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Characterization of Mine Leachates and the Development of a Ground-Water Monitoring Strategy for Mine Sites

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by

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Notice

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Section 1

Introduction

The total number of mining sites, both active and inactive, in the United States has been estimated to be as high as 82,000 (Office of Technology Assessment, 1984). Approximately 80 percent of the current mining activity in this country is associated with the recovery of gold and copper. The specific segment of the mining industry that has shown the greatest growth in the past 20 years is the use of cyanide heap leaching to recover gold. Although this technology is more than 100 years old (Murrey and Moeller, 1985), the commercial application of this process has recently increased because (1) gold can now be recovered from low grade ores that are not considered economically viable with conventional mining techniques, (2) the procedure is amenable to either small-scale or large-scale operations and has a shorter start up period compared to conventional gold-mining techniques, and (3) the start up costs are generally lower than conventional gold mining operations (Hoye, 1988). An estimated 300 heap leaching facilities are now operational in the United States and approximately one-third of them are located in the State of Nevada.

The quantity of mine wastes produced in the United States is enormous. It has been estimated that 20,000 active mines processed 1.5 billion tons of ore annually (EPA, 1985) and the cumulative quantity of mine waste produced has been estimated at 50 billion tons (Zilka, 1992). The vast majority of the mined ore is discarded in waste piles, tailings basins, abandoned mines, and heap leaching pads. It has been estimated that global mining activity will disturb 240,000 km^2 by the year 2000 (Moore and Luoma, 1990).

When the Resource, Conservation, and Recovery Act program was initiated by the U.S. Environmental Protection Agency, the emphasis was placed on developing approaches to classifying wastes (U.S. EPA, 1990). At that time, seventeen industries including mining were originally exempted from RCRA monitoring requirements because the wastes were generated in large quantity and were considered to have low toxicity. Subsequently, the Agency determined that most mining waste may pose an unacceptable environmental risk if they are not properly managed (EPA, 1987). This decision raised the issue of how to properly monitor the environmental effects of mine waste disposal:

1. The composition and environmental behavior of mine waste leachates is poorly understood.
2. The problem of how to effectively sample the large areas covered by tailings ponds, that may range in size from hundreds to thousands of acres, has never been addressed.
3. The parameters that should be monitored in ground water and surface water adjacent to mine waste disposal sites to detect fugitive mine waste leachate have not been selected and evaluated.

In order to address these points, a research project was initiated to identify appropriate parameters to reliably monitor mine waste leachates.

The approach that was used during this study was to access, compile, and analyze reports and data that have been submitted to state regulatory agencies as part of routine, on-going monitoring programs at mining facilities throughout the southwestern United States. This effort focused on cyanide heap leaching facilities in Nevada and copper mines in Arizona. This technique of using routine regulatory monitoring data, which was previously used to characterize ground water contamination in the vicinity of waste disposal sites (Plumb, 1992; Plumb and Pitchford, 1985; and Plumb and Fitzsimmons, 1984), was selected for several reasons:

1. Substantial monitoring data from a large number of sites can be compiled in a relatively short period of time.
2. The resultant project data base is more useful for identifying industry-specific trends than a single, detailed site investigation.
3. The use of historical records provides a means to assess possible temporal trends that may exceed the length of the project.

Since all of the constituents of mine waste leachate, except cyanide at the heap leaching sites, are naturally occurring substances that do not uniquely characterize these leachates, this research project utilized ionic ratios or multiple ion chemical signatures to fingerprint mine waste leachates. These data assessments are presented in a series of case studies for 22 heap leaching facilities in Nevada (Chapter 5) and 4 copper mines in Arizona (Chapter 6). Each of these examples demonstrate that mine waste leachates have a distinctive ionic composition that characterize it at the source and can be used to differentiate it from adjacent ground water or surface water. The set of parameters that define the leachate fingerprints have been suggested as key detection monitoring parameters for the mining industry. Furthermore, a multiple-phased monitoring strategy has been described for the detection and assessment of adverse impacts on ground water due to mining operations (Chapter 7). It is anticipated that these results will provide the improved technical guidance necessary to establish effective monitoring programs at mining sites.

Section 2

Data Collection

2.1 Data Sources

The conventional approach for this type of study is to select one or more facilities and establish long-term monitoring programs to obtain the required data. However, a consideration of the project constraints indicated that this approach would not be appropriate for a number of reasons. First, the project funding would only be sufficient for a limited sampling effort. While an acceptable site characterization program could be performed under these conditions, it would be difficult, if not impossible, to extrapolate the results and observations from one site to the mining industry in general. Second, it would be impossible to characterize temporal fluctuations with a periodicity equal to or greater than the duration of the project. Possible delays in gaining site access and installing monitoring equipment could further complicate this problem. Third, any incurred costs due to installing a monitoring well network would further reduce the amount of data that could be collected to characterize mine waste leachates. In order to avoid these potential problems, an alternative approach was used to obtain sufficient data to characterize mine waste leachates.

The approach that was selected to obtain data in this project was to access, tabulate, and evaluate routine monitoring data submitted to state regulatory agencies by mining companies. This technique has previously been used successfully to characterize ground-water conditions in the vicinity of hazardous waste disposal sites and municipal landfills (Plumb and Pitchford, 1985; Plumb, 1987; Plumb, 1991; Plumb, 1992) and offers several distinct advantages over a detailed site investigation. The primary benefit of this approach is that it provides characterization data from a larger number of facilities. Therefore, if a trend or pattern can be determined, the results are more representative of the mining industry. A second benefit of this approach is that it provides a means to assess those constituents that are currently being used in monitoring programs at mining facilities. A third benefit of this approach is that it can produce extensive temporal records to identify possible cyclic behavior patterns that may be present. Data records of three to 17 years in length were obtained for several facilities during the data collection process. A fourth benefit of this approach is that it leverages the project funding level. As a result, there is a much larger information base to characterize the composition of mine waste leachates and select potentially useful monitoring parameters.

The initial source of mine site monitoring data in this study was the Bureau of Mining Regulations of the Nevada Department of Environmental Protection. This agency was contacted because the State of Nevada has established extensive monitoring requirements for mining facilities and there are approximately 100 operational gold heap leaching facilities in the state. The agency consented to the use of their data in this study and their offices were visited in September, 1993.

The monitoring records for mining facilities in the State of Nevada were extremely well organized but only available in hard-copy format. The individual files were reviewed to select appropriate sites to be used in the project. The factors that were considered during the selection process included the following:

1. The amount of monitoring data that were available. Some facilities that were just starting operations or were in closure were excluded because there was limited data or no data.
2. The completeness of the data. The State of Nevada requires complete geochemical analyses, including pH and total dissolved solids, a trace metal scan, and cyanide analysis at heap leaching facilities.
3. A clear identification of the sampling locations. Depending on permit requirements, individual facilities monitored plant make up water, the barren pond, the pregnant pond, the tailings pond or tailings slurry, ground water in the vicinity of the mine, and a laboratory leachate of waste rock at the mine site (Nevada Meteoric Water Mobility Test). Site maps indicating sampling locations were obtained when possible.
4. A clear identification of the sampling dates. The individual sites generally contained quarterly monitoring results for a period of one to three years. These data are needed to assess possible temporal trends.

The monitoring records from 51 gold heap leaching facilities were reviewed in a three day period in September, 1993. The monitoring records from 36 of these sites were copied for more extensive evaluation during the project. The data from 26 of these facilities were used in the preparation of this report.

A second source of monitoring data for mining facilities in the southwest United States was the Arizona Department of Environmental Quality. The offices of this agency were visited in September, 1994 and again in May, 1995. A total of 10 site files were reviewed for the data characteristics identified above and the records from five copper mining operations were retained for use during this project. The data from the individual sites generally consisted of complete geochemical analyses and a trace metal scan for the facility tailings basin and several ground-water monitoring wells in the vicinity of the tailings basin. The period of record at the Arizona copper mining facilities ranged from two and a half years to 17 years.

A third source of data briefly discussed in this report is a laboratory study on the characterization of incinerated municipal waste ash leachate that was conducted on behalf of the U.S. Environmental Protection Agency (Plumb and Engelmann, 1991). This dataset includes geochemical and trace metal results for laboratory and field leachates from five ash monofills across the country. Although this study was not directly concerned with mining, it was pertinent to the characterization of mine waste leachates for two reasons. The first reason is that incinerated municipal waste ash is similar to mine waste in that it is essentially an inorganic matrix. The second reason is that the set of geochemical parameters was shown to be useful for fingerprinting these leachates and the same small set of geochemical ions were also the most abundant ions in mine waste leachates. Based on similar compositional characteristics of incinerated municipal waste ash leachates and mine leachates, the multiple ion fingerprinting technique developed for incinerated municipal waste ash leachate (Plumb and Engelmann, 1991) provided a useful approach for characterizing mine leachates.

2.2 Data Compilation

The monitoring results that were compiled to characterize mine waste leachates and identify appropriate monitoring parameters were obtained from several sources identified above. This approach can produce a substantial volume of data in a relatively short period of time. However, when using environmental data generated in response to different regulatory programs, there are certain circumstances and limiting conditions that must be recognized prior to using the information. These issues include (1) the format or organization of the data, (2) the completeness of the sample analyses, (3) the labeling of the sample results, and (4) the identification of the sampling location.

The first issue that is always encountered on reviewing data files is the variable format in which results are reported. Examples of this point are monitoring results listed alphabetically, monitoring results listed alphabetically by chemical symbol, monitoring results listed by analytical technique (anions, cations, trace metals), and monitoring results listed by regulatory concern (separate lists for chemicals with and without established criteria limits). In order to facilitate a compilation and comparison of the monitoring data from different mining facilities, all of the data were entered into a uniform spreadsheet format. The format selected for use in this study was Quattro Pro.

Separate Quattro Pro files were created for each mining facility. Except for two parameters, cyanide, and total dissolved solids, the data for 40 parameters were transcribed from the xeroxed records and entered alphabetically by chemical symbol into a spreadsheet as a function of sampling location (Well 1, Well 2, tailings pond, etc.) and sampling date. Cyanide was treated differently because it is a parameter of concern at the gold mining facilities but not at the copper mining facilities. The total dissolved solids data were treated separately to facilitate mass balance and charge balance calculations.

A second issue that became apparent on creating a project database is the fact that the extent of sample analysis can vary (1) between regulatory programs, (2) between different sampling locations on the same site, and (3) at the same site over time. For example, the Nevada Department of Environmental Protection currently requires analyses for 39 inorganic parameters and cyanide but the Arizona Department of Environmental Quality requires analyses for 23 inorganic parameters. In addition, the Nevada Department of Environmental Protection requires gold mining companies to analyze the process solutions (barren pond and pregnant pond) for the 39 inorganic parameters and cyanide but monitoring well samples must only be analyzed for 26 inorganic parameters and cyanide. Finally, individual site operators can seek a variance from the regulatory requirements if they can demonstrate to the regulatory agency that certain monitoring requirements are not useful or necessary. As a result of these factors, the composite project database is not highly structured. The spreadsheet matrix developed for the project was designed to accept the maximum number of analyses required by the Nevada Department of Environmental Protection.

As the monitoring results were entered into a spreadsheet, the following conventions were used:

1. If a particular analysis was not required or not reported, no entry was made in the spreadsheet. This permitted statistical functions (sample counts, averaging, calculation of standard deviations, etc.) to be applied to the data set.
2. If a particular analysis was reported as being below the limit of detection, the result was entered into the spreadsheet as less than the numerical value of the reported detection limit. [Quattro Pro treats a less than value as a sample entry when counting the number of samples analyzed but it treats the entry as a zero when calculating an average concentration or a

standard deviation of a sample set. By listing the actual sample detection limit, alternative values such as one-half the detection limit can be inserted at a later date if necessary.]

3. As the data were entered into the spreadsheets, the results for all parameters except pH were expressed in units of mg/L. This facilitated a direct comparison of data at the same location over time, between different locations at the same site, and at different sites.

A third issue that can arise when working with data from different sources is the proper labeling of the data. Specifically, when working with inorganic data, an important consideration is whether the sample is filtered prior to analysis. If available, this information is entered as a footnote in the spreadsheet to avoid comparing "dissolved" and "total" analyses.

A fourth issue that occasionally arises is uncertainty over the sampling location of the results being reported. Most cases can usually be resolved with a site map (which was obtained with the monitoring results) or careful scrutiny of laboratory traffic reports or analytical data sheets. If the sampling location could not be unequivocally defined, the data were not entered into the spreadsheet.

2.3 Quality Assurance Considerations

The routine regulatory monitoring data used in this project were generated by several different laboratories before the project began and are on file with two different state regulatory agencies. Consequently, these data were not generated in accordance with a single quality assurance project plan. In fact, although Nevada and Arizona both require mining companies to use state certified laboratories to produce monitoring data, the initial review of the site monitoring records produced no indication of a formal quality assurance program at any of the individual mining facilities. This does not mean that there was no attempt to control the quality of the data being generated but simply that there was no record in the files of any site-specific quality control requirements.

Since many of the conventional measures of data quality were absent from the site records (no replicate sample collection, no duplicate analysis, no check sample analysis, and no blank analysis), several internal data quality checks were established to assess the quality of the data and assure their suitability for use. The following approaches were used to evaluate the acceptability of the compiled monitoring data from mining facilities:

2.3.1 Accuracy Data Quality Objective

Mass Balance Considerations

A review of the data from each mining facility repeatedly demonstrated that a short list of geochemical parameters were the dominant ions in mine process solutions, mine waste leachates, tailings water, and ground water. These ions were Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, SO_4^{-2}, NO_3^{-}, Cl^{-}, and alkalinity (HCO_3^{-} and CO_3^{-2}). An internal data quality check was established based on the fact that the sum of the individual ions must equal the total dissolved solids concentration of the solution:

$$Ca^{+2} + Mg^{+2} + Na^{+} + K^{+} + SO_4^{-2} + NO_3^{-} + Cl^{-} + \text{alkalinity} = \text{TDS}.$$

The data quality objective used to check the data in this manner was that the sum of the ions should equal at least 80 percent but less than 120 percent of the total dissolved solids concentration in the sample. This approach does not verify the accuracy of the individual analyses. However, all of the analyses in the data set must be reasonably accurate in order for the mass balance requirement to be satisfied. If the results were outside the acceptable range, the data set was considered suspect because one or more of the analyses were in error or one or more analyses were missing.

The trace metal data were excluded from the mass balance calculations for two reasons. First, they collectively represented less than two percent of the total dissolved solids concentrations. Second, and more importantly, trace metals are frequently reported as "total" concentrations. Since particulate forms of trace metals would not be included in a total dissolved solids measurement, it would be erroneous to include them in a mass balance calculation.

Charge - Balance Considerations

A second balance technique that was used as an indirect check on the overall accuracy of the analyses for the most abundant ions in a mine waste leachate is that the sum of the anions (negative ions) must be equal to the sum of the cations (positive ions). This internal data check follows from the fundamental concept that all solutions must be electrically neutral. Therefore:

$$Ca^{+2} + Mg^{+2} + Na^{+} + K^{+} = SO_4^{-2} + NO_3^{-} + Cl^{-} + \text{alkalinity.}$$

In order to perform this check, reported constituent concentrations (in mg/L) were divided by the appropriate equivalent weight of each constituent to produce units of milliequivalents/L. The data quality objective used to check the data in this manner was that the ion balance should be within 20 percent relative standard deviation. This was calculated as:

$$\frac{(\text{(Sum of Cations)} - \text{(Sum of Anions)} * 100\ )}{\text{(Sum of Cations)} + \text{(Sum of Anions)}} < 20\ \%.$$

If the data set produced an acceptable mass balance and an acceptable charge balance, the accuracy of the data set was considered acceptable for use in the study.

Trace metals were also excluded from this calculation because of their low relative abundance and the fact that they are usually present as sorbed or particulate matter (i.e., they are not present as true ions which would be included in a charge balance equation). In addition, there was no information on the specific oxidation state of individual trace metals which precludes their use in charge balance calculations.

2.3.2 Precision Data Quality Objectives

As stated earlier, the original data sets did not contain any information that could be used to calculate the precision of the individual analyses. However, based on the extent of the spatial and temporal sampling that was reported, it was possible to define several indirect checks on the precision of the data sets. These checks were based on the relative abundance of the mine leachate constituents (major cations, major anions, total trace metals, and cyanide, where appropriate, were used for this purpose).

Temporal Sampling from the Same Location

One approach to assess the precision of individual data sets was to contrast measurements taken from the same location at different times. For example, the monitoring results from Well BAC1 in the tailings disposal area at the Phelps-Dodge facility in Clarksdale, Arizona are tabulated in Table 1. For this presentation, the actual concentrations of each constituent, in mg/L, was divided by the total dissolved solids concentration of the sample, also in mg/L. [Note that the sum of the ions represent 93 percent of the total dissolved solids concentration which is within the data quality acceptability range for accuracy]. The normalized concentration data were used to prepare a histogram that provided a graphical fingerprint for the ground water at this location. Regression analysis was then used to compare the analyte distribution pattern between the two sampling periods. In this case, the calculated r^2 value was 0.998 (i.e., there was a 99.8 percent match between the two histograms).

A formal data quality objective for this data assessment technique was not established because one of the project objectives was to determine whether mine waste leachates did, in fact, have some reproducible characteristics that could be used as a basis for selecting appropriate monitoring parameters. However, it was repeatedly noticed that the normalized concentration histograms from the same location produced regression coefficient r^2 values greater than 0.900 (90 percent match) while a regression analysis of histograms from different locations (such as a tailings basin and an upgradient monitoring well) produced regression coefficient r^2 values less than 0.100 (less than 10 percent match). Thus, consistency of the calculated regression coefficient provided a means to assess the reproducibility of the monitoring results from the same location at different times.

Simultaneous Sampling from Different Locations

A similar approach was used at several mining locations that had established multiple monitoring locations in the same area. For example, the Phelps-Dodge copper facility had six monitoring well locations within the designated tailings disposal area. If the selected monitoring parameters defined a pattern that was characteristically unique to the mine waste leachate, the histogram pattern produced at each of these locations should be similar. The same technique of regression analysis was used to compare the monitoring parameter histograms at each of the monitoring locations. The calculated r^2 values for these comparisons were generally greater than 0.95 (95 percent match). The high regression analysis coefficients suggest that the data are valid and that the recurring pattern is characteristic of mine waste leachate. If the data were of unacceptable quality, the regression coefficients would be smaller and more variable.

Different Sampling Locations in a Recirculating System

The heap leaching facilities in Nevada utilize a recirculating alkaline cyanide solution to extract gold from ore being processed. The Nevada Bureau of Mining Regulations requires individual facilities to sample several locations in the recirculating system on a quarterly basis. A comparison of monitoring results from two separate locations in a recirculating system is similar to comparing monitoring results from two different locations in the same area except that a recirculating system is a closed, well defined system. Regression analysis was used to compare the normalized concentration histograms defined by the major geochemical ions at each of these locations.

As stated above, no specific precision data quality objectives have been established for the project since one of the objectives is to assess the reproducibility of identifiable trends in mine waste leachate composition. However, the results indicate that the reproducibility of the multiple ion pattern or geochemical fingerprint observed in heap leaching process solutions is generally greater than 90 (regression coefficient r^2 values > 0.900).

2.3.3 Completeness Data Quality Objective

Because a graphical technique is being used to prepare multi-ion histograms for regression analysis, complete analysis for the identified geochemical parameters (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, SO_4^{-2}, NO_3^{-}, Cl^{-}, alkalinity, and total dissolved solids) were necessary. Therefore, the functional data quality objective for completeness was 100 percent of the required analyses for each sample.

2.3.4 Comparability Data Quality Objective

Since the data used in the project were derived from several sources, careful consideration was given to the units used to express the monitoring results. The reported concentration for all parameters except pH were expressed in units of mg/L as the data were reviewed and tabulated. This data conversion permitted the monitoring results from different sampling periods and different facilities to be directly compared with each other.

Section 3

Chemical Composition of Mine Waste Leachates

The routine regulatory monitoring data that were tabulated and reviewed provided estimates for the composition of three types of mine waste leachates. The three mine waste leachates that could be estimated with the project data base were (1) the composition of process solutions at heap leaching facilities in Nevada, (2) the composition of waste rock leachates at heap leaching facilities in Nevada, and (3) the composition of tailings water at copper mining operations in Arizona. The data from 26 heap leaching facilities in Nevada and 5 copper mining facilities in Arizona were composited in order to document the constituents for which analyses have been reported for each of these mine waste leachates and the concentrations at which these constituents have been detected.

3.1 Heap Leaching Process Solution

The process solution, which will be described in more detail later in the report, is an alkaline cyanide solution that extracts gold by complexation as it is recirculated through the ore. This solution represents a potential mine waste leachate if it migrates from the ore processing facility. The Nevada Bureau of Mining Regulation requires mine operators to conduct quarterly monitoring at several locations in the process solution system. Depending on the operations at each mine, these locations may include the barren pond, the pregnant pond, the tailings solution, and the tailings reclaim water. These samples are usually analyzed for 9 geochemical parameters, 27 trace metals, total dissolved solids, phosphorous, pH, and cyanide.

The composited monitoring results from the process solutions at 26 heap leaching facilities have been presented in Table 3-1. These results illustrate several characteristics of the process solution composition. First, the concentrations for each of the individual constituents are highly variable and non-normally distributed. This is indicated by the fact that the calculated standard deviation for each parameter is generally larger than the average concentration for that parameter (when the ratio of the standard deviation to the average for a set of values is greater than 1.0, the set of values is considered to be non-normally distributed). A second characteristic of the process solution is that a small suite of inorganic parameters consistently dominate the composition of the leachates.

As shown in Figure 3-1, the most abundant ions in the process solution are common geochemical constituents such as alkalinity (bicarbonate and carbonate), calcium, chloride, magnesium, sodium, and sulfate. Third, the process solutions have a high cyanide concentration and an elevated pH. The cyanide is purposely added to extract gold from the ore and the higher pH is necessary to maintain free cyanide ions in solution and prevent volatilization of cyanide gas. Finally, although the trace metals are minor constituents of the process solution, several are present at exceptionally high concentrations. Trace metal concentrations in excess of 10 mg/L, such as iron, copper, manganese, and zinc, are due to complexation with cyanide and/or measurement of particulate concentrations.

Table 3-1. Composite monitoring results from 26 heap leaching facilities in the State of Nevada.

Constituent	Samples	Average Concentration	Standard Deviation
Alkalinity	186	**787**	**1952**
Aluminum	148	**0.218**	**0.439**
Antimony	140	**0.105**	**0.768**
Arsenic	186	**0.469**	**0.874**
Barium	179	0.042	0.095
Beryllium	148	**0.057**	**0.145**
Bismuth	148	0.308	1.945
Cadmium	186	**0.100**	**0.245**
Calcium	182	245	**342**
Chloride	183	**674**	**1093**
Chromium	180	0.343	**0.816**
Cobalt	148	**1.885**	**3.127**
Copper	182	**158**	**570**
Fluoride	186	**26.72**	**79.12**
Gallium	148	0.013	0.070
Iron	182	**373**	**1076**
Lead	186	0.029	**0.217**
Lithium	148	0.354	1.006
Magnesium	181	**628**	**1742**
Manganese	179	**12.05**	**33.94**
Mercury	184	**1.194**	**2.901**
Molybdenum	148	**6.770**	**23.447**
Nickel	148	**1.026**	**2.618**
Nitrate	186	55.36	**70.17**
Phosphate	148	**99.61**	**258.76**
Potassium	182	42.29	85.74
Scandium	146	0.078	0.195
Selenium	186	**1.597**	**5.054**
Silver	178	**1.695**	**5.974**
Sodium	182	**680**	**603**
Strontium	148	3.757	4.869
Sulfate	186	**7956**	**19473**
Thallium	148	**0.006**	**0.029**
Tin	148	0.074	0.805
Titanium	148	0.627	1.801
Vanadium	129	0.037	0.115
Cyanide	183	**63.22**	**83.65**
Zinc	181	**12.33**	**77.52**
pH	186	8.71	**2.70**
TDS	180	**16953**	**35942**

All concentrations, except pH, expressed in units of mg/L.
Values in **bold** exceed one or more criteria.

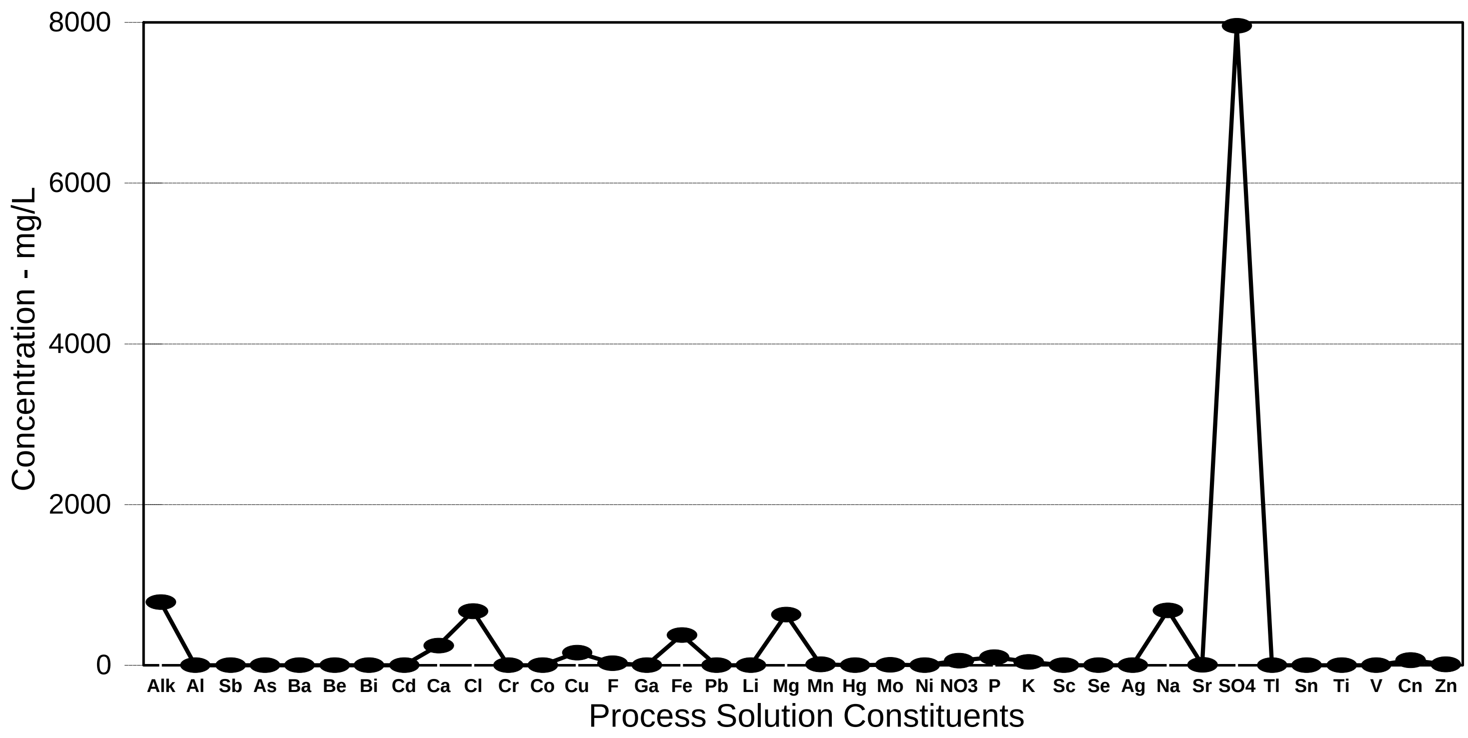


Figure 3-1. Composite process solution monitoring results.

The composited process solution data were evaluated to identify constituents that represent a potential environmental risk. This was accomplished by comparing the process solution data with screening criteria previously used by the U.S. Environmental Protection Agency to assess the potential environmental risks of other types of mining operations (EPA, 1990). These screening criteria were developed to evaluate the potential hazards of liquid wastes to human health via ingestion, to assess the potential adverse effects of contaminants on aquatic organisms, and to assess degradation of surface and ground-water quality. The screening criteria used to assess each of these risks were originally defined as follows (EPA, 1990):

> **Human Health Risk Level** is defined as 10 times the oral toxicity criteria for carcinogenic and non-carcinogenic effects. This assumes ingestion of 2 liters of contaminated water per day for 70 years.
>
> **Aquatic Ecological Risk Level** is defined as 100 times established ambient water quality criteria.
>
> **Surface and Ground-Water Quality Degradation Level** is defined as 10 times the maximum contaminant levels for drinking water. If drinking water criteria did not exist, EPA used the lower of 10 times the taste and odor threshold, 10 times the livestock watering guidelines, 10 times the irrigation guidelines, or 100 times the ambient water quality criteria for bioaccumulation by fish.

The screening criteria that were used by EPA, which are presented in Table 3-2, incorporate conservative dilution factors ranging from a ten-fold dilution for consumptive use of water to a 100-fold dilution for ecological effects. These variable dilution factors were originally selected to evaluate the intrinsic hazard of a mining waste stream and to limit the number of parameters for which a detailed risk assessment would be required (EPA, 1990). These screening criteria were used in this project to produce results that are consistent with the earlier EPA study (EPA, 1990).

The composite process solution monitoring results in Table 3-1 were compared to the EPA screening criteria in Table 3-2 to flag values above the criteria and identity parameters that represent a potential environmental risk. In performing this comparison, both the average concentration and the standard deviation in Table 3-1 were highlighted when the average concentration exceeded the criteria. However, if the average concentration was below the criteria but the higher concentrations for a parameter exceeded the criteria, only the standard deviation for that parameter was highlighted. This distinction provides a method to prioritize the process solution constituents (constituents with an average concentration above the screening criteria represent a more consistent or more frequent environmental risk than constituents that occasionally exceed the screening criteria).

There are 25 process solution parameters for which the average concentration exceeds one or more of the screening criteria in Table 3-2. This list of parameters includes alkalinity, aluminum, antimony, arsenic, beryllium, cadmium, chloride, chromium, cobalt, copper, fluoride, iron, magnesium, manganese, mercury, molybdenum, nickel, phosphorous, selenium, silver, sulfate, thallium, cyanide, zinc, and total dissolved solids. Although there are no established criteria for alkalinity or magnesium, both constituents have been flagged as a potential water quality problem because their high concentrations exceed the total dissolved solids criterion. In addition, there are five other parameters (calcium, chromium, lead, nitrate, and pH) that occasionally exceed the screening criteria even though the average concentrations are below the screening criteria. Thus, a total of 30 constituents have been reported in process solutions at gold heap leaching facilities at levels above screening criteria used to assess human health problems, water resources damage, and aquatic ecological risks. Although all of these 30 constituents will not be above screening criteria levels at all sites. However, the large number of parameters that represent a potential environmental risk establishes the need for effective monitoring at gold heap leaching facilities.

Table 3-2. Screening criteria used by EPA to identify contaminants of concern in mine waste leachates (EPA, 1990).

Constituent	Samples	Average Concentration	Standard Deviation
Alkalinity	186	**787**	**1952**
Aluminum	148	**0.218**	**0.439**
Antimony	140	**0.105**	**0.768**
Arsenic	186	**0.469**	**0.874**
Barium	179	0.042	0.095
Beryllium	148	**0.057**	**0.145**
Bismuth	148	0.308	1.945
Cadmium	186	**0.100**	**0.245**
Calcium	182	245	**342**
Chloride	183	**674**	**1093**
Chromium	180	0.343	**0.816**
Cobalt	148	**1.885**	**3.127**
Copper	182	**158**	**570**
Fluoride	186	**26.72**	**79.12**
Gallium	148	0.013	0.070
Iron	182	**373**	**1076**
Lead	186	0.029	**0.217**
Lithium	148	0.354	1.006
Magnesium	181	**628**	**1742**
Manganese	179	**12.05**	**33.94**
Mercury	184	**1.194**	**2.901**
Molybdenum	148	**6.770**	**23.447**
Nickel	148	**1.026**	**2.618**
Nitrate	186	55.36	**70.17**
Phosphate	148	**99.61**	**258.76**
Potassium	182	42.29	85.74
Scandium	146	0.078	0.195
Selenium	186	**1.597**	**5.054**
Silver	178	**1.695**	**5.974**
Sodium	182	**680**	**603**
Strontium	148	3.757	4.869
Sulfate	186	**7956**	**19473**
Thallium	148	**0.006**	**0.029**
Tin	148	0.074	0.805
Titanium	148	0.627	1.801
Vanadium	129	0.037	0.115
Cyanide	183	**63.22**	**83.65**
Zinc	181	**12.33**	**77.52**
pH	186	8.71	**2.70**
TDS	180	**16953**	**35942**

All concentrations, except pH, expressed in units of mg/L.
Values in **bold** exceed one or more criteria.

3.2 Meteoric Water Mobility Test Leachates

Another source of information on the composition of mine waste leachates at gold mining facilities are the results from the Meteoric Water Mobility Test (MWMT). The MWMT is a standardized leaching procedure using acidic distilled water to evaluate potential contaminant migration from overburden and waste rock at a mining site (NDEP, 1990). The test is performed by leaching a rather large sample of waste rock or overburden (5 kg) with approximately five liters of distilled water (pH adjusted to 5.5 to 6.0 with nitric acid) for 24 hours. After standing for one hour, a decanted sample of the leachate is analyzed for the same parameters listed in Table 3-1.

The composite results of 132 MWMT tests from 24 heap leaching facilities in Nevada have been summarized in Table 3-3. These results are similar to the process solution data in several respects. The data for the individual parameters are variable and non-normally distributed. This is undoubtedly due to inter-facility variability and the different sources of waste rock and overburden. Another characteristic of the MWMT leachates is that a relatively short list of inorganic constituents dominate the composition of these solutions. As shown in Figure 3-2, the five most abundant ions are geochemical parameters (alkalinity, calcium, chloride, sodium, and sulfate). In addition, four other geochemical parameters (fluoride, magnesium, nitrate, and potassium) and two trace metals (iron and barium) are noticeably present although at substantially lower levels. Finally, the trace metals are minor components that do not significantly define the composition of the MWMT leachates. Each of these characteristics were previously observed in the process solution data.

One noticeable difference between the process solution composition and the MWMT leachates is the lower concentrations in the MWMT leachates. The average total dissolved solids concentration of the MWMT leachates is only 698 mg/L and the only parameter with an average concentration above 100 mg/L is sulfate (136 mg/L). By comparison, the average total dissolved solids concentration of the process solutions is 16,953 mg/L, sulfate has an average concentration of 7,956 mg/L, and six other parameters have an average concentration in excess of 100 mg/L (alkalinity, calcium, chloride, copper, iron, and magnesium).

There are at least four factors that contribute to the differences in composition between the MWMT leachates and the process water solutions. First, the MWMT sample is only leached with distilled water whereas the process solutions are prepared from ground water, with some initial TDS level, that is supplemented with additions of cyanide salts and lye or lime salts to maintain an alkaline pH. Second, the MWMT leachate is the result of a single 24-hour leaching process whereas the process solution is produced by continually recirculating an alkaline lixiviant through an ore pile for periods up to three months. Third, the process water contains cyanide which forms soluble complexes that can enhance the mobility of some ore constituents compared to distilled water leaching in the MWMT. Fourth, depending on the individual mining operations, the ore to be processed may be subjected to a crushing and blending prior to leaching. This can produce a smaller particle size and a larger surface area from which constituents can be leached from the ore.

The composite MWMT leaching results in Table 3-3 were compared to the EPA screening criteria in Table 3-2 to identify parameters that represent potential environmental risks. As with the process solution data, both the average value and the standard deviation in Table 2 were highlighted if the average concentration exceeded the screening criteria. However, if the average concentration was below the screening criteria but one or more of the higher concentrations exceeded the criteria, only the standard deviation value was highlighted. This assessment suggests that five MWMT constituents regularly exceed the screening criteria and another 13 constituents occasionally exceed the screening criteria. Compared to the process solution assessment, the smaller number of MWMT constituents above screening criteria levels is consistent with the milder leaching conditions in the MWMT test and the lower concentrations that were observed.

Table 3-3. Composite Meteoric Water Mobility Test results from 24 Nevada heap leaching facilities.

Constituent	Samples	Average Concentration	Standard Deviation
Alkalinity	120	84.6	130
Aluminum	121	3.720	**36.52**
Antimony	124	0.037	**0.244**
Arsenic	132	0.173	**0.756**
Barium	132	0.823	**1.105**
Beryllium	120	0.003	**0.026**
Bismuth	121	0.012	0.124
Cadmium	132	0.013	**0.178**
Calcium	132	70.4	317
Chloride	121	26.1	92.3
Chromium	131	**0.041**	**0.384**
Cobalt	125	0.069	**0.721**
Copper	132	0.123	**0.914**
Fluoride	122	1.49	8.89
Gallium	121	0.056	1.096
Iron	131	**10.85**	**104**
Lead	132	0.031	**0.320**
Lithium	114	0.033	0.092
Magnesium	132	12.9	43.6
Manganese	132	0.403	**2.476**
Mercury	132	**0.004**	**0.036**
Molybdenum	121	0.052	**0.308**
Nickel	124	0.067	0.539
Nitrate	117	8.37	45.58
Phosphate	118	0.87	**9.396**
Potassium	129	16.8	33.6
Scandium	121	0.002	0.020
Selenium	132	0.016	0.078
Silver	132	**0.023**	**0.201**
Sodium	132	38.6	95.1
Strontium	121	0.283	0.872
Sulfate	122	136	429
Thallium	121	0.020	**0.108**
Tin	113	0.007	0.091
Titanium	121	0.017	0.139
Vanadium	118	0.056	0.545
Cyanide	64	0.009	0.104
Zinc	132	0.236	2.369
pH	104	7.64	**3.10**
TDS	97	698	**3563**

All concentrations, except pH, expressed in units of mg/L.

Values in **bold** exceed one or more criteria.

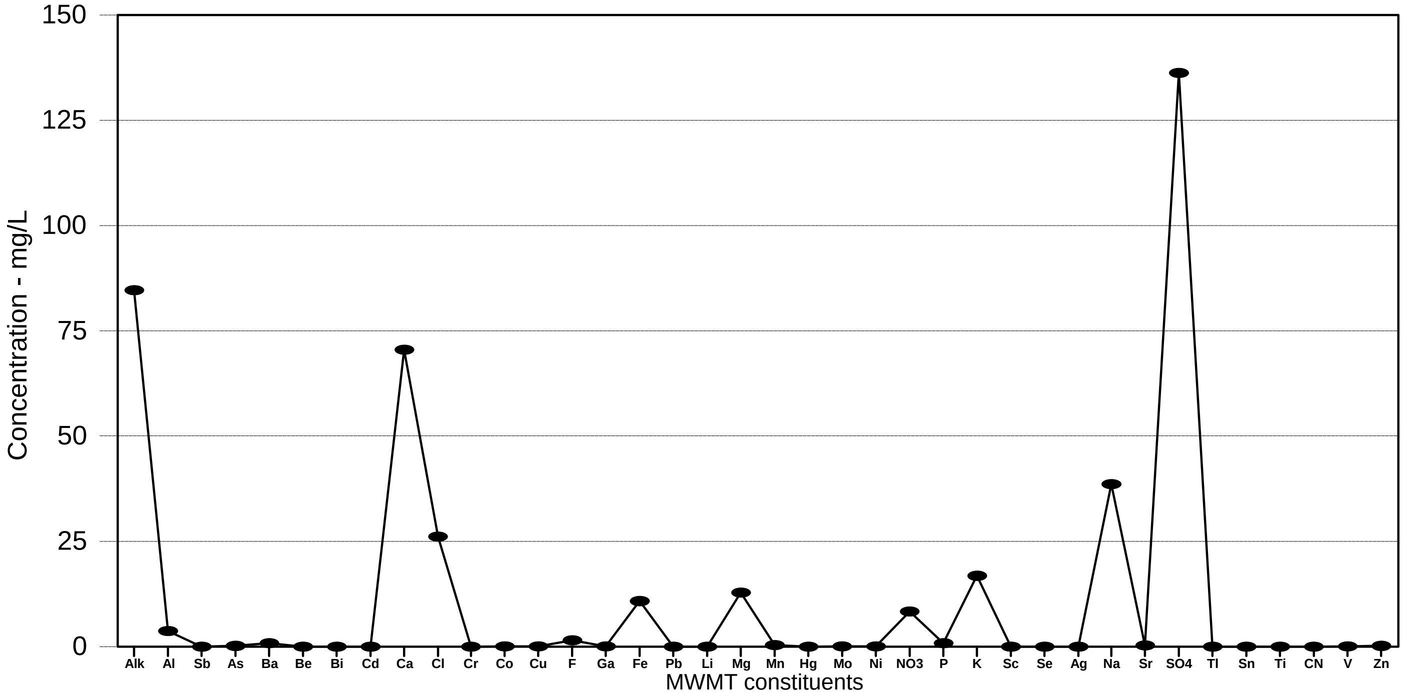


Figure 3-2. Composite Meteoric Water Mobility Test leaching results.

