conservative because it is more probable that the source-volume/target-volume ratio will be lower, which implies that the lowest source concentration must exceed 4 times the target horizon.

Screening the 50 potential ions with the noted geochemical evaluation yielded five ions that may serve as adequate indicator ions. Uranium and manganese are the best ions for monitoring leachate migration from the LCS to the LDS, and sodium, boron, and sulfate show the most potential for identifying leachate movement from the LDS to the HTW. Per the statistical protocols established for the OSDF monitoring systems, a control chart to evaluate leachate migration cannot be constructed unless the following three assumptions are true:

1. The data are normally distributed or can be transformed to a normal distribution (e.g., log normal).
2. Baseline data are uncontaminated by the OSDF and reflect chemical steady-state conditions.
3. Sample data are statistically independent (i.e., no serial correlation).

For Assumption 1, the Shapiro-Wilks Test of Normality and Dixon's Test for Outliers were performed to demonstrate that the data set had a normal or log normal distribution that was free of outlier values. The Mann-Kendall Trend Analysis and Sen's Slope Analysis were performed to determine if baseline data satisfied Assumption 2. Finally, Assumption 3 was tested using the Rank von Neumann Ratio Test.

Results from the statistical analysis indicate that no ion can serve as a universal leak indicator for all cells because trends occur in the data sets or the data show serial correlation (i.e., Assumptions 2 and 3 do not hold). None of the ions can be used to evaluate leachate migration from the LDS to the HTW in Cells 1 and 5. Also, as noted in the opening comments, there are insufficient chemical data to evaluate leachate migration from the LCS to the LDS in Cell 2. However, lack of water yield in the Cell 2 LDS provides an excellent indication that there is little or no leachate migration into the Cell 2 LDS. Useful ions for the target horizons of each cell are summarized below.

	Target Horizon	Indicator Ion
Cell 1	LDS	B, Mn
	HTW	None
Cell 2	LDS	Fe
	HTW	Mn, SO_4
Cell 3	LDS	Mn, U
	HTW	Na
Cell 4	LDS	U
	HTW	Na
Cell 5	LDS	Mn
	HTW	None
Cell 6	LDS	Mn, U
	HTW	Na
Cell 7	LDS	Mn, U
	HTW	U
Cell 8	LDS	U
	HTW	B

For the indicator ions identified for each target horizon, baseline data are sufficient to establish a control chart. However, the evaluation of leachate migration from the source to the target horizon must consider fluid dynamics in addition to chemical indicators. For example, if uranium in the HTW of Cell 7 begins to increase, and if one tracks this increase with a control chart, then eventually the chart will indicate that leakage is occurring, but this conclusion is reached independently of volume monitoring data for the overlying LDS in Cell 7. If no significant fluid is reaching the LDS of Cell 7, there is no hydraulic head to push the fluid into the HTW, and the conclusion of the control chart—that leachate is migrating—would be false. Therefore, the most important indicator of the potential for leachate migration is increases in fluid volume from the LDS.

Conclusions that can be drawn from this study are as follows:

1. Only a limited number of ions can serve as indicator ions because very few ions have concentrations in the source horizon that exceed their concentration in the target horizon by at least a factor of 4.
2. Many of the indicator ions in the target horizons show concentration trends or serial correlation, which precludes the use of control charts because steady-state conditions have not been established in the fluid-solid system.
3. Fluid volume is the key monitoring parameter to indicate the potential for leachate migration, and the sampling of and analysis for indicator ions are useful only if the hydraulic conditions permit leachate to migrate.

End of current text

1.0 Introduction

Beginning in May of 2005, water samples collected from the leachate collection system (LCS), leachate detection system (LDS), and horizontal till well (HTW)—successively deeper monitoring levels associated with each cell in the On-Site Disposal Facility (OSDF)—were analyzed for a comprehensive list of ions (Table 1–1) to establish the chemical composition of the fluids. Additionally, the gravel used to construct the LCS and LDS was leached with deionized water for 120 days to estimate a steady-state composition for rainwater contacting the gravel during construction activities. Fluid samples from this 120-day study were evaluated for the same ions in Table 1–1, as they must be considered natural source terms when evaluating common ions that are useful indicators of potential leachate leakage from the cells.

Table 1–1. Aqueous Ions Evaluated for the OSDF Monitoring Systems

Principal Components and Major Ions		
pH	Bicarbonate[a] – HCO_3	Calcium – Ca
Eh	Chloride – Cl	Magnesium – Mg
Total dissolved solids	Silica – SiO_2	Potassium – K
	Sulfate – SO_4	Sodium – Na
Minor Ions		
Boron – B	Iron – Fe	Total organic carbon – TOC
	Strontium – Sr	
Trace Ions		
Barium – Ba	Fluoride – F	Nickel – Ni
Cobalt – Co	Lithium – Li	Palladium – Pd
Copper – Cu	Manganese – Mn	Uranium – U
	Molybdenum – Mo	Zinc – Zn
Undetected Ions		
Aluminum – Al	Cesium – Cs	Selenium – Se
Ammonia – NH_3	Gold – Au	Silver – Ag
Antimony – Sb	Lead – Pb	Thorium – Th
Arsenic – As	Mercury – Hg	Tin – Sn
Beryllium – Be	Nitrate/nitrite – NO_3/NO_2	Total organic halogens – TOX
Cadmium – Cd	Phosphorous – P	Vanadium – V
Chromium – Cr	Platinum – Pt	Zircon – Zr

[a]Derived from alkalinity measurement

Ions in Table 1–1 were selected based on their common occurrence in surface waters and groundwaters (e.g., bicarbonate [HCO_3], sulfate [SO_4], calcium [Ca], magnesium [Mg]), classification as a constituent of concern (e.g., boron, [B], total organic halogens [TOX], uranium [U]), and their availability to be analyzed by the selected method (e.g., every element that could be analyzed by inductively coupled plasma/mass spectrometry ICP/MS was reported). This comprehensive list allowed a thorough review of the fluid chemistry to identify potential indicator ions for assessing the integrity of the OSDF liner systems.

Table 1–1 divides the ions into the following categories: major, minor, trace, and undetected. Major ions are defined as those whose concentration exceeds 10,000 μg/L (10 mg/L) in most samples. Minor ions have concentrations less than major ions and generally exceed 1,000 μg/L

(1 mg/L). Trace ions are present in the fluids at concentrations less than 500 µg/L (0.5 mg/L). Finally, undetected ions are those that were not detected in the majority of samples collected from a cell horizon (e.g., LCS, LDS, HTW) and from which a useful comparison could not be made.

1.1 Charge Balance

Major ions are the principal contributors to charge balance in the fluid. A fluid must maintain a zero charge balance; that is, the charge associated with cations (positive ions) must equal the charge of the anions (negative ions). The general quality of the analytical results can be evaluated by calculating the charge imbalance of the solution. Ideally, the sum of all cations and anions should yield a charge imbalance of zero. However, analytical accuracy is never 100 percent for all ions, and a charge imbalance will occur in the samples. As a rule of thumb, analytical results are acceptable if the sample has a charge imbalance within ± 5 percent. This criterion has been applied to the analytical results in this report, and approximately 25 percent of the sample results were rejected due to excessive charge imbalance (Figure 1–1).

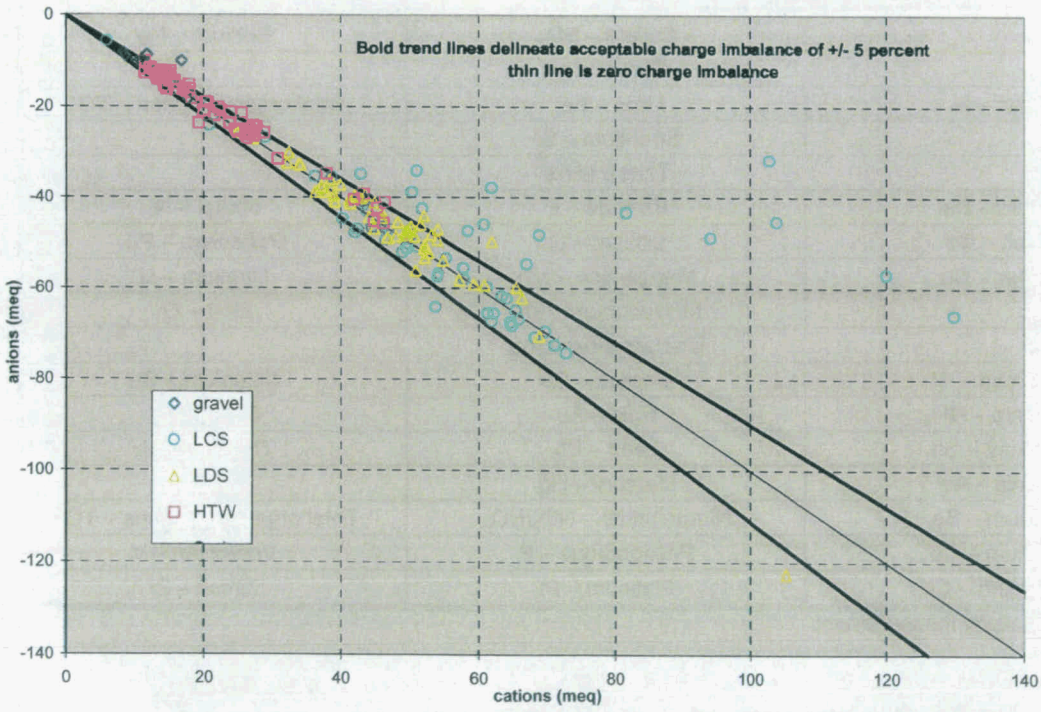

Figure 1–1. Charge Imbalance in Gravel, LCS, LDS, and HTW Fluids

Most of the rejected samples (85 percent) had a positive charge imbalance. This suggests that fine suspended solids were in the samples pulled for metal analysis. When the sample for metal analysis is preserved with acid, the low pH dissolves suspended material and increases the concentration of ions in solution. This acidified sample is no longer in charge equilibrium with the sample that was collected for general chemical analysis. Samples pulled for general chemical analysis, which provides concentration data for the anions (e.g., HCO_3, chloride [Cl], nitrate [NO_3], SO_4), are not acidified because the acids used to preserve samples contain the anions of interest (e.g., hydrochloric acid [HCl], nitric acid [HNO_3], sulfuric acid [H_2SO_4]). Therefore,

when the acidified sample is analyzed for metals, which generally form cations in solution, the extra cations produced by the dissolution of the suspended solids elevate the cation charge, relative to the anions in the general chemistry sample.

Most of the rejected samples in Figure 1–1 were collected from the LCS, which is the monitored horizon in contact with the waste placed in the cell. The LCS horizon has the greatest potential to contain suspended particulate in the fluid samples because part of this system remains open during the filling of the cell. This open system is also reflected in the ion concentration data (discussed below), which show a wide range of values for many constituents.

1.2 Fluid Mixing

When two fluids with different concentrations of a given ion are mixed together, the ion concentration in the mixture is determined by the following equation:

$$(\mu g/L)m = \{[(\mu g/L)_1 * \text{total } L_1] + [(\mu g/L)_2 * \text{total } L_2]\}/(\text{total } L_1 + \text{total } L_2)$$

where $(\mu g/L)_1$ and $(\mu g/L)_2$ are the mirograms of a given ion in a liter of Solution 1 and 2, respectively, and total L_1 and total L_2 are the total number of liters of each solution.

An examination of the equation reveals that if one of the solutions has a much greater volume, the concentration of the ion in the solution with a smaller volume must be much higher if the mixture is to have a concentration distinctly different from the solution with the greater volume.

For example, assuming 100 L Solution 1 and 10 L Solution 2, $(\mu g/L)_1$ equals 10 and $(\mu g/L)_2$ equals 20. Solving the above equation yields a mixture concentration of 11 $(\mu g/L)_m$. Although 11 is distinctly different from the concentration of 20 in Solution 2, it is not significantly different from the concentration of 10 in Solution 1 (NOTE: *Significantly different* is defined here as a mixed concentration that differs from the initial concentration plus or minus the laboratory uncertainty). EPA laboratories general state that the accuracy of the reported result is ± 20 percent. If the reported ion concentration is 10 µg/L, ± 20 percent implies that the accepted range for this sample is 10 ± 2 µg/L. Therefore, the true result for Solution 1 lies between 8 and 12 µg/L, and the mixture result of 11 is not significantly different from the concentration in Solution 1. The ion concentration in Solution 2 needs to be 4 times greater than that in Solution 1 before a significant detection is observed in the mixture.