3.3 Tailings Ponds at Copper Mines

A third estimate for the composition of mine waste leachates was developed using the monitoring results from several copper mining facilities in Arizona. The data obtained from these sources included most geochemical parameters and a shortened list of 17 trace metals. The composite results from these facilities are presented in Table 3-4 and Figure 3-3.

An inspection of the copper tailings pond monitoring results suggests that these solutions share many of the characteristics identified for heap leaching process solutions. First, the concentrations for the individual constituents are highly variable. The standard deviation for all but six of the parameters (alkalinity, chloride, fluoride, nickel, potassium, and sodium) listed in Table 3-4 are larger than the calculated average concentration. This indicates that the concentration data are non-normally distributed which is in agreement with the process solution and MWMT data. Second, the composition of the tailings water is dominated by a small number of ions (Figure 3-3). Sulfate is a particularly prominent ion while alkalinity, calcium, magnesium, and iron are abundant. Each of these parameters, except iron, is a major geochemical parameter. Finally, even though several of the individual trace metals may be present at elevated concentrations (i.e., copper, iron, and manganese), the trace metals are the least abundant class of inorganic constituents in tailings leachate and collectively represent less than five percent of the total dissolved solids concentration.

The composite tailings pond monitoring results in Table 3-4 were compared to the EPA screening criteria in Table 3-2 to identify parameters that represent potential environmental risks. As with the process solution data, both the average value and the standard deviation were highlighted if the average concentration in Table 3-3 exceeded the screening criteria. However, if the average value was below the screening criteria but one or more of the higher concentrations exceeded the criteria, only the standard deviation value was highlighted. This assessment suggests that 14 leachate constituents can regularly be expected to exceed the screening criteria. These parameters are arsenic, beryllium, cadmium, copper, iron, lead, magnesium, manganese, molybdenum, nickel, sulfate, zinc, pH, and total dissolved solids. In addition, calcium and chromium occasionally occur at levels that exceed the screening criteria.

3.4 Summary

The States of Nevada and Arizona have established extensive site monitoring programs for gold and copper mines operating within their jurisdiction. Routine monitoring data generated in accordance with these regulatory programs have been compiled to characterize the composition of mine waste leachates. This effort summarized the analyses for 40 constituents in 363 leachate samples from 26 gold mines and 5 copper mines.

An assessment of the composited information identified several trends or patterns associated with the composition of mine waste leachates. One important aspect of mine waste leachate composition is the variable concentrations that can be encountered with each of the constituents. A second important observation is that a small number of inorganic substances dominate the composition of mine waste leachates. The most abundant constituents in all three types of mine waste leachates were common geochemical parameters such as alkalinity, calcium, magnesium, sodium, chloride, and sulfate. The rank order for these parameters varied with each of the mine waste leachates but 9 of the top 13 constituents in process solutions, 9 of the top 11 constituents in MWMT leachates, and 9 of the top 15 constituents in copper tailings ponds were geochemical parameters (Table 3-5). A third observation is that the trace metals are usually the least abundant constituents in mine waste leachates. Occasionally, iron, manganese, and copper are present at relatively high concentrations but trace metals collectively represent less than five percent of the total dissolved solids concentration of mine waste leachates. (The high iron values in Table 3-1 and Table 3-3 may represent the analysis of particulate matter in the samples rather than mine waste leachates per se because concentrations of 100 mg/L at neutral pH greatly exceed the solubility product for iron hydroxide.)

Table 3-4. Composite monitoring results from three Arizona copper mine tailings basins.

Constituent	Samples	Average Concentration	Standard Deviation
Alkalinity	45	218	147
Aluminum	0		
Antimony	8	0.014	0.036
Arsenic	28	**0.069**	**0.095**
Barium	28	0.054	0.125
Beryllium	8	**0.228**	**0.237**
Bismuth	0		
Cadmium	28	**0.407**	**0.875**
Calcium	45	421	**508**
Chloride	45	31.9	24.2
Chromium	28	1.020	**2.253**
Cobalt	2	0	0
Copper	28	**47.00**	**99.45**
Fluoride	43	1.13	0.68
Gallium	0		
Iron	28	**173**	**355**
Lead	28	**0.182**	**0.422**
Lithium	0	0	
Magnesium	45	**874**	**912**
Manganese	28	**150**	**301**
Mercury	28	0.0	0.0
Molybdenum	8	**1.063**	**1.341**
Nickel	8	**1.613**	**1.201**
Nitrate	45	5.79	7.45
Phosphate	0		
Potassium	25	68.2	37.4
Scandium	0		
Selenium	28	0	0
Silver	28	0	0
Sodium	45	105	74.9
Strontium	2	7.25	4.869
Sulfate	45	**6978**	**8543**
Thallium	8	0	0
Tin	2	0	0
Titanium	0		
Vanadium	0		
Zinc	28	**85.05**	**186.4**
pH	21	**4.63**	**2.86**
TDS	45	**10155**	**13061**

All concentrations, except pH, expressed in units of mg/L.
Values in **bold** exceed one or more criteria.

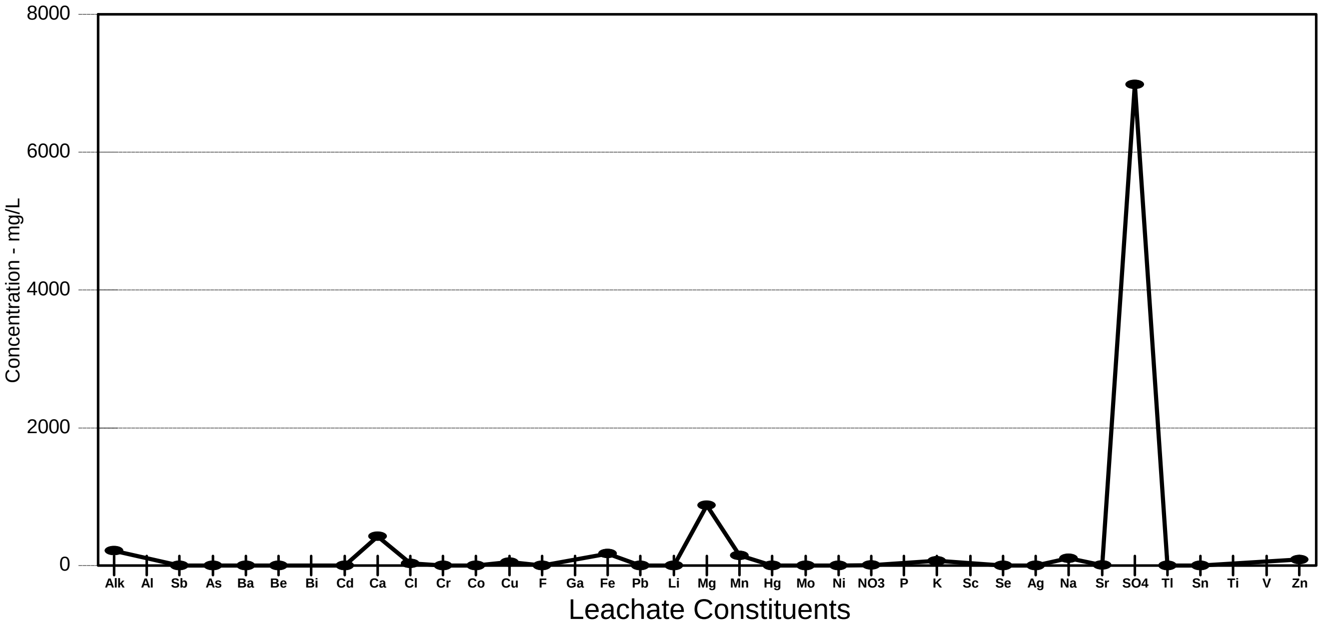


Figure 3-3. Composite monitoring results from copper mine tailings basins.

Table 3-5. Ranking of most abundant constituents in mine waste leachates at sites in project database.

Rank	Process Solution	MWMT Leachate	Tailings Ponds
1	Sulfate	Sulfate	Sulfate
2	Alkalinity	Alkalinity	Magnesium
3	Sodium	Calcium	Calcium
4	Chloride	Sodium	Alkalinity
5	Magnesium	Chloride	Iron
6	Iron	Potassium	Manganese
7	Calcium	Magnesium	Sodium
8	Copper	Iron	Zinc
9	Phosphorous	Nitrate	Potassium
10	Cyanide	Aluminum	Copper
11	Nitrate	Fluoride	Chloride
12	Potassium	Phosphorous	Strontium
13	Fluoride	Barium	Nitrate
14	Manganese	Strontium	Nickel
15	Zinc	Zinc	Fluoride

The composited information provided data on the composition of three types of mine waste leachates that were compared to screening criteria to identify potential contaminants of concern. This comparison indicated that 30 constituents in process solutions at heap leaching facilities may be present at concentrations above the screening criteria levels. The assessment also indicated that 18 parameters in MWMT leachates at Nevada gold mines and 16 parameters in Arizona tailings ponds may be present at concentrations above screening criteria levels. The potential contaminants of concern in mine waste leachates that were flagged in the screening criteria assessment included 8 geochemical parameters, 19 trace metals, phosphorus, cyanide, pH, and total dissolved solids. There were 10 contaminants of concern that were common to each of the mine waste leachates that were included in this study. These constituents were arsenic, cadmium, chromium, copper, iron, lead, manganese, pH, and total dissolved solids. The high number of constituents in mine leachate that are frequently present at concentrations that can potentially impair water quality emphasizes the need for effective monitoring programs at mining sites.

Section 4

Characterizing Solution Compositions Using Multiple-ion Fingerprint Patterns

The primary objective of this study is to identify an appropriate set of parameters that can be used for effective monitoring of mining sites. Ideally, these parameters should display several desirable characteristics associated with indicator parameters or tracers. The parameters should be unique to the mining facility to be monitored. This would provide a method to unequivocally identify the mine waste leachate and discriminate it from ambient conditions surrounding the operation. The parameters selected for monitoring should also have a low attenuation factor in the environment. This would allow the parameters to travel with the front edge of the plume and provide for early detection of migrating leachate if an unintentional spill or release occurs. Finally, standard analytical methods should be available to analyze for the selected parameters at anticipated concentration levels.

The monitoring results from mining operations in Nevada and Arizona have identified 40 constituents that may be present in mine waste leachates (Table 3-1, Table 3-3, Table 3-4). Unfortunately, when considered individually, these constituents do not possess all of the desirable characteristics of an indicator parameter or tracer. One limitation is that all of the constituents, except cyanide, are naturally occurring substances. Therefore, simple detection of any of these substances does not characterize the leachate or differentiate it from ambient ground water or surface water in the vicinity of the mine. A second limitation of the individual mine waste leachate constituents is the non-normal distribution associated with each parameter. This factor will complicate any attempt to define the concentration that differentiates a leachate constituent from the same substance in the surrounding environment. A third limitation that affects the suitability of individual leachate constituents as monitoring parameters is their chemical reactivity (attenuation) in the environment. Specifically, sorption and precipitation can reduce the rate of movement of trace metals and sorption and degradation can reduce the movement of cyanide. Therefore, these individual parameters would not be useful for early detection of mine waste leachate migration.

Since there are several readily identifiable problems that will limit the usefulness of individual mine leachate constituents as effective monitoring parameters, the possibility of using multiple ions to define chemical signatures or patterns that uniquely characterize mine waste leachates was explored in more detail. This concept is analogous to using fingerprints to identify individuals. However, rather than using the size and location of ridges and swirls on the fingertip, as is done with fingerprints, the relative abundance of several constituents is used to characterize the leachates. The graphical technique used to evaluate the feasibility of fingerprinting the composition of mine waste leachates was to prepare modified Stiff Diagrams with the site monitoring data.

4.1 Stiff Diagrams as a Multivariate Characterization Technique

A Stiff Diagram is a graphical technique of summarizing multiple water quality parameters for review. The conventional method of preparing Stiff Diagrams is to plot results for cations (calcium, magnesium, sodium, potassium, and ammonia) in one direction from a central axis and to plot results for anions (alkalinity, chloride, sulfate and nitrate) in the opposite direction from the same axis. As shown in Figure 4-1, the data points are then connected to form a distinctive shape (Stiff, 1951; Davis and DeWiest, 1966; Freeze and Cherry, 1979). Even though Stiff Diagrams are created using common and naturally occurring substances, the resulting patterns can uniquely characterize the water quality from a specific source.

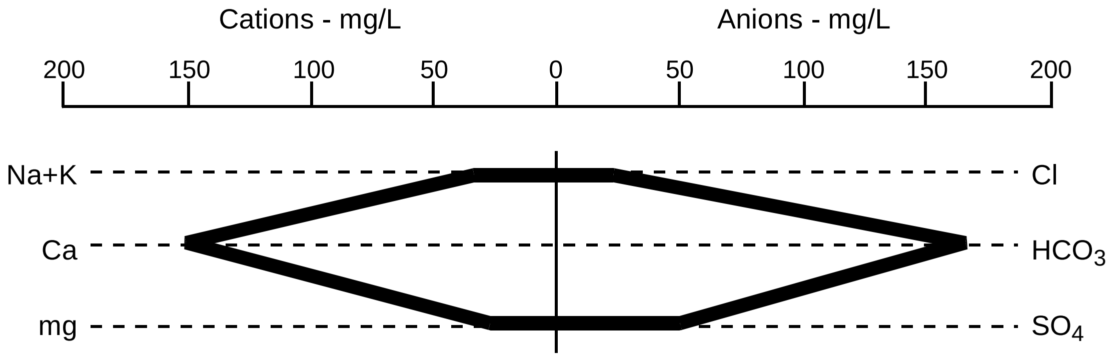


Figure 4-1. Example of Stiff Diagram used to characterize the composition of mine waste leachates.

Stiff Diagrams were initially used to characterize brine solutions in oil fields and ground water from different aquifers (Stiff, 1951; Davis and DeWiest, 1966). They have subsequently been used to characterize landfill leachate and monitor its migration through the environment (Tonjes et al., 1995; Kimmel and Braids, 1980; Dellaria et al., 1990; Black and Dellaria, 1992). The New York State Department of Environmental Conservation has accepted the Stiff Diagram data summary technique as a useful procedure for leachate release investigations (Tonjes et al., 1995).

Rahn et al. (1992) used histograms to characterize nonpoint sources of surface water contamination in a Rhode Island watershed. These investigators used monitoring data for eight common geochemical parameters (sodium, chloride, calcium, magnesium, bromide, iodide, potassium, and sulfate) to develop distinctive and reproducible chemical signatures for approximately 10 background and nonpoint sources in the watershed (Figure 4-2). The sources that were differentiated in this study included upper plateau streams, geological background, road salt leachate, septic tank effluent, tap water, and fertilizer leachate. An important aspect of this study was the demonstration that the chemical signatures from individual sources could be reproduced under controlled laboratory conditions. The observed agreement between laboratory and field results in this study reinforces the concept of using multiple ion signatures to characterize waste leachates.

4.2 Characterization of Incinerated Municipal Waste Ash Leachates

A study of the leaching characteristics of incinerated municipal waste ash provides another example of the feasibility of using multiple ion signatures to fingerprint the composition of waste solutions (Plumb and Engelmann, 1991). The literature review portion of the study demonstrated that a small number of parameters repeatedly dominated the composition of ash leachates (Table 4-1).

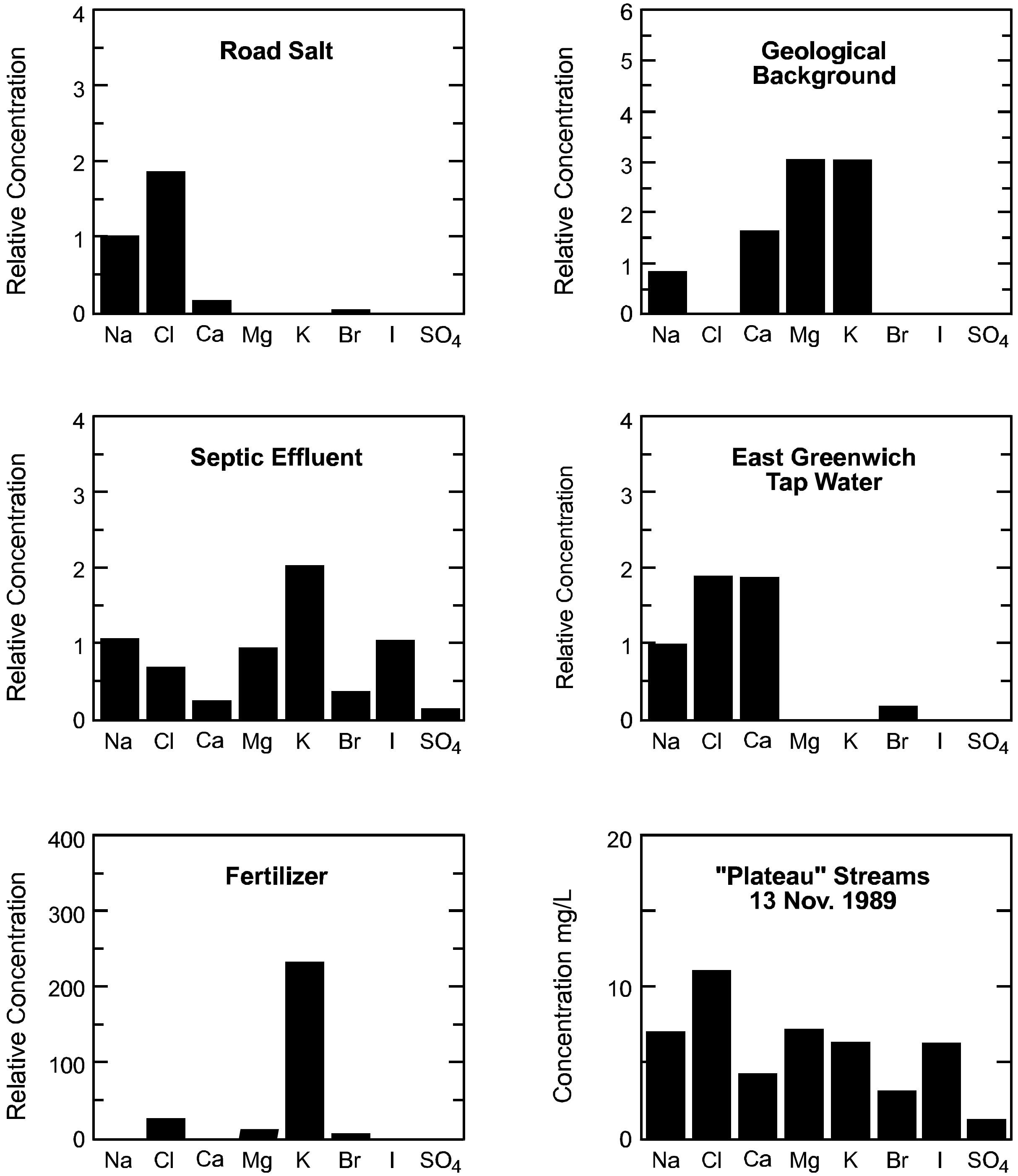


Figure 4-2. Examples of characteristic nonpoint source fingerprints identified by Rahn et al. (1995).

Table 4-1. Concentrations of inorganic constituents leached from incinerated municipal waste ash (VERSAR, 1987; NUS, 1987).

Inorganic Parameter	Fly Ash (mg/L)	Combined Ash (mg/L)
Arsenic	0.005 - 0.005	0.005 - 0.050
Barium	0.190 - 1.680	0.150 - 0.390
Cadmium	0.005 - 0.170	0.005 - 0.030
Chromium	0.002 - 0.150	0.002 - 0.020
Lead	0.025 - 35.000	0.025 - 2.980
Mercury	0.010 - 0.020	0.010 - 0.100
Selenium	0.002 - 0.108	0.002 - 0.050
Silver	0.020 - 0.050	ND - 0.050
Aluminum	0.090 - 0.250	0.170 - 29.400
Beryllium	0.010 - 0.010	ND - 0.010
Boron	1.790 - 3.540	0.100 - 0.220
Calcium	896.000 - 4620.000	122.000 - 536.000
Cobalt	0.030 - 0.030	0.010 - 0.030
Copper	0.002 - 0.089	0.002 - 0.190
Iron	0.002 - 0.167	0.002 - 0.038
Lithium	0.270 - 0.380	0.010 - 0.050
Magnesium	0.030 - 37.600	ND - 0.190
Manganese	0.001 - 0.052	ND - 0.010
Molybdenum	0.220 - 0.340	0.070 - 0.100
Nickel	ND - 0.090	0.007 - 0.090
Potassium	702.000 - 2530.000	85.000 - 120.000
Sodium	587.000 - 971.000	68.000 - 85.000
Strontium	2.600 - 17.700	0.580 - 3.190
Tin	0.090 - 0.090	0.020 - 0.090
Titanium	0.050 - 0.050	0.010 - 0.050
Vanadium	0.020 - 0.020	0.020 - 0.030
Yttrium	0.050 - 0.050	0.010 - 0.050
Zinc	0.005 - 4.150	0.001 - 0.960
Chloride		209.000 - 644.000
Sulfate		156.000 - 571.000

The short list of abundant ions, which generally represented more than 95 percent of the total dissolved solids concentration of the leachates, included the geochemical parameters that are used to prepare conventional Stiff Diagrams.

A controlled series of leaching experiments were conducted to specifically evaluate the possibility of using the geochemical data to fingerprint ash leachates. An example of the leaching results using ash samples from an ash monofill in New York State are shown in Figure 4-3. The geochemical parameters defined a reproducible leachate fingerprint that is characterized by a high chloride concentration, a relatively high sulfate concentration, and a sodium-potassium doublet. A regression analysis of the data sets suggests there is a 99 percent match between the geochemical fingerprint patterns (average regression coefficient = 0.991).

The geochemical patterns for ash leachate from six ash monofills across the country are presented in Figure 4-4. This information displays two characteristics of the leachate fingerprints. First, even for a relatively simple ash - distilled water leaching system, each source of ash produces a leachate with a distinctive chemical signature (i.e., the strong calcium - chloride signal in the Oregon facility is discernibly different from the truncated signal at the Illinois facility). Second, the relatively small 95 percent confidence intervals for each Stiff Diagram constituent indicates the reproducibility of these patterns. The observed variability for individual constituents does not have an apparent effect on the leachate composition pattern at a facility.

The final phase of the ash leachate study consisted of comparing the laboratory leachate fingerprints with field monitoring data. An example of this comparison for the ash monofill in Minnesota is presented in Figure 4-5. The laboratory leachate fingerprint, as shown on the left of the Figure, was dependent on the solid-liquid ratio used during the leaching process. As the solid-liquid ratio was increased, the presence of certain constituents (i.e., chloride and sodium) became more pronounced. The field leachates from the Minnesota facility are presented on the right side of the Figure. This information demonstrates that a characteristic fingerprint was obtained between July, 1988 and July, 1989 even though the total dissolved solids concentration of the leachate increased by more than 100 percent (from 7140 mg/L to 16,390 mg/L). The actual field fingerprints are similar to the laboratory leachates prepared at relatively high solid-liquid ratios (> 35 g/200 mL).

A comparison of laboratory and field leachate fingerprints at a second ash monofill are presented in Figure 4-6. The laboratory results from this facility also show the influence of solid-liquid ratio during leaching. As the solid-liquid ratio is increased, chloride becomes a more abundant anion than sulfate and the sodium-potassium doublet is enhanced. The partial field monitoring results (there were no data for potassium) indicate a recurring composition pattern that is similar to laboratory leachates prepared at higher solid-liquid ratios (> 35 g/200 mL).

The ash leachate characterization study demonstrated the potential for fingerprinting the composition of waste leachates. Each ash leachate had a distinctive multivariant composition defined by the relative abundance of the common geochemical ions (calcium, sodium, magnesium, potassium, alkalinity, chloride, and sulfate). Since the same chemical fingerprint occurred in field monitoring data and controlled laboratory leaching data, it was suggested that the same parameters would be effective monitoring parameters for incinerated municipal waste ash monofills (Plumb and Engelmann, 1991).

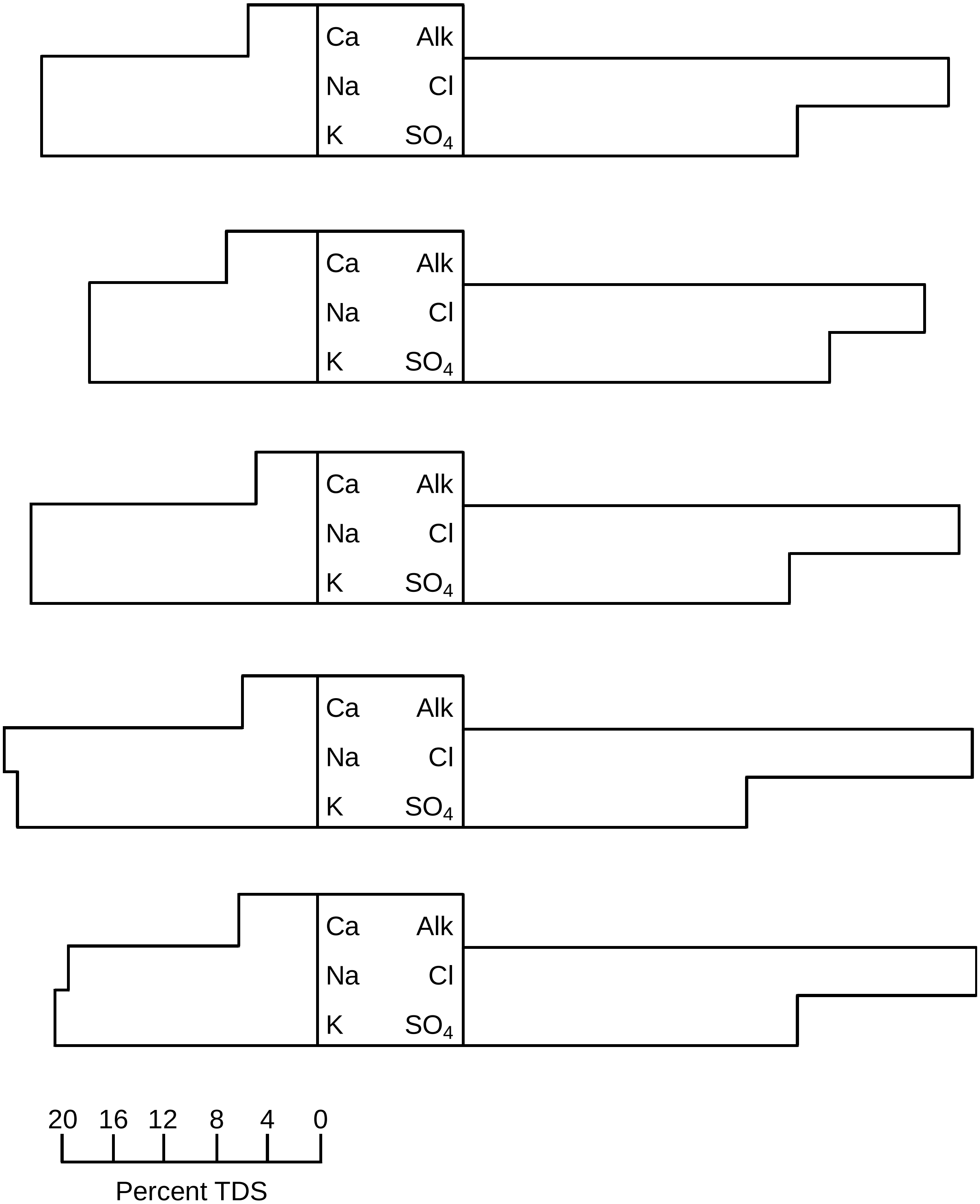


Figure 4-3. Characteristic multivariant fingerprint for incinerated municipal waste ash leachate from New York State.

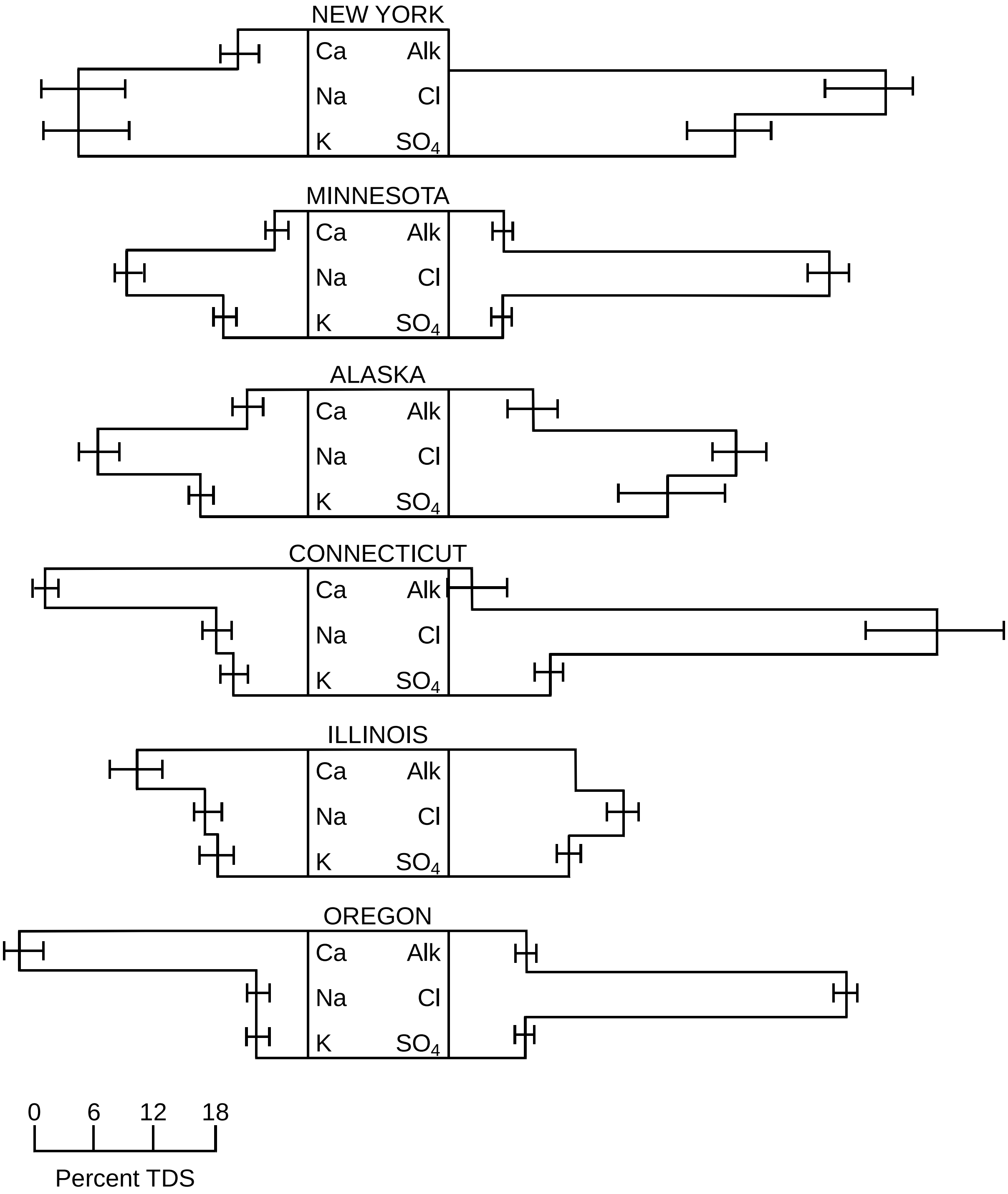


Figure 4-4. Comparison of ash leachate fingerprints from six ash monofill facilities across the country. The error bars indicate calculated 95 percent confidence limits.

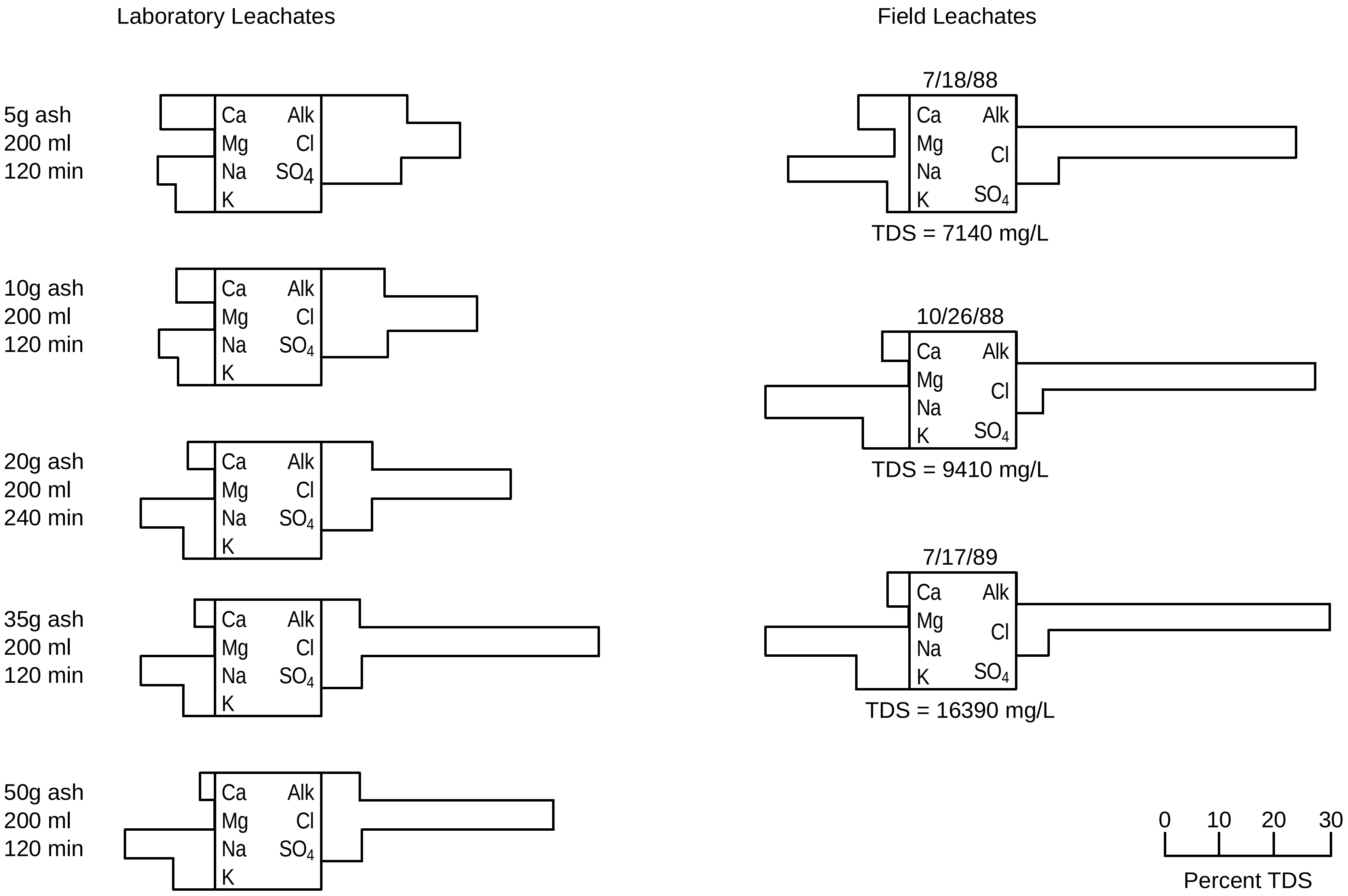


Figure 4-5. Comparison of laboratory ash leachate fingerprint and field leachate fingerprint for an ash monofill in Minnesota.

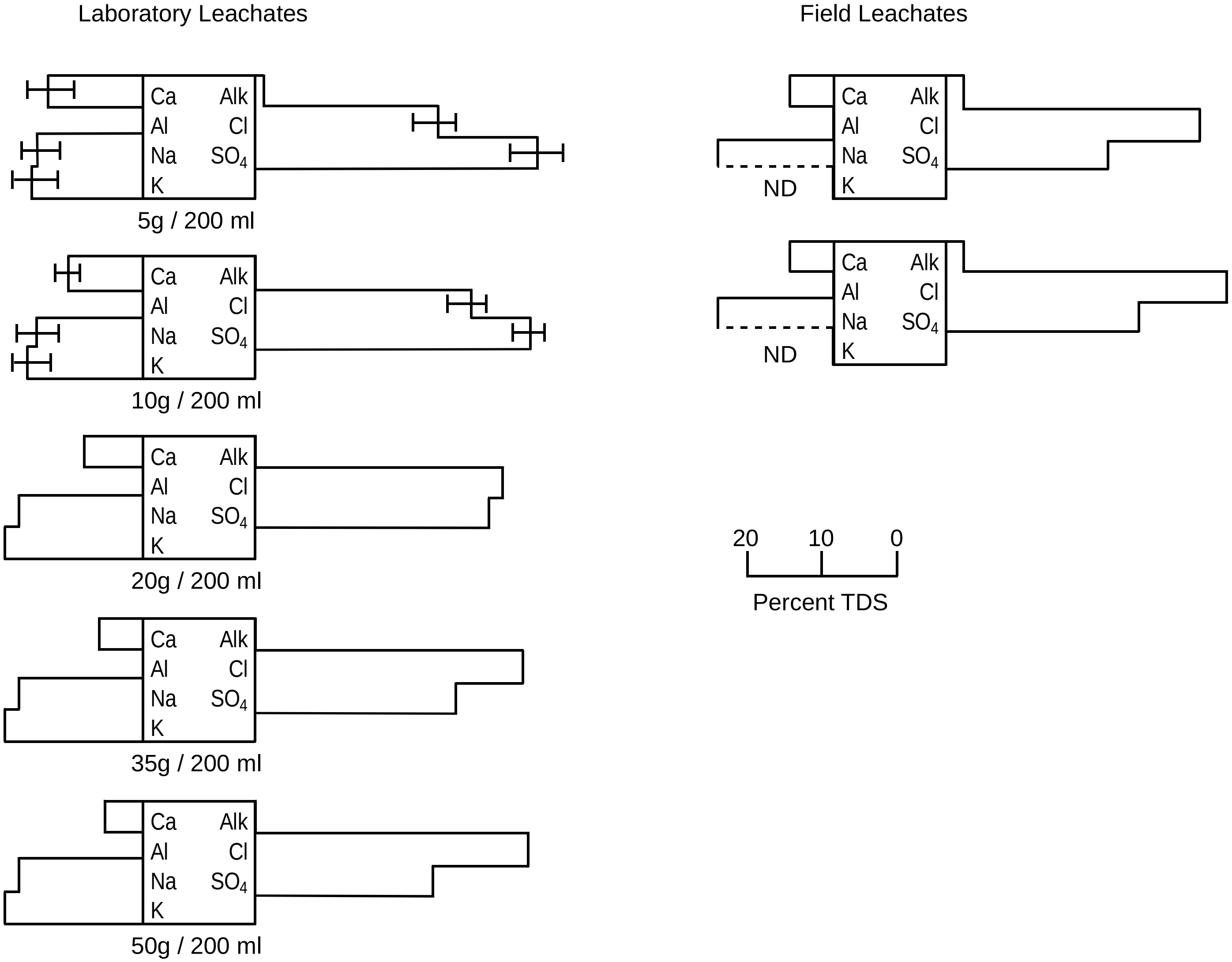


Figure 4-6. Comparison of ash leachate fingerprints and field leachate fingerprints at an ash monofill located in New York State.

4.3 Application to Mine Waste Leachate Characterization

The previous discussion identified several situations for which it has been possible to use Stiff Diagrams to uniquely define the composition of ground water or waste leachates. These examples include ground-water aquifers (Davis and DeWiest, 1966; Freeze and Cherry, 1979), municipal landfill leachates (Tonjes et al., 1995; Kimmel and Braids, 1992), and incinerated municipal waste ash leachate (Plumb and Engelmann, 1991). Each of these case studies share several common features that contribute to the usefulness of the Stiff Diagrams. These features are:

1. A small number of ions define the leachate composition. Usually, there are six to eight ions in the fingerprint.
2. The small number of ions that dominate the composition of the solution usually represent more than 90 percent of the reported total dissolved solids concentration.
3. The same set of geochemical parameters, calcium, magnesium, sodium, potassium, alkalinity, chloride, and sulfate were the dominant ions in each example.