The importance of the above example is readily seen when we evaluate leachate leakage from the OSDF cells. Stratigraphically, the LCS horizon is above the LDS, and the LDS is above the HTW. When a higher horizon (source) leaks to a lower horizon (target), the leakage volume is generally much smaller than the volume of fluid in the lower horizon. As noted in the example above, if the leakage volume is 1/10 of the volume of fluid in the lower horizon (a generous leakage volume), the ion concentration in the leakage volume must be at least 4 times as great as the ion concentration in the lower horizon if the mixture concentration is to be significantly different from the ion concentration in the lower horizon.

The relationship between the volume ratio of the source and the target, and the concentration ratio of the source and the target, is shown in Figure 1–2, which indicates that as the volume ratio decreases, the concentration ratio must increase. Therefore, for a more common case of very

little leachate leakage (say, 1/1000 of the target volume), the concentration in the source leachate would have to be 230 times higher than the target concentration if it is to be detected in the target horizon. That is, the higher the concentration ratio, the greater the probability that the leachate will be detected in the source horizon.

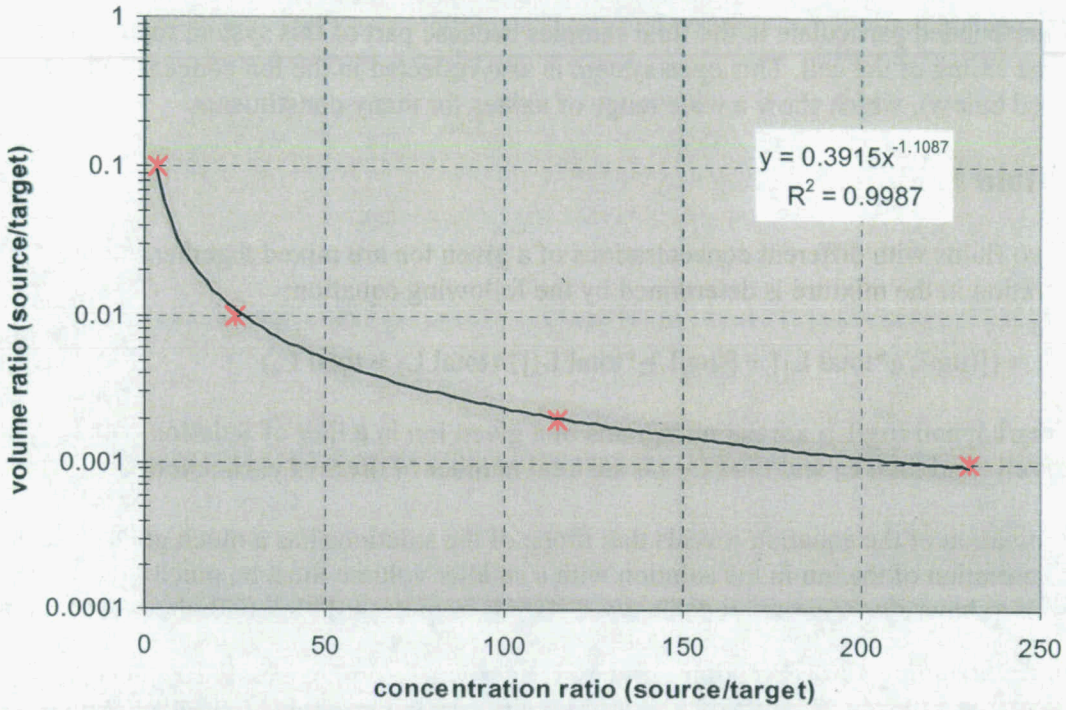

Figure 1–2. Volume and Concentration Ratios Needed to Detect the Source in the Target Horizon

For this review, ions will be screened as potential indicator ions if the ion concentration in the source fluid is at least 4 times greater than the fluid in the target horizon, assuming the source volume is 1/10 of the volume in the target horizon. There are no field data to support a selection of 1/10 as the screening volume ratio, but a larger ratio (e.g., 1/2) seems less probable and more difficult to justify when considering the engineered properties of the liner materials (i.e., the massive failure of the liner is highly improbable).

2.0 Assessment of Ion Trends

Many dissolved ions have their concentrations controlled by dissolution and precipitation of mineral phases (e.g., Ca, Mg, and CO_3 in calcite and dolomite), adsorption and desorption from the surface of clay minerals (e.g., potassium [K], sodium [Na]), and surface runoff from anthropogenic sources (e.g., calcium chloride [CaCl2] used for deicing road surfaces). Additionally—and this is most applicable to the LCS samples—large storm-events can dilute the ion concentrations in surface waters, and extended dry weather can concentrate the ions by the evaporation of water. All of these processes interact dynamically to produce the fluid compositions observed in the OSDF's monitoring systems.

For the LCS, LDS, and HTW, carbonate minerals (i.e., calcite and dolomite) are the dominant solids in contact with the fluid in these horizons. The glacial till surrounding the HTW is composed of 40 to 70 percent carbonate minerals (dolomite and calcite), and the gravel used to construct the LDS and LCS was obtained from crushed dolomitic limestone. Additionally, the majority of material placed as waste in the OSDF is contaminated glacial till, which contains the noted 40 to 70 percent carbonate minerals. Therefore, the Ca, Mg, and CO_3 ions, produced by the dissolution of carbonate minerals, are present in all horizons.

Dissolution of waste materials in the OSDF may produce fluid compositions in the LCS that are distinctly different from water in the LDS and HTW horizons below the LCS, and these differences are the basis for identifying which common ions in the monitoring horizons can be useful as indicators of a leaking liner system. For example, the large amount of structural steel placed in some cells will result in elevated iron (Fe) levels in the LCS when the dissolved oxygen levels in the cell decrease with time (i.e., the redox potential, or Eh, decreases with time). Likewise, U is the principal contaminant on the glacial till placed in the cell, and U levels in the LCS will be elevated relative to the LDS and HTW. A convenient way to evaluate the ion levels in the different horizons is to plot ion variation diagrams.

2.1 Major Ions

Figure 2–1 plots Ca plus Mg versus HCO_3 to examine how carbonate minerals control the fluid composition. The concentrations have been converted to mmol/L to aid in the interpretation of trends that arise from the dissolution of minerals. For example, the dissolution of carbonate minerals will produce equal moles of Ca plus Mg and CO_3 (note that the CO_3 is instantly converted to HCO_3 at near neutral pH). Therefore, if carbonate minerals are the only contributing phases to the solution chemistry, a plot of Ca+Mg versus HCO_3 should yield a sample trend along the calcite-dolomite dissolution line. However, most samples plot above the dissolution line, which indicates that other sources are contributing Ca and Mg ions to the fluid.

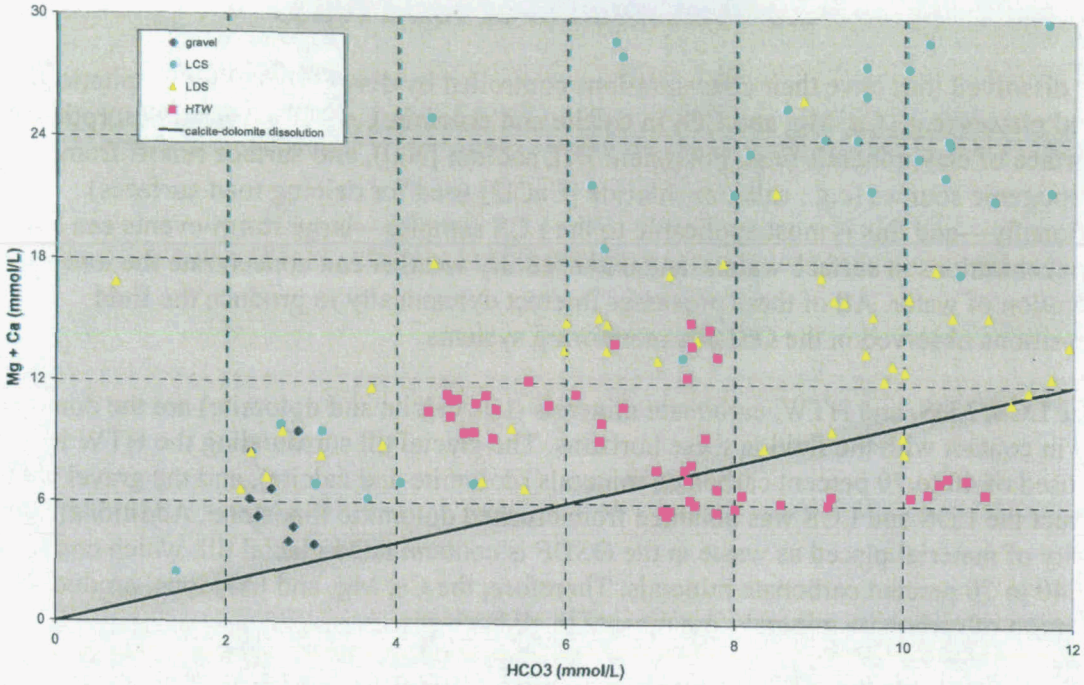

Figure 2–1. Variation of Magnesium plus Calcium as a Function of Bicarbonate Concentration

The scatter of data points in Figure 2–1 shows significant overlap of the LCS, LDS, and HTW fluids; this overlap is expected because carbonate minerals exist in all horizons. Because the ions are present over similar concentration ranges in all horizons, they are not suitable indicator ions for leakage of leachate from the cells. This is confirmed in Table 2–1, where the average HCO_3, Ca, and Mg concentrations for each horizon are tabulated to demonstrate that no adjacent horizons (i.e., LCS and LDS; LDS and HTW) have HCO_3, Ca, or Mg concentrations that differ by a factor of 4 or more (see the above discussion on fluid mixing). An exception is the Mg result for 12339D, which is not an average but a single result from November 5, 2005. The reported values for this analysis are suspect, as they result in an unacceptable charge imbalance. However, this point was not omitted (contrary to the discussion above on charge balance) because it is the only sample available for 12339D. Additional samples from 12339D were not collected due to the lack of fluid in the LDS for Cell 2.

The dolomitic limestone rock that was crushed to provide gravel for the LCS and LDS was leached with deionized water, and the fluid compositions in Figure 2–1 do not trend along the carbonate dissolution line. This is due to the presence of trace amounts of sulfate minerals in the carbonate rock. All carbonate rocks contain some sulfate minerals, and Ca and Mg are the principal elements associated with the sulfate minerals. Therefore, when carbonate rocks are dissolved, the major ions in solution will be Mg, Ca, HCO_3, and SO_4.