A review of the composite mine site monitoring data in Table 3-1, Table 3-2, and Table 3-3 indicates that these leachates are similar to those solutions that have been successfully characterized with Stiff Diagrams. The composition of each of the mine waste leachates is dominated by a small number (5 to 10) of substances. Also, the most abundant ions in the mine waste leachates include the common geochemical ions (calcium, magnesium, sodium, potassium, nitrate, alkalinity, chloride, and sulfate) that proved to be useful with previous applications of Stiff Diagrams. The high concentrations associated with each of the geochemical parameters should eliminate or minimize the problem of dealing with non-detectable results. Finally, the geochemical ions represent 70 to 100 percent of the total dissolved solids concentration of mine waste leachates. Based on these conditions, Stiff Diagrams were selected to identify and characterize multivariant compositional patterns associated with mine waste leachates.

4.4 Stiff Diagram Modifications

The conventional approach to preparing Stiff Diagrams is to plot anion and cation concentrations in opposite direction from a common axis as shown in Figure 4-1. However, the basic Stiff Diagram was modified for this study. As indicated in Figure 4-7, the components of a Stiff Diagram were rotated about the center axis. The resultant data summary still produces a two-dimensional figure to characterize the mine waste leachates but the shape is now a histogram rather than a geometric pattern. This modified version of a Stiff Diagram was used as a matter of convenience to facilitate preparation of the graphical fingerprints. As a result, readily available software (Quattro Pro) could be used to prepare the data summaries rather than using more specialized geotechnical software.

A second property of conventional Stiff Diagrams that was modified during this study was the concentration units used to express the data. The usual approach is to present data in units of mg/L or meq/L. However, when the results to be summarized and compared display considerable variability, as is the case with mining data, a wide concentration range can complicate any attempt to compare graphical fingerprints (Tonjes et al., 1995). However, rather than using a sliding scale as has been suggested for landfill leachates (Tonjes et al., 1995), an alternative approach was used. The monitoring results for each parameter were normalized to the total dissolved solids concentration of the sample. This approach offers the following advantages.

1. The vertical scale for all of the modified Stiff Diagrams are fixed in the range of 0.0 to 1.0 for all parameters since the concentration for an individual mine waste leachate constituent must be less than the total dissolved solids concentration of the leachate. The use of a common scale permits graphical fingerprints from different sampling locations or different sampling times to be directly compared.
2. The data manipulation step does not alter the chemical fingerprint since all the data from one location are divided by a constant factor (the total dissolved solids concentration).
3. The use of normalized data can rapidly identify some data quality problems in the results. For example, when the normalized concentration for a parameter exceeds a value of 1.0, either the parameter result is high and/or the total dissolved solids concentration is low. After inspection, the data can be flagged as suspect and used or discarded, as appropriate. Also, if the sum of the normalized concentration exceeds a value of 1.0 (or the upper data quality objective), there is one or more suspect result in the data set.

The comparison of Stiff Diagrams has historically been a subjective process. One final adaptation used in this study to address this issue was the application of a statistical procedure to provide a more quantitative comparison of the mine waste leachate fingerprints. Regression analysis was used to estimate the similarity of the modified Stiff histograms prepared with two sets of geochemical data. The calculated regression coefficient (r), which ranges from 0 to 1, estimates the variability in one set of data that can be explained by the variability in a second set of data. The square of the calculated regression coefficient (r^2) provides a numerical estimate of the match between two fingerprints or the precision (reproducibility) of a single pattern.

4.5 Summary

Composite monitoring results for mine waste leachates in Nevada and Arizona demonstrate that these solutions are composed of naturally occurring substances. A recurring pattern that has been identified in three types of mine waste leachates, process solutions at Nevada gold mines, MWMT leachates at Nevada gold mines, and tailings ponds at Arizona copper mines, is that a small suite of common geochemical ions are the most abundant constituents in mine waste leachates while trace metals are present at much lower and highly variable concentrations. This distribution is similar to that observed in ground water, landfill leachates, and incinerated municipal waste ash leachates which have all been successfully characterized using graphical multivariant techniques such as Stiff Diagrams. Therefore, Stiff Diagrams were selected to identify multivariant compositional patterns that could be used to uniquely characterize mine waste leachates.

The conventional approach to Stiff Diagrams was modified in several ways for this study. First, all of the data were plotted on a common axis. As a result, the graphical summaries were in the form of a histogram rather than an abstract geometric shape. Second, all of the monitoring data were normalized to the total dissolved solids concentration. This had the effect of creating a uniform y-axis that facilitated a comparison of individual data sets despite large concentration fluctuations. Third, regression analyses were used to develop a numerical estimate of the similarity between different graphical patterns.

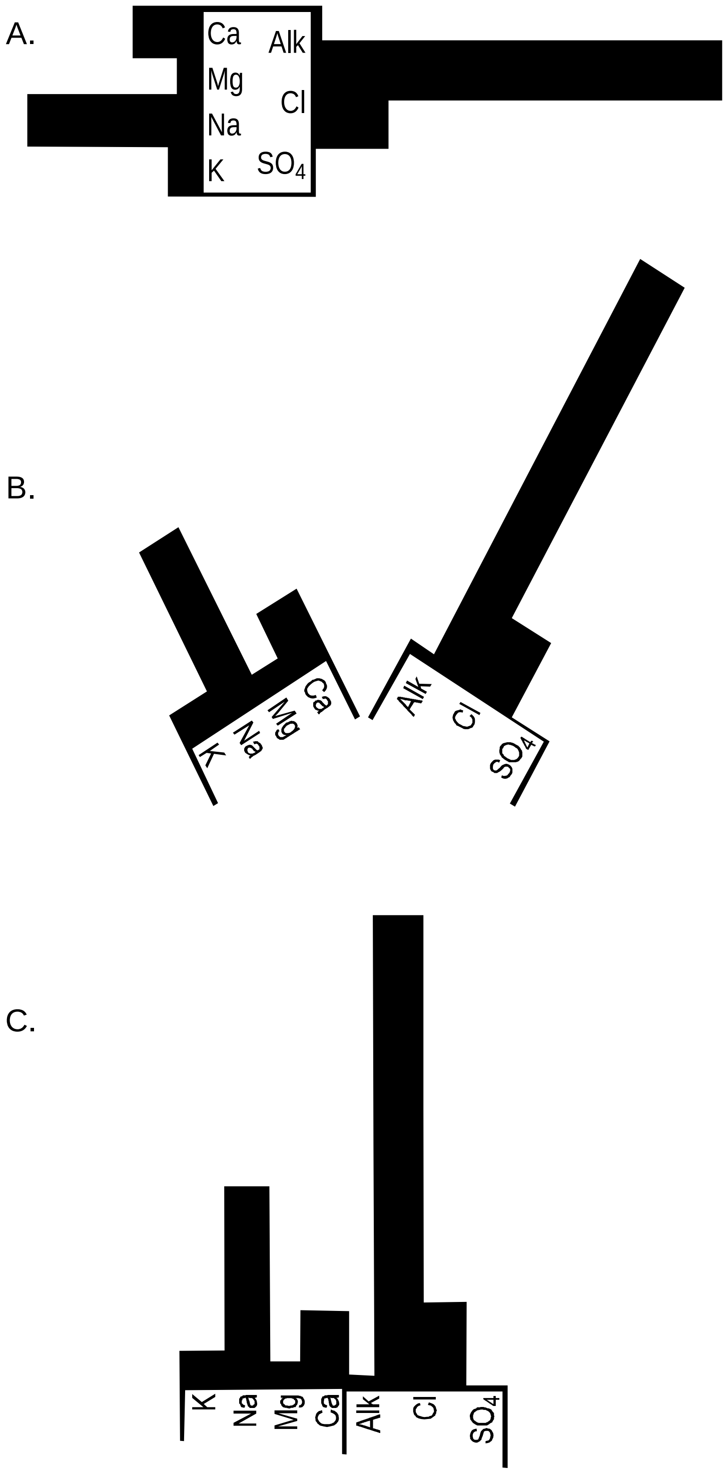


Figure 4-7. Transformation of conventional Stiff Diagram (A) into modified Stiff histogram (C) used to characterize mine waste leachates.

Section 5

Assessment of Monitoring Results From Gold Heap Leaching Facilities in Nevada

The process of using cyanide to complex and recover gold is more than 100 years old (Murrey and Moeller, 1985). However, the first small scale application of this technique did not occur in the United States until the late 1960's (Hiskey, 1985). Several years later, the first large scale heap leaching facility began operating in Nevada (Dorey, et al., 1988). The number of facilities has continued to increase in the past 15 years with approximately 300 now in operation.

There are several factors that have contributed to the rapid growth in this sector of the mining industry. First, gold can now be recovered from low-grade ores that are not considered economically viable with conventional mining techniques. The process has been applied to oxidized ores with gold concentrations as low as 0.05 oz/ton (Hoye, 1988). Second, the procedure is amenable to either small-scale or large-scale operations and has a shorter start up period compared to conventional gold mining techniques. Third, the capital costs for heap leaching operations are 60 - 80 percent lower than conventional gold mining operations (Hoye, 1988). As a result, heap leaching has become the fastest growing sector in the mining industry in the United States and the largest number of these operations are located in the State of Nevada.

5.1 Description of Heap Leaching Process

The heap leaching process is schematically summarized in Figure 5-1. The gold-bearing ore to be processed is removed from the mine pit and stockpiled. Depending on the ore supply, the preparation of the ore can range from no treatment, to crushing only, to crushing and agglomeration with lime or cement (Norman and Raforth, 1995; Strachan and van Zyl, 1987). The crushing process increases the surface area of the ore from which gold can be extracted and the agglomeration process increases the permeability of the ore pile to be leached.

The prepared ore is stacked in benches or layers 20 to 30 feet high on an impervious leaching pad (Strachan and van Zyl, 1987; Hoye, 1988). The leaching pads are usually constructed of compacted clay and/or synthetic liners to produce a final permeability of less than 1×10^{-6} cm/s (Norman and Raforth, 1995, Strachan and van Zyl, 1987, Comba, et al., 1992). Leaching pads can range in size from less than 1 acre to 50 acres (Hoye, 1988).

An alkaline cyanide solution, composed of plant make-up water, sodium cyanide and either sodium hydroxide or lime is pumped from the barren reservoir and sprinkled on the ore benches at a rate of 0.003 to 0.05 gal/min/ft^2 which is sufficient to percolate into the pile but not cause erosion of the pile (Norman and Raforth, 1995). The cyanide concentration in the lixiviant solution ranges from 250 mg/L to 800 mg/L and the solution pH is 9 - 11 s.u. (Hoye, 1988, Norman and Raforth, 1995). As the cyanide solution percolates through the benches, it extracts gold, silver, and other semi-precious

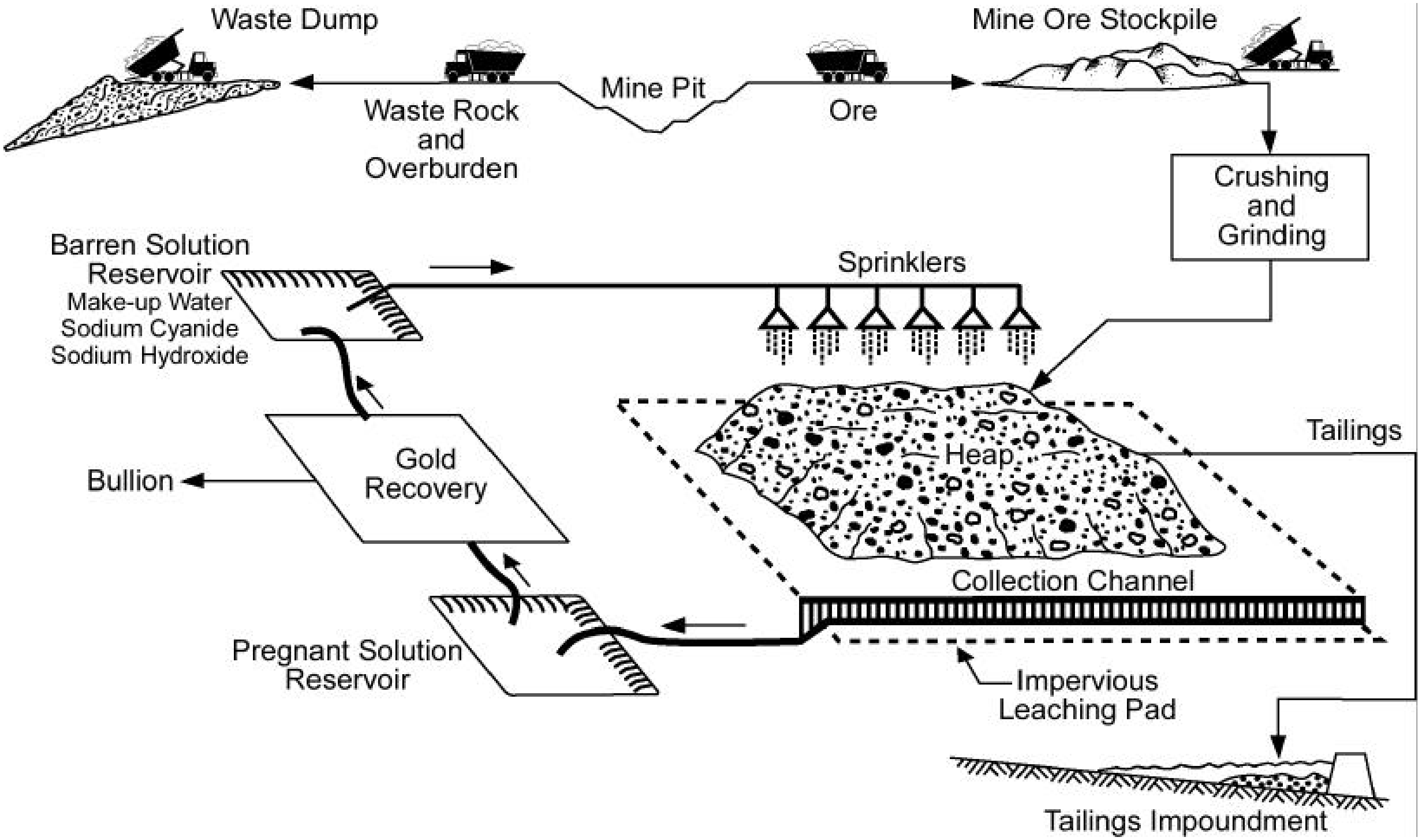


Figure 5-1. Schematic diagram of a heap leaching operation.

metals (mercury, zinc, copper, iron, nickel and lead) from the prepared ore by complexation (Norman and Raforth, 1995). The gold-enriched solution is collected and pumped to a pregnant pond reservoir. Gold is recovered from the process solution by a zinc precipitation process or an activated carbon absorption and electrowinning (Norman and Raforth, 1995). The gold-depleted solution is pumped back to the barren pond where it is reconstituted and recirculated through the ore pile (Figure 5-1).

When the ore on the leaching pad is exhausted, the mining process is continued using one of the following options:

1. Additional benches of fresh ore are added to the pile on the leaching pad. This permits continued usage of the original pad but is usually limited to two or three additional benches.
2. Leave the spent ore in place and expand the size of the leaching pad.
3. Transfer the spent ore to a tailings basin and place fresh ore on the original leaching pad.

The selection of one of these options is usually determined by factors such as hauling distances, land availability, and local topography (Norman and Raforth, 1995).

5.2 Fingerprinting Heap Leaching Process Solutions

The Nevada Division of Environmental Protection has established a comprehensive monitoring program for heap leaching facilities (NDEP, 1989). Although some of the specific details will fluctuate from site to site, the general program requires monitoring of the barren pond and the pregnant pond (Figure 5-1), the tailings slurry or the tailings reclaim water (if a tailings pond is used), the make-up water used by the facility, and the ground water in the vicinity of the operation. An initial review of composite data from 26 heap leaching facilities suggested that a small number of common inorganic constituents repeatedly dominated the composition of mine waste leachates (Chapter 3) and that a graphical data summation technique, such as the Stiff Diagram, could be useful to define characteristic multi-variant compositional patterns or fingerprints for mine waste leachates (Chapter 4). If it is possible to fingerprint the composition of mine waste leachate, then those parameters that define the fingerprint become candidates for effective detection monitoring parameters at mining sites. The remainder of this Chapter shall use the monitoring results from the Nevada heap leaching facilities as a series of case studies to explore the possibility of fingerprinting mine waste leachates.

The following approach will be used to present the data from the individual case studies. First, the data will be presented for the pregnant pond monitoring location to illustrate the identification of a recurring geochemical fingerprint pattern. Second, the pregnant pond fingerprint pattern will be compared to the geochemical pattern at other locations within the recirculating system used at heap leaching facilities (i.e., the barren pond and tailings pond). If the geochemical fingerprint is a characteristic feature of the mine process solution, a comparable fingerprint should be seen at each location. Third, the process solution fingerprint pattern will be compared to the geochemical fingerprint for the mine make up water. If the geochemical fingerprint is a characteristic property of the mine process solution, the two geochemical fingerprints should be distinctly different. Finally, the process solution fingerprint will be compared to ground-water fingerprints from monitoring locations in the vicinity of the mine. The objective of this effort is to determine whether the fingerprint pattern can be used to monitor mine leachate migration through the environment. Although this approach will introduce some redundancy in the presentation, it is considered necessary to illustrate the potential for fingerprinting mine leachates.

5.2.1 Lone Tree Gold Mine

The first gold mining facility to be discussed is the Lone Tree Gold Mine in west-central Nevada. This facility uses a conventional heap leaching process and the site monitoring program includes quarterly monitoring of the pregnant pond, the barren pond, the mill water supply, and three monitoring wells. The data set obtained from the Nevada Department of Environmental Protection for this mine included 10 sets of quarterly data collected between March, 1991 and May, 1993.

The monitoring results from the Lone Tree pregnant pond are presented in Table 5-1. This information displays many of the characteristics that were identified in the composite data set (Table 3-1). The suite of nine geochemical parameters (alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, and sulfate) represent 98 percent of the total dissolved solids concentration in the pregnant pond. The trace metals collectively represent less than two percent of the total dissolved solids concentration and half of them display non-normal distributions. Finally, 19 of the leachate constituents listed in Table 5-1 exceed one or more of the screening criteria presented in Table 3-2.

The data for the individual quarterly surveys at the pregnant pond location are presented as a series of histograms in Figure 5-2. The x-axis of this histogram identifies each of the major geochemical parameters usually incorporated in a Stiff diagram. In addition, the x-axis includes a separate entry for cyanide (CN), copper (Cu), and total trace metals (TTM). These last three parameters are not used in conventional Stiff Diagrams but have been incorporated into the graphical summaries because of their importance in heap leaching operations. Cyanide is the primary agent used to extract gold from the ore by complexation and can be present at high concentrations. Copper has been included as a separate entry because it is often reported at high concentrations in heap leaching process solutions. Finally, the individual trace metals except copper have been summed to produce a total trace metals value (TTM). These extra values in the histograms provide for maximum use of the available data and ensure that major concentration fluctuations that might impact the solution fingerprint are not missed.

The results from eight quarterly surveys at the Lone Tree pregnant pond demonstrate the variability observed for individual leachate constituents (Figure 5-2). For example, total dissolved solids varied from 3000 mg/L to 6500 mg/L, sulfate varied from 1000 mg/L to more than 2500 mg/L, chloride varied from less than 1000 mg/L to 2000 mg/L, and calcium varied from 500 mg/L to more than 3000 mg/L. However, despite these fluctuations, there is an indication of a repetitive composition pattern for this solution. Specifically, sulfate is the most abundant geochemical ion, sodium and chloride are the second most abundant ions, calcium is the third most abundant ion, alkalinity is a minor constituent in the pattern, and the remaining ions do not make a significant contribution to the pattern.

The quarterly monitoring data from the Lone Tree pregnant pond were divided by the total dissolved solids concentration reported for each survey. These normalized data are presented in Figure 5-3. This data transformation serves two purposes. First, it creates a standardized y-axis for the histograms that ranges from 0.0 to 1.0 that facilitates a comparison of the leachate composition patterns. This follows from the fact that the concentration for an individual ion must be less than the total dissolved solids concentration for a solution. Second, the common axis demonstrates the recurring multiple ion signature that defines the composition of the pregnant pond solution at the Lone Tree mine. Even though the total dissolved solids concentration varied by more than 3300

Table 5-1. Monitoring results from the pregnant pond at the Lone Tree Gold Mine.

	Pregnant Pond Sampling Date								
Constituent	**8/91**	**11/91**	**2/92**	**5/92**	**10/92**	**1/93**	**4/93**	**Average Concentration**	**Standard Deviation**
Alkalinity	214	148	313	143	214	291	258	216	63
Calcium			650	340	490	339	465	449	106
Chloride	1060	1900	1248	971	824	756	643	1040	369
Fluoride	3.6	3.8	5.6	5.1	5.4	4.7	5.5	5.0	1.0
Magnesium			24	58	28	13	18	26	15
Nitrate	1.7	66	47	38	37	30	16	34	18
Potassium			35	34	39	39	21	34	6
Sodium			985	854	798	700	464	782	166
Sulfate	2592	1800	1600	1720	1604	1030	969	1582	478
Cyanide	89	108	220	91	130	130	141	126	40
Copper			36	100	77	65	51	68	20
TTM	0.41	0.32	5.97	209	63	10.5	14.4	44	66
TDS	5559	6573	5132	4552	4464	3229	3230	4692	1051
pH	9.6	9.2	9.6	8.8	9.4	10.6	9.9	9.5	0.5
Aluminum				0.1	0.1	0.4	1.1	0.3	0.4
Antimony				<0.5	<0.5	<0.5	<0.5	0.0	0.0
Arsenic	0.33	0.02	0.01	0.03	0.13	0.04	0.20	0.13	0.12
Barium			0.4	0.1	<0.1	0.04	0.2	0.08	0.15
Beryllium				<0.1	<0.1	<0.1	<0.1	0.00	0.00
Bismuth				0.1	<0.1	<0.1	<0.1	0.02	0.04
Cadmium	0.04	0.2	0.2	0.1	0.1	0.2	0.3	0.2	0.10
Chromium			<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1
Cobalt				5.9	1.2	0.8	0.6	2.0	2.0
Gallium				0.1	<0.1	<0.1	<0.1	0.02	0.05
Iron	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Lead	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Lithium				0.2	<0.1	<0.1	<0.1	0.04	0.08
Manganese			0.07	6.6	<0.1	0.1	0.5	1.21	2.42
Mercury	0.02	0.06	0.06	0.02	0.07	0.04	0.04	0.04	0.02
Molybdenum				0.3	<0.5	<0.5	<0.5	0.06	0.12
Nickel				3.1	1.1	1.1	1.0	1.54	0.79
Phosphate				160	50	<0.1	<0.1	49	58
Scandium				<0.1	<0.1	<0.1	<0.1	0.00	0.00
Selenium	0.00	0.00	0.12	0.13	0.52	0.06	0.04	0.13	0.16
Silver	0.03	0.03	0.05	0.03	0.10	0.06	0.05	0.05	0.02
Strontium				19	5.4	4.2	3.7	7.8	5.7
Thallium				<2	<1	<1	<1	0.00	0.00
Tin				<1	<2	<1	<1	0.00	0.00
Titanium				<0.01	<0.01	<0.01	<0.01	0.00	0.00
Vanadium				<0.1	<0.1	<0.1	<0.1	0.00	0.00
Zinc			4.5	1.7	2.4	2.9	4.0	2.76	1.20

All concentrations, except pH, expressed in mg/L.

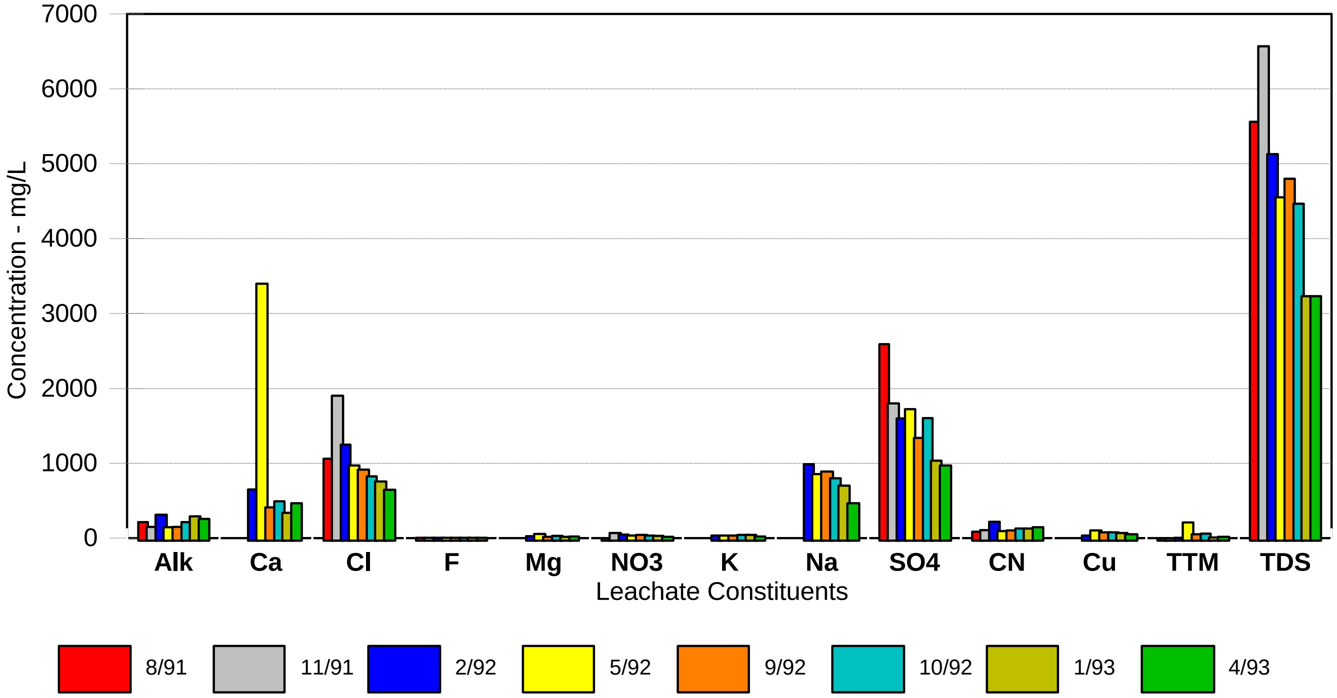


Figure 5-2. Monitoring results from the Lone Tree Mine pregnant pond.

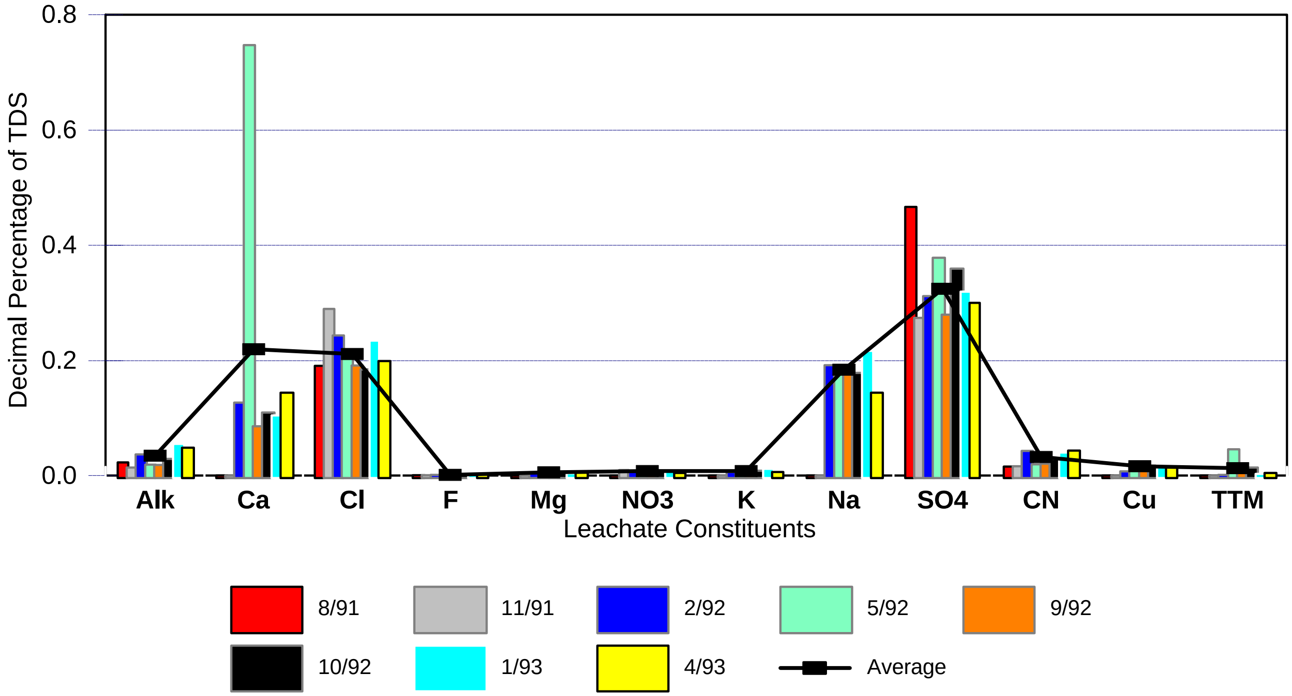


Figure 5-3. Normalized monitoring results from the Lone Tree pregnant pond.

mg/L, and the sulfate concentration varied by more than 1600 mg/L, sulfate consistently represented 35 percent of the total dissolved solids concentration in eight surveys over a two year period. Similarly, even though chloride varied by more than 1200 mg/L between 1991 and 1993, chloride consistently represented 20 percent of the total dissolved solids concentration. Except for a single calcium result in May, 1992, sodium, calcium, alkalinity, and the less abundant pregnant pond constituents also represented a constant percentage of the leachate total dissolved solids concentration.

A more quantitative estimate of the reproducibility of the geochemical fingerprint was evaluated further by performing a regression analysis between the individual quarterly surveys. The regression coefficient varies between 0.0 and 1.0 and the square of the regression coefficient (r^2), which also varies between 0.0 and 1.0, provides an estimate of the similarity between two sets of data. As shown in Table 5-2, the square of the regression coefficient for the Lone Tree pregnant pond data ranged from 0.094 to 0.990. If the May, 1992 survey results are excluded because of the extraneous calcium results, the values for the square of the regression coefficient ranged from 0.646 to 0.990 with an average value of 0.817 (i.e., there was an 81.7 percent match between the fingerprints for seven quarterly surveys). If the August, 1991 and November, 1991 results are excluded because of incomplete sample analyses (there are no results for calcium, magnesium, potassium, and sodium), the average r^2 value increases to 0.966 (a 96.6 percent match).

The normalized concentration results in Figure 5-3 illustrate another benefit of this approach. The initial results suggest that calcium represents 75 percent of the total dissolved solids concentration in May, 1992. However, since sodium represents 20 percent of the total dissolved solids concentration, sulfate represents 35 percent of the total dissolved solids concentration, chloride represents 20 percent of the total dissolved solids concentration, and there are several lesser constituents, the May, 1992 data contain one or more errors because the sum of the ions exceeds 150 percent of the total dissolved solids concentration. The most probable error in the May, 1992 data is the calcium result because it is not compatible with the calcium values in other surveys and the ratio of concentration to total dissolved solids is rather constant over time for the remaining geochemical parameters.

The normalized trace metal data from the Lone Tree pregnant pond are presented in Figure 5-4. The trace metal distribution pattern is much less reproducible than the geochemical distribution pattern. This is more clearly indicated in the regression analysis table in which the inter-survey r^2 values range from 0.000 to 0.995. The average r^2 value for the trace metal data is only 0.162 which is considerably lower than the 0.817 for seven quarters of geochemical monitoring data. The low and variable concentrations for each of the trace metals and the low inter-survey r^2 value (an average match of only 16 percent) suggests that the pregnant pond leachate does not have a consistent, characteristic trace metal pattern or fingerprint.

A second location that has been monitored at the Lone Tree mine is the barren pond. The normalized results from eight quarterly surveys at this location have been summarized in Figure 5-5. The multi-ion fingerprint pattern indicated for this location is composed of 35 percent sulfate, 20 percent chloride, 15 to 20 percent sodium, 10 to 15 percent calcium, and approximately five percent alkalinity. If the May, 1992 survey is excluded because of the suspect value for calcium, the average regression analysis r^2 value for the remaining seven surveys is 0.792.

The assessment of the barren pond monitoring data suggests that the mine process solution has a reproducible chemical fingerprint at this location. A more important observation is the fact that the barren pond fingerprint (Figure 5-5) is essentially identical with the pregnant pond fingerprint

(Figure 5-3). A regression analysis of the two data sets indicates that there is a 99.5 percent match (r^2 = 0.995) between the barren pond signature and the pregnant pond signature. While this result might be anticipated because both monitoring locations are part of the same recirculating system (Figure 5-1), the similarity of the solution fingerprint in these two sets of data is encouraging.

Table 5-2. Regression analysis table for the Lone Tree pregnant pond monitoring results, 1991-1993.

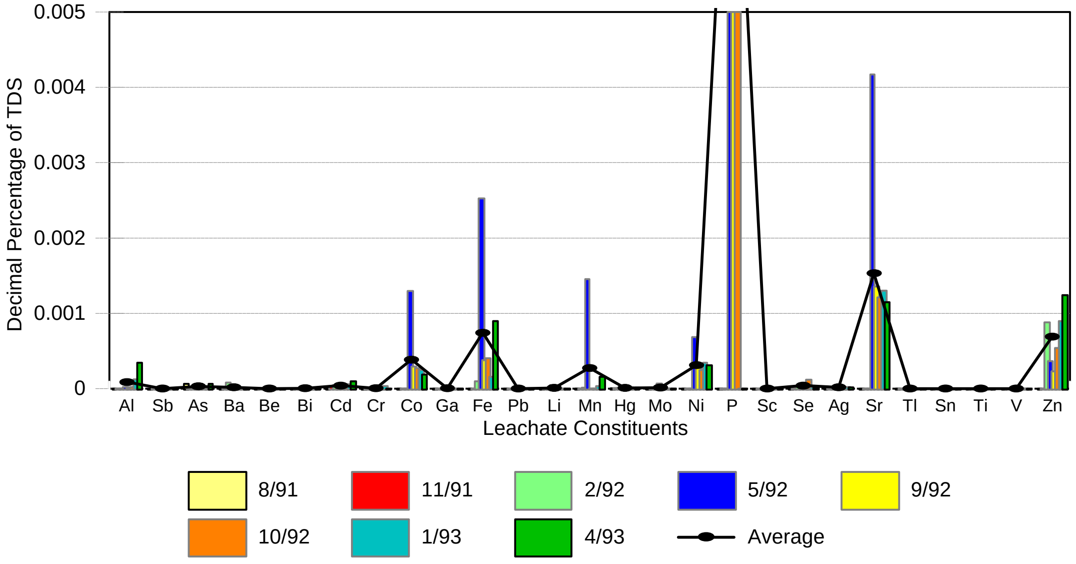
	8/91	**11/91**	**2/92**	**5/92**	**9/92**	**10/92**	**1/93**	**4/93**
8/91	1.000	0.798	0.656	0.123	0.662	0.768	0.649	0.707
11/91		1.000	0.680	0.094	0.637	0.636	0.646	0.664
2/92			1.000	0.376	0.980	0.951	0.988	0.974
5/92				1.000	0.313	0.350	0.308	0.469
9/92					1.000	0.970	0.990	0.939
10/92						1.000	0.956	0.959
1/93							1.000	0.949
4/93								1.000

Average r^2 value for all comparisons is 0.685.

The data set from the Lone Tree mine also included six quarterly surveys for the mine water supply or the make-up water. These data are compared to the average process solution fingerprint in Figure 5-6. The mine water supply has a reproducible multi-ion fingerprint in which alkalinity is the most abundant ion (40 percent of TDS), sodium is the second most abundant ion (20 percent of TDS), while calcium, chloride, magnesium, and sulfate are minor components of the fingerprint (5 to 10 percent of TDS). The reproducibility of the mill water supply fingerprint, as estimated from a regression analysis of the six sampling events between August, 1991 and October, 1992, is 0.993.

The most important observation on reviewing the data in Figure 5-6 is the fact that there is a distinctive shift in the composition of the mine process water (barren pond and pregnant pond) compared to the mine water supply. Even though there is a highly variable quantity of material leached from the ore pile (total dissolved solids varied from 3000 mg/L to 6500 mg/L, sulfate varied from 900 mg/L to 2800 mg/L), the process solution had a consistent multi-ion fingerprint over time and the resulting chemical signature could be differentiated from the water supply fingerprint. When comparing the two fingerprints, the process solutions are relatively depleted in alkalinity and sodium but are enriched in sulfate, chloride, and calcium. A regression analysis of the two patterns indicates that there is only a 3.5 percent match (r^2 = 0.035) between the water supply and the pregnant solution and a 4.9 percent match between the water supply and the barren solution.

Monitoring results from three Lone Tree wells are summarized and contrasted with the process solution fingerprint in Figure 5-7. There is a consistent ground-water fingerprint at each of these locations. However, there is an indication of a compositional shift that could be due to mine waste leachate (Table 5-3). The ground-water fingerprint at Well 1 is very similar to the mine water supply (r^2 = 0.962) and dissimilar from the process solution fingerprint (r^2 = 0.102). The ground-water fingerprint at Well 3 is less similar to the water supply fingerprint (r^2 = 0.107) and more similar to the process solution fingerprint (r^2 = 0.352). Although the distinctive process solution fingerprint is not evident, Well 3 indicates a simultaneous drop in alkalinity, an increase in sulfate, an increase in total dissolved solids, and a shift in composition to more closely resemble the mine process solution. Each of these concurrent changes would be expected if process solution were migrating from the source.



Regression analysis table for the Lone Tree pregnant pond trace metal data

	8/91	**11/91**	**2/92**	**5/92**	**9/92**	**10/92**	**1/93**	**4/93**
8/91	1.000	0.019	0.003	0.004	0.003	0.003	0.007	0.006
11/91		1.000	0.000	0.005	0.006	0.005	0.006	0.007
2/92			1.000	0.002	0.001	0.000	0.259	0.414
5/92				1.000	0.993	0.995	0.001	0.000
9/92					1.000	0.994	0.007	0.002
10/92						1.000	0.001	0.000
1/93							1.000	0.779
4/93								1.000

Average r squared value = 0.162

Figure 5-4. Normalized trace metal distribution patterns in the Lone Tree pregnant pond.

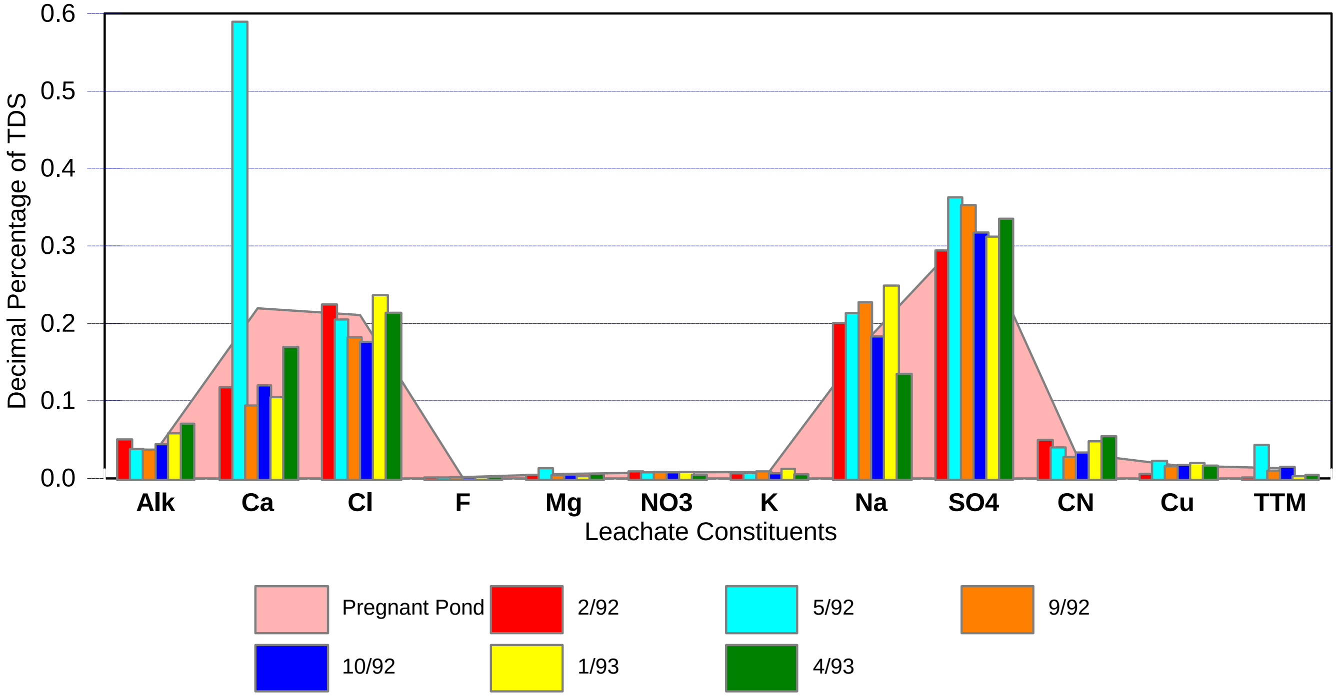


Figure 5-5. Normalized monitoring results for the Lone Tree barren pond.

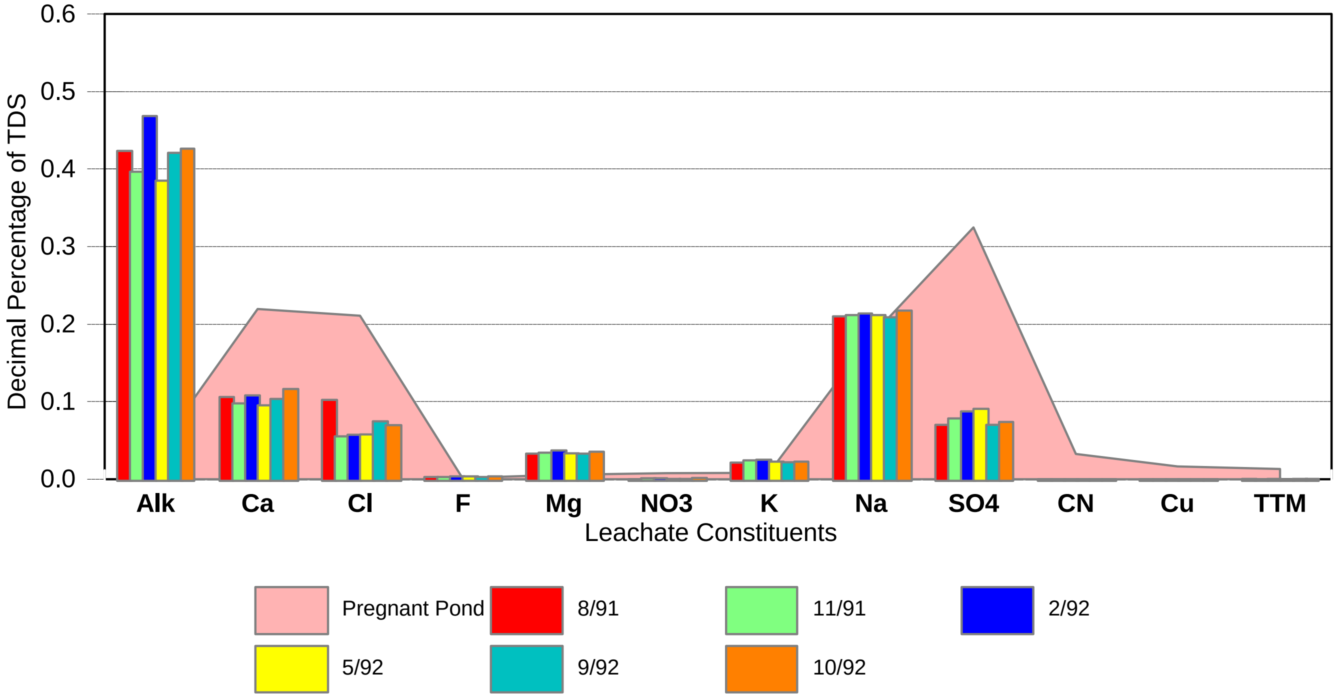


Figure 5-6. Comparison of water supply fingerprint and the Lone Tree pregnant pond fingerprint.

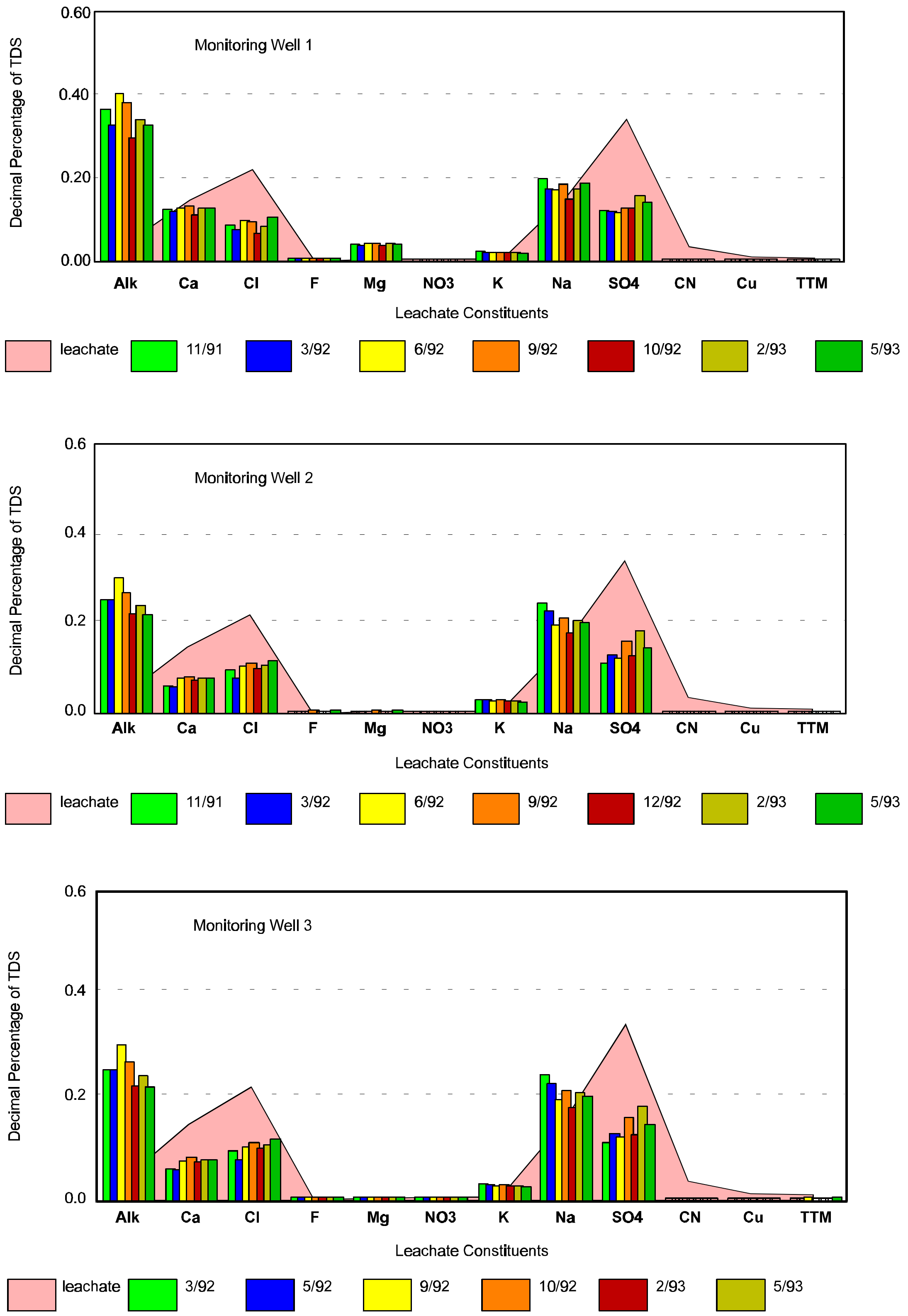


Figure 5-7. Comparison of ground-water fingerprints with the Lone Tree pregnant solution fingerprint.

Table 5-3. Regression analysis comparison of the Lone Tree pregnant solution fingerprint with ground-water fingerprints from the vicinity of the mine.

	Monitoring Well 1	Monitoring Well 2	Monitoring Well 3
Process Solution	0.102	0.277	0.352
Water Supply	0.962	0.843	0.107

Tabulated value is the r^2 value for a regression analysis between the two indicated fingerprints.

Lone Tree Summary

Monitoring data from the Lone Tree mine were evaluated to identify a unique feature or characteristic of the process solution at this facility. This effort demonstrated that the geochemical parameters (alkalinity, calcium, chloride, magnesium, nitrate, potassium, sodium, and sulfate) defined a reproducible, multi-ion fingerprint that was distinctive for the Lone Tree process solution. Even though the individual geochemical parameters concentrations varied by as much as 100 percent over a two-year period, the data defined a chemical signature for the recirculating process solution that was consistent over time and space. The process solution fingerprint was graphically and statistically distinct from the mine water supply. This suggests that the process solution fingerprint is a unique property of the heap leaching process itself and it is not an artifact of the water used at the mine site.

5.2.2 Green Springs Gold Mine

The Green Springs Mine is located in eastern Nevada. At the time that data were being gathered for this project, this mine was on standby status and scheduled to be closed. Therefore, only a limited amount of monitoring information was obtained for this facility. This data set include seven quarters of monitoring data for the barren pond and four quarters of monitoring data from a single monitoring well.

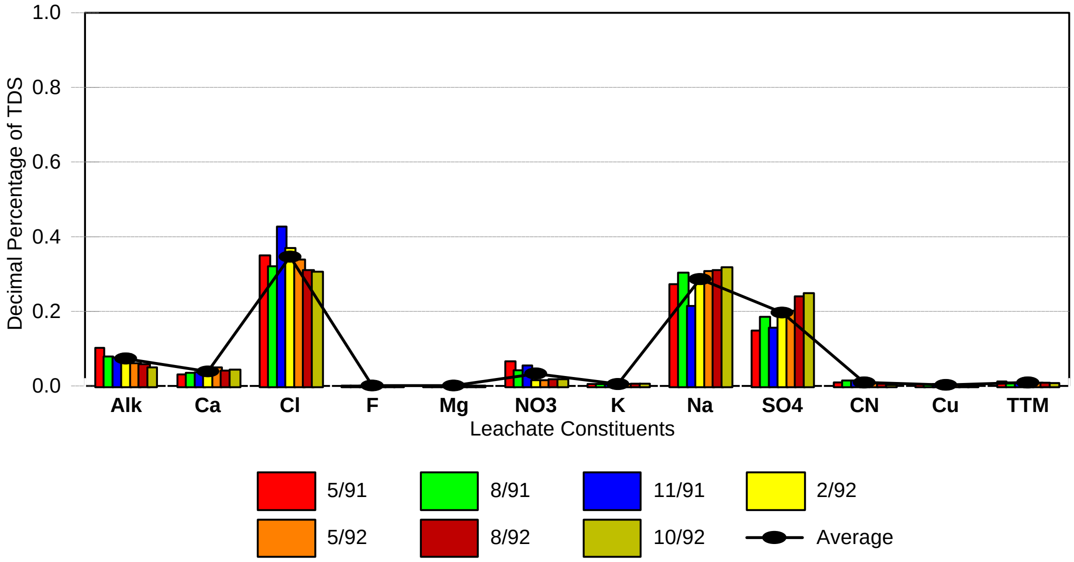
The monitoring results from the Green Springs barren pond are presented in Table 5-4. These data are consistent with the barren pond compositions observed at other mines. Specifically, the most abundant ions in the barren solution are all common geochemical ions. At the Green Springs Mine, the three most abundant ions are chloride, sodium, and sulfate. Also, the trace metals are the least abundant ions and collectively represent only 1.3 percent of the total dissolved solids concentration.

The barren pond monitoring results were normalized to the total dissolved solids concentration and presented in a series of histograms in Figure 5-8. Although the concentrations for the individual parameters were quite variable (alkalinity ranged from 89 mg/L to 190 mg/L, chloride ranged from 481 mg/L to 895 mg/L, and sulfate ranged from 277 mg/L to 444 mg/L), the data from seven quarterly surveys defined a reproducible pattern or fingerprint that characterizes the barren solution at this mine. This specific fingerprint consists of a bimodal pattern that emphasizes the relatively high chloride (30-35 percent of TDS), sodium (30 percent of TDS), and sulfate (20 percent of TDS). A regression analysis of the quarterly fingerprint patterns produced an average r^2 value of 0.944. That is, the percentage of the variability in one multi-ion pattern that is explained by the variability in a second pattern, or the extent to which the two patterns matched, is 94.4 percent.

Table 5-4. Green Springs Mine barren pond monitoring results.

	Sampling Date							Average Concentration	Standard Deviation
	5/20/91	8/28/91	11/15/91	2/18/92	5/8/92	8/19/92	10/2/92		
Akalinity	190.0	150.0	160.0	144.0	117.0	90.0	89.0	122.7	42.0
Calcium	58.0	67.0	77.0	59.0	94.0	64.0	78.0	64.5	19.3
Chloride	655.0	612.0	895.0	630.0	651.0	481.0	547.0	581.1	178.2
Fluoride	0.9	1.0	1.1	1.1	0.9	0.9	0.9	0.9	0.2
Magnesium	0.4	0.3	1.9	0.8	0.4	0.7	1.1	0.8	0.5
Nitrate	123.0	80.0	115.0	27.1	30.2	28.2	32.0	58.9	36.1
Potassium	9.1	9.5	7.9	7.9	9.1	9.2	11.0	8.2	2.3
Sodium	510.0	580.0	450.0	470.0	590.0	480.0	570.0	472.6	130.7
Sulfate	277.0	354.0	328.0	339.0	387.0	372.0	444.0	324.2	92.8
Cyanide	17.0	29.0	31.0	9.0	18.0	9.5	4.2	15.8	8.7
Copper	6.4	8.0	11.0	4.1	6.0	0.4	0.3	4.9	3.2
Total Trace Metals	23.6	18.5	18.3	14.7	16.5	12.7	13.1	15.3	4.8
TDS	1780	2090	1810					1554	537
pH	10.35	10.11	9.92	10.21	9.99	9.58	9.54	9.01	2.38
Aluminum	0.210	0.150	2.000	0.150	0.240	0.170	3.100	0.875	0.979
Antimony	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.000	0.000
Arsenic	2.900	1.200	1.100	1.000	1.100	0.570	0.960	1.184	0.642
Barium	<0.1	<0.1	<0.1	<0.1	<0.5	<0.1	<0.1	0.000	0.000
Beryllium	0.110	0.050	0.050	<0.05	<0.05	<0.05	<0.05	0.031	0.035
Bismuth	<0.1	<0.1	<0.1	<0.05	<0.05	<0.05	<0.05	0.000	0.000
Cadmium	0.070	0.013	0.011	0.020	<0.005	<0.005	<0.005	0.017	0.020
Chromium	0.330	0.380	0.300	0.310	0.420	0.210	0.290	0.291	0.090
Cobalt	0.550	0.610	0.570	0.580	0.670	0.480	0.740	0.544	0.155
Gallium	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.000	0.000
Iron	0.890	0.810	1.600	0.430	0.720	0.420	1.900	0.907	0.489
Lead	<0.025	<0.025	<0.025	<0.005	<0.005	<0.005	<0.005	0.000	0.000
Lithium	0.500	0.500	0.500	<0.05	<0.5	<0.5	<0.5	0.215	0.218
Manganese	<0.05	<0.03	0.080	<0.03	<0.03	<0.03	<0.03	0.013	0.025
Mercury	2.200	1.000	0.520	1.200	0.870	0.210	0.120	0.838	0.586
Molybdenum	0.450	0.440	0.330	0.340	0.370	0.110	0.320	0.309	0.115
Nickel	10.000	9.300	8.200	8.700	10.000	3.500	2.600	6.901	2.904
Phosphorus	0.430	0.480	0.230	0.450	0.420	6.200	1.900	1.486	1.776
Scandium	0.500	0.500	0.500	<0.5	<0.5	<0.5		0.245	0.217
Selenium	0.038	0.092	0.018	0.029	0.170	0.037		0.061	0.046
Silver	0.050	0.110	0.025	<0.025	0.130	0.079	<0.5	0.055	0.043
Strontium	0.920	1.800	0.690	0.720	0.790	0.600	0.890	0.848	0.372
Thallium	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	0.000	0.000
Tin	<0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.000	0.000
Titanium	0.094	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.015	0.029
Vanadium	0.310	0.130	0.020	0.130	0.500	0.098	0.120	0.180	0.134
Zinc	3.000	0.940	1.600	0.640	0.130	0.061	0.110	0.919	0.875

All concentrations except pH in mg/L.



Green Springs Barren Pond Regression Analysis Matrix

	5/91	8/91	11/91	2/92	5/92	8/92	10/92
5/91	1.000	0.972	0.997	0.971	0.952	0.909	0.892
8/91		1.000	0.888	0.979	0.992	0.977	0.968
11/91			1.000	0.942	0.889	0.830	0.808
2/92				1.000	0.985	0.960	0.946
5/92					1.000	0.986	0.982
8/92						1.000	0.999
10/92							1.000

Average r squared value = 0.944

Figure 5-8. Normalized geochemical monitoring results from the Green Springs barren pond.

The normalized monitoring results for trace metals in the barren pond are presented in Figure 5-9. The average r^2 value for these data is 0.586. Although the trace metal pattern at this mine is more consistent than the trace metal pattern observed at the Lone Tree mine, the trace metal pattern is still less reproducible than the geochemical pattern at the same mine.

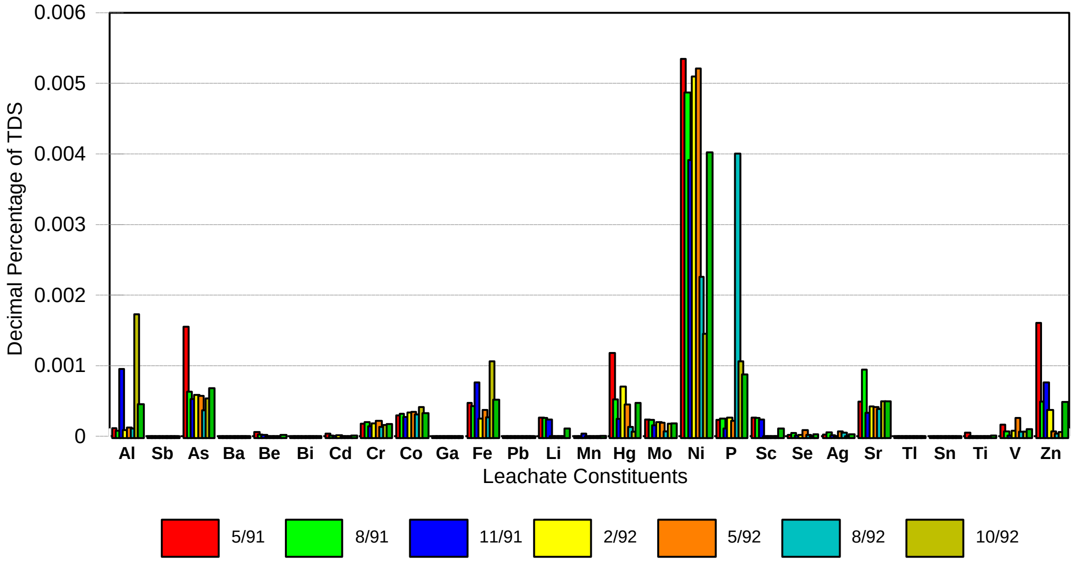
The data file for this facility did not have any information on the make up water and only had data from a single monitoring well. As might be expected, the geochemical parameters were the most abundant ground water constituents and produced a distinctive fingerprint pattern (Figure 5-10). This pattern is defined by a single dominant alkalinity spike (50 percent of TDS), a smaller peak due to calcium (20 percent of TDS), and minor peaks due to magnesium and sulfate (10 percent of TDS). The average regression analysis r^2 value for the four surveys at monitoring Well 1 was 0.988 (i.e., there was a 98.8 percent match of the ground-water pattern at Well 1 between surveys over time). An inspection of Figure 5-8 and 5-10 indicates that the same small set of common geochemical parameters defined a reproducible but distinctly different fingerprint for the barren pond and the ground water at the Green Springs Mine. A regression analysis of the two patterns produced an average r^2 value of 0.000.

Green Springs Summary

The monitoring data set for the Green Springs Mine was limited to several sets of quarterly monitoring data for the barren pond and a single monitoring well. However, these data still illustrated several characteristics of mine waste leachate.

1. Seven geochemical parameters represented 105 percent of the total dissolved solids concentration in the barren pond. The geochemical data from seven sets of quarterly surveys produced a reproducible and distinctive multi-ion fingerprint for the barren pond solution. A regression analysis comparison of the individual survey results over a two-year period produced an average r^2 value of 0.944.
2. The trace metals only represented 1.3 percent of the total dissolved solids concentration of the barren pond solution. The compositional pattern defined by these parameters was less reproducible than the pattern defined by the geochemical parameters (average r^2 value was 0.586).
3. The geochemical parameters also defined a reproducible pattern at the single monitoring well. The ground-water pattern, based on four quarterly surveys, had an average regression analysis r^2 value of 0.988. The alkalinity-rich ground-water pattern was also distinctively different from the barren pond fingerprint that had relatively high levels of chloride, sodium, and sulfate.

The data from this mine demonstrate that it is possible to develop a multi-ion fingerprint to characterize mine waste leachate. Furthermore, this fingerprint is graphically and statistically distinct from the local ground-water fingerprint. It should be possible to track the migration of mine waste leachate through the environment based on its unique composition. However, there was insufficient spatial sampling in the vicinity of the Green Springs Mine to explore this possibility in more detail.

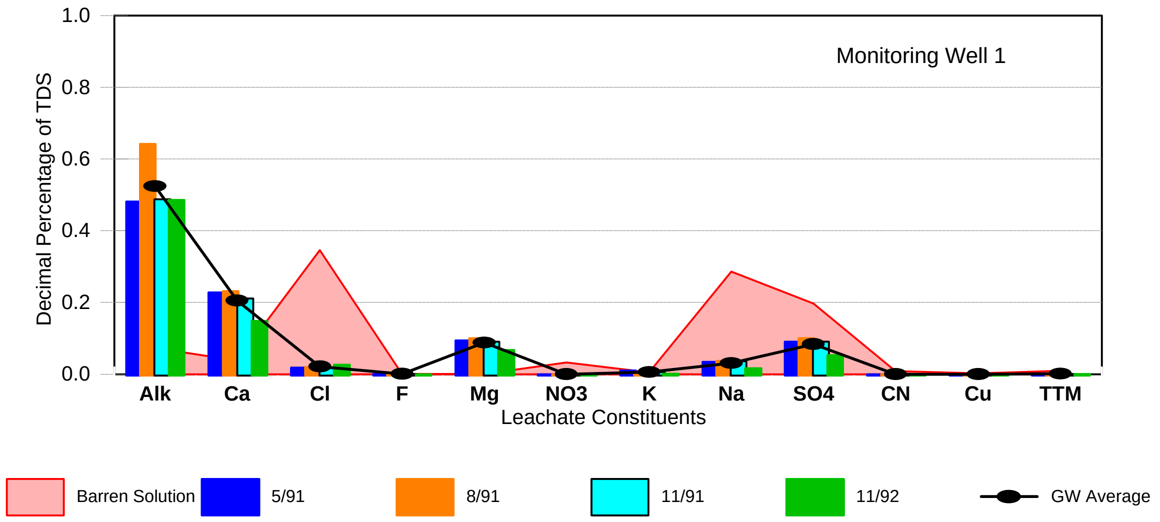


Regression analysis matrix for Green Springs barren pond trace metal data.

Sampling Date	**5/91**	**8/91**	**11/91**	**2/92**	**5/92**	**8/92**	**10/92**
5/91	1.000	0.920	0.885	0.924	0.885	0.190	0.248
8/91		1.000	0.915	0.981	0.974	0.232	0.292
11/91			1.000	0.910	0.904	0.189	0.459
2/92				1.000	0.991	0.240	0.284
5/92					1.000	0.236	0.299
8/92						1.000	0.342
10/92							1.000

Average r squared value = 0.586

Figure 5-9. Normalized trace metal distribution patterns in the Green Springs Mine barren pond.



Green Springs Monitoring Well Regression Analysis Matrix

	5/91	8/91	11/91	11/92
5/91	1.000	0.989	0.999	0.971
8/91		1.000	0.995	0.994
11/91			1.000	0.980
11/92				1.000

Average r squared value = 0.988

Regression Analysis: Barren Pond vs Well 1 0.00004

Figure 5-10. Comparison of monitoring Well 1 fingerprint with the Green Springs barren pond fingerprint.

5.2.3 Alligator Ridge Mine

The Alligator Ridge Mine is located in east-central Nevada. The monitoring results for this facility included the following sets of data:

1. Three sets of quarterly data at the pregnant pond.
2. Three sets of quarterly data at the barren pond.
3. Three sets of quarterly data at the production well.
4. Three sets of quarterly data at eight monitoring wells.

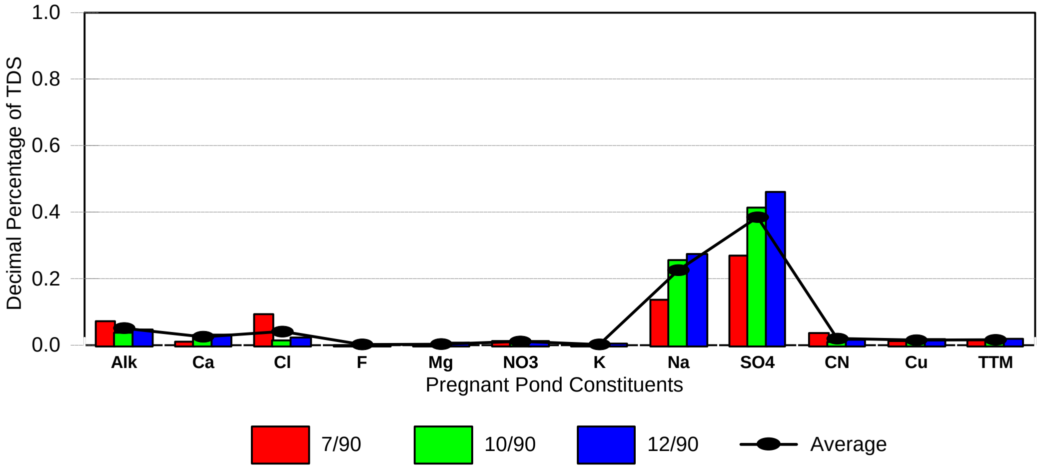
The data from each of these sources have been summarized in a series of histograms to identify multi-ion compositional patterns.

The monitoring data for the Alligator Ridge pregnant pond are presented in Figure 5-11. This information suggests that there is a recurring compositional pattern at this location that is defined by a very dominant sulfate spike (40 percent of TDS), a high sodium spike (20 percent of TDS), and a small amount of noise for alkalinity, calcium, and chloride. Even though the total dissolved solids concentration fluctuated between 3500 mg/L and 5500 mg/L, the average regression analysis r^2 value for this set of data was 0.920 due to the strong sodium-sulfate doublet in the chemical signature.

The monitoring data from the Alligator Ridge barren pond are summarized in Figure 5-12. The chemical signature in the barren pond is essentially identical to the pregnant pond fingerprint. A regression analysis of the barren pond data produced an average r^2 value of 0.907. A regression analysis of the pregnant pond pattern with the barren pond pattern produced an r^2 value of 0.951. Thus, data from two locations in the recirculating heap leaching system demonstrate that the process solution at the Alligator Ridge Mine has a consistent and reproducible fingerprint.

The normalized geochemical fingerprint for the three production wells used as make up water are compared with the Alligator Ridge process solution fingerprint in Figure 5-13. The three production wells define a reproducible pattern in which alkalinity represents 40 percent of the TDS, calcium represents 20 percent of the TDS, and sulfate represents 10 percent of the TDS. The process solution fingerprint at this mine can be easily differentiated from the production well fingerprint because of the lower alkalinity, lower calcium, higher sodium, and higher sulfate concentrations. A regression analysis of the two patterns demonstrates that they can also be statistically differentiated from each other. The average regression coefficient r^2 value for these two sets of data is only 0.052 (a 5.2 percent match).

The Alligator Ridge process solution fingerprint is compared to the ground-water fingerprint at Well M-23 in Figure 5-14. The ground-water pattern indicates a dominant peak for sulfate (40 percent of TDS), a major peak for sodium (20 percent of TDS), and small quantities of alkalinity and the other geochemical parameters. This geochemical distribution is nearly identical with the process solution fingerprint (regression analysis r^2 value = 0.956). The similarity of the two fingerprints would indicate that the ground water at Well M-23, which is located in the leach pad area, has been contaminated by leakage or spillage from the facility. A more important observation is the fact that the geochemical signature, which can be used to characterize the process solution at its source, maintains its identity as the process solution migrates through the environment.

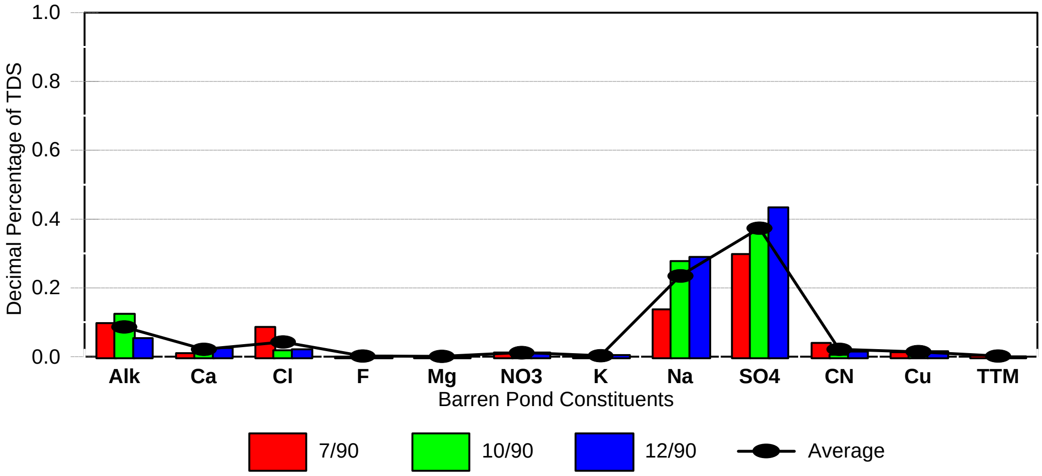


Regression Analysis matrix for Alligator Ridge new pregnant pond

Sampling Date	7/90	10/90	12/90
7/90	1.000	0.874	0.888
10/90		1.000	0.999
12/90			1.000

Average r squared value = 0.920

Figure 5-11. Normalized geochemical monitoring results from the Alligator Ridge new pregnant pond.

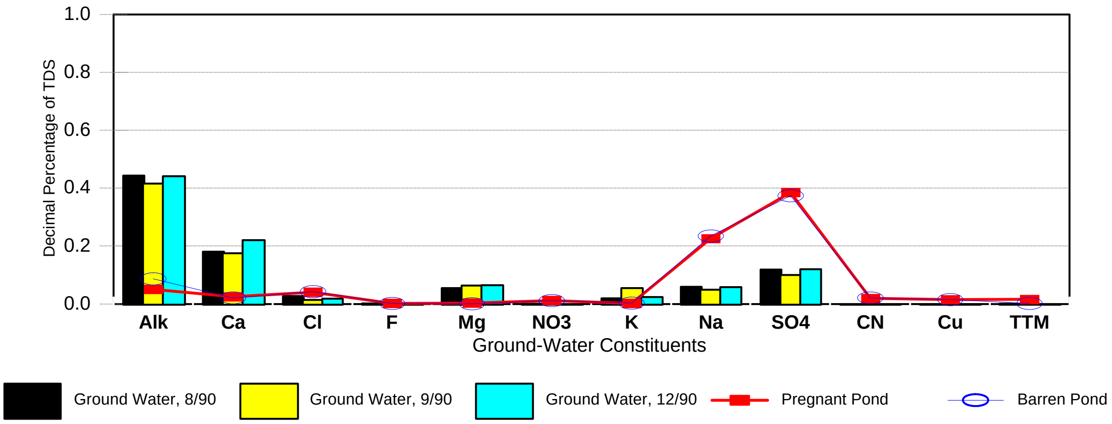


Regression Analysis matrix for Alligator Ridge barren pond

Sampling Date	**7/90**	**10/90**	**12/90**
7/90	1.000	0.881	0.872
10/90		1.000	0.967
12/90			1.000

Average r squared value = 0.907

Figure 5-12. Normalized geochemical monitoring results from the Alligator Ridge barren pond.

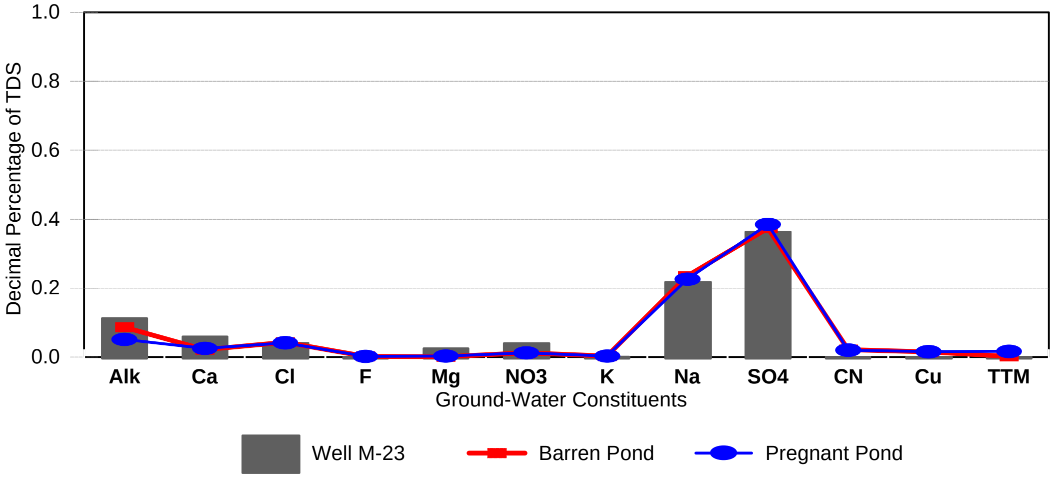


Regression analysis matrix between process solution and production wells

	Well 1	Well 2	Well 3
Pregnant Pond	0.019	0.009	0.016
Barren Pond	0.102	0.076	0.090

Average r squared value = 0.052

Figure 5-13. Comparison of the production well and process solution fingerprints at the Alligator Ridge Mine.



Regression analysis matrix between process solution and Well M-23

	New Pregnant Pond	Barren Pond
Well M-23	0.942	0.970

Average r squared value = 0.956

Figure 5-14. Comparison of Well M-23 fingerprint with the Alligator Ridge process solution fingerprint.

Monitoring results from a second well at the Alligator Ridge facility are compared to the pregnant pond fingerprint in Figure 5-15. The data from three surveys at Well 44-B, located east of the leach pad area, produce a consistent geochemical fingerprint ($r^2 = 0.979$). Furthermore, the Well 44-B fingerprint bears a strong resemblance to the process solution fingerprint. These data also suggest that the process solution fingerprint maintains its chemical identity as the solution migrates from the source.

Alligator Ridge Summary

The data from this heap leaching facility illustrate three features of the fingerprinting process. The first feature is that the geochemical parameters define a consistent and reproducible chemical signature or fingerprint for the process solution at this mine. This signature, defined by 40 percent sulfate, 20 percent sodium, and 10 percent alkalinity, can be used to characterize heap leaching process solutions at their source. The second feature is that the same geochemical parameters also define a reproducible fingerprint for the make up water used at the mine. Therefore, the geochemical fingerprint can be used to differentiate between local ground water and a mine process solution. The third feature of the geochemical fingerprint is that it maintains its chemical identity while migrating through a ground-water environment. Thus, the monitoring results from the Alligator Ridge Mine indicate that the geochemical fingerprint can be used to track the migration of mine waste leachates.

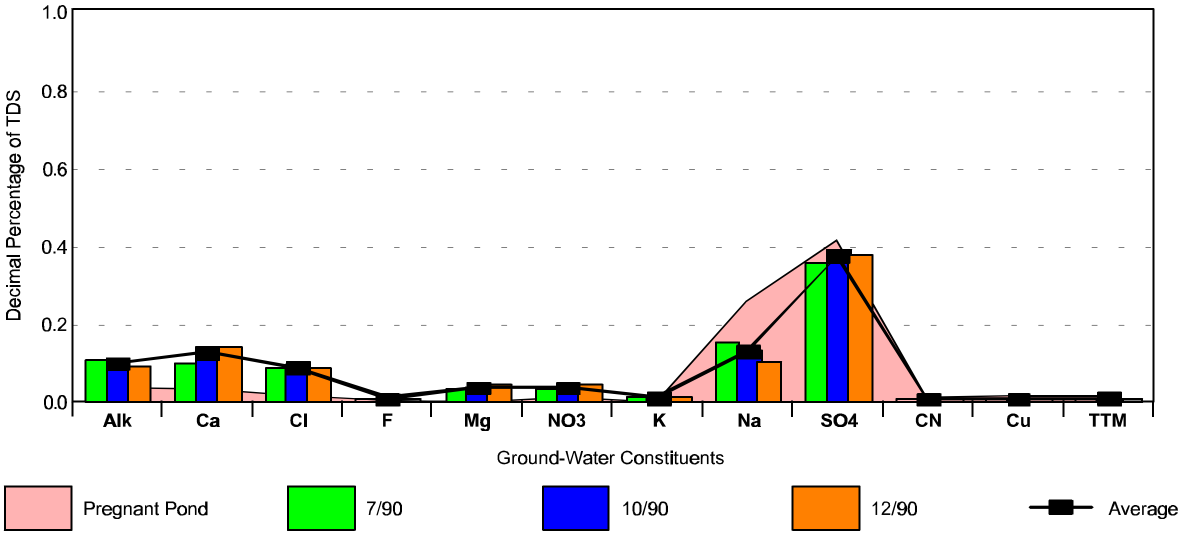
5.2.4 Oliver Hills Mine

This mining facility is located in west central Nevada. The monitoring results for the Oliver Hills Mine cover the period from September, 1990 until June, 1993. However, during 1992, there was no active mining at the site and only fresh water was circulated through the ore pile. As a result, only low, residual levels of cyanide were reported in the barren and pregnant ponds (generally less than 2 mg/L) and the pH was lower than active heap leaching operations (pH 7.5 - 8.2).

Monitoring results from six quarterly surveys at the Oliver Hills pregnant pond are presented in Figure 5-16. Except for the first survey in September, 1990, the geochemical data define a consistent multi-ion signature for this solution. The pregnant fingerprint is characterized by 30-35 percent sulfate, 15 percent sodium, 10-15 percent calcium, and small amounts of the other parameters. The average regression analysis r^2 value for all surveys is 0.865. If the September, 1990 results are excluded, the r^2 value increases to 0.924.

The monitoring data from six surveys at the barren pond are presented in Figure 5-17. Again, except for a single alkalinity value in March, 1992, the geochemical data define a reproducible pattern that is very similar to the pregnant pond pattern. A regression analysis of the individual barren pond surveys produced an average r^2 value of 0.834. A regression analysis of the pregnant pond pattern with the barren pond pattern produced an r^2 value of 0.972. Thus, there was a 97 percent match between the solution fingerprints from two locations in the recirculating process solution.

The normalized composition of the Oliver Hills pregnant pond is contrasted with the make up water used at the mine in Figure 5-18. Although the relatively high levels of sulfate in the make up water are unusual, the two fingerprints can be distinguished. A regression analysis of the process solution fingerprints and the make up water fingerprint produced an average r^2 value of 0.537.