Table 2–1. Average Concentrations for Major Ions in the OSDF Monitoring Horizons Data Collected May 2005 through February 2007

			Millimoles per Liter						
	Horizon	**Location**	**Cl**	**HCO_3**	**SO_4**	**Ca**	**Mg**	**K**	**Na**
Cell 1	LCS	12338C	1.08	10.5	13.1	12.8	6.35	0.463	0.686
	LDS	12338D	**3.28**	6.74	20.2	9.22	6.32	**0.431**	**19.0**
	HTW	12338	**0.714**	4.65	8.10	6.73	3.53	**0.087**	**0.867**
Cell 2	LCS	12339C	0.35	11.4	16.2	13.3	8.06	0.514	0.629
	LDS	12339D	3.16	2.62	**58.3**	11.4	**19.3**	**0.972**	**43.0**
	HTW	12339	6.03	4.85	**7.38**	7.13	**3.95**	**0.093**	**4.35**
Cell 3	LCS	12340C	0.922	10.0	18.6	15.2	7.98	0.698	1.10
	LDS	12340D	1.73	4.53	13.0	4.94	4.54	0.302	**13.8**
	HTW	12340	4.41	6.00	6.43	6.81	3.72	0.099	**2.57**
Cell 4	LCS	12341C	2.55	8.30	25.7	13.6	15.9	0.562	1.98
	LDS	12341D	2.04	6.56	**19.1**	8.53	7.49	**0.888**	**16.9**
	HTW	12341	0.899	7.30	**1.88**	3.52	2.29	**0.052**	**0.672**
Cell 5	LCS	12342C	2.31	10.3	27.2	13.0	17.8	0.586	2.81
	LDS	12342D	1.21	11.2	**13.7**	7.76	4.58	**0.301**	**15.3**
	HTW	12342	1.46	10.3	**1.31**	4.84	2.03	**0.039**	**0.861**
Cell 6	LCS	12343C	3.14	9.46	20.4	12.3	13.1	0.519	2.15
	LDS	12343D	1.56	8.67	**18.6**	8.91	6.57	**0.689**	**17.7**
	HTW	12343	0.702	7.43	**4.33**	4.26	3.23	**0.085**	**2.09**
Cell 7	LCS	12344C	2.18	5.47	16.5	9.16	9.27	0.692	2.16
	LDS	12344D	1.42	7.85	**17.9**	5.58	3.31	**0.513**	**27.8**
	HTW	12344	2.28	8.30	**1.07**	3.98	2.03	**0.062**	**0.94**
Cell 8	LCS	12345C	2.51	4.12	8.94	6.51	5.10	0.319	1.77
	LDS	12345D	1.44	7.64	**25.8**	12.6	9.64	**1.54**	14.8
	HTW	12345	29.9	7.43	**1.22**	8.81	4.42	**0.070**	14.9

Bold numbers indicate that the LCS or LDS is at least 4 times greater than the underlying horizon.

Figure 2–2 shows the dissolution trend for carbonate and sulfate minerals that contain Mg and Ca. Note that the gravel samples lie very close to and parallel the dissolution trend, which indicates that carbonate and sulfate minerals account for the Mg, Ca, HCO_3, and SO_4 ion concentrations observed in the fluid contacting the dolomitic limestone gravel. Most samples fall below the dissolution line, and this suggests that Mg and Ca have been removed by ion exchange reactions with Na and K. This is most probable for the LDS samples since they lie the greatest distance below the line. The HTW points that lie above the line indicate that Ca, Mg, or both have been added to these samples from the dissolution of non-carbonate and non-sulfate phases (e.g., CaCl2 used for road deicing). The resolution of the LCS and LDS samples into distinct fields is the result of elevated sulfate levels. Sulfate is concentrated in the fluid by evaporation, and it can also be diluted by precipitation. The addition of water to, and the evaporation of water from, the LCS samples during the construction of the cells explains the trend parallel to the dissolution line over the entire range of observed concentrations.

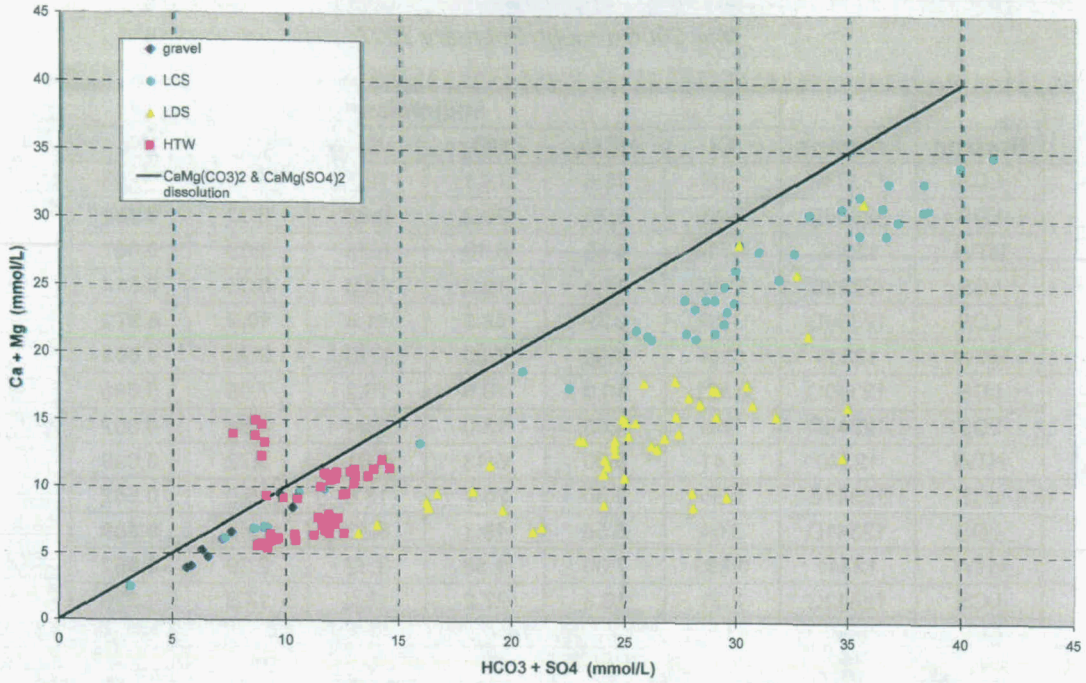

Figure 2–2. Variation of Magnesium plus Calcium as a Function of Bicarbonate plus Sulfate

On Figure 2–3, the SO_4 in LDS samples is observed to be greater than the gravel and HTW samples. The gravel samples follow the SO_4 dissolution line, indicating that SO_4 minerals continued to dissolve over the 120-day leach period (fluid samples were obtained at 30, 60, 90, and 120 days). Greater SO_4 values in the LDS samples, which represent the same rock as the leached gravel, suggest concentration of the ions by evaporation or a longer residence time for the fluid contacting the crushed rock. The elevated SO_4 values for the LDS samples indicate that SO_4 can be used as an indicator of leachate leakage from the LDS to the HTW. Table 2–1 shows that average SO_4 values in the LDS horizon for Cells 2, 4, 5, 6, 7, and 8 exceed the SO4 values in the HTW by at least a factor of 4. As noted above, the results for 12339D (Cell 2, LDS) are anomalously high, and the SO_4 result is included because it is the only result available for this horizon.

Figure 2–4 shows a dissolution line for halite (NaCl). Halite is present in carbonate rocks in trace amounts, in the waste material placed in the OSDF cells and in the environment (i.e., deicer for roads). Most LCS and HTW samples fall on or near the dissolution line, and the LDS and gravel results lie above the dissolution line, indicating another source for Na in these samples (possibly ion exchange with Ca or release from silica minerals). The Cl values are similar for most LCS, LDS, and HTW samples, the exception being the high Cl values for the HTW samples from Cell 8 and the low Cl results for the LCS samples from Cell 2. However, most of the LDS samples have Na values that are significantly higher than LCS and HTW samples. The two LDS samples with low Na values (12345D, August and November of 2005) appear to be an anomaly because later samples from this cell are much higher and agree with other LDS cells. Therefore, Na can be a useful indicator ion to monitor leachate leakage from the LDS to the HTW.

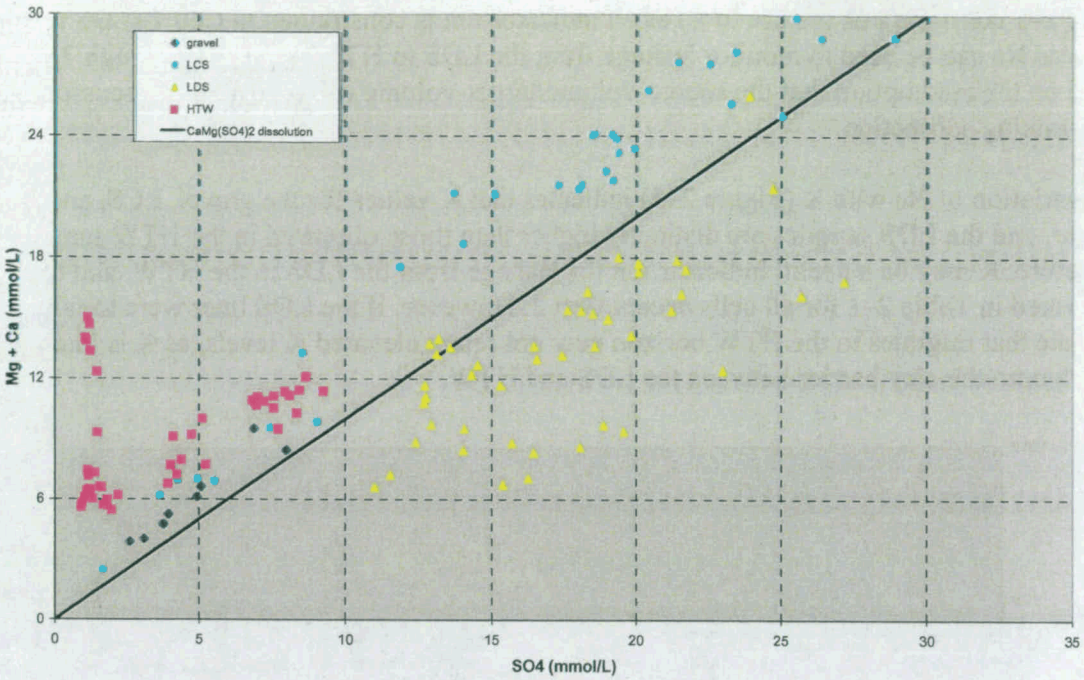

Figure 2–3. Variation of Magnesium plus Calcium as a Function of Sulfate Concentration

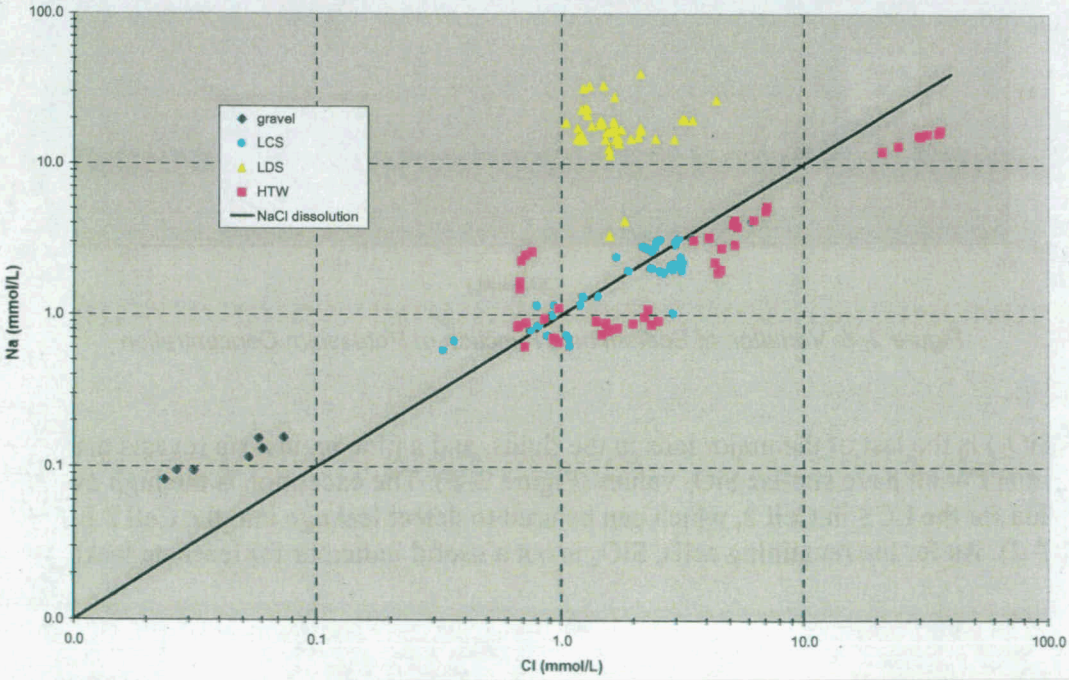

Figure 2–4. Variation of Sodium as a Function of Chloride Concentration

Table 2–1 confirms that the use of Cl as an indicator ion is constrained to Cell 1 (LDS to HTW) whereas Na can be used to monitor leakage from the LDS to HTW in Cells 1 through 7. This is based on the assumption that the source-volume/target-volume ratio is 1/10, as discussed in the fluid-mixing subsection.

The variation of Na with K (Figure 2–5) indicates that K values for the gravel, LCS, and LDS are similar, and the LDS samples are distinctly higher than those observed in the HTW samples. Therefore, K may be a useful indicator ion for leakage from the LDS to the HTW, and this is confirmed in Table 2–1 for all cells except Cell 2. However, if the LDS liner were to fail, the leachate that migrates to the HTW horizon may not retain elevated K levels, as K is likely to adsorb onto the clay barrier between the LDS and HTW.

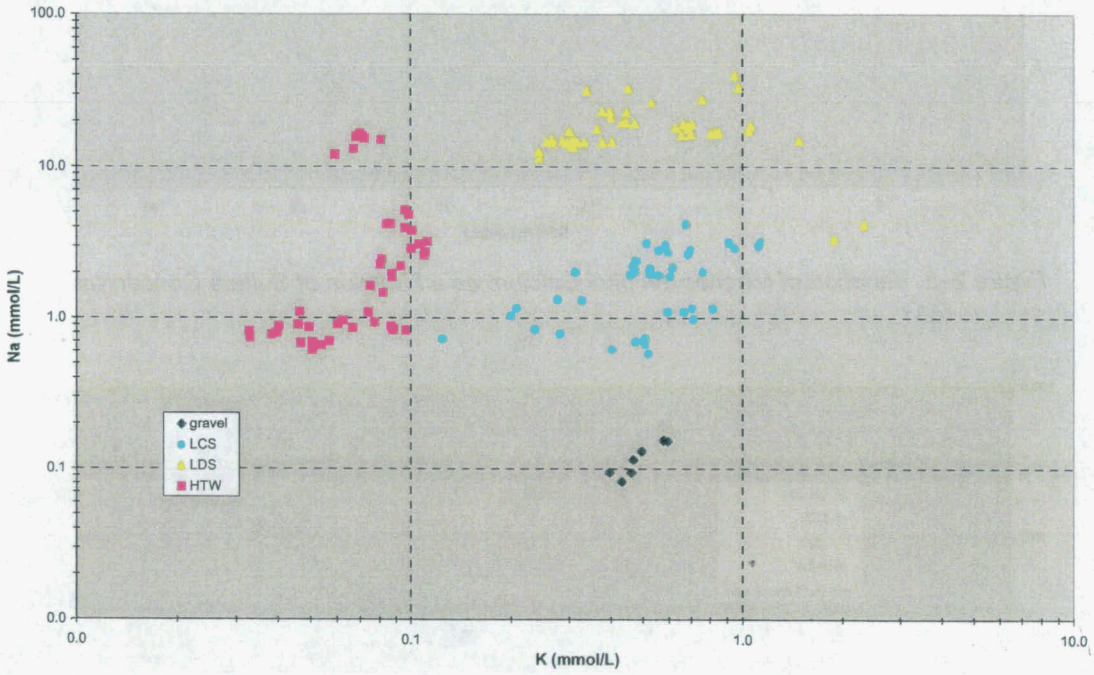

Figure 2–5. Variation of Sodium as a Function of Potassium Concentration

Silica (SiO_2) is the last of the major ions in the fluids, and a plot against Na reveals that the LCS, LDS, and HTW all have similar SiO_2 values (Figure 2–6). The exception is the high average SiO_2 value for the LCS in Cell 2, which can be used to detect leakage into the Cell 2 LDS (Table 2–2). As for the remaining cells, SiO_2 is not a useful indicator for leachate leakage.

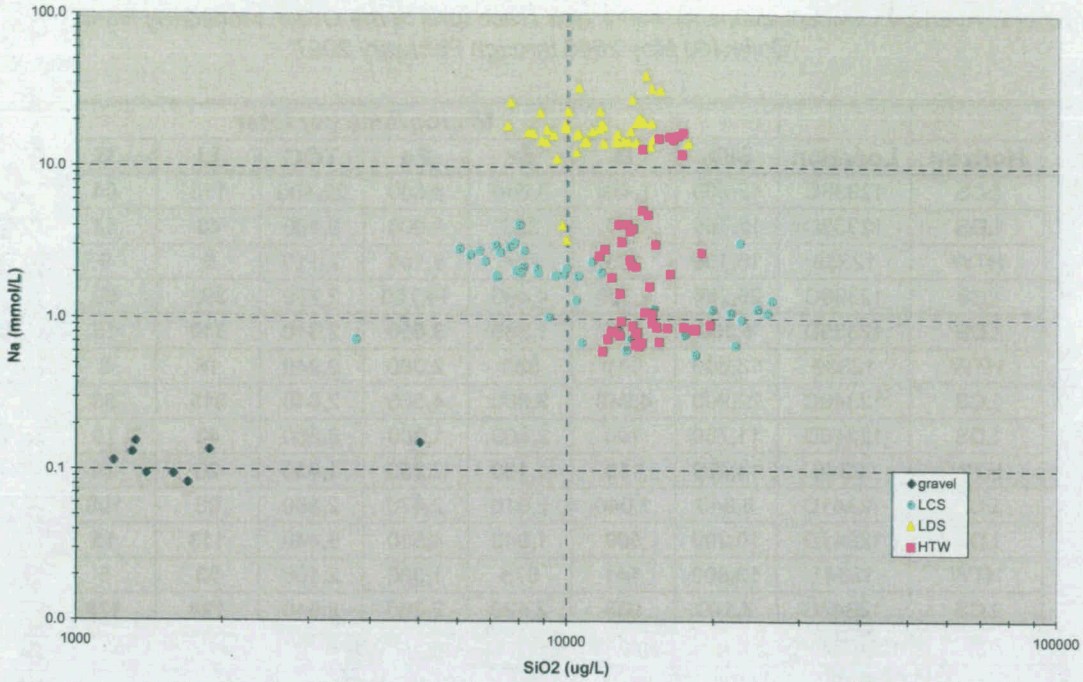

Figure 2–6. Variation of Sodium as a Function of Silica Concentration

2.2 Minor Ions

Boron (B) and strontium (Sr) are present in the dolomite rock used to construct the LCS and LDS layers. When the dolomitic limestone gravel is leached, B and Sr are released to the fluid and reach concentrations near 1,000 µg/L (Figure 2–7). The LCS and LDS samples straddle the gravel samples, with most of the LCS samples exhibiting higher concentrations, and the LDS samples lower concentrations, relative to the gravel samples. This linear trend through the gravel samples arises from the dilution and evaporation of the water in contact with the crushed dolomitic rock, and the depletion of the B and Sr from the crushed rock surface over time. HTW samples anchor the trend at low concentrations, with the exception of the single point plotted at a B concentration of 960 µg/L (Cell 3, 12340, August 2006). All laboratory results for other samples collected from well 12340 show B results near 100 µg/L. Therefore, it is likely that this result is 96 µg/L, and the laboratory failed to perform the correct dilution calculation prior to reporting the result.

Table 2–2 shows that B is a useful indicator ion to detect leakage from the LCS to the LDS in Cells 1, 2, and 3, and from the LDS to the HTW in Cells 2, 4, 5, 6, 7, and 8. Note that the anomalous B value of 960 µg/L for an HTW sample from Cell 3 (discussed above) was omitted when the average B value was calculated for Table 2–2. Although Sr levels in the HTW are less than those in the LDS, the difference in the values is less than a factor of 4, and Sr is not a useful indicator ion for leachate leakage.

Table 2–2. Average Concentrations for Minor and Trace Ions in the OSDF Monitoring Horizons Data Collected May 2005 through February 2007

			Micrograms per Liter							
	Horizon	**Location**	**SiO_2**	**B**	**Sr**	**Fe**	**TOC**	**Li**	**U**	**Ba**
Cell 1	LCS	12338C	12,500	**1,440**	3,040	3,600	20,400	115	**94**	64.7
	LDS	12338D	12,700	**240**	905	1,900	6,160	**48**	**14**	15.6
	HTW	12338	15,100	185	724	5,190	2,110	**9**	9	48.9
Cell 2	LCS	12339C	**20,200**	**2,730**	4,490	**16,700**	2,770	392	**80**	61.1
	LDS	12339D	**4,350**	**535**	1,360	**3,610**	2,310	**310**	**16**	16.7
	HTW	12339	13,600	141	853	2,080	2,240	**18**	8	61.2
Cell 3	LCS	12340C	22,900	**4,940**	3,800	4,580	2,640	**815**	**66**	48.7
	LDS	12340D	11,700	**106**	2,800	1,300	6,680	**43**	**15**	19.1
	HTW	12340	14,400	110	1,150	2,250	1,950	26	20	37.7
Cell 4	LCS	12341C	8,340	1,040	2,510	2,470	2,850	98	**106**	27.6
	LDS	12341D	10,200	**509**	1,940	4,510	5,440	**113**	**15**	32.6
	HTW	12341	13,800	**141**	673	1,330	2,100	**13**	5	59.4
Cell 5	LCS	12342C	7,140	933	2,420	2,650	2,910	128	**178**	26.1
	LDS	12342D	12,600	**267**	1,170	1,860	8,140	**55**	**23**	24.3
	HTW	12342	13,700	**65**	534	2,460	2,930	**6**	8	81.1
Cell 6	LCS	12343C	9,400	928	2,090	2,520	2,860	84	**148**	33.6
	LDS	12343D	10,600	**433**	1,640	1,830	6,470	**79**	**23**	31.7
	HTW	12343	13,200	**87**	562	1,140	2,300	**12**	13	34.3
Cell 7	LCS	12344C	12,700	787	1,850	3,950	2,580	79	**169**	54.6
	LDS	12344D	12,800	**309**	1,380	1,490	6,660	**89**	**25**	30.9
	HTW	12344	16,300	**25**	463	1,280	2,090	**9**	**3**	109
Cell 8	LCS	12345C	11,500	313	1,160	1,660	2,620	43	**104**	67.5
	LDS	12345D	9,310	**1,410**	3,570	3,890	3,390	**148**	**19**	42.6
	HTW	12345	16,200	**77**	891	2,000	1,910	**15**	5	360

Bold numbers indicate that the LCS or LDS is at least 4 times greater than the underlying horizon.

Total organic carbon (TOC) and Fe are the remaining minor ions in the fluids, and values for TOC are more tightly clustered for each horizon (Figure 2–8). For example, most LDS samples have TOC levels between 4,000 and 10,000 µg/L (a factor of 2.5), and Fe ranges from 500 to 5,000 µg/L (a factor of 10). The larger range observed for Fe is tied to the amount of oxygen in the fluid and the steel debris in the cells. As the oxygen level decreases (i.e., as Eh decreases), the Fe concentration increases. When the cells are first constructed, oxygen levels are high, and they decrease with time as the cells are filled, capped, and isolated from rain and the atmosphere. Therefore, Fe concentrations are expected to increase with time, most notably in cells that contain abundant structural iron debris.