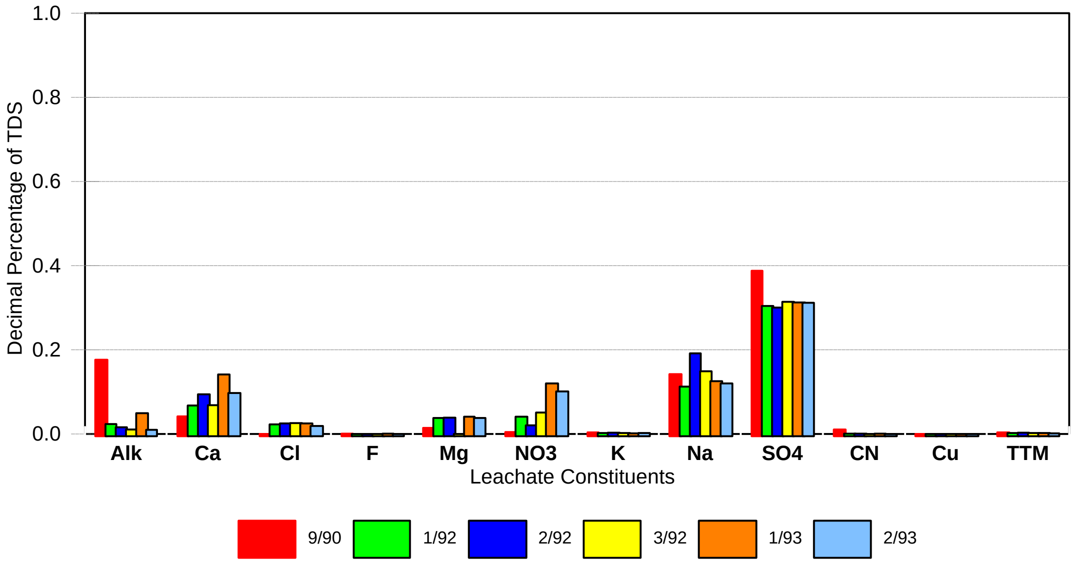


Regression analysis matrix for ground water at Well 44B

Sampling Date	7/90	10/90	12/90
7/90	1.000	0.984	0.962
10/90		1.000	0.992
12/90			1.000

Average r squared value = 0.979

Figure 5-15. Comparison of Well 44B fingerprint with the Alligator Ridge process solution fingerprint.

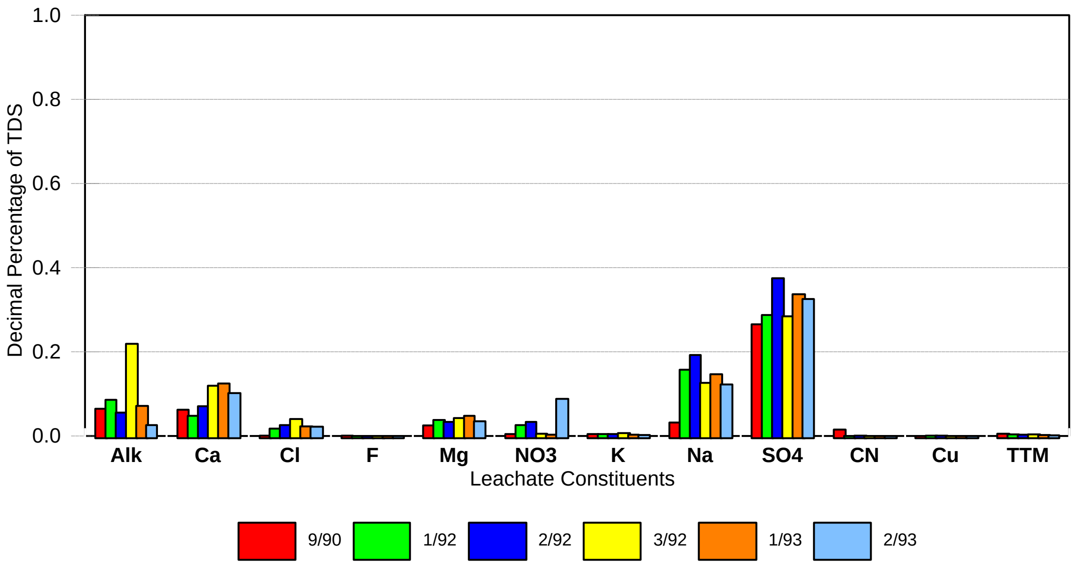


Regression analysis matrix for Oliver Springs Pregnant Pond

Sampling Date	9/90	1/92	2/92	3/92	1/93	2/93
9/90	1.000	0.820	0.746	0.781	0.695	0.695
1/92		1.000	0.932	0.971	0.907	0.955
2/92			1.000	0.952	0.832	0.880
3/92				1.000	0.893	0.946
1/93					1.000	0.972
2/93						1.000

Average r squared value = 0.865

Figure 5-16. Pregnant pond fingerprint at the Oliver Hills Mine.

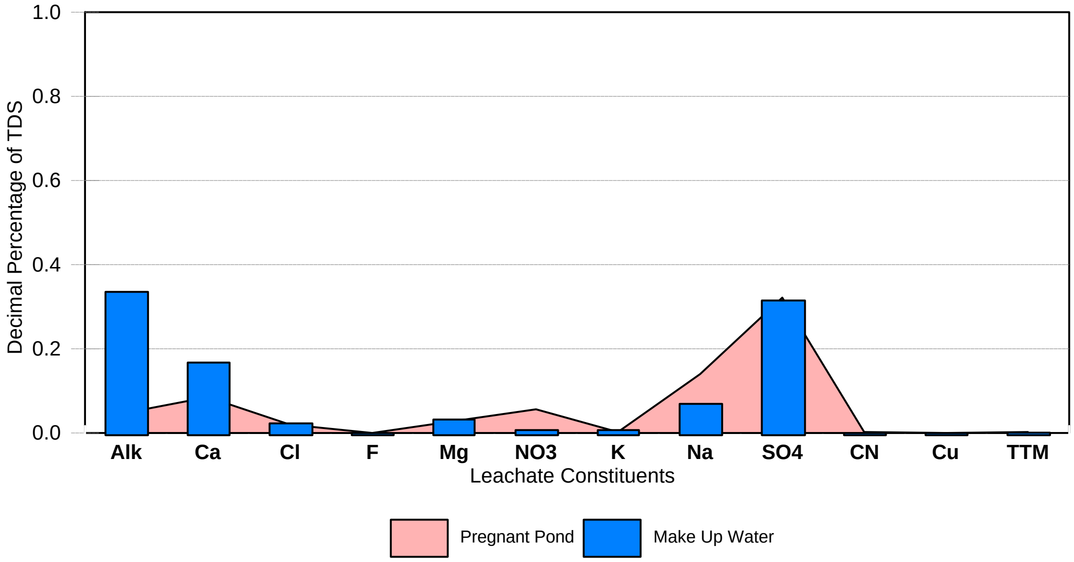


Regression analysis matrix for Oliver Springs Barren Pond

Sampling Date	9/90	1/92	2/92	3/92	1/93	2/93
9/90	1.000	0.817	0.825	0.745	0.885	0.833
1/92		1.000	0.977	0.784	0.931	0.868
2/92			1.000	0.690	0.948	0.926
3/92				1.000	0.783	0.601
1/93					1.000	0.904
2/93						1.000

Average r squared value = 0.834

Figure 5-17. Barren pond fingerprint at the Oliver Hills Mine.



Regression analysis matrix between process solution and make up water

	Pregnant Pond	Barren Pond
Make Up Water	0.466	0.609

Figure 5-18. Comparison of pregnant pond and make up water fingerprints.

The geochemical monitoring data from two wells near the mining operation are compared with the process solution fingerprint in Figure 5-19. The single most abundant ion in the ground water is alkalinity followed in decreasing order by calcium, sulfate, sodium, and chloride. The consistency of the ground-water fingerprint is indicated by the fact that the calculated r^2 value is 0.927. However, when the ground-water fingerprint is compared to the process solution fingerprint, the r^2 value drops to 0.233. Based on the consistent differences between the process solution fingerprint and the ground-water fingerprint, this mining operation has not had an impact on the ground water in the limited areas where monitoring has been conducted.

Oliver Hills Summary

The file for this mine contained six sets of quarterly monitoring data for the pregnant pond and the barren pond. Each set of data defined a consistent geochemical signature with a high level of reproducibility. The r^2 value for the process ponds was 0.972. An interesting aspect of this site is that the process solution fingerprint has remained constant over time even though there was no active mining during 1992.

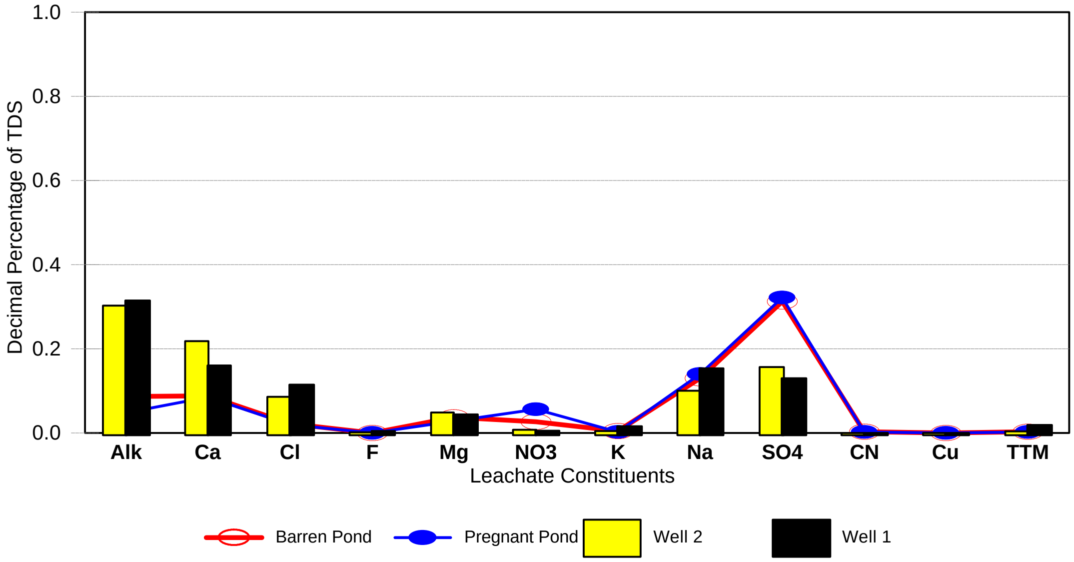
The same set of geochemical parameters also defined a reproducible fingerprint for the ground water that was distinctly different, both graphically and statistically, from the process solution fingerprint. Based on the fingerprint differences, and the limited spatial sampling that has been conducted (only two wells), this facility has not had an impact on the local ground water.

5.2.5 Barrick Goldstrike Mine

The Barrick Goldstrike Mine is a major gold mining facility located in north-eastern Nevada. The data set for this mine includes monitoring results for the pregnant pond, the barren pond, tailings water, a tailings reclaim solution, and more than a dozen wells. These data were generated between 1991 and 1993.

Three years of monitoring data for the Barrick Goldstrike pregnant pond are presented in Figure 5-20. There are two points illustrated with these results. The first point is that there are obvious data quality problems with the August, 1992 data. This is indicated by the fact that the reported sulfate results represent approximately 110 percent of the total dissolved solids concentration. Since this is not physically possible, either the sulfate data are biased high or the total dissolved solids concentration data are biased low. Based on the similarity of the normalized concentrations for the other pregnant pond constituents, it is likely that the reported sulfate results are in error. The second point illustrated with the pregnant pond data is that there is a recurring multiple ion chemical signature. In each data set, sulfate is the singular most abundant ion, sodium is the second most abundant ion, and calcium, alkalinity, and chloride and minor constituents of the chemical signature.

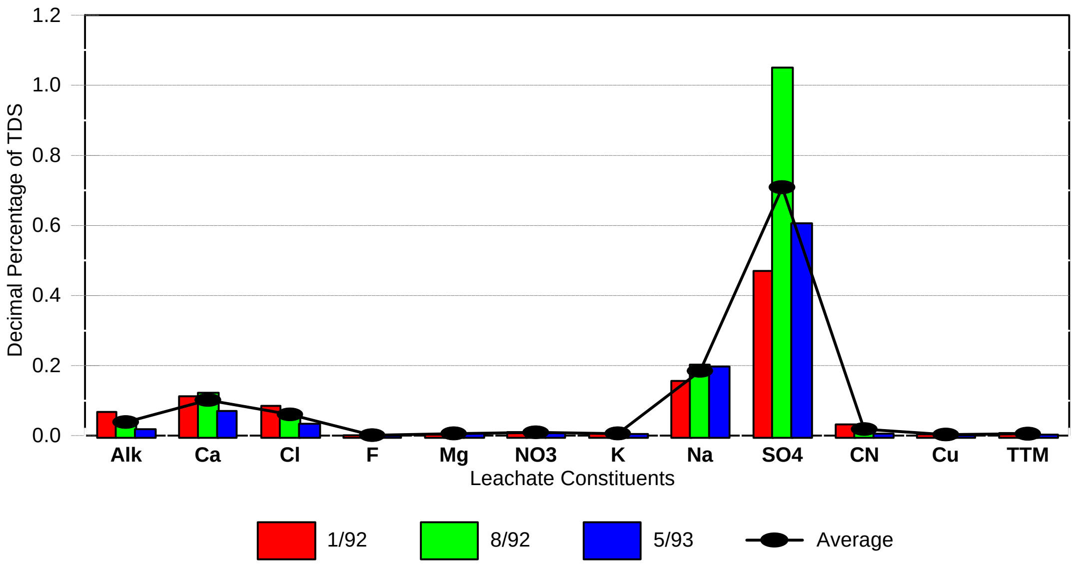
A regression analysis comparison of the individual pregnant pond surveys produced r^2 values ranging from 0.961 to 0.982. The average r^2 value was 0.970 (a 97 percent match). The erroneous sulfate data did not have a significant effect on the regression analysis due to the fact that sulfate was the most abundant constituent in the pregnant solution.



Regression Analysis Matrix between Process Solutions and Ground Water

	Well 1	**Well 2**	**Barren Pond**	**Pregnant Pond**
Well 1	1.000	0.927	0.259	0.156
Well 2		1.000	0.314	0.202
Barren Pond			1.000	0.972
Pregnant Pond				1.000

Figure 5-19. Comparison of Oliver Hills process solution fingerprint with the local ground-water fingerprint.



Regression analysis matrix for Barrick pregnant pond

Sampling Date	1/92	8/92	5/93
1/92	1.000	0.961	0.968
8/92		1.000	0.982
5/93			1.000

Average r squared value = 0.970

Figure 5-20. Pregnant pond fingerprint at the Barrick Goldstrike Mine.

The geochemical monitoring results for the barren pond at this facility are presented in Figure 5-21. The repetitive chemical signature seen at this location suggests that sulfate represents 50 to 60 percent of TDS, sodium represents 20 percent of TDS, and alkalinity, calcium, and chloride are all present but each represents less than 10 percent of the TDS. The average regression analysis r^2 value for this set of data is 0.970.

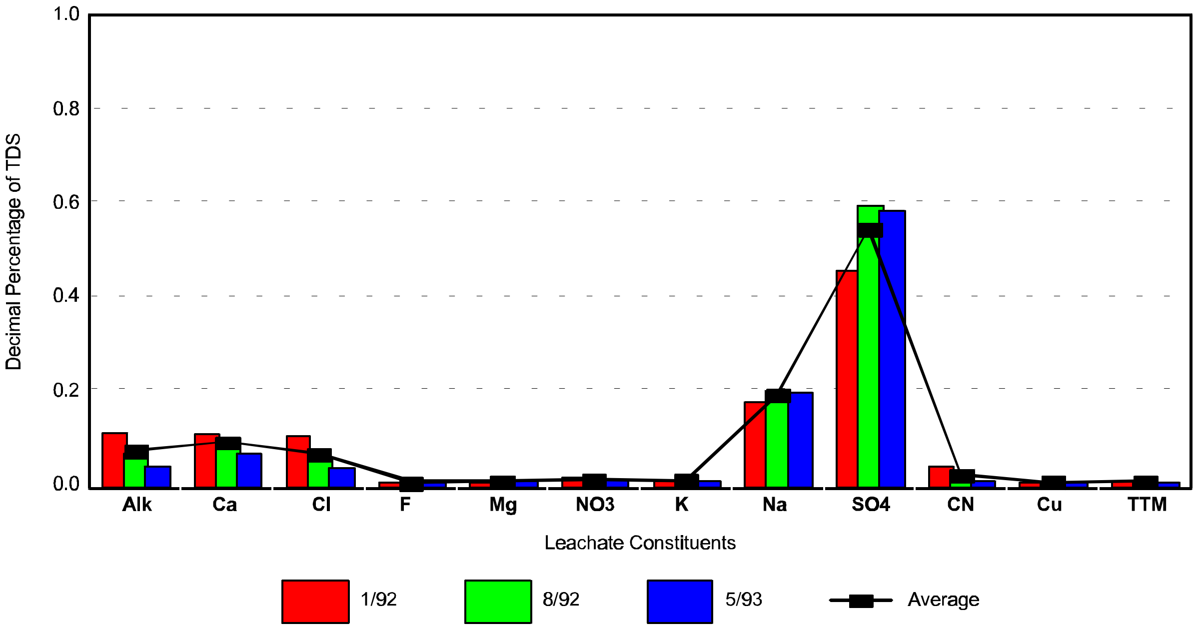
A comparison of the pregnant pond fingerprint (Figure 5-20) with the barren pond fingerprint indicates that the same chemical signature is present at these two locations in the recirculating heap leach operation. Each of these fingerprints share the same features of a dominant sulfate peak, a secondary peak due to sodium, and small amounts of alkalinity, calcium, and sodium. A regression analysis of the two sets of data produced an r^2 value of 0.999. Also, the similarity of the chemical fingerprint at these two locations, with the exception of the pregnant pond sulfate data in 1992, would support the assessment that the sulfate data for that survey is biased high.

The monitoring program at this facility included routine monitoring of tailings water and tailings reclaim water. The monitoring data from these two locations are compared to the pregnant pond and barren pond data in Figure 5-22. All four sets of data share a common geochemical fingerprint that is defined by 60 percent sulfate, 15 percent sodium, 10 to 15 percent calcium, and less than 10 percent alkalinity and chloride. Each of these locations serve as an independent estimate of the source fingerprint at this mine and the results define a consistent geochemical fingerprint (the average r^2 value is 0.964).

The trace metal data from the pregnant pond, the barren pond, the tailings water, and the tailings reclaim water at the Barrick Goldstrike Mine are presented in Figure 5-23. This information indicates that there is no consistent trace metal fingerprint in the mine waste leachates at this facility. The regression analysis r^2 values ranged from 0.001 to 0.843 with an average value of 0.196. That is, the match between each of these source terms ranged from a low of 0.1 percent to a high of 84.3 percent. Even though the geochemical parameters defined a reproducible fingerprint between locations and over time ($r^2 = 0.970$), the reproducibility of the trace metal signature was only 19.6 percent. Some of the factors that contribute to the increased trace metal variability include a lower abundance, lower solubilities and a more complex aquatic chemistry (sorption to particulate matter, complexation by cyanide, and lower precipitation).

The site monitoring program at this facility includes more than a dozen monitoring wells. Geochemical monitoring results for five quarterly surveys at Well 7A are presented and contrasted to the mine waste leachate fingerprint in Figure 5-24. These results demonstrate that the local ground water also has a reproducible and characteristic fingerprint. The ground-water fingerprint pattern is defined by 50 percent alkalinity, 20 percent sulfate, 15 percent calcium, and small amounts of chloride, magnesium, and sodium. A regression analysis of the ground-water pattern produced r^2 values that ranged from a low of 0.976 to a high of 0.999. Over the five quarters for which data are available, the ground-water pattern had a reproducibility of 99.2 percent.

An equally important observation is the fact that the ground-water fingerprint is graphically and statistically distinct from the Barrick Goldstrike mine waste leachate fingerprint. While the ground water is relatively rich in alkalinity and poor in sulfate, the composition of the mine waste leachates has shifted to one that is rich in sulfate and poor in alkalinity. The regression analysis confirms the distinction between the two fingerprint patterns ($r^2 = 0.121$).

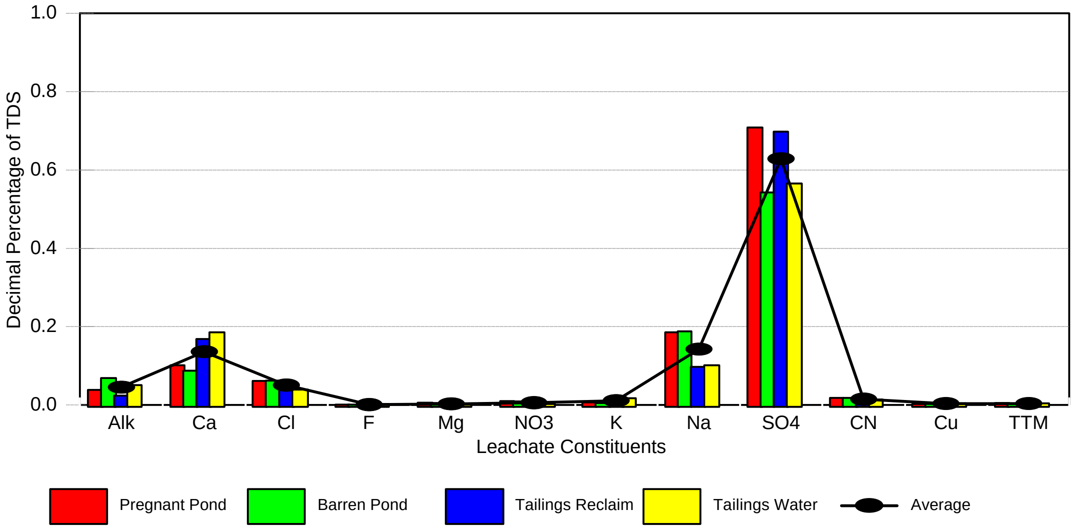


Regression analysis matrix for Barrick barren pond

Sampling Date	1/92	8/92	5/93
1/92	1.000	0.969	0.946
8/92		1.000	0.996
5/93			1.000

Average r squared value = 0.970

Figure 5-21. Barren pond fingerprint at the Barrick Goldstrike Mine.

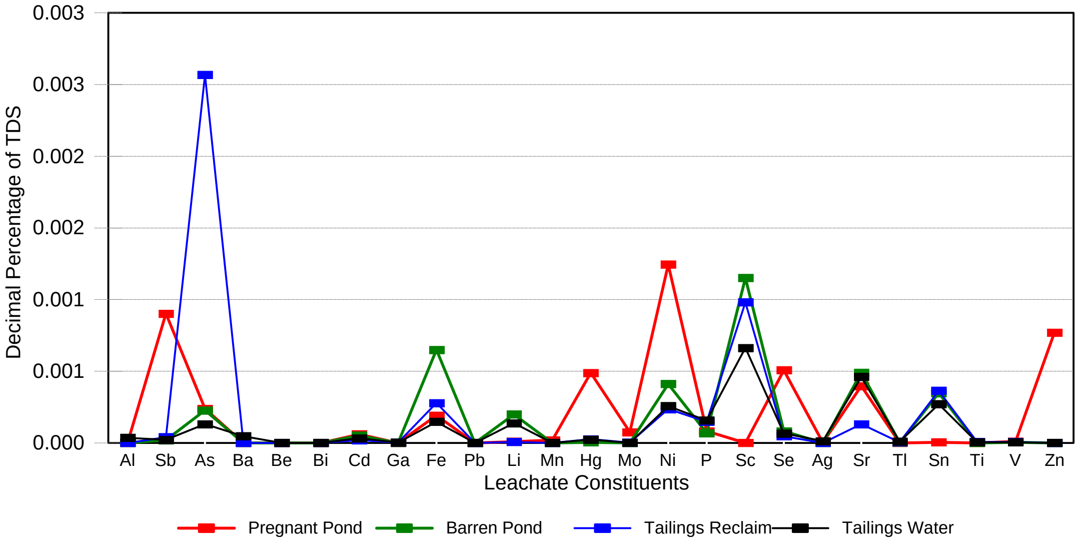


Regression analysis matrix for Barrick geochemical fingerprint

Sampling location	**Pregnant pond**	**Barren pond**	**Tailings reclaim**	**Tailings water**
Pregnant pond	1.000	0.989	0.971	0.954
Barren pond		1.000	0.940	0.935
Tailings reclaim			1.000	0.991
Tailings water				1.000

Average r squared value = 0.964

Figure 5-22. Geochemical fingerprint comparison for Barrick Goldstrike mine waste leachates.

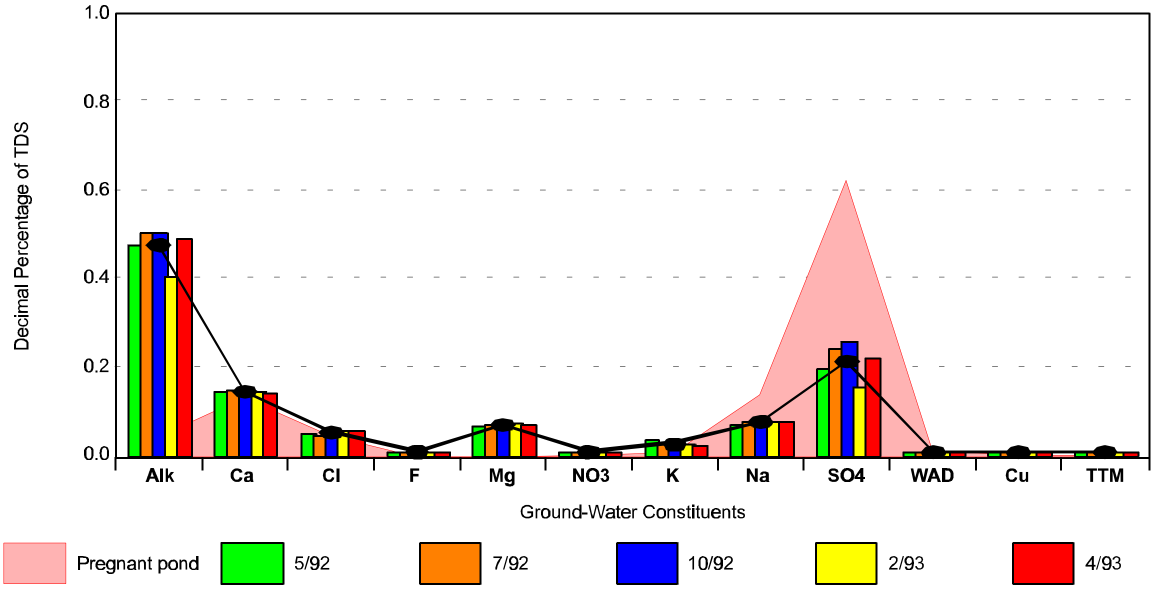


Regression analysis matrix for Barrick trace metal fingerprint

Sampling location	Pregnant pond	Barren pond	Tailings reclaim	Tailings water
Pregnant pond	1.000	0.009	0.001	0.012
Barren pond		1.000	0.171	0.843
Tailings reclaim			1.000	0.143
Tailings water				1.000

Average r squared value = 0.196

Figure 5-23. Trace metal fingerprint comparison for Barrick Goldstrike Mine waste leachates.



Regression analysis matrix for monitoring Well 7A

	Sampling Date				
	5/92	**7/92**	**10/92**	**2/93**	**4/93**
Pregnant Pond	0.101	0.141	0.159	0.083	0.121
5/92	1.000	0.995	0.991	0.992	0.997
7/92		1.000	0.999	0.982	0.999
10/92			1.000	0.976	0.997
2/93				1.000	0.987
4/93					1.000

Average r squared value = 0.992

Figure 5-24. Geochemical fingerprint for ground water at Barrick Goldstrike Well 7A.

Each monitoring well was sampled five to nine times between 1990 and 1993. The results for 47 sampling events at seven wells have been summarized in Figure 5-25. Except for some fluctuation in the height of the alkalinity peak, each data set defined a geochemical fingerprint that was identical to the ground-water fingerprint at Well 7A. This pattern consists of 30 to 50 percent alkalinity, 10 to 20 percent sulfate, 15 percent calcium, and less than 10 percent chloride, magnesium, sodium, and potassium. A regression analysis of these patterns indicates a reproducibility of 94.9 percent. Thus, the ground-water fingerprint is consistent over time and space and can be differentiated from the mine waste leachate fingerprint at this facility ($r^2 = 0.140$).

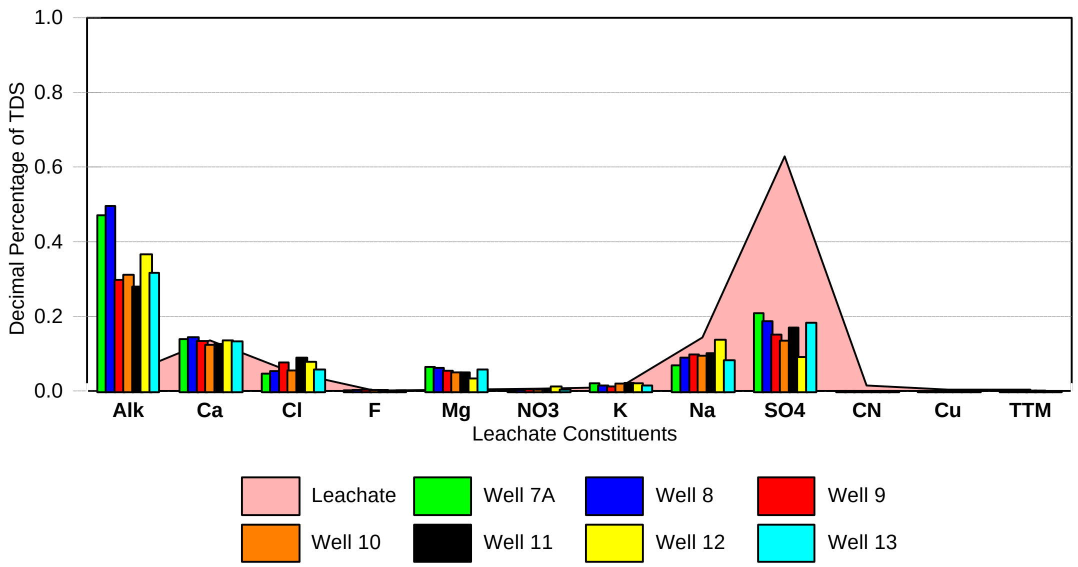
The Barrick Goldstrike data set also contained monitoring results for a well labeled as Leach Pad Observation Port 9 (LPOP 9). The top portion of Figure 5-26 contrasts monitoring results from LPOP 9 on 6/17/91 with the Barrick Goldstrike process solution fingerprint. The ground-water fingerprint on this occasion is defined by approximately 50 percent alkalinity, 15 percent calcium, 15 percent nitrate, 10 percent sodium, and 10 percent sulfate. Since this pattern is quite similar to that observed at other monitoring wells (Figure 5-24, Figure 5-25), and dissimilar from the process solution fingerprint ($r^2 = 0.027$), the conclusion is that mine waste leachates are not impacting this location on this date.

The bottom portion of Figure 5-26 contrasts monitoring results from LPOP 9 on 7/11/91 with the Barrick Goldstrike process solution fingerprint. At this later date, there has been a shift in the ground-water composition at LPOP 9. The ground-water pattern now consists of 40 percent sulfate, 20 percent sodium, and 10 percent alkalinity, calcium, and chloride. This pattern bears a very strong resemblance to the process solution fingerprint ($r^2 = 0.912$). The observed compositional shift at LPOP 9 would indicate that the ground water has been impacted by the migration of mine waste leachate.

Barrick Goldstrike Summary

The data set for this mine contained monitoring data for the barren pond and the pregnant pond for a period of three years. The geochemical data from these surveys defined a consistent pattern that characterized the process solutions and tailings water at this facility. Even with erroneously high and suspect sulfate data for one year, a regression analysis of the individual geochemical patterns produced an average r^2 value of 0.97 (a 97 percent match over time). Although a reproducible geochemical fingerprint was observed and identified, an evaluation of the trace metal data demonstrated that their abundance was extremely variable. The extent to which trace metal distribution patterns in individual mine waste leachate streams matched ranged from 0.1 percent to 84.3 percent with an average value of 19.6 percent. Thus, the geochemical parameters defined a multi-ion signature that characterized the composition of the mine waste leachates at this mine and the trace metals displayed an erratic abundance.

There was no plant make up water data associated with this file. Therefore, it was not possible to demonstrate that the process solution fingerprint was the result of a composition shift during ore processing. However, the sulfate-rich, alkalinity-poor signature that characterized the Barrick Goldstrike process solutions was graphically and statistically distinguishable from the sulfate-poor, alkalinity-rich signature that characterized the ground water at more than a dozen monitoring locations.

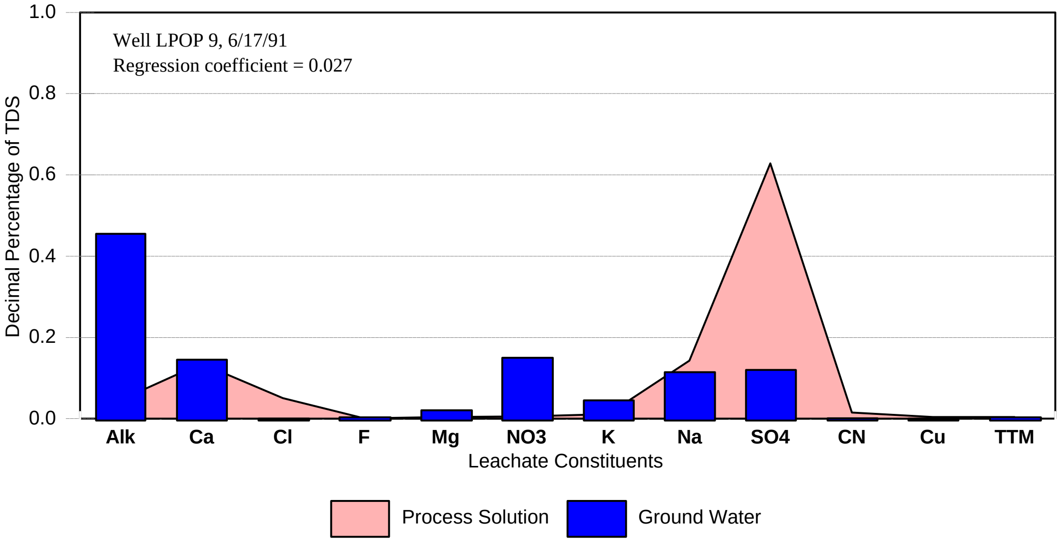


Regression analysis matrix for Barrick ground-water monitoring results

	Sampling Location						
	Well 7A	**Well 8**	**Well 9**	**Well 10**	**Well 11**	**Well 12**	**Well 13**
Pregnant pond	0.123	0.090	0.167	0.123	0.229	0.037	0.214
Well 7A	1.000	0.994	0.943	0.969	0.917	0.887	0.968
Well 8		1.000	0.948	0.978	0.915	0.926	0.958
Well 9			1.000	0.989	0.990	0.928	0.985
Well 10				1.000	0.965	0.954	0.979
Well 11					1.000	0.888	0.979
Well 12						1.000	0.878
Well 13							1.000

Average r squared value = 0.949

Figure 5-25. Geochemical fingerprint comparison for ground water from seven wells at the Barrick Goldstrike facility.



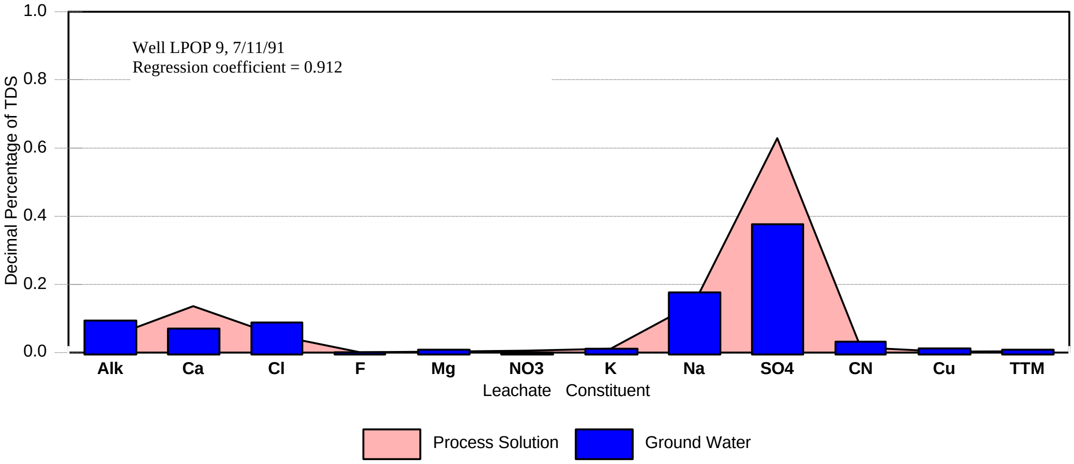


Figure 5-26. Comparison of ground-water monitoring results at Well LPOP 9 with the Barrick process solution fingerprint.

An interesting sequence of events was identified at a monitoring location near the heap leaching pad (LPOP 9). The geochemical signature at this location in June, 1991 was characterized by a high abundance of alkalinity (45 percent) and a low abundance of sulfate (15 percent). This distribution pattern was consistent with the ground-water pattern observed at other wells ($r^2 = 0.826$) but distinguishable from the sulfate-rich, alkalinity-poor distribution of the mine process solutions ($r^2 = 0.027$). One month later, the chemical distribution at LPOP 9 had changed significantly. In July, 1991, sulfate now represented 40 percent of the total dissolved solids concentration and alkalinity only represented 10 percent of the total dissolved solids concentration. As a result of this composition shift, the geochemical fingerprint no longer matched the ground-water fingerprint ($r^2 = 0.202$) but was very similar to the process solution fingerprint ($r^2 = 0.912$). This example illustrates the following characteristics of the fingerprinting concept:

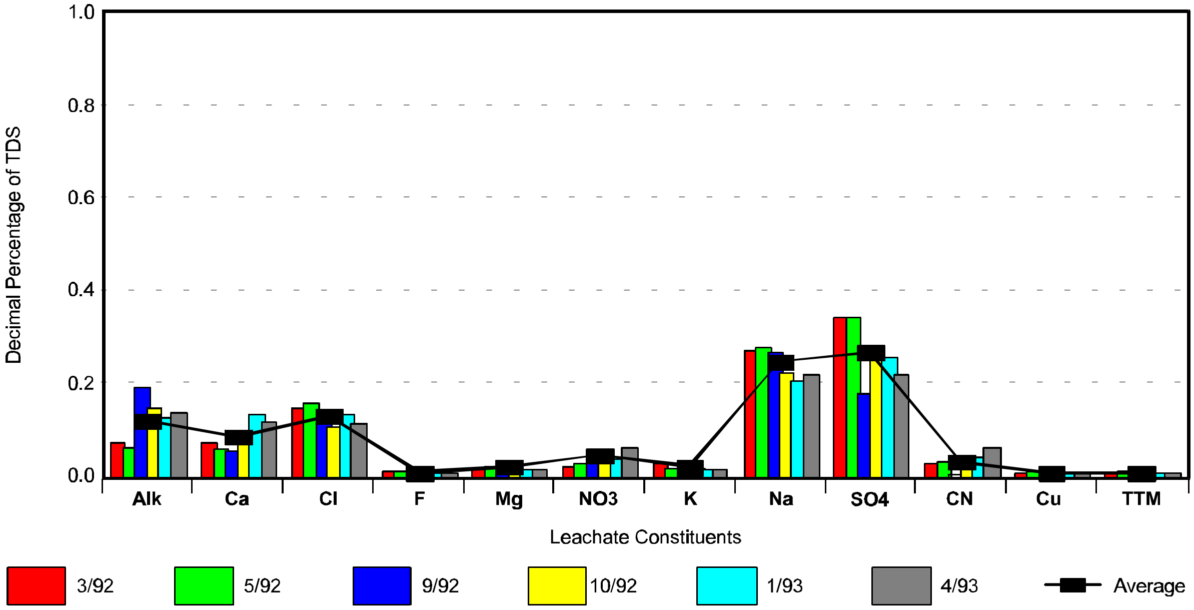
1. The geochemical parameters define a reproducible chemical signature that characterizes the composition of process solutions and tailings water at the source.
2. Although trace metals are generally recognized as the usual constituents of concern in mine waste leachates, their relative abundance and concentrations are too variable to define a characteristic fingerprint pattern.
3. The same suite of geochemical parameters that define the composition of process solutions and tailings water can also be used to characterize ground water in the vicinity of a mining operation. The resulting fingerprints can be used to differentiate mine process solutions from ground water.
4. The July, 1991 monitoring results from LPOP 9 indicate that the mine process solution maintains its chemical identity as it migrates away from the source. This, in turn, suggests that the same geochemical parameters that can be used to characterize process solutions at the source can also be used to detect and monitor the movement of process solutions through the environment.

5.2.6 Rabbit Creek Mine

The Rabbit Creek Mine is located in north-western Nevada and the company uses a conventional heap leaching operation to recover gold from the ore being mined. The monitoring program established for this facility includes routine monitoring of the pregnant pond, the barren pond, the tailings reclaim water, the make up water, and five monitoring wells. The available data for this site cover the period from November, 1990 through May, 1993.

The results from six sets of quarterly monitoring data at the Rabbit Creek pregnant pond are presented in Figure 5-27. The geochemical parameters define a recurring pattern in which the dominant feature is a sodium-sulfate doublet. A regression analysis comparison of the individual survey results suggests that there is an 85.7 percent match for the geochemical fingerprints (average r^2 value = 0.857).

The pregnant pond fingerprint pattern is compared to the geochemical monitoring results for the Rabbit Creek barren pond in Figure 5-28. The barren pond data define a similar pattern in which sodium and sulfate create a dominant doublet and calcium, chloride, and alkalinity create a smaller triplet. A regression analysis of the pregnant pond pattern with the barren pond pattern suggests a reproducibility of 88.8 percent ($r^2 = 0.888$). A similar analysis of the individual barren pond results only produces an r^2 value of 0.656. However, if one excludes the January, 1993 results, the average r^2 value increase to 0.801. (The flagging of this data set is reasonable based on identifiable data quality concerns. The high sulfate result causes a high mass balance and the combination of a high sulfate result and a low sodium result causes a charge imbalance.)

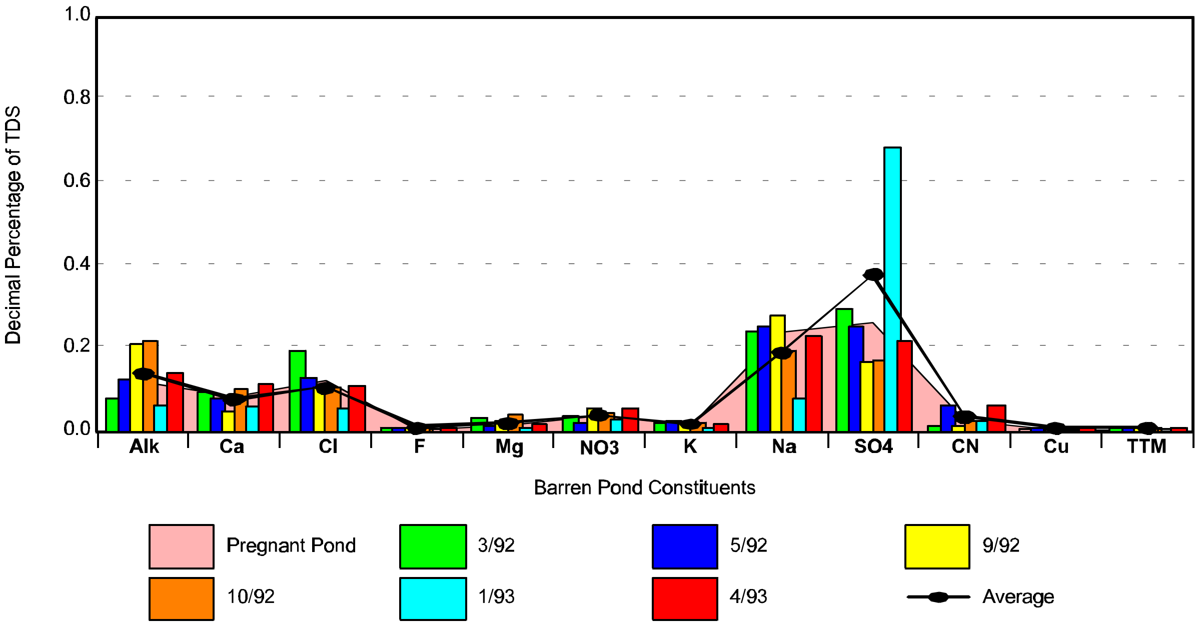


Regression analysis matrix for Rabbit Creek pregnant pond.

Sampling Date	3/92	5/92	9/92	10/92	1/93	4/93
3/92	1.000	0.994	0.684	0.890	0.894	0.849
5/92		1.000	0.667	0.865	0.863	0.823
9/92			1.000	0.873	0.760	0.842
10/92				1.000	0.946	0.951
1/93					1.000	0.966
4/93						1.000

Average r squared value = 0.857

Figure 5-27. Pregnant pond fingerprint at the Rabbit Creek Mine.



Regression analysis matrix for Rabbit Creek barren pond.

Sampling Date	3/92	5/92	9/92	10/92	1/93	4/93
3/92	1.000	0.901	0.623	0.601	0.535	0.828
5/92		1.000	0.793	0.748	0.474	0.959
9/92			1.000	0.898	0.177	0.832
10/92				1.000	0.238	0.836
1/93					1.000	0.401
4/93						1.000

Average r squared value = 0.656
Pregnant pond - barren pond comparison = 0.888

Figure 5-28. Barren pond fingerprint at the Rabbit Creek Mine.

The Rabbit Creek facility also monitors a tailings delivery pipe and the tailings reclaim water on a quarterly basis. Since these two sampling locations might be considered extensions of the recirculating heap leaching solution, the monitoring results for the tailings delivery pipe and the tailings reclaim water were compared to the process solution fingerprint. As shown in Figure 5-29, the geochemical data for the tailings solutions define the same chemical signature identified in the process solutions. An analysis of the individual mine waste leachate fingerprints suggests that the reproducibility of this pattern is on the order of 93 percent. As with the other examples that have been presented earlier, the results from this site demonstrate that the geochemical monitoring results define a chemical fingerprint that can characterize the composition of mine waste leachates.

The geochemical monitoring results from four quarterly surveys of the mine make up water are compared to the pregnant pond fingerprint in Figure 5-30. This information illustrates that the make up water has a consistent fingerprint over time and that this pattern is defined by relatively high concentrations of alkalinity (40 percent) and lesser quantities of sulfate (18 percent), calcium (15 percent), and sodium (10 percent). The reproducibility of this pattern over time was 98.4 percent.

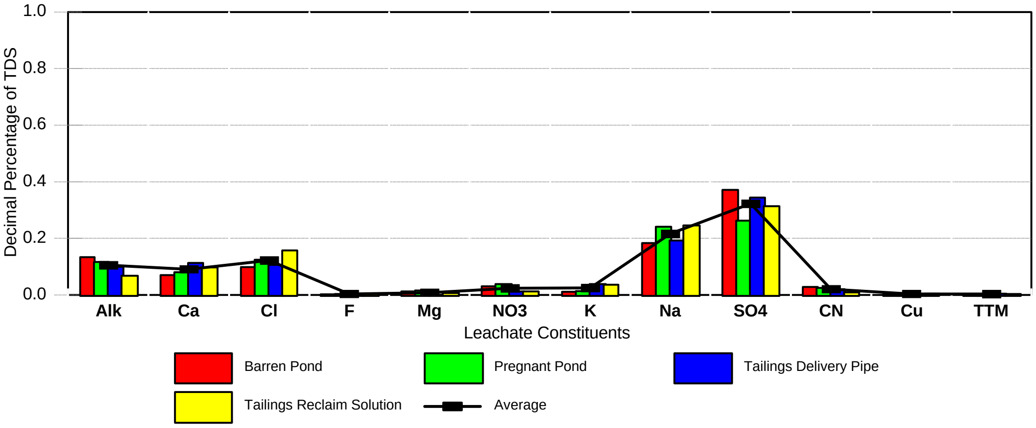
A comparison of the pregnant pond fingerprint with the make up water fingerprint demonstrates the compositional shift that has occurred in the Rabbit Creek process solution (Figure 5-30). The make up water is characterized by a relatively high alkalinity spike and a secondary spike for sulfate and calcium. By comparison, the pregnant pond has enriched levels of both sodium and sulfate and a reduced level of alkalinity. These differences are sufficient to statistically differentiate the mine process solution from the make up water ($r^2 = 0.318$).

The ground-water monitoring results for 11 quarterly surveys between December, 1990 and May, 1993 have been presented in Figure 5-31. Each of these data sets defines a consistent pattern as indicated by the high regression coefficient r^2 value (0.992). This pattern is characterized by a relatively high alkalinity (30 to 35 percent), lesser amounts of calcium (10 to 15 percent) and sodium (10 to 15 percent), and minor amounts of the other geochemical parameters. As in the previous example with make up water, the ground-water fingerprint in the vicinity of the Rabbit Creek Mine is graphically and statistically distinct from the pregnant pond fingerprint ($r^2 = 0.240$).

Rabbit Creek Summary

The Rabbit Creek monitoring program generates data for the pregnant pond, barren pond, tailings delivery pipe, and the tailings reclaim water at the facility. With the exception of a single survey at the barren pond location, which was flagged because of data quality considerations (high mass balance and an anion-cation imbalance), the monitoring results defined a consistent geochemical pattern. This fingerprint was characterized by a sodium - sulfate doublet and a smaller alkalinity - calcium - chloride triplet. The reproducibility of this pattern, as indicated by regression analysis, was 93 percent.

The make up water at the Rabbit Creek Mine also had a consistent fingerprint. The make up water fingerprint, which is typical of most natural water system, is characterized by a relatively high abundance of alkalinity, small quantities of calcium and sulfate, and minor amounts of the other geochemical parameters. Since the make up water has a fingerprint that is consistent over time, and the process solution has a fingerprint that is graphically and statistically distinct from the make up water, the process solution fingerprint must be a characteristic property of the heap leaching solutions and mine waste leachates at this facility.

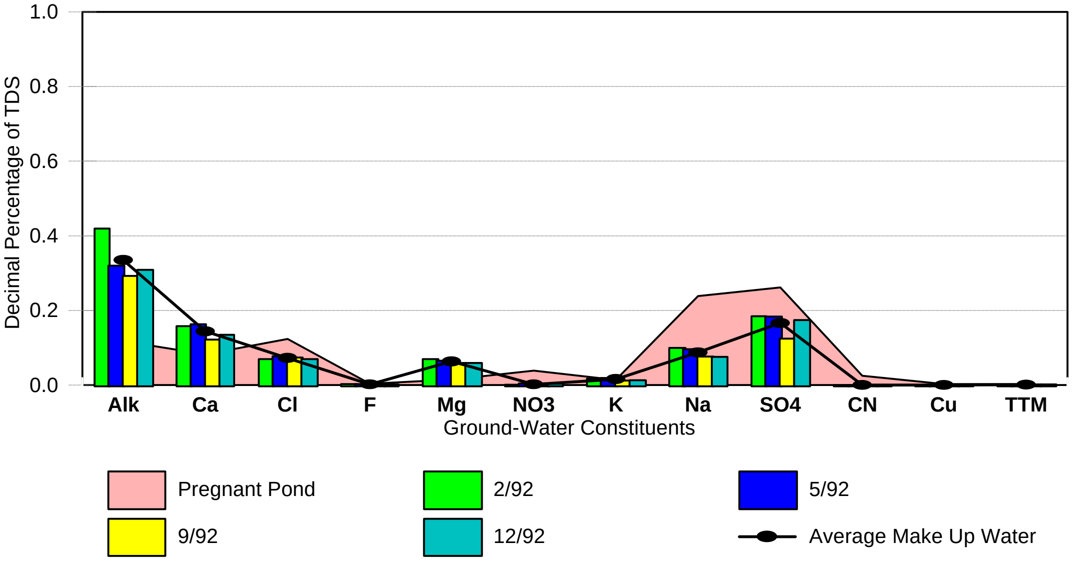


Regression analysis matrix for Rabbit Creek mine waste leachates.

Mine Waste Leachate	Pregnant pond	Barren pond	Tailings delivery	Tailings reclaim
Pregnant pond	1.000	0.887	0.873	0.962
Barren pond		1.000	0.948	0.961
Tailings delivery			1.000	0.968
Tailings reclaim				1.000

Average r squared value = 0.933

Figure 5-29. Comparison of the geochemical fingerprints for mine waste leachates at the Rabbit Creek Mine.

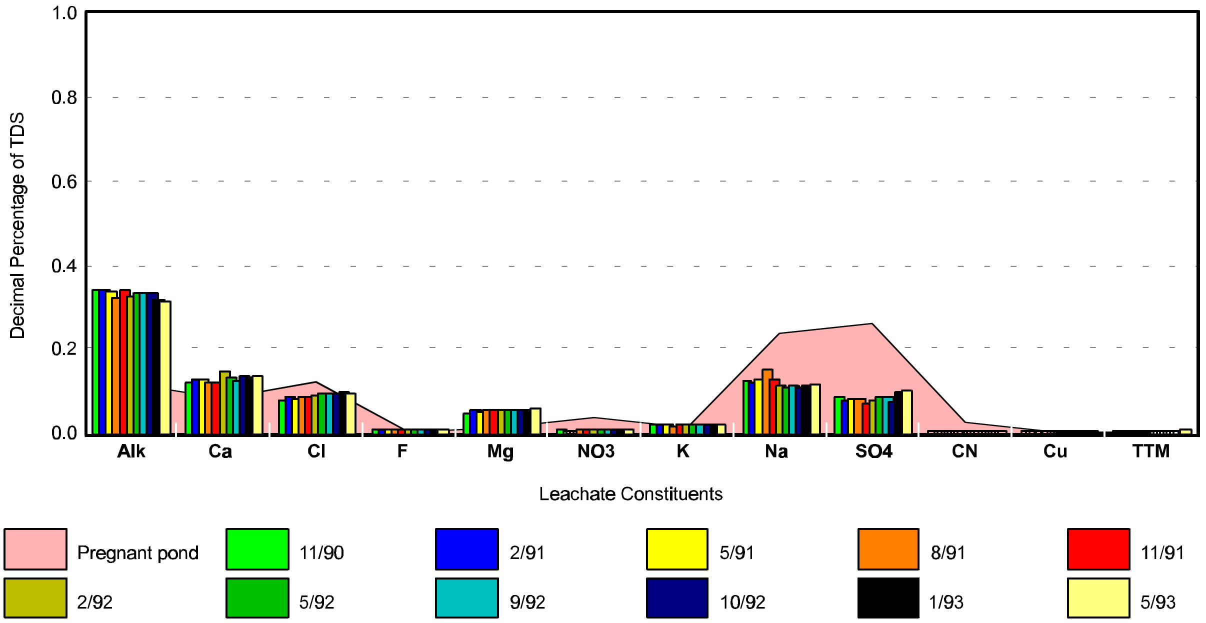


Regression analysis matrix for Rabbit Creek make up water.

	Sampling Date			
	2/92	**5/92**	**9/92**	**12/92**
Pregnant pond	0.276	0.368	0.286	0.343
2/92	1.000	0.976	0.991	0.985
5/92		1.000	0.979	0.994
9/92			1.000	0.981
12/92				1.000

Average r squared value = 0.984

Figure 5-30. Comparison of the pregnant pond fingerprint with the make up water fingerprint at the Rabbit Creek Mine.



Regression analysis matrix for Rabbit Creek ground-water data.

	Monitoring Well 5 sampling date										
	11/90	**2/91**	**5/91**	**8/91**	**11/91**	**2/92**	**5/92**	**9/92**	**10/92**	**1/93**	**5/93**
Pregnant pond	0.242	0.222	0.240	0.291	0.216	0.216	0.223	0.233	0.207	0.268	0.280
11/90	1.000	0.998	0.998	0.986	0.996	0.988	0.994	0.996	0.992	0.990	0.989
2/91		1.000	0.999	0.986	0.998	0.994	0.998	0.998	0.997	0.992	0.990
5/91			1.000	0.991	0.997	0.992	0.994	0.995	0.994	0.990	0.990
8/91				1.000	0.989	0.974	0.977	0.982	0.976	0.976	0.979
11/91					1.000	0.987	0.993	0.995	0.993	0.984	0.983
2/92						1.000	0.996	0.993	0.998	0.991	0.992
5/92							1.000	0.999	0.999	0.996	0.994
9/92								1.000	0.998	0.996	0.994
10/92									1.000	0.993	0.991
1/93										1.000	0.999
5/93											1.000

Average r squared value = 0.992
Ground-water - pregnant pond comparison = 0.240

Figure 5-31. Comparison of the ground-water fingerprint with the Rabbit Creek pregnant pond fingerprint.

The information for this mine also contained monitoring results from five wells. The geochemical pattern at each of these locations consisted of a relatively high abundance of alkalinity, smaller amounts of calcium and sulfate, and lower quantities of chloride, magnesium, and sodium. This reproducible pattern (r^2 = 0.984) is identical to the make up water fingerprint and distinctly different from the process solution fingerprint (r^2 = 0.318). This combination of observations indicates that local ground water is used as make up water at the mine and that the mine process solutions have not adversely impacted the locations being monitored.

5.2.7 Aurora Partnership Mine

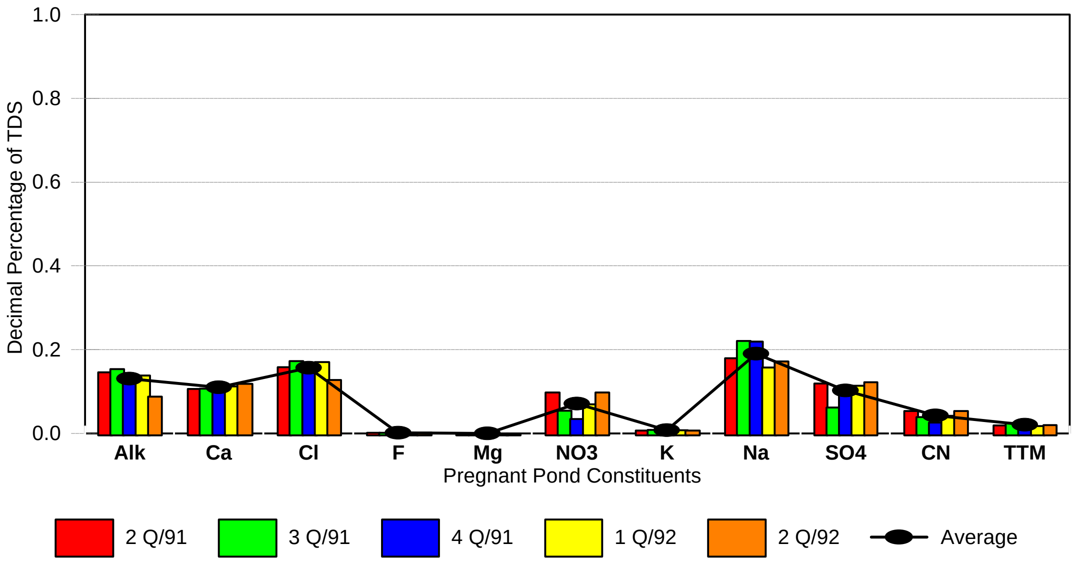
Five sets of quarterly monitoring results for the pregnant pond at the Aurora Partnership Mine are presented in Figure 5-32. Although this pattern lacks a single, prominent constituent, the geochemical data define a reproducible fingerprint for this solution. The regression analysis results to assess the inter-survey similarity of this pattern ranged from a low of 0.754 to a high of 0.967. The average regression analysis r^2 value for these data sets was 0.879 (i.e., an 88 percent similarity or match between the fingerprint patterns defined by the geochemical parameters).

The data from five quarterly surveys at the barren pond of this facility are presented in Figure 5-33. Even though this pattern is non-descript, compared to some of the other mining facilities that have been evaluated, there is a reproducible composition pattern. The calculated regression analysis r^2 values ranged from a low of 0.633 to a high of 0.983 with an average of 0.810. These values are slightly lower than those observed in data sets at other mines but the solution composition clearly shows a consistent, repeatable pattern. The lower r^2 values for this set of data are probably due to the similar peak heights for each of the constituents and the absence of a single dominant constituent.

The Aurora Partnership Mine file contained multiple estimates for the composition of the process solution. The monitoring results suggested that there was a recurring geochemical fingerprint in both the pregnant pond (r^2 = 0.879) and the barren pond (r^2 = 0.810). A regression analysis of these two data patterns produced an r^2 value of 0.977 (98 percent match). Thus, the geochemical parameters defined an identical solution fingerprint for these two locations in the recirculating heap leach solution at the Aurora Partnership Mine.

The Aurora Partnership file only contained the results from a single sampling of the mine make up water. The geochemical results from this sampling event are compared to the composition of the mine process solutions in Figure 5-34. Although there are no estimates of solution composition variability, the resulting make up water fingerprint is typical of most ground-water and surface water systems. Specifically, alkalinity is the single dominant ion (50 percent) in the solution with successively smaller amounts of sulfate (18 percent), calcium (17 percent), sodium (11 percent), and chloride (7 percent).

The information presented in Figure 5-34 demonstrates that the process solution fingerprint is distinctly different from the make up water fingerprint. A regression analysis produced an r^2 value of 0.230 between the barren pond and the make up water and an r^2 value of 0.302 between the pregnant pond and the make up water. Since the process solution fingerprint is different from the make up water and consistent over time, the process solution fingerprint is not just make up water passing through the plant and must be characteristic of the specific mining operation.

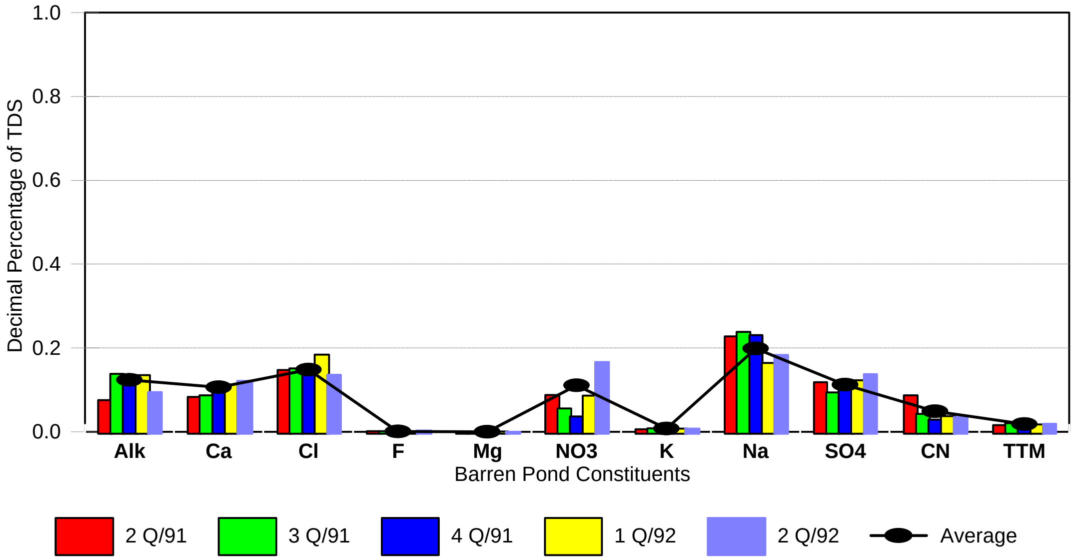


Regression analysis matrix for Aurora pregnant pond.

Sampling Date	2 Q/91	3 Q/91	4 Q/91	1 Q/92	2 Q/92
2 Q/91	1.000	0.876	0.878	0.967	0.916
3 Q/91		1.000	0.958	0.877	0.754
4 Q/91			1.000	0.890	0.808
1 Q/92				1.000	0.870
2 Q/92					1.000

Average r squared value = 0.879

Figure 5-32. Pregnant pond fingerprint at the Aurora Partnership Mine.

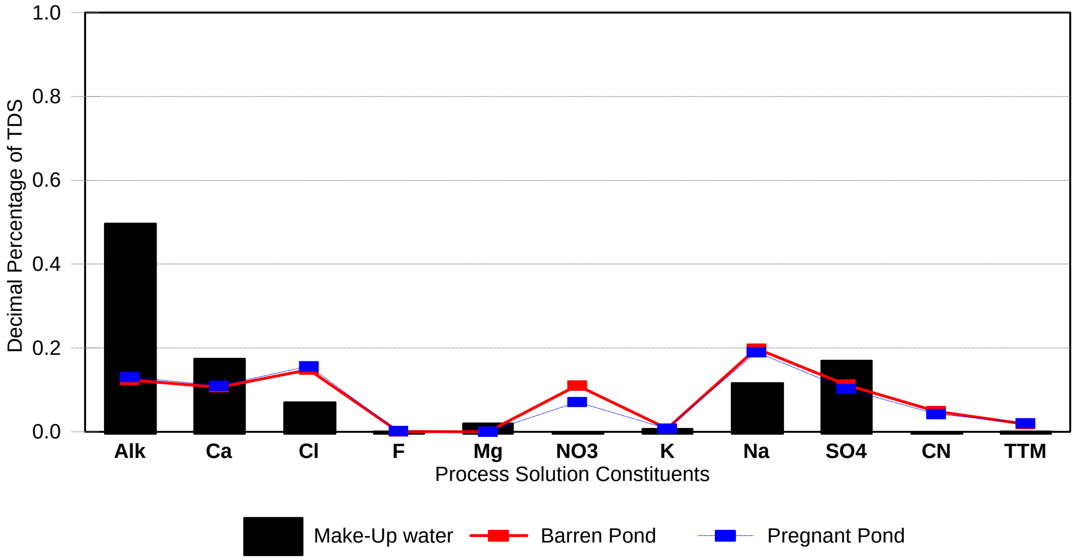


Regression analysis matrix for Aurora barren pond.

Sampling Date	2 Q/91	3 Q/91	4 Q/91	1 Q/92	2 Q/92
2 Q/91	1.000	0.865	0.829	0.764	0.757
3 Q/91		1.000	0.983	0.892	0.664
4 Q/91			1.000	0.837	0.635
1 Q/92				1.000	0.878
2 Q/92					1.000

Average r squared value = 0.810
Barren pond - pregnant pond comparison = 0.977

Figure 5-33. Barren pond fingerprint at the Aurora Partnership Mine.



Make Up Water - Process Solution Comparison

	Pregnant Pond	Barren Pond
Make Up Water	0.303	0.211

Figure 5-34. Comparison of make up water fingerprint with the Aurora Partnership process solution fingerprint.

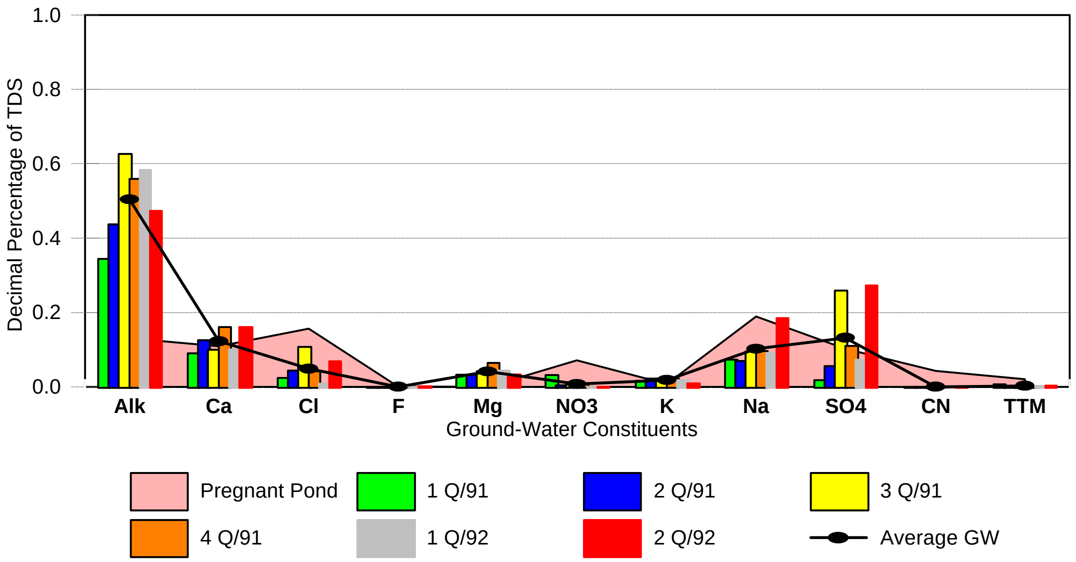
The site file contained the results for six quarterly surveys at a single monitoring well. Although there is some variability due to possible data quality problems (poor mass balance), the results indicate a reasonably consistent ground-water fingerprint (Figure 5-35). The major feature of this pattern is the dominant alkalinity spike that represents 50 percent of the total dissolved solids concentration. Regression analysis of these patterns produced r^2 values ranging from a low of 0.729 to a high of 0.992 with an average of 0.898 (a 90 percent match). The ground-water fingerprint at the one site monitoring well is identical to the make up water fingerprint and distinctly different from the mine process solution fingerprint ($r^2 = 0.222$).

Aurora Partnership summary

The limited data obtained for the Aurora Partnership Gold Mine were used to explore the possibility of using geochemical parameters to fingerprint process solutions at heap leaching facilities. The data from five quarterly surveys between 1991 and 1992 demonstrated that routine monitoring results for ten common geochemical parameters (alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, sulfate, and total dissolved solids) could be used to develop a reproducible multi-ion fingerprint for the mine process solutions. The inter-survey regression analysis of the pregnant pond data produced r^2 values of 0.754 - 0.976 (average = 0.879) and a similar analysis of the barren pond data produced r^2 values of 0.635 - 0.983 (average = 0.810). These values are slightly lower than those calculated with data sets at other mining operations in Nevada and is attributed to the rather simple pattern at this mine that lacks a dominant feature. However, the results from this site again demonstrate that the geochemical parameters can be used to develop a reproducible chemical signature to characterize the process solutions as there was a 98 percent match between the barren pond and pregnant pond fingerprints.

Another important aspect of this data assessment is that the mine process solution fingerprint was shown to be different from the make up water and ground-water fingerprints. Since the process solution composition is consistently different from the make up water (r^2 ranged from 0.230 to 0.302), the process solution fingerprint can not be an artifact of the make up water used at the mine and must be characteristic of the heap leaching process. Also, the difference between the process solution fingerprint and the ground-water fingerprint (r^2 ranged from 0.169 to 0.228) should make it possible to differentiate fugitive leachates from the regional ground water.

Although the monitoring data from the Aurora Partnership Mine are useful for demonstrating that heap leaching process solutions can be fingerprinted at the source, and that this fingerprint can be differentiated from the local ground-water fingerprint, this data set is not useful for tracking the migration of process solutions through the environment. This is due to the fact that the site monitoring program only reported data from a single well which was not impacted by the mining operation (the ground-water fingerprint was similar to the make up water fingerprint but different from the process solution fingerprint). The limited available data makes it impossible to distinguish between (1) a mining operation that is not impacting the ground water or (2) a mining operation that is impacting ground water but it is not being detected because of limited spatial sampling.



Regression analysis matrix for Aurora ground water.

	Sampling Date					
	1 Q/91	**2 Q/91**	**3 Q/91**	**4 Q/91**	**1 Q/92**	**2 Q/92**
Pregnant pond	0.191	0.194	0.231	0.191	0.151	0.374
1 Q/91	1.000	0.980	0.823	0.965	0.974	0.729
2 Q/91		1.000	0.889	0.992	0.981	0.795
3 Q/91			1.000	0.917	0.898	0.913
4 Q/91				1.000	0.983	0.842
1 Q/92					1.000	0.789
2 Q/92						1.000

Average r squared value = 0.898
Ground water - process solution comparison = 0.222

Figure 5-35. Comparison of the ground-water fingerprint with the Aurora Partnership pregnant pond fingerprint.

5.2.8 Cortez Gold Mine

The Cortez Gold Mine, which uses a conventional heap leaching process, is located in central Nevada. The facility utilizes a fixed leaching pad and places the spent ore in a series of tailings basins. The monitoring information that was obtained for this particular operation included the following:

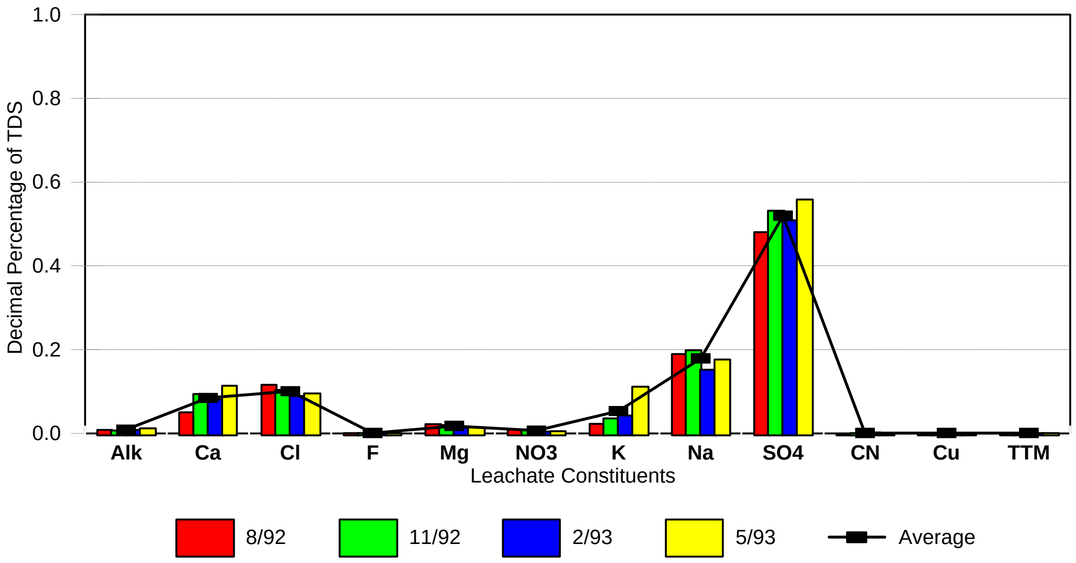
1. Pregnant pond monitoring results.
2. Barren pond monitoring results.
3. Tailings pond #6 monitoring results.
4. Tailings reclaim solution monitoring results.
5. Solution pond 1 monitoring results.
6. Water storage reservoir monitoring results.
7. Ground-water monitoring results from 40 wells.

A minimum of four surveys were conducted at each of the locations identified above between 1991 and 1993. Each of the samples were analyzed for complete geochemical analyses, total dissolved solids, pH, weak acid dissociable cyanide, and trace metals as specified by the Nevada Department of Environmental Protection. Approximately 10,000 analyses have been tabulated and reviewed for this site.

The pregnant pond is part of the recirculating process solution system and represents the location at which the ore pile leachate is collected. The monitoring results from four surveys at the Cortez Gold Mine pregnant pond are presented graphically in Figure 5-36. These data indicate that the pregnant pond has a consistent geochemical composition over time. This characteristic pattern consists of 50 percent sulfate, 20 percent sodium, 10 percent calcium, and 10 percent chloride. A regression analysis comparison of the individual survey results at this location produced an average r^2 value of 0.980.

The barren pond is the location at which the process solution is made up prior to spraying on the ore pile. Generally, a cyanide salt is added to extract the gold and the solution pH is adjusted into the alkaline range ($pH > 10$) to ionize the cyanide and keep it in solution. The data from four surveys at the Cortez Gold Mine barren pond between August, 1992 and May, 1993 are presented in Figure 5-37. The data from these surveys produce a repeatable pattern that is characterized by 50 percent sulfate, 20 percent sodium, 10 percent calcium, and 10 percent chloride. Even though the reported concentrations for the individual constituents displayed considerable apparent variability (total dissolved solids ranged from 7220 mg/L to 11,000 mg/L; calcium ranged from 475 mg/L to 1120 mg/L; chloride ranged from 504 mg/L to 1400 mg/L; and potassium ranged from 81 mg/L to 150 mg/L), the barren solution maintained a consistent multi-ion composition or fingerprint over time. A regression analysis comparison of the individual barren pond surveys produced an average r^2 value of 0.986.

The data set from the Cortez Gold Mine contained information from four locations that can be used to characterize the process solution at this facility. In addition to the pregnant pond and the barren pond, the site file also contained information for the tailings reclaim solution and a solution pond.

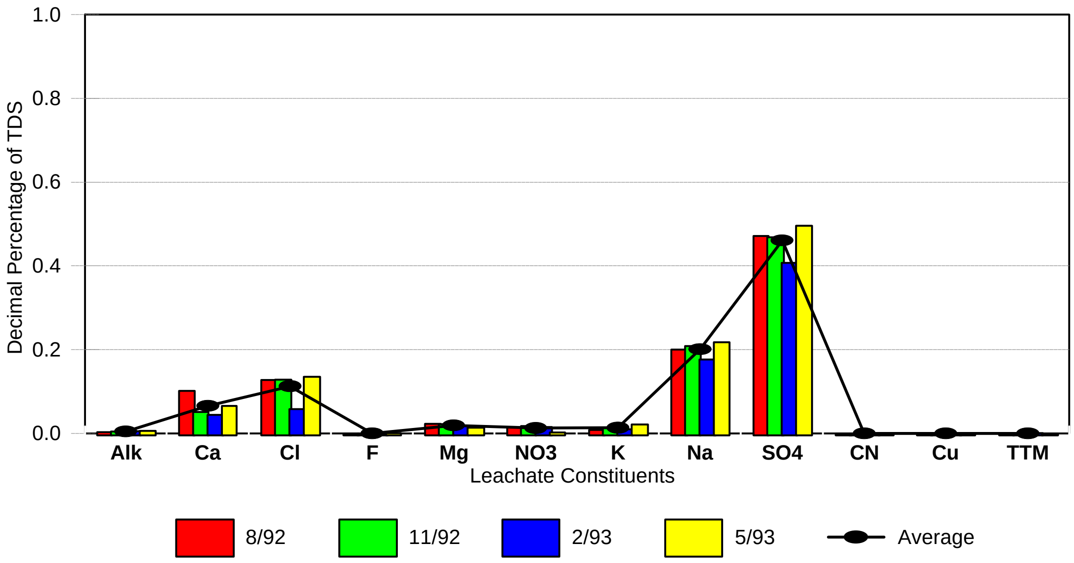


Regression analysis matrix for Cortez pregnant pond #2

Sampling Date	**8/92**	**11/92**	**2/93**	**5/93**
8/92	1.000	0.988	0.975	0.992
11/92		1.000	0.984	0.998
2/93			1.000	0.981
5/93				1.000

Average r squared value = 0.986

Figure 5-36. Pregnant pond fingerprint at the Cortez Gold Mine.



Regression analysis matrix for Cortez barren pond

	Sampling date			
	8/92	**11/92**	**2/93**	**5/93**
8/92	1.000	0.991	0.981	0.952
11/92		1.000	0.994	0.976
2/93			1.000	0.985
5/93				1.000

Average r squared value = 0.980

Figure 5-37. Barren pond fingerprint at the Cortez Gold Mine.

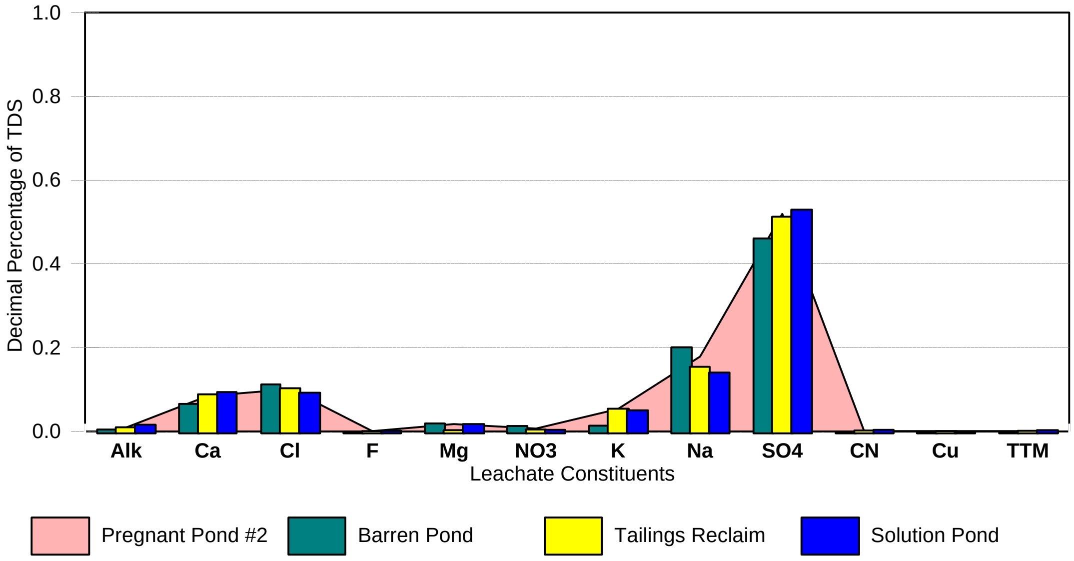
Average geochemical monitoring results from each of these four locations are compared in Figure 5-38. The data from each location define a reproducible pattern in which sulfate is the single dominant ion (50 percent), sodium, chloride, and calcium are minor constituents (10 to 20 percent), and the other constituents (alkalinity, fluoride, copper, cyanide, and total trace metals) are essentially absent from the solution fingerprint.