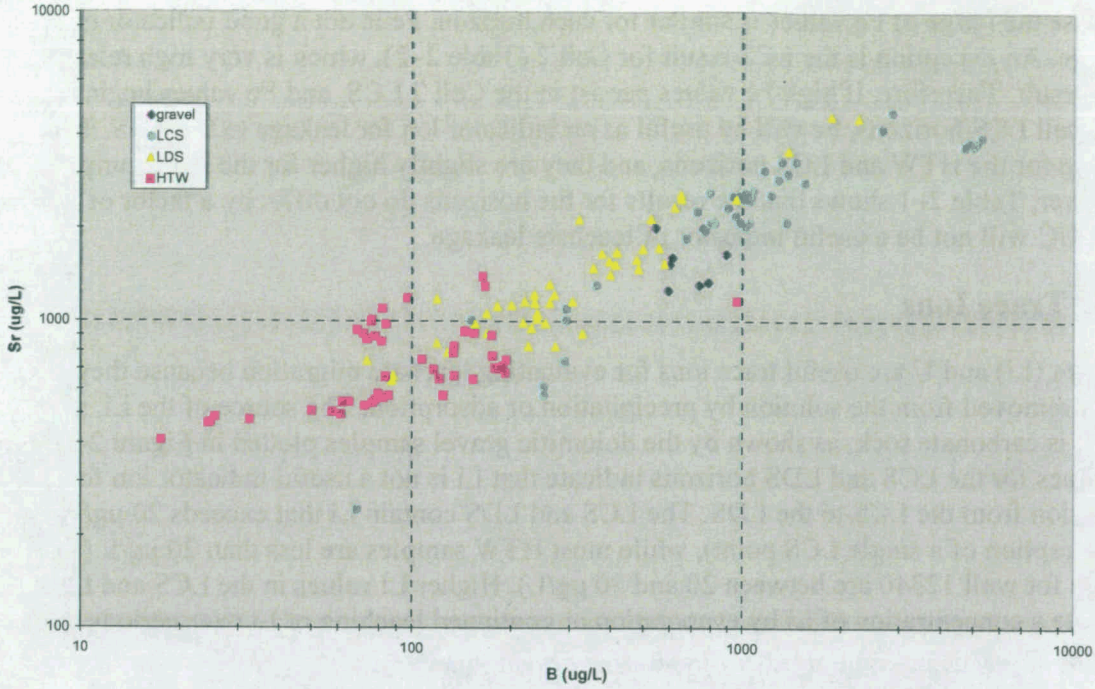

Figure 2–7. Variation of Strontium as a Function of Boron Concentration

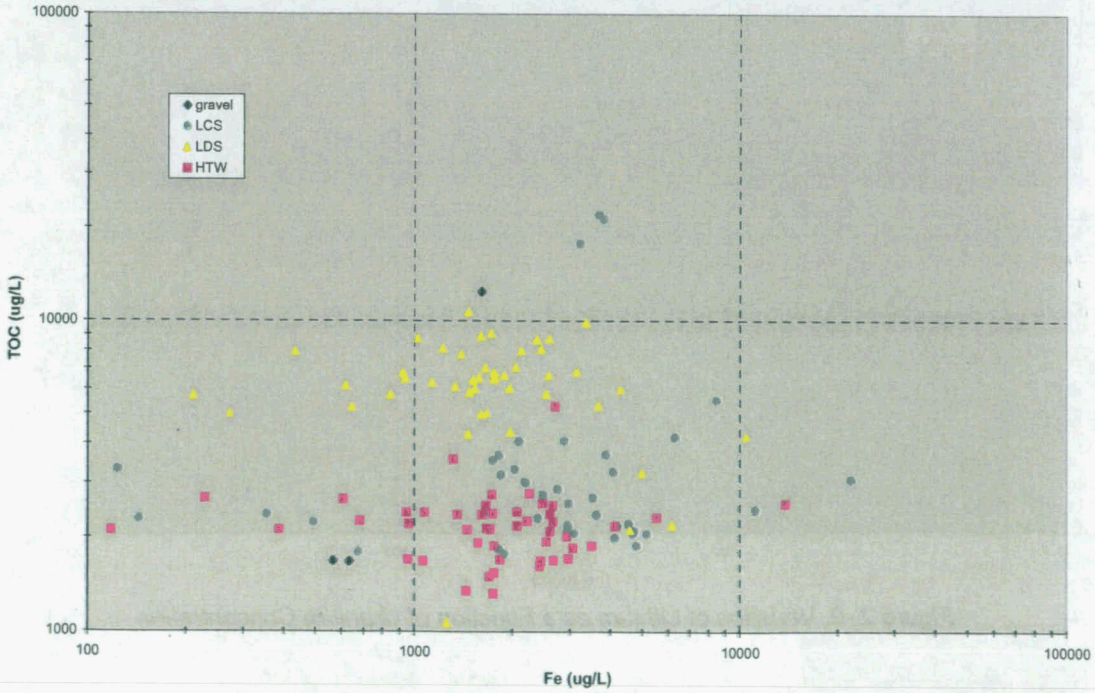

Figure 2–8. Variation of Total Organic Carbon as a Function of Iron Concentration

Because the range of Fe values is similar for each horizon, Fe is not a good indicator of leachate leakage. An exception is the LCS result for Cell 2 (Table 2–2), which is very high relative to the LDS result. Therefore, if high Fe values persist in the Cell 2 LCS, and Fe values begin to rise in other cell LCS horizons, Fe will be useful as an indicator ion for leakage to the LDS. TOC values overlap for the HTW and LCS horizons, and they are slightly higher for the LDS samples. However, Table 2–1 shows that the results for the horizons do not differ by a factor of 4 or more, and TOC will not be a useful indicator of leachate leakage.

2.3 Trace Ions

Lithium (Li) and U are useful trace ions for evaluating leachate migration because they are not easily removed from the solution by precipitation or adsorption. The source of the Li, and part of the U, is carbonate rock, as shown by the dolomitic gravel samples plotted in Figure 2–9. Similar Li values for the LCS and LDS horizons indicate that Li is not a useful indicator ion for leachate migration from the LCS to the LDS. The LCS and LDS contain Li that exceeds 20 µg/L (with the exception of a single LCS point), while most HTW samples are less than 20 µg/L (all Li results for well 12340 are between 20 and 30 µg/L). Higher Li values in the LCS and LDS indicate a concentration of Li by evaporation or continued leaching of Li over periods longer than 120 days (the maximum leach time for the gravel samples).

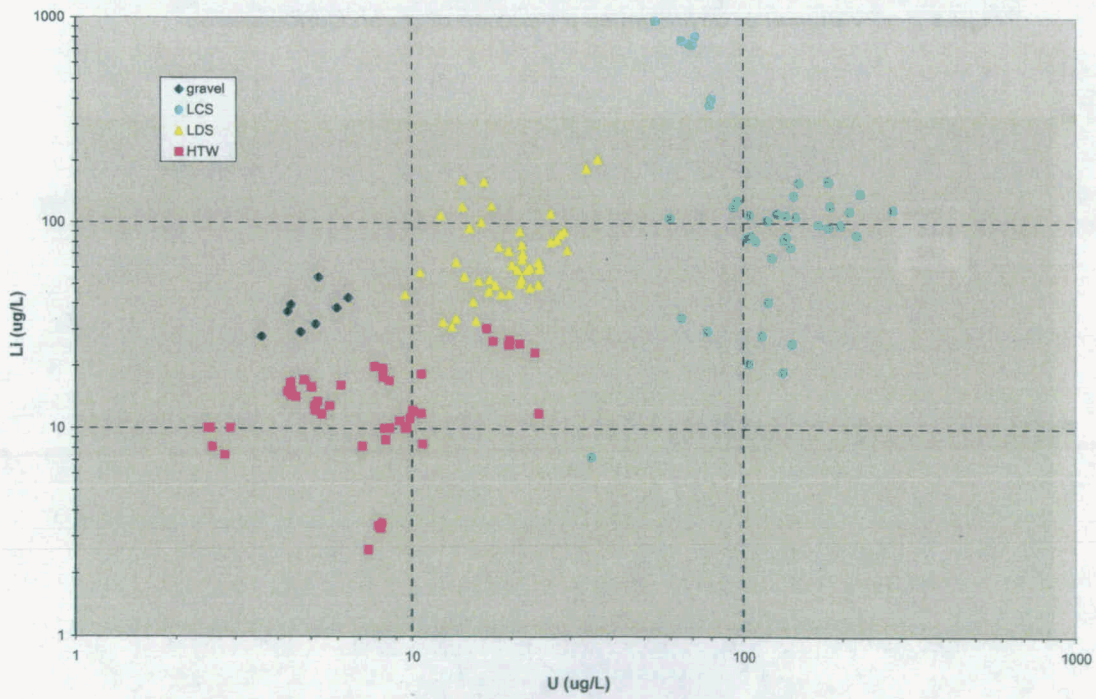

Figure 2–9. Variation of Lithium as a Function of Uranium Concentration

Table 2–2 indicates that levels of Li in the LDS are significantly higher than most HTW samples, the exception being Cell 3. Therefore, Li can be used as an indicator ion for leachate leakage from the LDS to the HTW. For Cell 3, the very high Li value in the Cell 3 LCS makes Li a useful indicator ion for leakage from the Cell 2 LCS to the LDS. Turning to U, the LDS and HTW values overlap, but the LCS values are elevated over LDS results. Table 2–2 indicates that U is the best indicator ion for leachate leakage from LCS to LDS, for all cells. The higher U values in the LCS samples arise from the leaching of U from the waste materials placed in the

cells. Additionally, there is a significant difference in the U values for the Cell 7 LDS and HTW samples, and U can be used as an indicator of leachate migration from the LDS to HTW horizon for Cell 7.

Barium (Ba) is plotted against SO_4 (Figure 2–9) because barite ($BaSO_4$) solubility generally controls the levels of Ba in solution when sulfate is present. Many of the points on Figure 2–10 follow the solubility curve for barite, but many also lie above the curve. Samples that plot far above the solubility curve may have elevated Ba levels from dissolution of fine carbonate suspended in the sample collected for metal analysis. When the metal sample is acidified to a pH of less than 2, the fine carbonate suspended in solution is dissolved, releasing Ba that is present in the carbonate phases as a trace element. Alternatively, Ba may be present as a trace element in the CaCl2 spread to deice the roads in the former construction areas; this appears to hold for the samples from HTW 12345, as they have elevated Ca, Ba, and Cl, relative to other HTW locations. However, the LCS and LDS results are not sufficiently elevated, relative to the underlying horizon, for Ba to serve as a useful indicator ion.

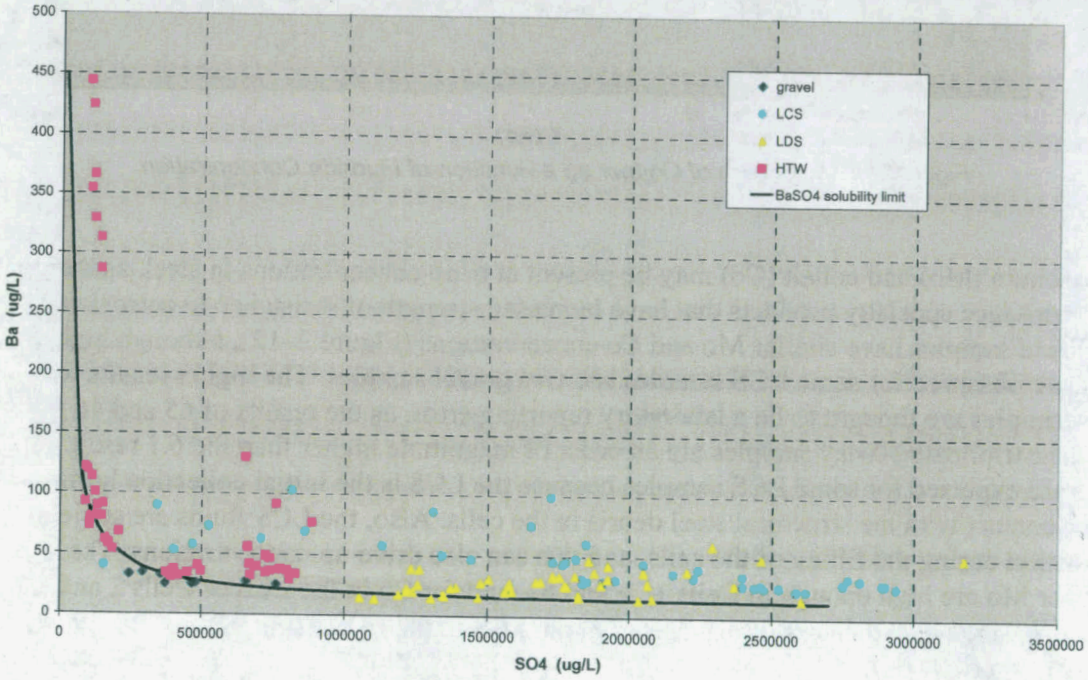

Figure 2–10. Variation of Barium as a Function of Sulfate Concentration

Figure 2–11 shows the range of fluoride (F) and copper (Cu) values in the fluid samples. The F levels in the LCS, LDS, and HTW samples are similar, but they are much greater than the levels that are derived from the leaching of the dolomite gravel. As F levels in the fluid in contact with the gravel continued to increase over the 120-day leach period, higher levels in the LCS, LDS, and HTW samples may indicate that F continues to be released from the carbonate rock until it reaches a solubility limit (F concentrations in groundwater are generally limited by the solubility of the mineral apatite). Values for Cu are similar for LCS and LDS samples, but many of the HTW samples have lower Cu concentrations. Table 2–3 indicates that F is not a useful indicator ion, but Cu may be useful for monitoring leachate migration from the LDS to the HTW for Cells 4, 7, and 8.