The monitoring results for this mine contained 16 sets of data (four quarterly surveys from four different locations) that were used to characterize the process solution composition. A regression analysis was performed to estimate the reproducibility of the multi-ion compositional pattern described by these surveys. This effort demonstrated that the solution fingerprint had a very high degree of consistency. The calculated r^2 values ranged from a low of 0.980 for the pregnant pond surveys to a high of 0.990 for the solution pond surveys. In addition, a comparison of the geochemical pattern at different locations in the recirculating system produced a similarly high degree of comparability ($r^2 = 0.984$). The consistent nature of the geochemical fingerprint at four monitoring locations over a period of one year, even though the observed concentrations for the individual leachate constituents fluctuated by more than 50 percent, strongly suggests that the chemical signature is characteristic of the process solution at the facility.

The average trace metal composition patterns at each of the four process solution sampling locations used to develop the geochemical fingerprint for the Cortez Mine are contrasted in Figure 5-39. These data indicate that certain metals such as zinc, strontium, molybdenum, iron, and arsenic are often present in these solutions. However, despite the consistent geochemical pattern defined at these sampling locations, the trace metal patterns demonstrated considerable variability. The calculated regression analysis r^2 values for the trace metal patterns ranged from a low of 0.000 (between the pregnant pond and the barren pond) to a high of 0.622 (between the tailings reclaim water and the solution pond). The average regression analysis r^2 value for all trace metal data was only 0.186.

An evaluation of 16 sets of quarterly monitoring data for the Cortez process solution indicates that the trace metal abundance is highly variable. Factors that contribute to this situation include the following:

1. The relative abundance of trace metals at a single location in the recirculating system varies with time. A regression analysis comparison of the trace metal patterns ranged from a low of 0.234 at the pregnant pond to a high of 0.861 at the barren pond.
2. The relative trace metal abundance varies considerably between different locations in the recirculating system. As indicated in Figure 5-39, the regression analysis r^2 values for different sampling locations ranged from 0.000 to 0.622.
3. Because the trace metal component is such a small and variable component of the process solution composition, data quality checks such as mass balance and charge balance that are used with the geochemical parameters are not effective with trace metals. As a result, data quality problems that could contribute to the low r^2 values for the trace metal patterns are not readily detectable.
4. A decision to monitor "total concentrations" of trace metals rather than "dissolved concentrations", or improper sampling can cause considerable fluctuation in apparent trace metal concentrations. Since trace metals are the least abundant constituents in the process solution, these fluctuations can mask any trace metal pattern that may be present.

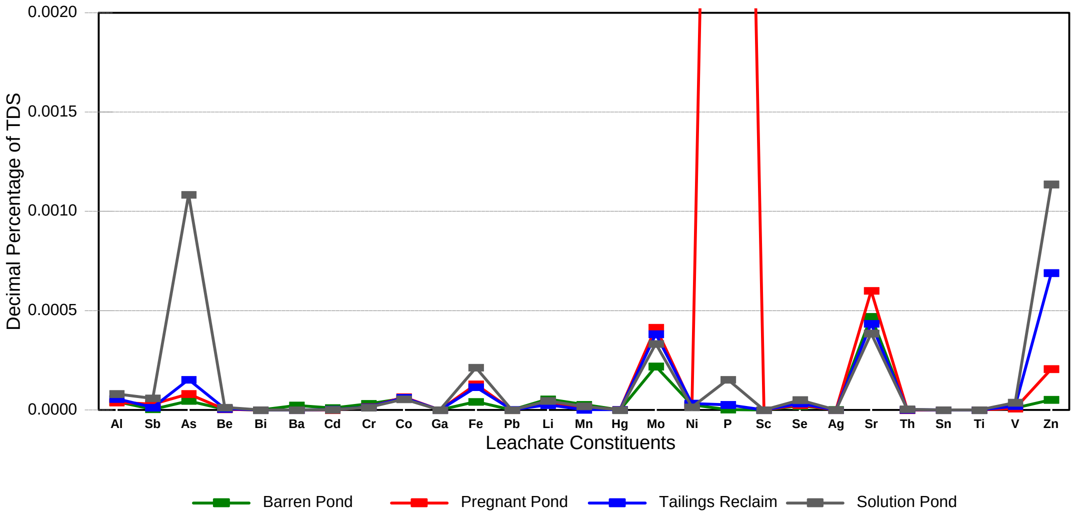


Cortez Process Solution Regression Analysis Matrix

Sampling Location	Barren Pond	Pregnant Pond	Tailings Reclaim Solution	Solution Pond
Barren Pond	1.000	0.983	0.972	0.960
Pregnant Pond		1.000	0.997	0.993
Tailings Reclaim			1.000	0.997
Solution Pond				1.000

Average r squared value = 0.984

Figure 5-38. Comparison of the geochemical fingerprint for mine waste leachates at the Cortez Gold Mine.



Trace metal regression analysis matrix for Cortez mine waste leachates

Sampling Location	Barren Pond	Pregnant Pond	Tailings Reclaim	Solution Pond
Barren Pond	1.000	0.000	0.397	0.094
Pregnant Pond		1.000	0.000	0.002
Tailings Reclaim			1.000	0.622
Solution Pond				1.000

Average r squared value = 0.186

Figure 5-39. Comparison of trace metal fingerprints for mine waste leachates at the Cortez Gold Mine.

Two years of quarterly monitoring data at Well 2 are compared to the Cortez process solution fingerprint in Figure 5-40. These data define a repeatable pattern for the ground water at this location. This pattern is characterized by 30 percent sodium, 20 percent sulfate, 20 percent alkalinity, and 15 percent chloride. The reproducibility of this fingerprint during eight sampling events is approximately 91 percent ($r^2 = 0.911$). In addition, the ground-water pattern can be distinguished from the Cortez process solution fingerprint because of the higher relative abundance of alkalinity and the lower relative abundance of sulfate. A regression analysis comparison of the two fingerprints produced a relatively low r^2 value of 0.501.

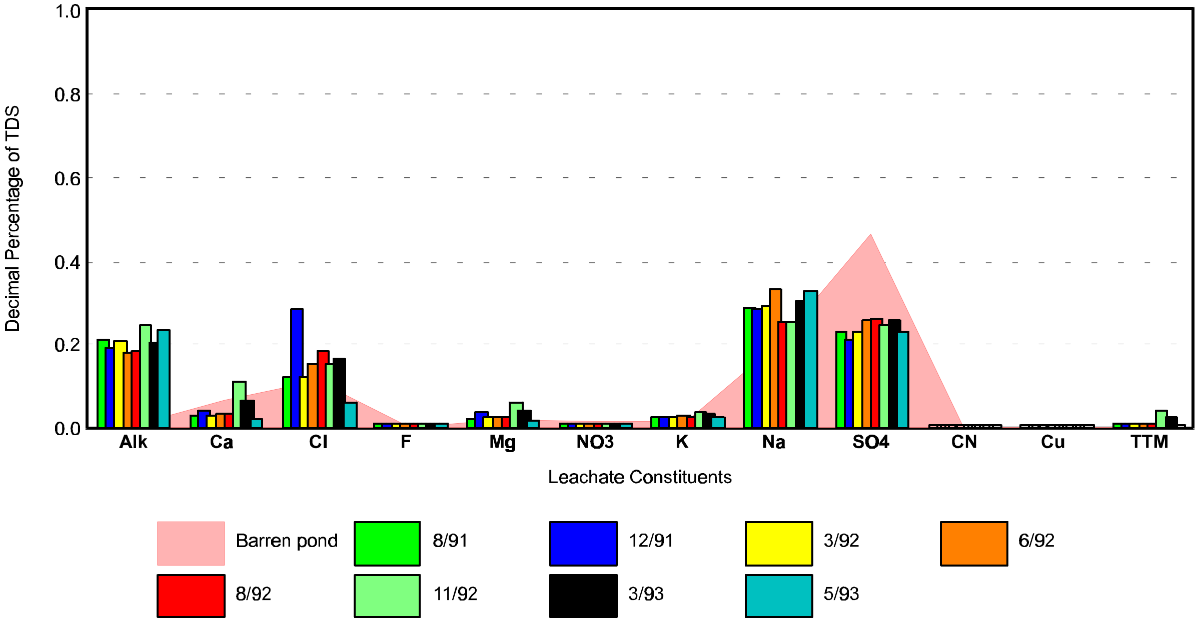
Ground-water monitoring results from eight wells are compared to the Cortez process solution fingerprint in Figure 5-41. In each of these examples, when compared to the process solution fingerprint, the ground-water pattern is enriched in alkalinity and depleted in sulfate. Although there was some fluctuation in the height of the alkalinity peak, the reproducibility of the ground-water pattern was 81 percent ($r^2 = 0.815$). This typical ground-water pattern was easily differentiated from the mine process solution ($r^2 = 0.211$).

Results from eight quarterly surveys at Well 1 between August, 1991 and May, 1993 have been summarized in Figure 5-42. This pattern represents a compositional shift from the ground-water pattern identified in Figure 5-41. The changes that have occurred at Well 1 include a lower relative abundance of alkalinity (from more than 20 percent to less than 5 percent), a lower relative abundance of calcium (from 15 percent to 10 percent), and a higher relative abundance of sulfate (from 20 percent to 40 percent). Each of these changes, along with a substantial increase in total dissolved solids concentration, were simultaneously detected at Well 1.

There are three important observations concerning the ground-water composition shifts that occurred at Well 1. First, the apparent shift is not due to suspect quality data. This position is supported by the fact that the geochemical ions consistently represent 90 to 110 percent of the total dissolved solids concentration (i.e., an acceptable mass balance). Second, the geochemical pattern is identical for each of the eight quarterly surveys. The average regression coefficient r^2 value for the Well 1 monitoring data is 0.994. Third, each of the simultaneous changes that occurred at Well 1 have produced a ground-water fingerprint that is very similar to the Cortez process solution fingerprint. A regression analysis comparison of the two fingerprint patterns suggests that there is an 83 percent match between the Well 1 data and the mine process solution.

Since the assessment of the geochemical monitoring data from Well 1 indicated that process solution from the mine was impacting ground water, the trace metal data were examined in greater detail. The quarterly monitoring results from Well 1 are compared to the pregnant pond trace metal distribution in Figure 5-43, top panel. Most of the trace metal peaks that are prominent in the pregnant pond solution, including phosphorus, molybdenum, strontium, zinc, cobalt, and aluminum, are greatly diminished in the ground water at Well 1. In fact, the only process solution trace metal that appears to show up in ground water at the same relative abundance is iron. These monitoring results indicate that the trace metal components of the mine process solution do not migrate as rapidly as the geochemical constituents of the process solution.

The same quarterly monitoring results for trace metals at Well 1 are also compared to the typical trace metal distribution for ground water that has not been impacted by process solution (Figure 5-43, bottom panel). Well 59 was chosen for this comparison because it has a low total dissolved solids concentration that is typical of background ground-water conditions (300 mg/L) and it has a geochemical fingerprint that is representative of background ground water (Figure 5-41). Both of

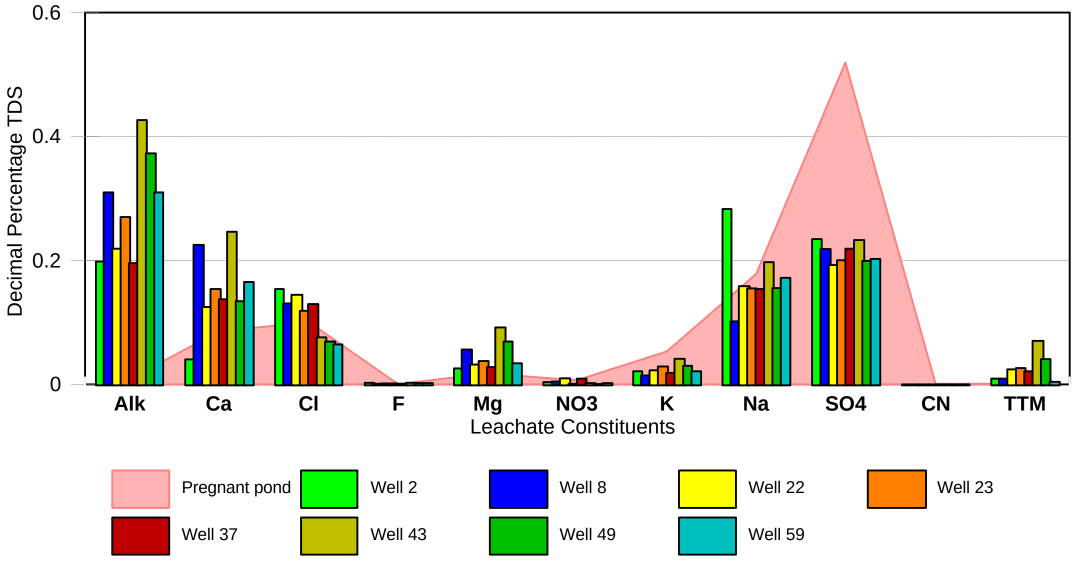


Regression analysis matrix for Cortez monitoring Well 2

	8/91	**12/91**	**3/92**	**6/92**	**8/92**	**11/92**	**3/93**	**5/93**
8/91	1.000	0.819	1.000	0.978	0.948	0.924	0.980	0.963
12/91		1.000	0.819	0.852	0.912	0.800	0.872	0.666
3/92			1.000	0.982	0.944	0.919	0.980	0.966
6/92				1.000	0.960	0.882	0.984	0.922
8/92					1.000	0.908	0.975	0.835
11/92						1.000	0.948	0.857
3/93							1.000	0.908
5/93								1.000

Average inter-survey comparison for Well 2 = 0.911
Average comparison between Well 2 and barren pond = 0.501

Figure 5-40. Comparison of the ground-water fingerprint at Well 2 with the Cortez process solution fingerprint.



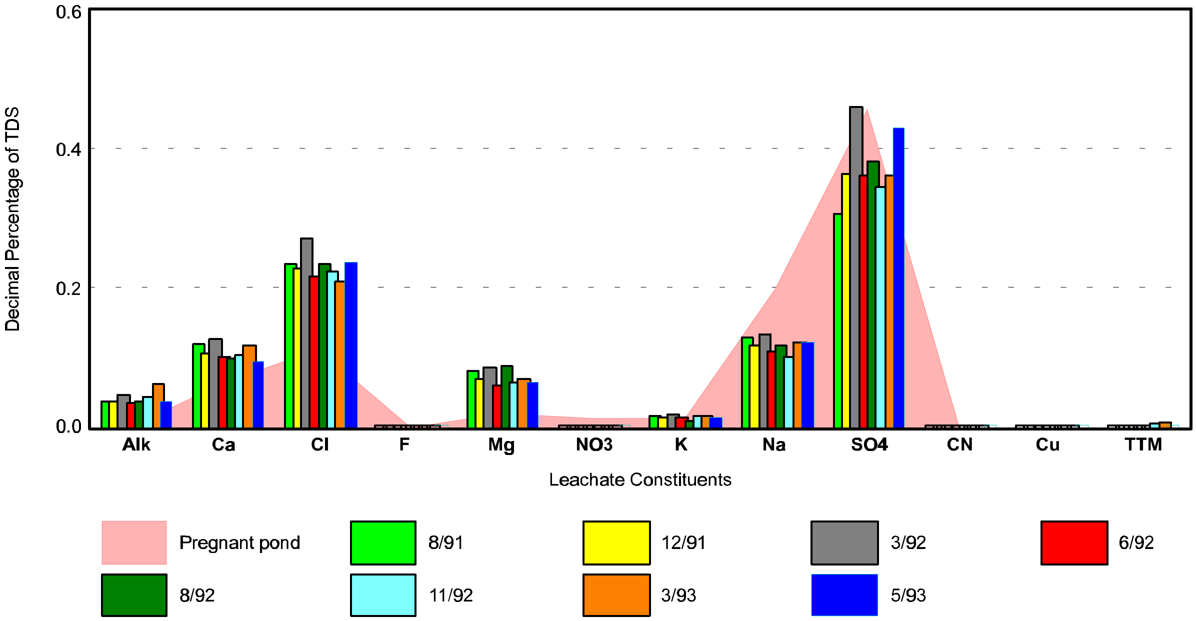
Regression analysis matrix for uncontaminated Cortez ground water

	Sampling Location							
	Well 2	**Well 8**	**Well 22**	**Well 23**	**Well 37**	**Well 43**	**Well 49**	**Well 59**
Pregnant Pond	0.434	0.190	0.072	0.085	0.464	0.113	0.122	0.202
Well 2	1.000	0.436	0.794	0.678	0.777	0.460	0.534	0.612
Well 8		1.000	0.847	0.927	0.838	0.889	0.842	0.894
Well 22			1.000	0.962	0.976	0.777	0.793	0.871
Well 23				1.000	0.936	0.909	0.905	0.961
Well 37					1.000	0.742	0.736	0.860
Well 43						1.000	0.959	0.955
Well 49							1.000	0.947
Well 59								1.000

Average r squared value = 0.815

Average ground water - pregnant pond comparison = 0.211

Figure 5-41. Comparison of Cortez process solution fingerprint with the ground-water fingerprint at 8 uncontaminated wells.



Regression analysis matrix for Cortez monitoring Well 1

	Sampling Date							
	8/91	**12/91**	**3/92**	**6/92**	**8/92**	**11/92**	**3/93**	**5/93**
8/91	1.000	0.979	0.968	0.969	0.974	0.978	0.968	0.948
12/91		1.000	0.998	0.999	0.997	0.998	0.992	0.992
3/92			1.000	0.999	0.998	0.997	0.992	0.996
6/92				1.000	0.996	0.997	0.992	0.996
8/92					1.000	0.995	0.988	0.992
11/92						1.000	0.991	0.989
3/93							1.000	0.985
5/93								1.000

Average inter-survey comparison for Well 1 = 0.994
Average comparison between Well 1 and pregnant pond = 0.833

Figure 5-42. Comparison of the ground-water fingerprint at Well 1 with the Cortez process solution fingerprint.

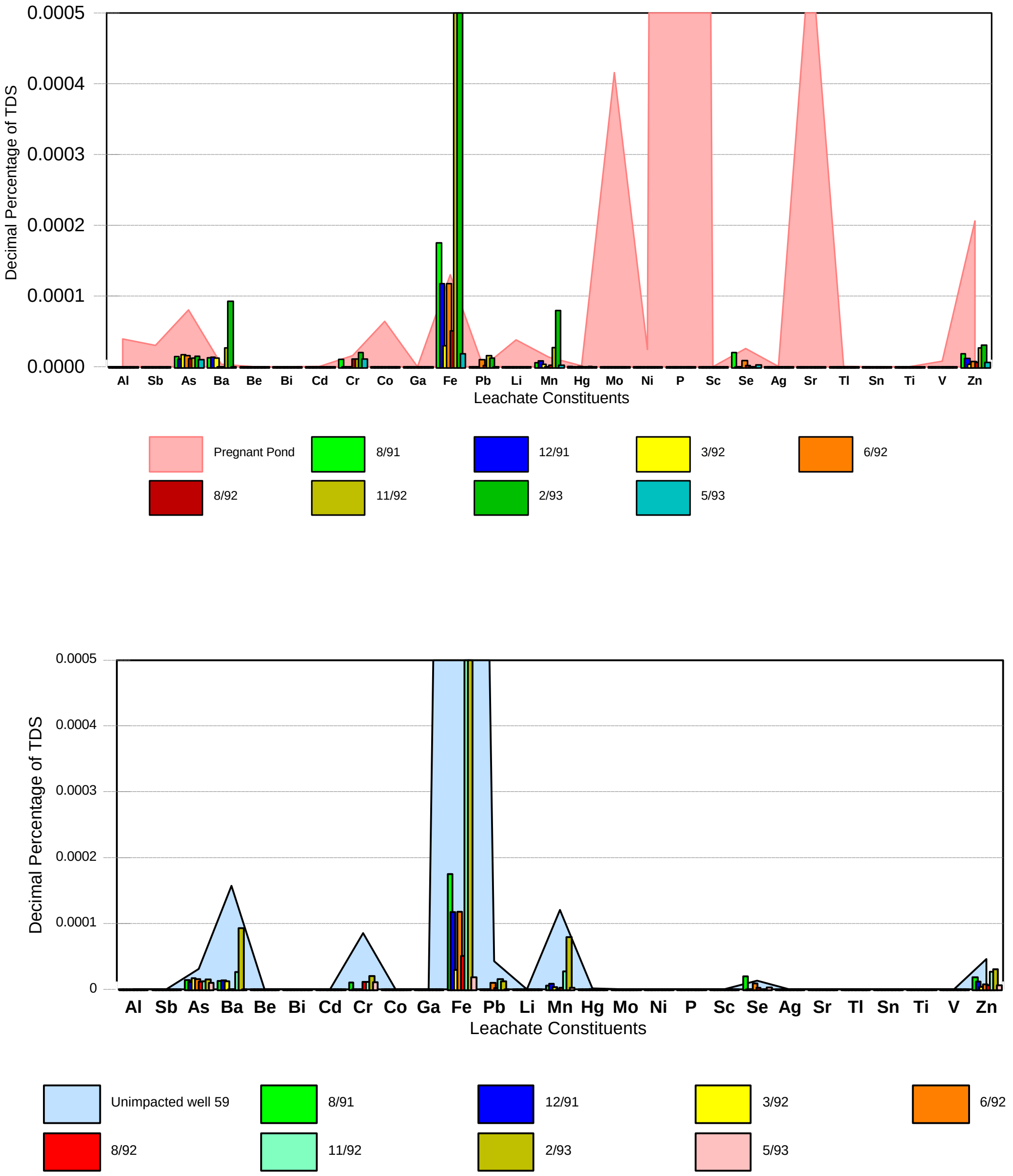


Figure 5-43. Comparison of the trace metal distribution patterns at monitoring Well 1, the Cortez pregnant pond, and background ground water.

these patterns have a relatively high iron peak and all of the smaller peaks for arsenic, barium, chromium, manganese, tin, and zinc. The similarity of these two patterns suggests that the trace metal pattern at Well 1 is essentially identical to an unimpacted background well.

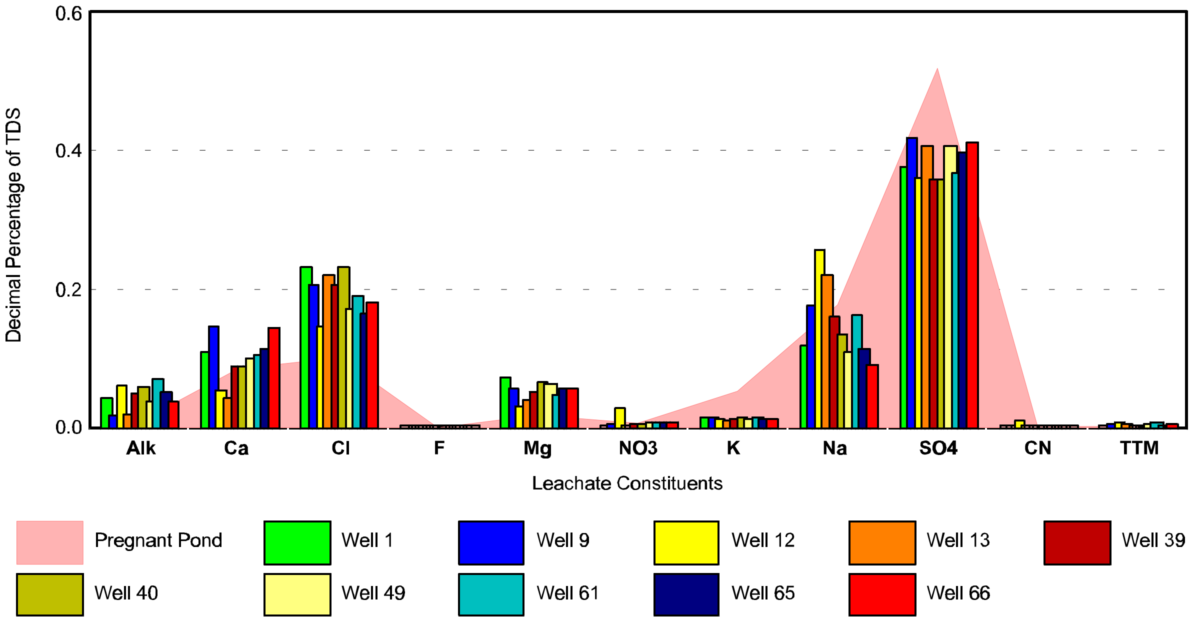
The monitoring results from Well 1 at the Cortez Mine have a direct bearing on the selection of monitoring parameters for mining sites. First, the geochemical pattern that characterized the mine process solution at the source was also detected at Well 1. This condition suggests that the same set of geochemical parameters can be used to characterize, detect, and track the migration of mine process solution. Second, even though the ground water at Well 1 has been impacted by the mining operation for at least eight consecutive quarters, the trace metal pattern at this location still resembles background conditions. Since the trace metal distribution has not been altered more than two years after the well was impacted by process solution from the mine, this suggests that trace metals would not be effective monitoring parameters to detect the initial migration of mine waste leachates and process solutions because the greater attenuation of the trace metals does not allow for early detection.

Monitoring Well 1 was not the only location at which the ground water has been affected by the mining operations. As shown in Figure 5-44, an assessment of the Cortez monitoring data has identified at least 10 wells that are impacted. The ground water conditions at each of these wells has a substantially higher total dissolved solids concentration, a reduced relative abundance of alkalinity, and an elevated relative abundance of sulfate. The geochemical pattern at each of these locations is very similar to the Cortez process solution fingerprint ($r^2 = 0.890$).

The sampling coordinates for each of the impacted wells also define a consistent pattern with respect to operations at the facility. Well 13 is located in the center of the original tailings disposal area. Well 9 and Well 12 are located between the heap leaching pad and the tailings ponds. Wells 39, 40, and 61 are located along the northern perimeter of an active tailings pond. Well 44 is located some distance northeast of the active tailings pond (the site map did not contain a scale reference). Finally, Well 49 is located at an even greater distance northeast of the active tailings pond. Thus, the characteristic fingerprint pattern clearly identifies the process solution at its source and tracks its migration beyond the northern perimeter of the tailings basin and in a northeasterly direction away from the site.

Trace metal monitoring results from Well 9, which is located between the tailings disposal area and the heap leaching pad, are compared to the trace metal pattern for process solution and background ground water in Figure 5-45. The trace metal pattern at Well 9 (Figure 5-45, top panel) does not contain any of the major peaks associated with the mine process solution. In addition, smaller peaks due to aluminum, arsenic, cobalt, and possibly zinc are not readily apparent at Well 9. There are some high results for barium and chromium that are not related to the mine process solution pattern and may possibly represent a data quality problem. However, the trace metal pattern at Well 9 is clearly different from the Cortez process solution trace metal pattern.

The trace metal pattern at Well 9 is contrasted with the trace metal pattern from unimpacted wells in the vicinity of the mine in Figure 5-45, bottom panel. The relatively high iron peak matches well with the background pattern. Also, the smaller Well 9 peaks due to arsenic, barium, chromium, manganese, tin, and zinc are in complete agreement with the background pattern. Again, as at Well 1, even though Well 9 has been impacted by the mining operation (a significant TDS increase, a ground-water composition shift, and the presence of the characteristic process solution fingerprint),



Regression analysis matrix for contaminated ground water and Cortez pregnant pond

	Sampling Location									
	Well 1	**Well 9**	**Well 12**	**Well 13**	**Well 39**	**Well 40**	**Well 49**	**Well 61**	**Well 65**	**Well 66**
Pregnant Pond	0.817	0.892	0.855	0.864	0.858	0.807	0.916	0.878	0.916	0.876
Well 1	1.000	0.961	0.780	0.910	0.977	0.992	0.968	0.964	0.964	0.961
Well 9		1.000	0.859	0.930	0.973	0.950	0.964	0.973	0.969	0.957
Well 12			1.000	0.941	0.888	0.822	0.809	0.896	0.916	0.738
Well 13				1.000	0.969	0.937	0.901	0.949	0.893	0.840
Well 39					1.000	0.989	0.956	0.992	0.957	0.928
Well 40						1.000	0.952	0.975	0.949	0.930
Well 49							1.000	0.961	0.997	0.985
Well 61								1.000	0.969	0.937
Well 65									1.000	0.988
Well 66										1.000

Average r squared value = 0.931
Average ground water - pregnant pond comparison = 0.890

Figure 5-44. Comparison of Cortez process solution fingerprint with ground water monitoring results from 10 impacted wells.

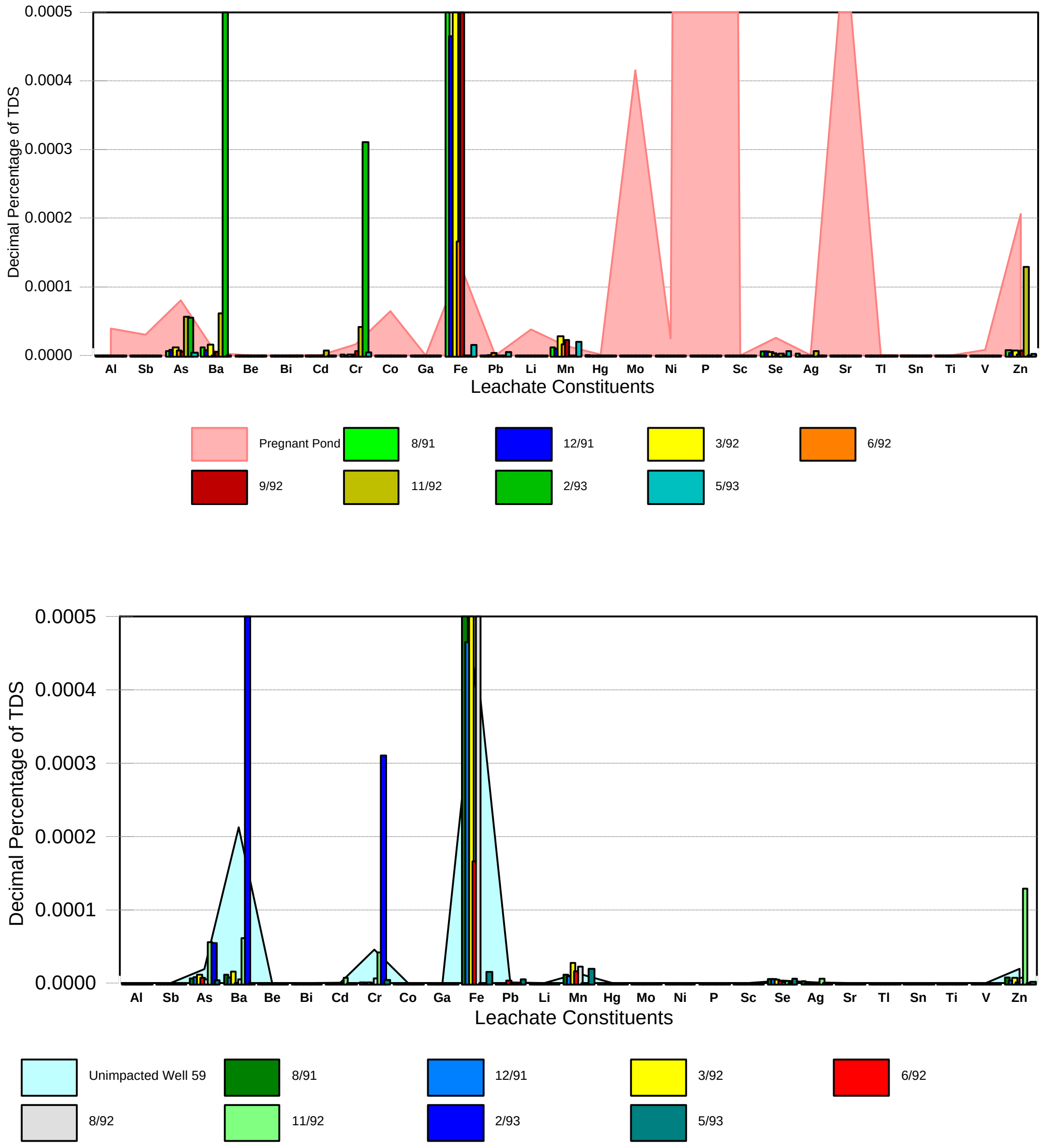


Figure 5-45. Comparison of Well 9 trace metal results to process solution (top) and background ground water (bottom).

the trace metals associated with the process solution have not been detected at Well 9. In fact, except for a single barium result and a single chromium result, the trace metal results from this well define a pattern that is identical to the background ground-water pattern. Once again, the mine process solution has apparently migrated from its source, the process solution has maintained its characteristic chemical signature as it migrated, but the ambient trace metal pattern has not been altered. This is another indication that the trace metals do not migrate as fast as the geochemical parameters and that they would not provide for early detection of mine waste leachate migration.

The trace metal monitoring results from Well 65 are presented in Figure 5-46. As shown in the top panel, the trace metal pattern does not resemble the trace metal distribution in the mine process solution. The observed trace metal distribution at Well 65 overestimates the iron peak and misses the reminder of the trace metal peaks in the process solution. By comparison, the trace metal pattern at Well 65 has the relatively high iron peak and all of the minor trace metal peaks reported at the unimpacted wells. Again, these results indicate that fugitive process solution from the mine has not altered the trace metal distribution pattern at Well 65. Therefore, since this location has been impacted for at least two years, the trace metals would not be suitable parameters for early detection of mine waste leachate and process solution migration.

Cortez Gold Mine Summary

The monitoring information obtained for this facility included a total of 16 quarterly surveys from four locations in the process solution and tailings disposal area. As previously observed with monitoring results from other mining operations, the geochemical results from each of these surveys defined a chemical signature that was consistent within the recirculating leaching system and over time. The process solution signature at this mine was defined by 50 percent sulfate, 20 percent sodium, 10 percent calcium, and 10 percent chloride. The reproducibility of this fingerprint pattern was estimated by regression analysis to be 98 percent.

An assessment of the ground-water monitoring results from 18 wells in the vicinity of the Cortez facility identified two discrete chemical signatures or fingerprints. One ground water pattern occurred at wells with low total dissolved solids concentrations (approximately 400 mg/L) and was characterized by a relatively high alkalinity content (20 to 40 percent) and a relatively low sulfate content (20 percent). This alkalinity-rich, sulfate-poor pattern, which is generally typical of most natural water systems, was distinctly different from the Cortez process solution fingerprint (r^2 = 0.211). The second ground water pattern was observed at 10 wells with an elevated total dissolved solids concentration (approximately 4,000 mg/L). The characteristic features of the second ground-water fingerprint were the reduced alkalinity content (5 percent) and the higher sulfate content (40 percent). This fingerprint was very similar to the Cortez process solution fingerprint (r^2 = 0.833).

The identification of a sulfate-rich, alkalinity-poor fingerprint in the ground water near the mining operation indicates that fugitive process solution is impacting the local ground water. However, the most pertinent observation is the fact that the process solution maintains its characteristic fingerprint pattern as it migrates away from the source. As a result, the same set of geochemical parameters that have been shown to be useful for characterizing process solutions at heap leaching facilities can also be used for detecting and tracking the migration of process solution through the environment.

A review of the Cortez monitoring data also provided insight into the occurrence and behavior of trace metals associated with mine process solutions. Although the process solution at this facility had

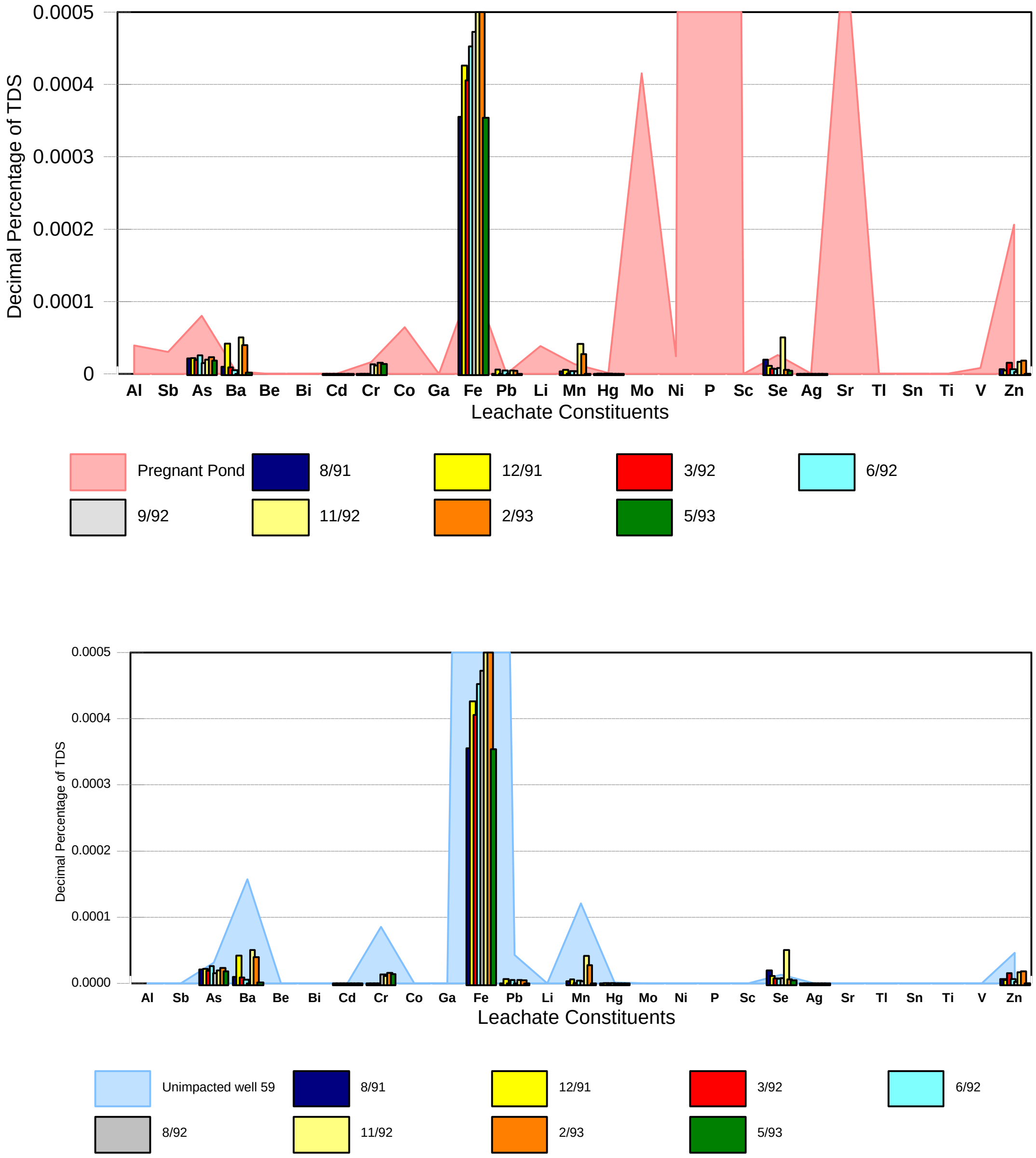


Figure 5-46. Comparison of Well 65 trace metal results to process solution (top) and background ground water (bottom).

a reproducible geochemical composition, the trace metal pattern in the same solutions was highly variable. Thus, while the reproduciblity of the geochemical fingerprint was estimated to be 0.986, the reproducibility of the trace metal pattern was only 0.186. The implication of this result is that the trace metal pattern does not provide a means to uniquely characterize or identify process solutions at heap leaching facilities.

One of the properties of process solution trace metals that was demonstrated through a review of the ground-water monitoring data was the slower rate of migration of these constituents. Ground water at several monitoring locations had substantially higher total dissolved solids concentrations, a change in the geochemical composition, and a resultant geochemical fingerprint that matched the Cortez process solution fingerprint. However, even though these distinctive changes were recognizable over eight consecutive quarters at ten wells, the occurrence and distribution of trace metals was still identical to that observed at adjacent, unimpacted wells. This situation means that the trace metals in process solution do not migrate as rapidly as the geochemical constituents. Because of their slower movement, monitoring for trace metals would not result in the early detection of process solution migrating through the ground water.