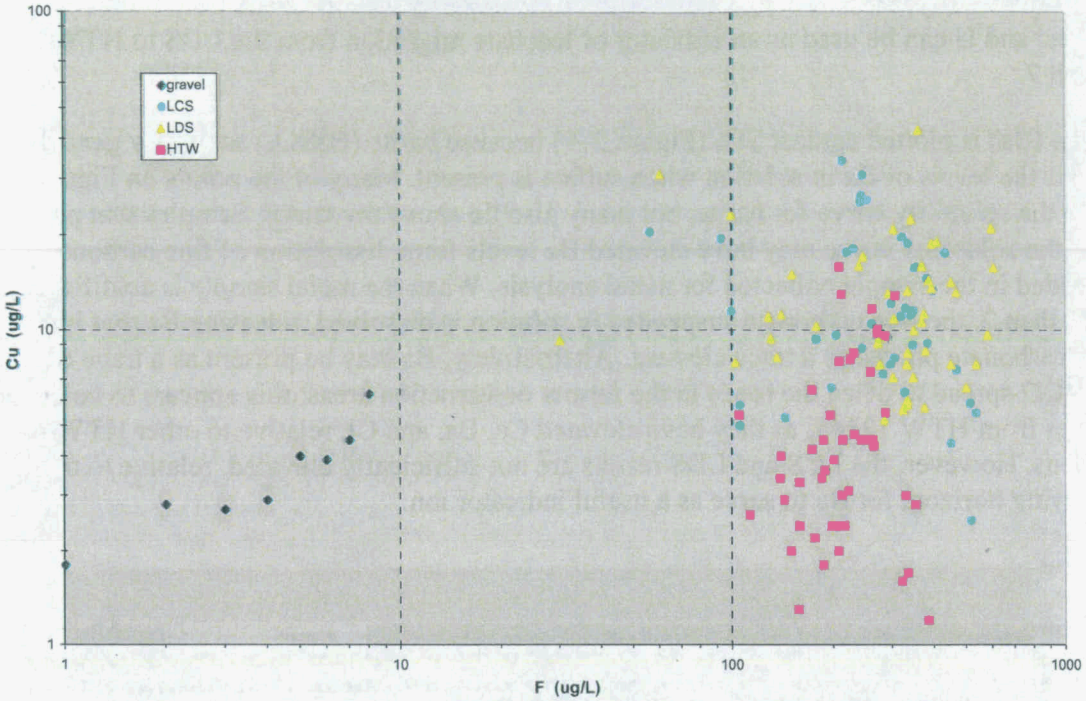

Figure 2–11. Variation of Copper as a Function of Fluoride Concentration

Molybdenum (Mo) and cobalt (Co) may be present at trace concentrations in steel, as they are used to produce specialty products that have increased strength or resistance to corrosion. Most of the fluid samples have similar Mo and Co concentrations (Figure 2–12), although higher values are observed for some LCS samples and two gravel samples. The higher results for the gravel samples are thought to be a laboratory reporting error, as the results of 65 and 46 µg/L for two of the triplicate 30-day samples are an order of magnitude higher than the 6.1 result. Higher results are expected for some LCS samples because the LCS is the initial collection horizon for fluid in contact with the structural steel debris in the cells. Also, the LCS fluids are subject to evaporation during the filling of the cells, and this can also drive up concentrations. The LCS levels for Mo are high enough in Cells 1, 2, and 8—and for Co in the LCS of Cells 2 and 3—for these ions to serve as indicators of leakage from the LCS to the LDS (Table 2–3).

In the Cell 7 LDS, the Mo concentration is nearly 10 times that in the HTW horizon, and Mo is useful to detect migration of fluid from the LDS to the HTW for this cell.

Figure 2–13 shows the positive co-variation of nickel (Ni) and palladium (Pd). These trace metals are found together in ore deposits and, during the smelting process, Ni is generally not purified to the extent that all Pd is removed. As noted above for Mo and Co, Ni is also used to produce specialty steel products, and Pd will be in these products due to its association with Ni. The highest Ni values are found in the LCS samples for Cells 2 and 3, and Ni is sufficiently low enough in the LDS of Cell 3 for Ni to serve as an indicator ion for this cell (Table 2–3). Average results for Pd are not significantly different between adjacent horizons in Cells 1 through 7, but in Cell 8 it may be useful as an indicator ion for leakage from the LDS to the HTW.

Table 2–3. Average Concentrations for Trace Ions in the OSDF Monitoring Horizons Data Collected May 2005 through February 2007

			Micrograms per Liter							
	Horizon	**Location**	**F**	**Cu**	**Mo**	**Co**	**Ni**	**Pd**	**Mn**	**Zn**
Cell 1	LCS	12338C	241	12.3	**11.4**	4.83	19.7	1.73	**579**	47.7
	LDS	12338D	121	12.6	**1.82**	1.33	19.8	0.57	**41.8**	273
	HTW	12338	207	9.92	1.60	1.14	6.96	0.59	61.32	218
Cell 2	LCS	12339C	99	12.7	**41.3**	**42.5**	81.6	3.50	**5,630**	46.9
	LDS	12339D	390	14.5	**3.10**	**3.50**	21.5	0.93	**418**	284
	HTW	12339	235	6.95	1.70	1.26	7.58	0.71	**47.1**	86.2
Cell 3	LCS	12340C	135	10.7	5.28	**34.1**	**87.3**	2.36	**5,880**	26.3
	LDS	12340D	328	8.63	5.89	**0.73**	**6.15**	0.65	**24.7**	84.0
	HTW	12340	248	6.27	1.37	1.33	7.26	0.78	189	106
Cell 4	LCS	12341C	331	15.9	1.80	2.62	21.3	1.83	411	18.2
	LDS	12341D	303	**12.4**	1.93	2.18	14.4	1.31	297	166
	HTW	12341	345	**2.06**	1.26	2.18	6.44	0.38	263	76.2
Cell 5	LCS	12342C	291	15.5	1.30	4.66	32.9	1.84	**1,230**	18.4
	LDS	12342D	297	10.6	1.51	1.50	14.5	0.85	**120**	33.4
	HTW	12342	179	2.77	1.01	2.44	9.04	0.33	842	19.1
Cell 6	LCS	12343C	334	13.7	1.57	1.98	24.5	1.65	**418**	13.9
	LDS	12343D	367	13.9	2.94	1.13	12.8	1.31	**15.3**	41.3
	HTW	12343	246	6.90	3.98	0.89	7.46	0.45	270	1,570
Cell 7	LCS	12344C	367	14.0	4.10	2.65	12.3	1.49	**108**	23.9
	LDS	12344D	503	**12.0**	**8.83**	0.70	8.39	1.03	**8.24**	21.2
	HTW	12344	161	**2.72**	**0.85**	0.78	4.52	0.38	28.1	139
Cell 8	LCS	12345C	339	8.15	**6.35**	1.63	8.92	0.85	51.7	11.9
	LDS	12345D	213	**22.2**	**1.39**	1.90	17.1	**2.78**	208	80.3
	HTW	12345	177	**3.27**	0.85	1.00	9.49	**0.64**	59.5	282

Bold numbers indicate that the LCS or LDS is at least 4 times greater than the underlying horizon.

Manganese (Mn) and zinc (Zn) are the last of the trace ions that have been detected in the fluid samples. Figure 2–14 indicates that the samples have a large variation in Mn concentrations, with most samples containing less than 100 µg/L of Zn. A wide variation in Mn is partly due to the dependence of Mn concentration on the amount of oxygen in the system (as discussed above for Fe) and the presence of steel debris placed in the cells. LCS samples reach the highest Mn, Ni, and Co concentrations in Cells 2 and 3; this is due to the large amount of steel debris placed in these cells. The elevated Zn results for the HTW samples are from the February 2007 sample event, and it is unclear whether contamination was introduced to the samples or the laboratory failed to make the correct dilution adjustment before reporting the result.

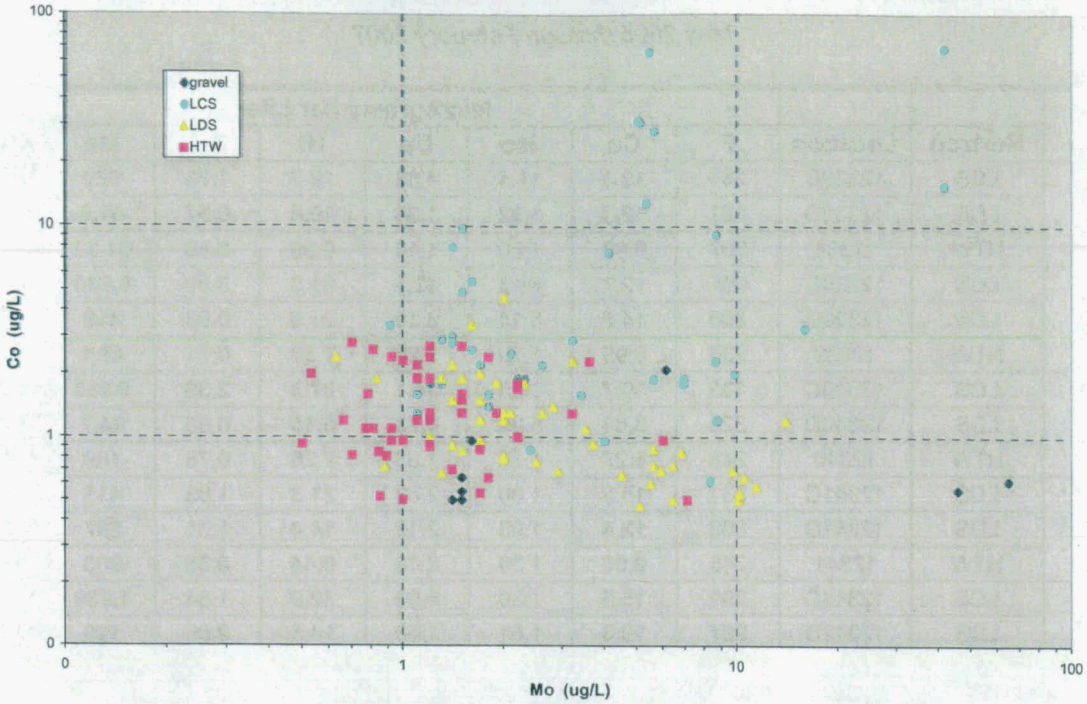

Figure 2–12. Variation of Cobalt as a Function of Molybdenum Concentration

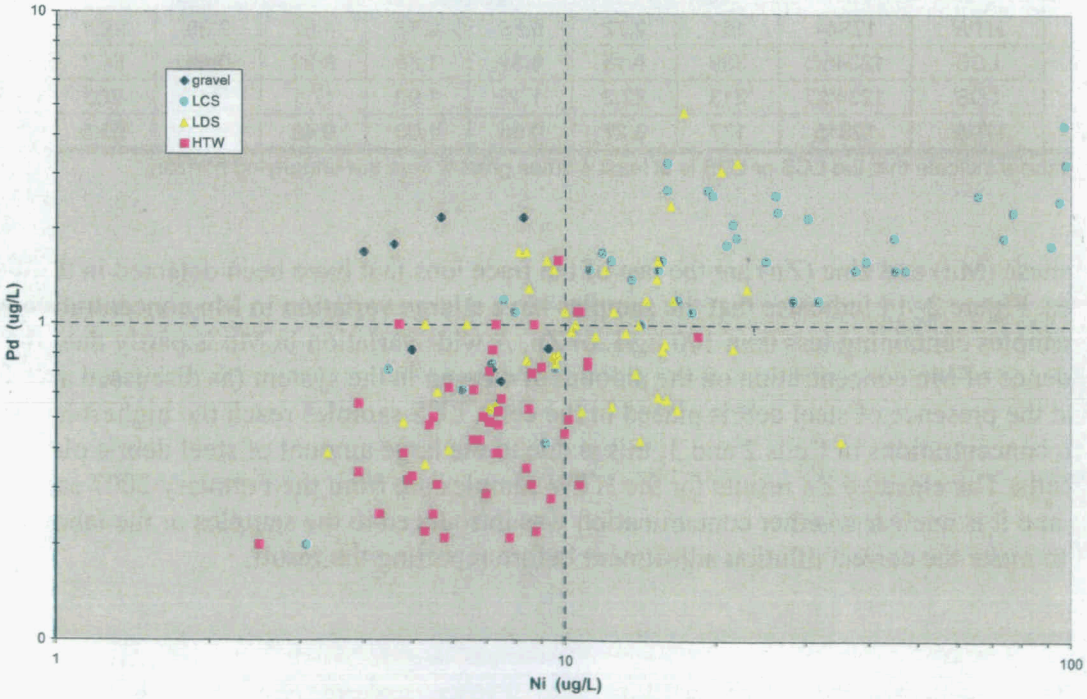

Figure 2–13. Variation of Palladium as a Function of Nickel Concentration

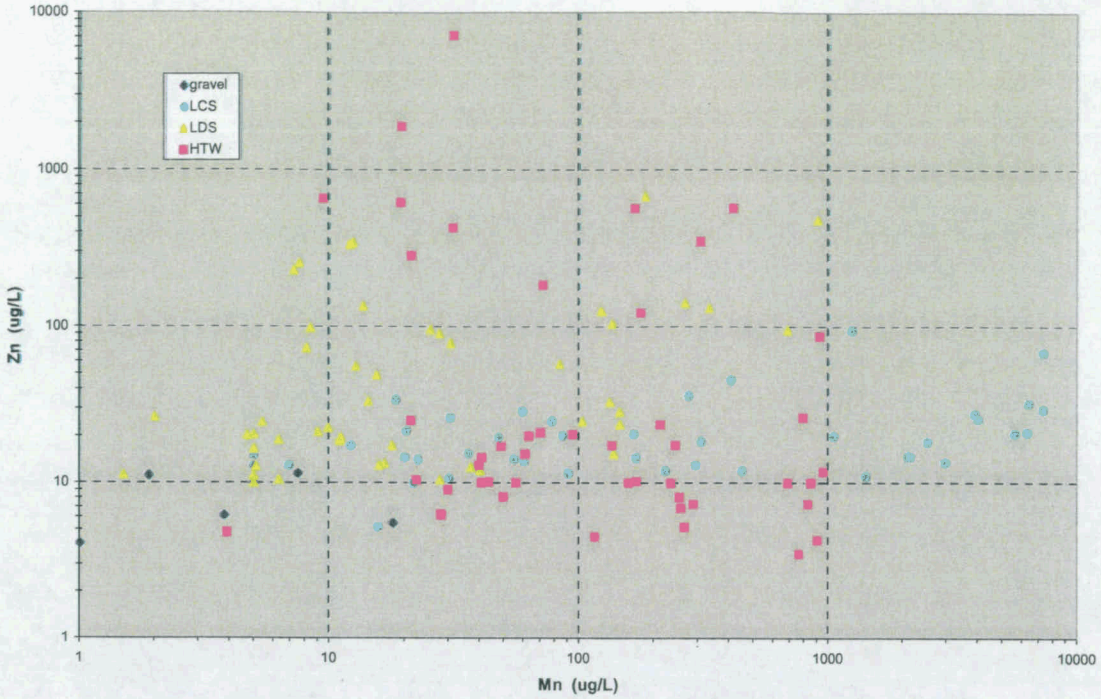

Figure 2–14. Variation of Zinc as a Function of Manganese Concentration

Table 2–3 indicates that the Mn concentrations are sufficiently high in the LCS samples for this ion to be useful as an indicator of leakage from the LCS to the LDS in all cells except Cells 4 and 8. In the LDS horizon for Cell 2, Mn is about 9 times greater than the HTW value, and Mn may be useful to indicate leakage from the LDS to the HTW for Cell 2. Average Zn results reported in Table 2–3 indicate that the highest Zn values are found in HTW horizons, and Zn will not be a useful indicator of leakage. However, the suspect Zn results for the February 2007 sampling round are biasing the results in Table 2–3 to high values, and Zn results are inconclusive with respect to monitoring decisions at this time.

End of current text

3.0 Statistical Analysis of Ion Data

Appendix B of the Technical Memorandum for the On-Site Disposal Facility Cells 1, 2 & 3 Baseline Groundwater Conditions (DOE 2002) defines the basis for statistical tests that must be performed on groundwater data prior to establishing a control chart for a given monitoring well. As of March 2007, eight samples had been collected from each of the HTW below Cells 1 through 8, and up to eight samples had also been collected from the LDS and LCS for each cell. Based on the discussion above, the magnitude of the ion concentrations in the LCS, LDS, and HTW horizons will determine the appropriate ions for monitoring. These ions are U and Mn for the LDS horizon, and Na, SO_4, and B for the HTW. Statistical tests were performed only on the noted ions for the data sets available on the LDS and HTW horizons since these are the monitoring zones that could detect leachate migration from the LCS and LDS horizons (i.e., LCS to LDS and LDS to HTW).

Per the protocols established in Appendix B of DOE (2002), a control chart cannot be established for a given well unless the following three assumptions are met:

1) The data are normally distributed or can be transformed to a normal distribution (e.g., log normal).
2) Baseline data are from a well uncontaminated by the OSDF and reflect chemical steady-state conditions.
3) Sample data are statistically independent (i.e., no serial correlation).

Statistical tests were performed on the ion data sets to verify the above assumptions. For Assumption 1, the Shapiro-Wilks Test of Normality and Dixon's Test for Outliers were performed to demonstrate that the data set had a normal or log normal distribution that was free of outlier values. The Mann-Kendall Trend Analysis and Sen's Slope Analysis were performed to determine if baseline data satisfied Assumption 2. Finally, Assumption 3 was tested using the Rank von Neumann Ratio Test. All calculations were performed with the ChemStat software package, and summary reports generated by the software are provided as Attachment 1.

3.1 Uranium Results

The concentration of U in the LCS horizon of all cells is sufficiently greater than that in all LDS horizons, which makes U the best indicator of leachate migration from the LCS to the LDS horizon. In Cell 7, the U concentration in the LDS is sufficiently greater than that observed in the HTW, making U a useful leak indicator in the HTW for Cell 7. U is not an appropriate ion for leak detection in the remaining HTW because the levels in the overlying LDS are too low, relative to the HTW horizon.

U concentrations are normally distributed in the LDS of Cells 1, 3, 4, 5, 6, and 7, and the HTW of Cell 7, but a log normal distribution is present in the LDS of Cell 8 (Table 3–1). Statistical tests could not be performed for the LDS horizon of Cell 2 since only a single analysis is available (there has been insufficient fluid for a sample since the first sample was obtained in May 2005). The Mann-Kendall and Sen's Slope tests indicate that U is exhibiting an upward trend in Cell 1, and Cells 3 through 8 have no trend for U. Results for the Rank von Neumann Ratio Test indicate that the data are independent and lack serial correlation. There were no outliers detected in any of the horizons.

Table 3–1. Summary of Statistical Tests for Uranium LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Distribution	Trend	Serial Correlation	Outliers	
					Present	Removed
Cell 1	LDS	normal	upward	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 2	LDS	insuf. data	insuf. data	insuf. data	insuf. data	insuf. data
	HTW	NC	NC	NC	NC	NC
Cell 3	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 4	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 5	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 6	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 7	LDS	normal	none	no	no	NA
	HTW	normal	none	no	no	NA
Cell 8	LDS	log normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC

Distribution determined by Shapiro-Wilks Test of Normality
Trend determined by Mann-Kendall Trend Analysis and Sens Slope Analysis
Serial Correlation determined by Rank von Neumann Ratio Test
Outliers determined by Dixon's Test; outliers were removed if Shapiro-Wilks test failed
NA – not applicable
NC – not considered because the uranium concentration is inappropriate for use as a detection ion in this horizon

Based on the results in Table 3–1, the upward trend in Cell 1 and lack of data for Cell 2 indicate that a U control chart cannot be used in Cells 1 & 2 to monitor leakage from the LCS to the LDS. U data from the LDS horizon of Cells 3 through 8, and the HTW of Cell 7, meet the three assumptions outlined above and are adequate to establish baseline conditions in these horizons. Therefore, future data can be compared against these baseline conditions using a control chart.

3.2 Manganese Results

Mn concentrations in the LCS horizon of Cells 1, 3, 5, 6, and 7 are sufficiently greater than those observed in the LDS, and Mn can serve as an indicator of leachate leakage from the LCS to the LDS. In Cell 2, Mn in the HTW is much lower than the single observation obtained for Mn in the LDS, and the statistical tests were run for the HTW samples with the added assumption that future Mn levels in the LDS of Cell 2 will be similar to the result for the initial sample. Mn is not an appropriate ion for leak detection in Cells 4 and 8 or in the HTW for Cells 1, 3, 5, 6, and 7 because the levels in the overlying LCS, the LDS, or both are too low, relative to the LDS and HTW horizons.

For the LDS of Cells 3, 5, 6, and 7 and the HTW of Cell 2, Mn concentrations are normally distributed (Table 3–2). A log normal distribution is observed for the samples obtained from the LDS of Cell 1. Statistical tests could not be performed for the LDS horizon of Cell 2 because only a single analysis is available (there has been insufficient fluid for a sample since the first sample was obtained in May 2005). The Mann-Kendall and Sen's Slope tests indicate that Mn

has no trend in the horizons that were evaluated. Results for the Rank von Neumann Ratio Test indicate that the data are independent and lack serial correlation. There was a single outlier detected in the LDS of Cell 3, and once it was removed, the distribution passed the Shapiro-Wilks Test for Normality. There were no other outliers detected in the remaining horizons.

Table 3–2. Summary of Statistical Tests for Manganese LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Distribution	Trend	Serial Correlation	Outliers	
					Present	Removed
Cell 1	LDS	log normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 2	LDS	insuf. data	insuf. data	insuf. data	insuf. data	insuf. data
	HTW	normal	none	no	no	NA
Cell 3	LDS	normal	none	no	yes	yes
	HTW	NC	NC	NC	NC	NC
Cell 4	LDS	NC	NC	NC	NC	NC
	HTW	NC	NC	NC	NC	NC
Cell 5	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 6	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 7	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 8	LDS	NC	NC	NC	NC	NC
	HTW	NC	NC	NC	NC	NC

Distribution determined by Shapiro-Wilks Test of Normality
Trend determined by Mann-Kendall Trend Analysis and Sens Slope Analysis
Serial Correlation determined by Rank von Neumann Ratio Test
Outliers determined by Dixon's Test; outliers were removed if Shapiro-Wilks test failed
NA – not applicable
NC – not considered because the manganese concentration is inappropriate for use as a detection ion in this horizon

Based on the results in Table 3–2, the lack of data for Cell 2 and the concentration ranges in Cells 4 and 8 indicate that a control chart for Mn cannot be used for Cells 2, 4, & 8 to monitor leakage from the LCS to the LDS. Mn data from the LDS horizon of Cells 1, 3, 5, 6, and 7 and the HTW of Cell 2 meet the three assumptions outlined above and are adequate to establish baseline conditions in these horizons. Therefore, future data can be compared against these baseline conditions using a control chart.

3.3 Sodium Results

Na concentrations in the LDS horizon of Cells 1 through 7 are sufficiently greater than those observed in the HTW, and Na can serve as an indicator of leachate leakage from the LDS to the HTW. However, Na is not an appropriate ion for leak detection in the HTW of Cell 8 or in the LDS for Cells 1 through 8 because the Na levels in the overlying LCS, the LDS, or both are too low, relative to the LDS and HTW horizons.

For the HTW of Cells 1 through 7, Na concentrations exhibit a normal distribution (Table 3–3). The Mann-Kendall and Sen's Slope tests indicate that Na shows a downward trend in Cells 1, 2,

and 8; an upward trend in Cell 5; and no trend in Cells 3, 4, and 7. Results for the Rank von Neumann Ratio Test indicate that the data from Cells 1 through 7 are independent and lack serial correlation. There were no outliers detected by Dixon's Test.

Table 3–3. Summary of Statistical Tests for Sodium LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Distribution	Trend	Serial Correlation	Outliers	
					Present	Removed
Cell 1	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	no	no	NA
Cell 2	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	no	no	NA
Cell 3	LDS	NC	NC	NC	NC	NC
	HTW	normal	none	no	no	NA
Cell 4	LDS	NC	NC	NC	NC	NC
	HTW	normal	none	no	no	NA
Cell 5	LDS	NC	NC	NC	NC	NC
	HTW	normal	Up	no	no	NA
Cell 6	LDS	NC	NC	NC	NC	NC
	HTW	normal	none	no	no	NA
Cell 7	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	no	no	NA
Cell 8	LDS	NC	NC	NC	NC	NC
	HTW	NC	NC	NC	NC	NC

Distribution determined by Shapiro-Wilks Test of Normality
Trend determined by Mann-Kendall Trend Analysis and Sens Slope Analysis
Serial Correlation determined by Rank von Neumann Ratio Test
Outliers determined by Dixon's Test; outliers were removed if Shapiro-Wilks test failed
NA – not applicable
NC – not considered because the sodium concentration is inappropriate for use as a detection ion in this horizon

Based on the results in Table 3–3, the Na trends in Cells 1, 2, 5 and 7 and the concentration ranges in Cell 8 indicate that a control chart for Na cannot be used to monitor leakage from the LDS to the HTW in these cells. Na data from the HTW horizon of Cells 3, 4, and 6 meet the three assumptions outlined above and are adequate to establish baseline conditions in these horizons. Therefore, future data can be compared against the baseline conditions in Cells 3, 4, and 6 using a control chart.

3.4 Sulfate Results

SO_4 concentrations in the LDS horizon of Cells 2, 4, 5, 6, 7, and 8 are sufficiently greater than those observed in the HTW, and SO_4 can serve as an indicator of leachate leakage from the LDS to the HTW. However, SO_4 is not an appropriate ion for leak detection in the HTW of Cells 1 and 3 or in the LDS for Cells 1 through 8 because the SO_4 levels in the overlying LCS, the LDS, or both are too low, relative to the LDS and HTW horizons.

For the HTW of Cells 2, 4, 5, and 6, SO_4 concentrations exhibit a normal distribution (Table 3–4), while the distribution is log normal for Cells 7 and 8. The Mann-Kendall and Sen's Slope tests indicate that SO_4 shows a downward trend in Cells 6 and 7; an upward trend in Cells

4, 5, and 8; and no trend in Cell 2. Results for the Rank von Neumann Ratio Test indicate that the data from Cells 2, 4, and 7 are independent, while Cells 5, 6, and 8 show serial correlation. There were no outliers detected by Dixon's Test.

Table 3–4. Summary of Statistical Tests for Sulfate LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Distribution	Trend	Serial Correlation	Outliers	
					Present	Removed
Cell 1	LDS	NC	NC	NC	NC	NC
	HTW	NC	NC	NC	NC	NC
Cell 2	LDS	NC	NC	NC	NC	NC
	HTW	normal	none	no	no	NA
Cell 3	LDS	NC	NC	NC	NC	NC
	HTW	NC	NC	NC	NC	NC
Cell 4	LDS	NC	NC	NC	NC	NC
	HTW	normal	Up	no	no	NA
Cell 5	LDS	NC	NC	NC	NC	NC
	HTW	normal	Up	yes	no	NA
Cell 6	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	yes	no	NA
Cell 7	LDS	NC	NC	NC	NC	NC
	HTW	log normal	down	no	no	NA
Cell 8	LDS	NC	NC	NC	NC	NC
	HTW	log normal	up	yes	no	NA

Distribution determined by Shapiro-Wilks Test of Normality
Trend determined by Mann-Kendall Trend Analysis and Sens Slope Analysis
Serial Correlation determined by Rank von Neumann Ratio Test
Outliers determined by Dixon's Test; outliers were removed if Shapiro-Wilks test failed
NA – not applicable
NC – not considered because the sulfate concentration is inappropriate for use as a detection ion in this horizon

Based on the results in Table 3–4, the SO_4 trends in Cells 4 through 8 and the serial correlation in Cells 5, 6, and 8 indicate that a control chart for SO_4 cannot be used to monitor leakage from the LDS to the HTW in these cells. SO_4 data from the HTW horizon of Cell 2 meets the three assumptions outlined above and are adequate to establish baseline conditions in this horizon. Therefore, future data can be compared against the baseline conditions in Cell 3 using a control chart.

3.5 Boron Results

The concentration of B in the LCS horizon of all Cells 1 and 3 is sufficiently greater than that in the LDS horizons, which allows B to be used as an indicator of leachate migration from the LCS to the LDS horizon. In Cells 2, 4, 5, 6, 7, and 8, the B concentration in the LDS is sufficiently greater than that observed in the HTW, making B a useful leak indicator for leakage from the LDS to the HTW. B is not an appropriate ion for leak detection in the LDS of Cells 2, 4, 5, 6, 7, and 8 and the HTW of Cells 1 and 3 because the levels in the overlying LCS and LDS are too low, relative to the LDS and HTW horizons.

B concentrations are normally distributed in the LDS of Cells 1 and 3 and in the HTW of Cells 2, 5, 6, 7, and 8, while a log normal distribution is present in the HTW of Cell 4 (Table 3–5). Statistical tests could not be performed for the LDS horizon of Cell 2, as only a single analysis is available (there has been insufficient fluid for a sample since the first sample was obtained in May 2005). The Mann-Kendall and Sen's Slope tests indicate that B is exhibiting an upward trend in the HTW of Cell 2; a downward trend in the LDS of Cell 3 and the HTW of Cells 4, 6, and 7; and no trend for the LDS in Cell 1 and the HTW in Cell 8. Results for the Rank von Neumann Ratio Test indicate there is a serial correlation in the LDS of Cell 3 and the HTW of Cells 2 and 4, while data in the remaining horizons are independent and lack serial correlation. There were no outliers detected in any of the horizons.

Table 3–5. Summary of Statistical Tests for Boron LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Distribution	Trend	Serial Correlation	Outliers	
					Present	Removed
Cell 1	LDS	normal	none	no	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 2	LDS	insuf. data	insuf. data	insuf. data	insuf. data	insuf. data
	HTW	normal	up	yes	no	NA
Cell 3	LDS	normal	down	yes	no	NA
	HTW	NC	NC	NC	NC	NC
Cell 4	LDS	NC	NC	NC	NC	NC
	HTW	log normal	down	yes	no	NA
Cell 5	LDS	NC	NC	NC	NC	NC
	HTW	normal	up	no	no	NA
Cell 6	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	no	no	NA
Cell 7	LDS	NC	NC	NC	NC	NC
	HTW	normal	down	no	no	NA
Cell 8	LDS	NC	NC	NC	NC	NC
	HTW	normal	none	no	no	NA

Distribution determined by Shapiro-Wilks Test of Normality
Trend determined by Mann-Kendall Trend Analysis and Sens Slope Analysis
Serial Correlation determined by Rank von Neumann Ratio Test
Outliers determined by Dixon's Test; outliers were removed if Shapiro-Wilks test failed
NA – not applicable
NC – not considered because the boron concentration is inappropriate for use as a detection ion in this horizon

Based on the results in Table 3–5, the data trends in Cells 2 through 7 indicate that a B control chart cannot be used to monitor leakage in these horizons. B data from the LDS horizon of Cell 1 and the HTW of Cell 8 meet the three assumptions outlined above and are adequate to establish baseline conditions in these horizons. Therefore, for Cells 1 and 8, future data can be compared against these baseline conditions using a control chart.

3.6 Statistical Summary

Table 3–6 is a summary of each parameter that can be used to monitor leakage in the LDS and HTW horizons, based on the results of the statistical tests. As only a single analysis is available for the LDS of Cell 2, there is no statistical evaluation possible for this horizon. For the HTW of

Cells 1 and 5, the statistical tests indicate that the parameter concentrations are not at steady state, and monitoring via control charts is not possible.

Table 3–6. Summary of Indicator Parameters for LDS and HTW Monitoring Horizons of the OSDF

	Horizon	Parameter
Cell 1	LDS	B, Mn
	HTW	None
Cell 2	LDS	Fe[a]
	HTW	Mn, SO_4
Cell 3	LDS	Mn, U
	HTW	Na
Cell 4	LDS	U
	HTW	Na
Cell 5	LDS	Mn
	HTW	None
Cell 6	LDS	Mn, U
	HTW	Na
Cell 7	LDS	Mn, U
	HTW	U
Cell 8	LDS	U
	HTW	B

[a]Based on a single analysis for iron in the LDS

In Cell 1, B and Mn are useful monitoring ions in the LDS horizon. The HTW of Cell 2 can be monitored using Mn and SO_4. For Cell 3, Mn and U can be used in the LDS, while Na is useful in the HTW. Cell 4 can be monitored using U in the LDS and Na in the HTW. The LDS of Cell 5 can be monitored with Mn. In Cell 6, Mn and U can be used in the LDS and Na in the HTW. For Cell 7, Mn and U can be used in the LDS and U in the HTW. Finally, Cell 8 can be monitored using U in the LDS and B in the HTW.

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4.0 Conclusions

A preliminary analysis of the common ions in the monitoring horizons of the OSDF suggests that Mn and U are the most useful ions for evaluating leachate migration from the LCS to the LDS. Relative to the LDS, elevated Mn and U values in the LCS are derived from the waste materials placed in the cells. Mn concentrations in the LCS exceed those in the LDS by 10 to 230 times, with the exception of Cell 8, where the LDS Mn value is 4 times greater than the LCS. This latter case is puzzling, but it may reflect that less structural iron is present in Cell 8. The U levels in the LCS are 4 to 7 times greater than the LDS, and these elevated concentrations are clearly tied to the leaching of U from the waste materials placed in the cells. As noted at the end of the section on minor ions, Fe may be a useful indicator ion for LCS-to-LDS migration in Cell 2, but the single analysis available for the LDS precludes a robust statistical analysis at this time.

Ions that are the most useful for monitoring leachate migration from the LDS to the HTW horizon include B, Na, and SO_4. All cells have B concentrations in the LDS that exceed those in the HTW by a factor of 4 to 12, and this is the most useful ion for monitoring leaking from the LDS. A definitive source for the elevated Na concentrations in the LDS has not been identified, but Na concentrations in the HTW of Cells 1 through 7 are 6 to 27 times less, which indicates that Na is useful to monitor fluid communication between these horizons. Cells 2, 4, 5, 6, 7, and 8 have SO_4 values in the LDS that exceed those in the HTW by 5 to 20 times.

Statistical tests show that many of the ion data sets for the LDS and HTW horizons fail the trend analysis and serial correlation tests, indicating that the chemical conditions are not at steady state. There is no single ion that can serve as a universal monitoring indicator for all cells. For the LDS horizon, U is useful for Cells 3, 4, 6, 7, and 8, while Mn is useful in Cells 1, 3, 5, 6, and 7. Cell 2 results for the LDS are constrained to a single analysis, and no statistical conclusion can be drawn until additional fluid volume appears in the LDS horizon. In the HTW horizon, Na is useful in Cells 3, 4, and 6; Mn and SO_4 in Cell 2; U in Cell 7; and B in Cell 8. There are no useful monitoring parameters for the HTW in Cells 1 and 5.

The above recommendations on potential monitoring ions are based on the assumption that the volume of leachate from the source horizon that enters the target horizon is 1/10 of the volume found in the target horizon. The validity of this assumption has not been tested. However, if the volume of leachate from the source horizon is much less than 1/10 of the fluid volume in the target horizon (a more probable case), detection of leachate migration will not be possible unless the ion concentration in the source is much higher than that in the target horizon (Figure 1–2). For example, the Mn concentration in the LCS of Cell 3 is 230 times greater than that in the LDS, and an LCS leachate volume as low as 1/1000 of the LDS volume can be detected in the LDS via the monitoring of Mn levels.

A final note on the monitoring of common ions in the LDS and HTW horizons is of interest. If sufficient volumes of fluid do not enter the LDS layers of the cells, monitoring the LDS and HTW horizons for chemical constituents is meaningless from the perspective of leachate migration because there is no hydraulic head to drive leachate out of the LDS. Therefore, it is recommended that monitoring for chemical constituents in the LDS and HTW be discontinued until fluid volumes in the LDS indicate that flow to the HTW is possible.

End of current text

5.0 References

DOE (U.S. Department of Energy), 2002. Technical Memorandum for the On-Site Disposal Facility Cells 1, 2 & 3 Baseline Groundwater Conditions, 20100-RP-0021, Rev. B, U.S. Department of Energy, Cincinnati, Ohio.