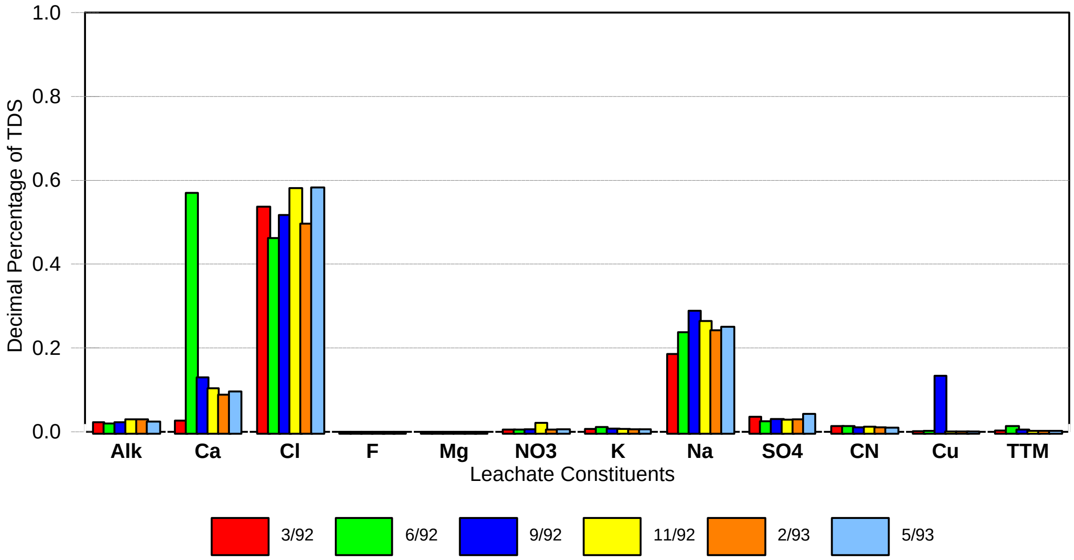
5.2.9 Florida Canyon Mine

This mine is located in Pershing County, Nevada. The facility processed 12,000,000 tons of ore and waste rock in 1991 to produce 80,000 ounces of gold and 20,000 ounces of silver using heap leaching technology. The data set for the Florida Canyon mine includes six quarterly surveys of the barren and pregnant pond and six sets of quarterly monitoring data from each of two monitoring wells.

Six sets of quarterly monitoring data for the Florida Canyon pregnant pond are presented graphically in Figure 5-47. With the exception of a single calcium value in June, 1992, these results suggest that the pregnant pond has a constant composition over time. The chemical signature for this solution is defined by 50 percent chloride, 20 percent sodium, and 10 percent calcium. A regression analysis of the six survey patterns produced an average r^2 value of 0.748.

There are several indications that the calcium value for the June, 1992 survey is suspect. First, the reported concentration of 3600 mg/L is outside the range of 140 mg/L to 810 mg/L reported for the remaining five samples. This difference is excessive even for the variable concentrations that have been observed in mine waste leachates. Second, the reported calcium concentration represents almost 60 percent of the total dissolved solids concentration and the sum of the individual geochemical constituents in June, 1992 represents 135 percent of the total dissolved solids concentration (Table 5-5). This value is high compared to the other five surveys that are in the generally acceptable range. Third, a charge balance of the June, 1992 results suggests that they are off by +94 percent (an excess of cations). The March, 1992 survey is off by -54 percent, which is probably due to the low mass balance, and the remaining four surveys have a mass balance within 20 percent. The high mass balance and the high charge balance for the June, 1992 results indicates that one or more of the analyses are in error and the most likely suspect is the very high calcium value.

The results of the June, 1992 survey were dropped from the data set because of identified data quality concerns. A regression analysis performed on the remaining five surveys produced an average r^2 value of 0.961. This example illustrates two characteristics of the leachate fingerprinting concept. First, it demonstrates again that it is possible to define a reproducible geochemical fingerprint pattern for mine waste leachates. Second, since the individual geochemical ions represent essentially all of the total dissolved solids concentration of a leachate, it is possible to use mass



Regression Analysis Matrix for Florida Canyon Pregnant Pond

	3/92	**6/92**	**9/92**	**11/92**	**2/93**	**5/93**
3/92	1.000	0.388	0.889	0.975	0.969	0.982
6/92		1.000	0.573	0.514	0.511	0.503
9/92			1.000	0.934	0.938	0.931
11/92				1.000	0.998	0.998
2/93					1.000	0.996
5/93						1.000

Average r squared value = 0.748

Figure 5-47. Pregnant pond fingerprint at the Florida Canyon Mine.

Table 5-5. Data quality assessment of the Florida Canyon pregnant pond geochemical monitoring results.

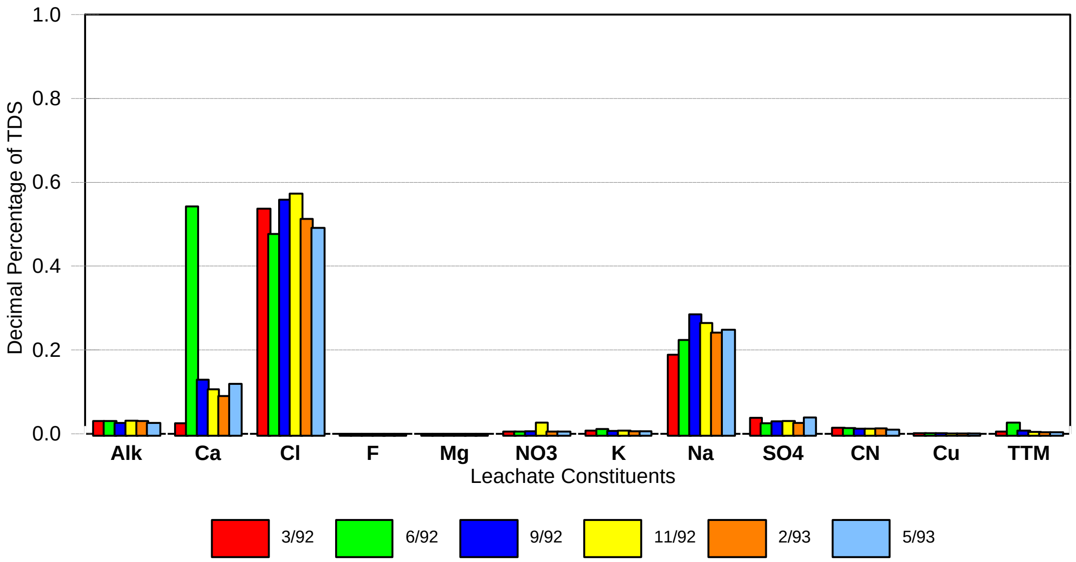
Survey Date	Mass Balance	Charge Balance
3/92	83.3%	-54%
6/92	134.5%	94%
9/92	114.6%	19%
11/92	104.7%	-7%
2/93	90.8%	-2%
5/93	101.9%	-12%

balance and charge balance calculations to evaluate the quality of the monitoring data being produced. In this case, the suspect data could be identified but not corrected. However, if this technique were actively applied as the data were being generated, the error could be identified and corrected in a timely manner and acceptable data could be produced in the monitoring program.

The monitoring results from the Florida Canyon barren pond are presented in Figure 5-48. The fingerprint pattern at this location in the recirculating heap leaching process consists of 50 percent chloride, 20 percent sodium, and 10 percent calcium. This data set also contains an apparently erroneous value for calcium in the June, 1992 survey (high calcium concentration, high mass balance, high charge balance). If this survey is omitted because of data quality concerns, a regression analysis of the remaining five barren pond surveys produces an average regression analysis r^2 value of 0.982. A regression analysis of the pregnant pond pattern with the barren pond pattern produced an r^2 value of 0.996.

Monitoring results from Florida Canyon Well 4 are presented in Figure 5-49. There is a reproducible geochemical pattern at this location that is graphically and statistically distinct from the Florida Canyon process solution fingerprint. The ground-water composition pattern consists of 30 percent alkalinity and 15 percent calcium, chloride, sodium, and sulfate. A regression analysis of the ground-water patterns produced an r^2 value of 0.934. A regression analysis of the ground-water fingerprint with the process solution fingerprint produced an r^2 value of only 0.141. Based on this assessment, the ground water at Well 4 has not been impacted by process solution from the mine.

Monitoring data from a second well on the Florida Canyon property are summarized in Figure 5-50. These data also suggest a consistent geochemical pattern (average r^2 value = 0.992) at this location. However, the geochemical fingerprint at Well 7 has been shifted from that observed at Well 4. The fingerprint at Well 7, which is located closer to the heap leach pad than Well 4, has a reduced abundance of alkalinity (20 percent vs 30 percent), an increased abundance of chloride (35 percent vs 15 percent), and an increased abundance of sodium (35 percent vs 15 percent). Each of these changes are consistent with those that could be caused by the Florida Canyon process solution. In fact, a regression analysis indicates that the Well 7 fingerprint more closely resembles the process solution fingerprint than Well 4 (r^2 = 0.661). These results suggest that fugitive process solution from the heap leaching facility may be impacting the ground water in the vicinity of Well 7. Unfortunately, there are no additional monitoring locations that can be used to investigate or confirm the cause of the shift in ground-water composition that has been observed at Well 7.

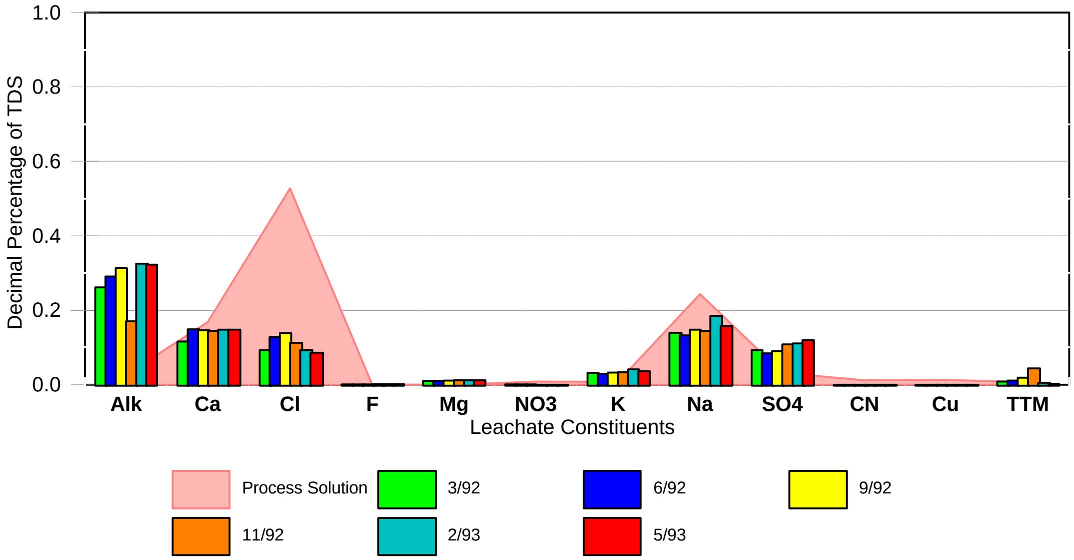


Regression Analysis Matrix for Florida Canyon Barren Pond

	3/92	6/92	9/92	11/92	2/93	5/93
3/92	1.000	0.422	0.949	0.972	0.973	0.948
6/92		1.000	0.595	0.553	0.546	0.603
9/92			1.000	0.995	0.996	0.999
11/92				1.000	0.998	0.994
2/93					1.000	0.995
5/93						1.000

Average r squared value = 0.836

Figure 5-48. Florida Canyon barren pond fingerprint pattern.

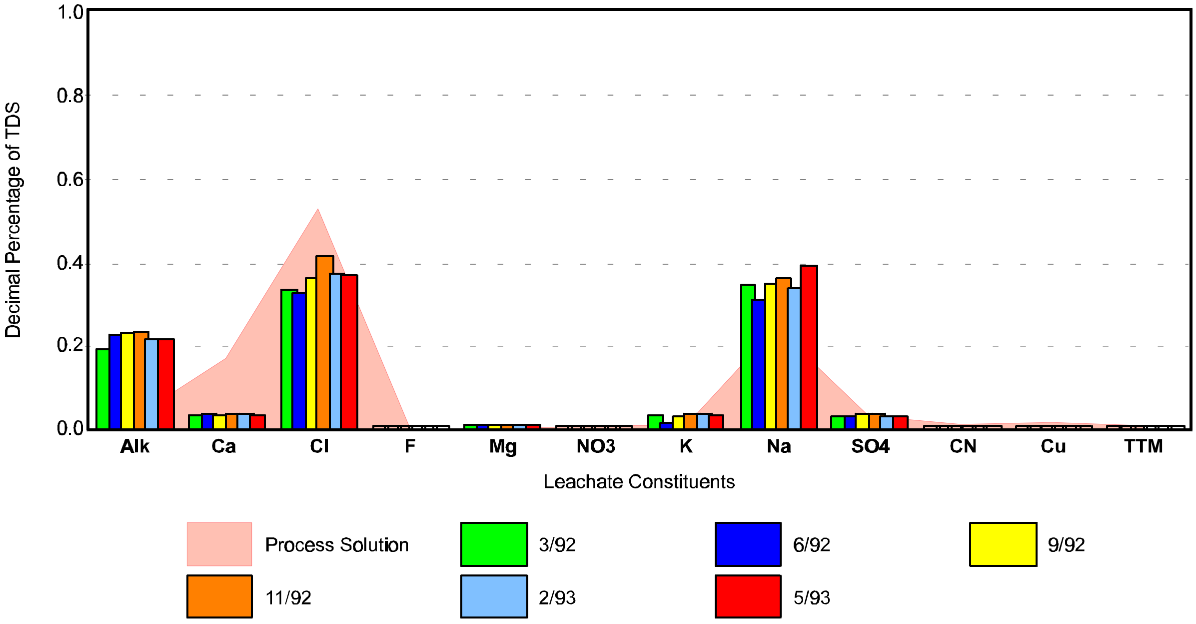


Regression Analysis Matrix for Florida Canyon Monitoring Well 4

	3/92	6/92	9/92	11/92	2/93	5/93
Process Solution	0.110	0.158	0.158	0.269	0.083	0.065
3/92	1.000	0.977	0.984	0.859	0.994	0.991
6/92		1.000	0.977	0.859	0.959	0.962
9/92			1.000	0.854	0.963	0.962
11/92				1.000	0.845	0.829
2/93					1.000	0.993
5/93						1.000

Average r squared value = 0.934

Figure 5-49. Comparison of the ground-water fingerprint at Well 4 to the Florida Canyon process solution fingerprint.



Regression Analysis Matrix for Florida Canyon Monitoring Well 7

	3/92	6/92	9/92	11/92	2/93	5/93
Process Solution	0.662	0.632	0.643	0.700	0.686	0.645
3/92	1.000	0.985	0.994	0.990	0.994	1.000
6/92		1.000	0.997	0.990	0.992	0.984
9/92			1.000	0.995	0.997	0.993
11/92				1.000	0.999	0.985
2/93					1.000	0.991
5/93						1.000

Average r squared value = 0.992

Figure 5-50. Comparison of the ground-water fingerprint at Well 7 to the Florida Canyon process solution fingerprint.

Florida Canyon Summary

An evaluation of the monitoring results from the Florida Canyon Mine demonstrated that the process solution has a constant relative composition or fingerprint. The geochemical signature for this facility, which was repeatedly observed at both the barren pond location and the pregnant pond location, consisted of 50 percent chloride, 20 percent sodium, and 10 percent calcium. The reproducibility of this pattern was estimated by regression analysis to be between 96 and 99 percent.

The process solution fingerprint for the Florida Canyon Mine is quite different from that observed at other mines. While most other process solutions have a dominant sulfate spike, the major process solution constituent at this facility is chloride. However, although the actual fingerprint may change from mine to mine, the important point to be recognized is that the same small set of geochemical parameters produced a distinctive fingerprint that is a characteristic property of the process solution at each mine. Therefore, the geochemical parameters (alkalinity, calcium, chloride, fluoride, magnesium, potassium, sodium, and sulfate) that define these fingerprint patterns should collectively function as useful monitoring parameters to characterize mine process solutions at the source and track their movement through the environment if a leak or spill should occur.

A second feature of the fingerprinting concept demonstrated with the Florida Canyon data is that the same set of geochemical parameters used to characterize process solution at the heap leaching facilities can also be used to characterize ground water in the vicinity of the mine. The resulting pattern can then be compared both graphically and statistically with the process solution fingerprint. At the Florida Canyon Mine, the alkalinity-dominant pattern was visually and statistically ($r^2 = 0.140$) distinct from the chloride dominant pattern of the process solution. However, at Well 7, the ground-water pattern had shifted to one that more closely resembles the process solution fingerprint ($r^2 = 0.661$). Although this specific example can not be pursued because of limited sampling, the simultaneous changes in total dissolved solids, increased relative abundance in chloride and sodium, a reduction in the relative abundance of alkalinity, and a shift in the ground-water composition to more closely resemble the process solution pattern strongly indicates that the ground water is being impacted by the mining operation.

A third feature of the fingerprinting concept that was demonstrated with the Florida Canyon data is the internal quality control checks that can be used to validate the monitoring data. One of these checks, based on the principle of conservation of mass, states that the sum of the ions in a solution must be equal to the total dissolved concentration. When this check was applied to the June, 1992 survey, the sum of the individual ions represented 135 percent of the total dissolved solids concentration. This condition suggests that one or more of the geochemical analyses were biased high and/or the total dissolved solids concentration was biased low. The second quality control check, based on the principle of conservation of charge, states that the sum of the cations must equal the sum of the anions. The application of this check to the June, 1992 data produced an unacceptably high cation balance of +94 percent. Since both of these unacceptable data quality conditions can be explained by the high calcium results reported in June, 1992, the data from this survey can reasonably be considered suspect. After excluding the June, 1992 survey data, the similarity of the Florida Canyon process solution fingerprint improved from 75 percent to 98 percent. Thus, basic quality assessment procedures can be routinely and rapidly applied to geochemical monitoring results to detect inaccurate data and improve characterization of the process solution fingerprints.

5.2.10 Alta Gold Mine

This facility is located in east-central Nevada. The data that were obtained for this mine from the Nevada Department of Environmental Protection consisted of several quarters of pregnant pond and barren pond results and four quarters of plant make up water results.

The normalized geochemical monitoring results for the pregnant pond at this mine are presented in Figure 5-51. An inspection of the ionic fingerprint demonstrates that some of monitoring data are of suspect quality. Specifically, the very high sodium result for the September, 1991 survey (85 percent of TDS) and the high sulfate result for the same survey (50 percent of TDS) produce a mass balance that is unacceptably high. However, despite the obvious data quality problems, the pregnant pond still appears to have a reasonably consistent composition. This pattern is defined by approximately 40 percent sulfate, 20 percent sodium, 10 to 15 percent chloride, and 10 percent alkalinity.

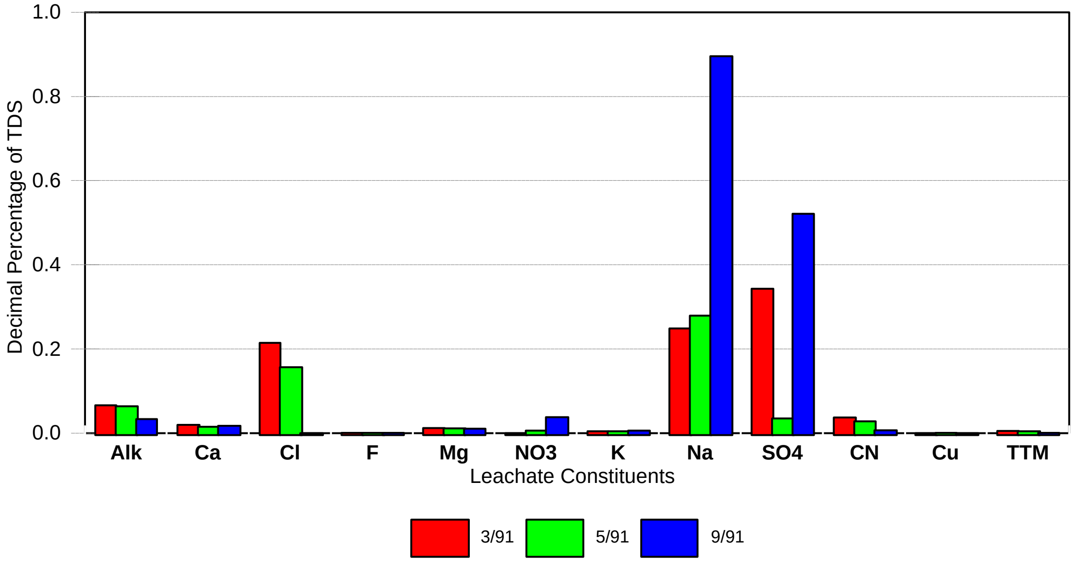
Three sets of quarterly monitoring data from the Alta barren pond are summarized in Figure 5-52. This data set also contains suspect quality data because the sum of the sodium and sulfate results represent more than 140 percent of the reported total dissolved solids concentration at that location. This condition indicates that the sodium and sulfate results are biased high or the total dissolved solids concentration is biased low. However, in spite of the data quality problems and the limited data, the results still suggest an ionic composition similar to that observed at the pregnant pond.

The monitoring results summarized in Figure 5-51 and Figure 5-52 suggest that the process solution at the Alta Gold Mine may have a distinctive geochemical fingerprint. However, the pattern is distorted or masked by poor quality data. Therefore, this mine was used as an example to demonstrate the internal data quality control checks that can be utilized in conjunction with the fingerprinting concept.

The quarterly monitoring results for the geochemical parameters in the Alta barren pond are presented in Table 5-6. The first data quality check is to perform a mass balance on the results. This is accomplished by adding 61 percent of the alkalinity concentration (a correction factor to compensate for the fact that alkalinity is reported in units of mg $CaCO_3$ /L) to the actual concentrations for the other geochemical parameters and comparing the sum to the total dissolved solids concentration of the barren pond. This ratio should fall in the range of 0.8 to 1.2 which is the range of acceptable data established for the project.

The mass balance for the March, 1991 survey was 95 percent which is in the range expected for good data. However, in comparison, the mass balance for the May, 1991 survey is only 60 percent which is in the unacceptable range. An inspection of the data indicates that the sulfate data is the cause for this discrepancy. The reported sulfate concentration of 103 mg/L is low compared to the other sulfate concentrations, the low sulfate concentration would account for the low mass balance, and the low sulfate concentration would account for the low anionic sum and the charge imbalance. The mass balance for the September, 1991 survey is more than 150 percent of the total dissolved solids concentration even though the chloride results, which represent approximately 18 percent of the total dissolved solids concentration, are missing or unreported. The value that stands out as erroneous is the sodium concentration that is almost equal to the total dissolved solids concentration. The high sodium result would account for the mass imbalance and the calculated charge imbalance.

The internal data consistency checks indicate that the sulfate data in the May survey and the sodium data in the September survey are suspect. If these data quality assessments were conducted as the

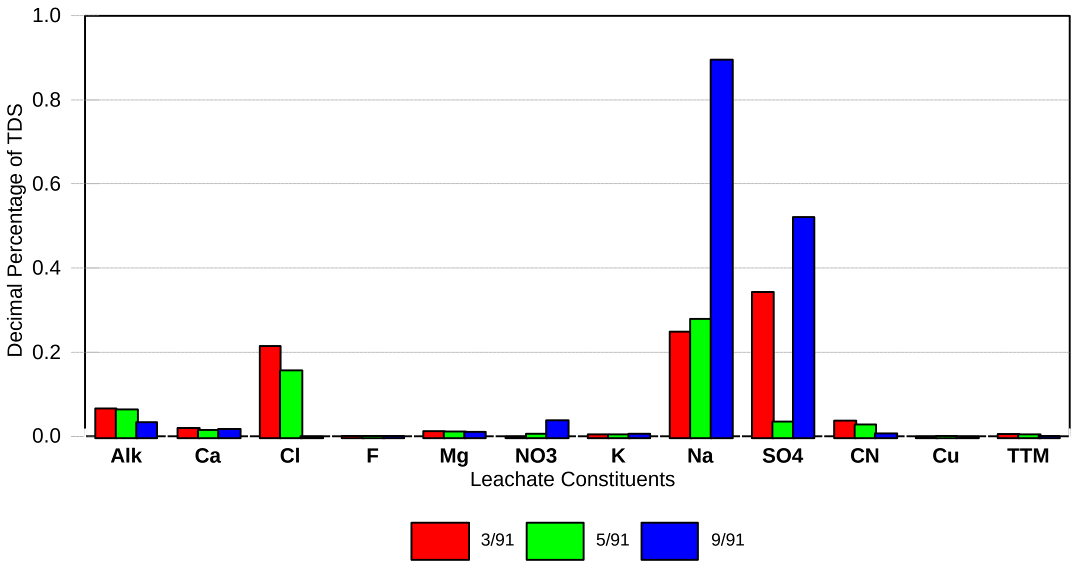


Regression analysis matrix for Alta Gold pregnant pond

	3/91	**5/91**	**9/91**	**12/91**
3/91	1.000	0.990	0.677	0.872
5/91		1.000	0.762	0.862
9/91			1.000	0.605
12/91				1.000

Average r squared value = 0.792

Figure 5-51. Pregnant pond fingerprint pattern at the Alta Gold Company Mine.



Regression analysis matrix for Alta Gold barren pond

	3/91	**5/91**	**9/91**	**12/91**
3/91	1.000	0.990	0.677	0.872
5/91		1.000	0.762	0.862
9/91			1.000	0.605
12/91				1.000

Average r squared value = 0.519
Pregnant pond - barren pond comparison = 0.922

Figure 5-52. Barren pond fingerprint pattern at the Alta Gold Company Mine.

Table 5-6. Quarterly monitoring results for the Alta Gold Company barren pond.

	Sampling Date		
	3/91	**5/91**	**9/91**
Alkalinity	298.0	308.0	446.0
Calcium	55.2	45.9	50.9
Chloride	595.0	464.0	
Fluoride	2.75	2.90	1.21
Magnesium	31.6	31.6	30.2
Nitrate	0.25	17.10	110.1
Potassium	11.4	12.6	16.8
Sodium	690.0	829.0	2578.0
Sulfate	951.0	103.0	1500.0
Cyanide	104.0	83.3	19.4
Copper	0.5	1.7	0.3
Total Trace Metals	0.0	0.0	0.0
TDS	2770	2970	2879
pH	9.59	9.40	9.80
All concentrations, except pH, expressed in units of mg/L.			
Mass Balance	0.947	0.599	1.530
Charge Balance	-12.93	14.26	71.19
anion sum	-46.68	-25.01	-42.75
cation sum	33.75	39.26	113.94
RSD	-0.322	0.444	0.909

sample results were being reported, it would be a relatively simple matter to repeat the analyses or review the initial results for dilution or transcription errors. For the purposes of this example, it is assumed that the sulfate data in May is a transcription error and the correct value should be 1030 mg/L and the correct sodium value in September should be 800 mg/L.

Modified barren pond results that include the adjusted values for sodium and sulfate are presented in Table 5-7. The mass balance check indicates that the new concentrations are reasonable since the mass balance for all three surveys is now in the good range (91 to 95 percent of the total dissolved solids concentration). Also, the charge imbalance has been corrected and is actually better in the modified data sets than it is in the March data set.

The modified data set was used to fingerprint the Alta barren pond. As can be seen in Figure 5-53, the geochemical pattern is more apparent than it was using the original suspect quality data (Figure 5-52). Also, the fingerprint is more consistent because the regression analysis r^2 value between quarterly surveys has increased from 0.512 to 0.839. It must be emphasized that the alternative concentration values used in this example were selected based on a consideration of the fundamental properties of mass balance and charge balance that must be satisfied in every solution. However, in doing so, the results also reaffirmed the characteristic nature of the process solution fingerprint.

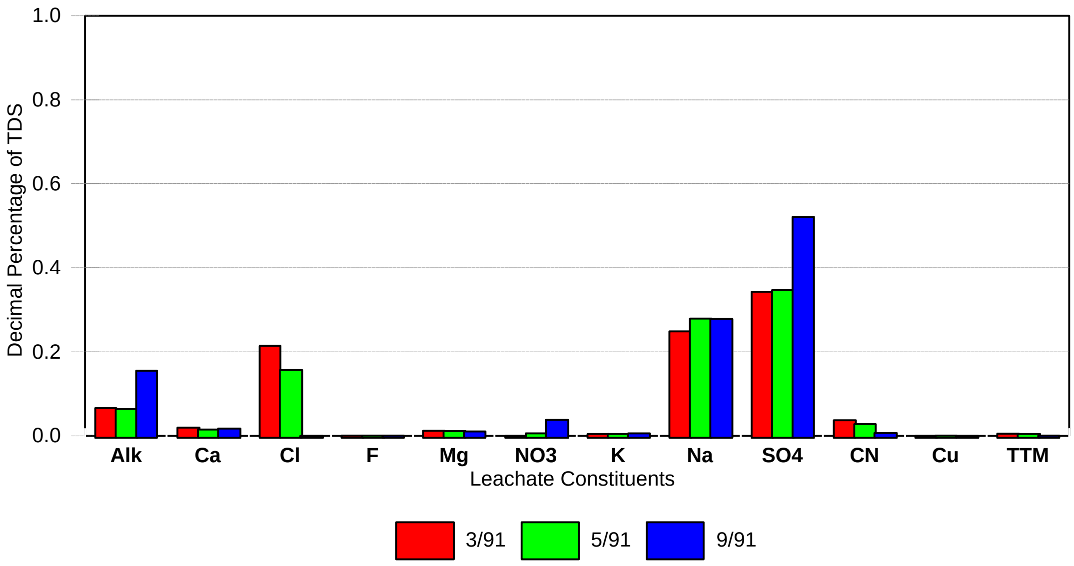
Table 5-7. Modified monitoring results for the Alta Gold Company barren pond.

	Sampling Date		
	3/91	**5/91**	**9/91**
Alkalinity	298.0	308.0	446.0
Calcium	55.2	45.9	50.9
Chloride	595.0	464.0	
Fluoride	2.75	2.90	1.21
Magnesium	31.6	31.6	30.2
Nitrate	0.25	17.10	110.1
Potassium	11.4	12.6	16.8
Sodium	690.0	829.0	800.0
Sulfate	951.0	1030.0	1500.0
Cyanide	104.0	83.3	19.4
Copper	0.5	1.7	0.3
Total Trace Metals	0.0	0.0	0.0
TDS	2770	2970	2879
pH	9.59	9.40	9.80
All concentrations, except pH, expressed in units of mg/L.			
Mass Balance	0.952	0.916	0.913
Charge Balance	-12.93	-5.06	-4.47
anion sum	-46.68	-44.32	-42.75
cation sum	33.75	39.26	38.29
RSD	-0.322	-0.121	-0.110

The monitoring records for the Alta Mine also included quarterly surveys of the facility water supply. The geochemical parameters defined a separate pattern for this source. As shown in Figure 5-54, the three prominent features of the water supply fingerprint are (1) an ionic composition characterized by a high alkalinity peak and a small sodium-sulfate doublet, (2) a pattern that is consistent and reproducible over time (r^2 = 0.984, and (3) a pattern that is visually and statistically (r^2 = 0.046) distinct from the process solution. These differences demonstrate that the process solution fingerprint is a result of the mining operation itself and is not an artifact of the water used at the mine.

Alta Gold Mine Summary

The initial records search only produced a limited amount of information for this mining operation. However, the results were still useful for demonstrating three properties of the process solution fingerprint. These properties were the constant relative composition of the mine process solution, the application of fundamental data quality assessment procedures for evaluating monitoring data, and the distinctive differences between the process solution fingerprint and the mine make up water fingerprint.

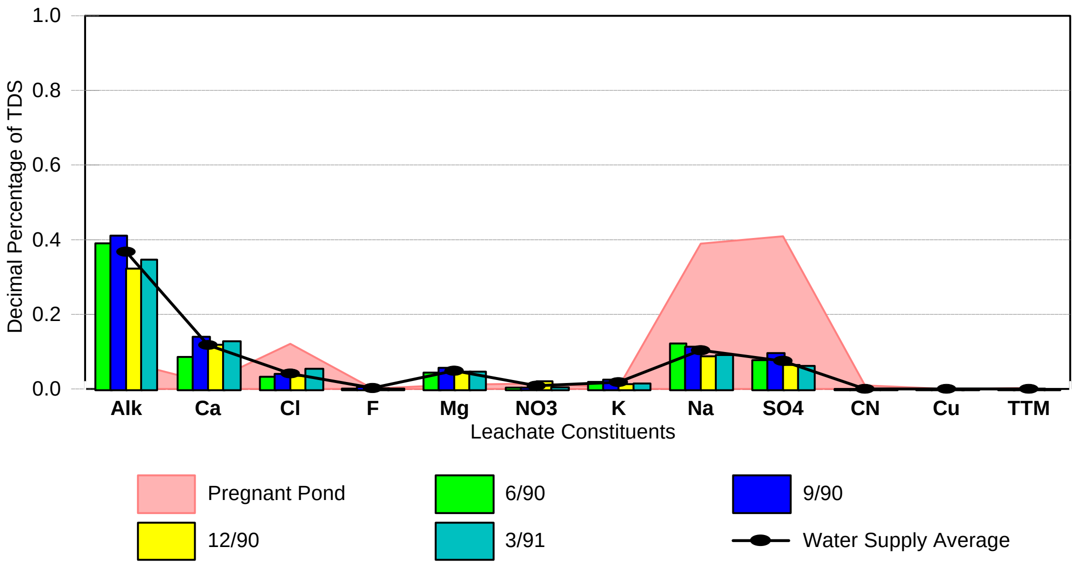


Regression analysis matrix for adjusted Alta Gold barren pond

	Sampling Date		
	3/91	**5/91**	**9/91**
3/91	1.000	0.972	0.721
5/91		1.000	0.823
9/91			1.000

Average r squared value = 0.839

Figure 5-53. Modified barren pond fingerprint at Alta Gold after adjusting results for suspect quality data.



Regression analysis matrix for Alta Gold water supply

Pregnant Pond	6/90	9/90	12/90	3/91
6/90	1.000	0.983	0.972	0.968
9/90		1.000	0.994	0.991
12/90			1.000	0.994
3/91				1.000

Average r squared value = 0.984
Water supply - pregnant pond comparison = 0.046

Figure 5-54. Comparison of the Alta Gold Company process solution fingerprint with the mine water supply fingerprint.

The first property to be demonstrated is that the pregnant pond and the barren pond had the same relative chemical composition which produced identical geochemical fingerprints. The similarity of the two fingerprint patterns was estimated by regression analysis to be 92 percent. The fact that monitoring data from two separate locations within the recirculating heap leaching process system produce a consistent and reproducible fingerprint is in agreement with similar observations at other mining sites.

The second property to be demonstrated was the ability to rapidly evaluate monitoring data quality. Based on the fundamental principles of mass conservation and charge conservation, it was possible to identify specific analytical results that were in error. If this approach were applied in an active data collection program, it would be a relatively simple matter to reanalyze the flagged results or check the analytical data package for transcription errors without conducting extensive resampling programs or statistical analysis of the monitoring data. An added benefit is that the resultant data provides a better resolution of the process solution fingerprint.

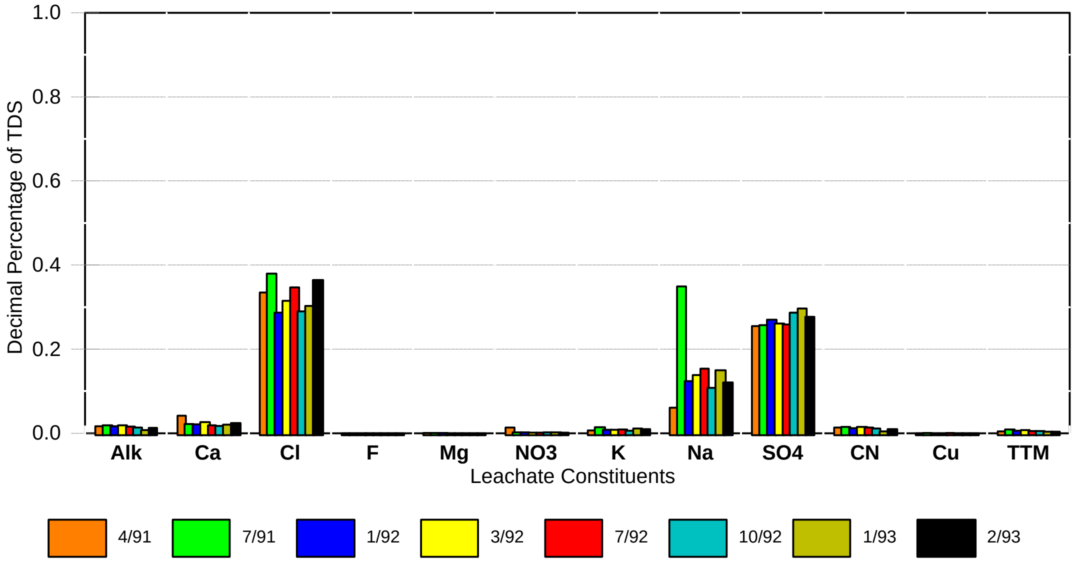
The third property demonstrated with the Alta monitoring results is that the plant make up water also had a distinctive geochemical fingerprint that could be readily distinguished from the process solution fingerprint. The significance of this observation, which has been documented at other mining facilities, is that the process solution fingerprint must be a characteristic property of the heap leaching process at the mine.

5.2.11 Hycroft Gold Mine

Another Nevada heap leaching facility for which monitoring records were obtained was the Hycroft Gold Mine. The results from eight quarterly surveys of the facility pregnant pond between April, 1991 and February, 1993 are presented graphically in Figure 5-55. Each of these surveys define a stable relative composition that is characterized by 35 percent chloride, 30 percent sulfate, and 15 percent sodium. The reproducibility of this pattern was estimated to be 93 percent. If the July, 1991 results are excluded from consideration because of the anomalous sodium result, the reproducibility of the geochemical pattern in the remaining seven surveys increases to 97 percent.

Geochemical monitoring results from the Hycroft barren pond are presented in Figure 5-56. These results have an ionic composition that is identical to that observed at the pregnant pond (Figure 5-55). This pattern consists of 35 percent chloride, 30 percent sulfate, and 15 percent sodium. A regression analysis comparison of the individual survey results at this location produced an average r^2 value of 0.933 while a comparison of the barren pond pattern with the pregnant pond pattern produced an r^2 value of 1.000. The fact that the barren pond and the pregnant pond have the same geochemical fingerprint is consistent with observations at other heap leaching facilities.

Monitoring results for 10 consecutive quarters of the mine make up water are compared with the barren pond fingerprint in Figure 5-57. An inspection of these results suggest that there is a data quality problem. This is most evident with the chloride results and the sodium results of the second quarter, 1991 survey because these two parameters represent almost 140 percent of the total dissolved solids concentration (i.e., either the concentrations for these two parameters are biased high or the total dissolved solids concentration is biased low). However, despite the uncertainty in the heights of the chloride and sodium peaks, the make up water has a repeatable geochemical fingerprint over time. The reproducibility of this fingerprint pattern, estimated by regression analysis, was 94 percent.

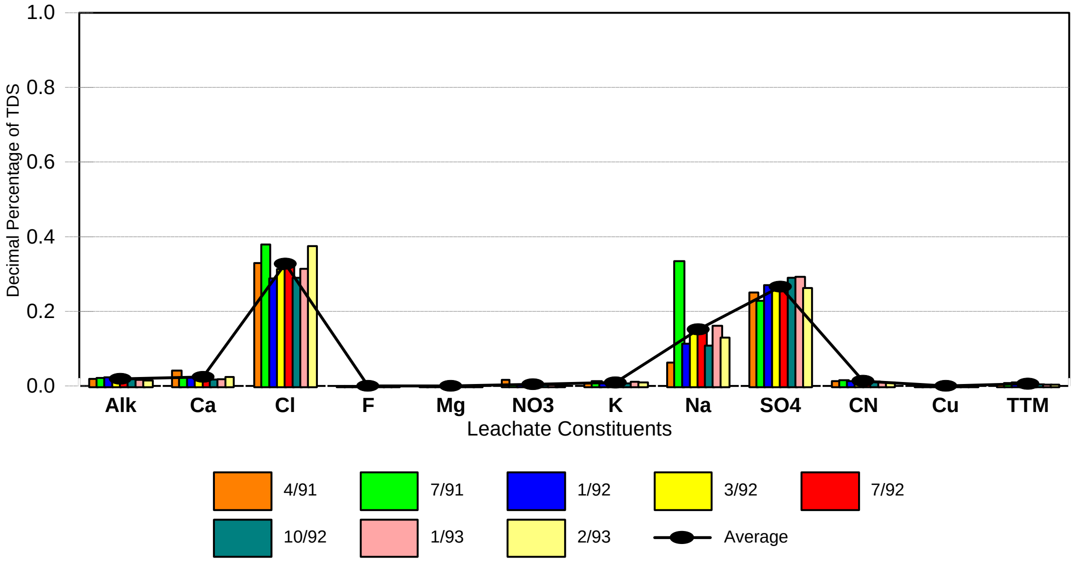


Regression analysis matrix for Hycroft pregnant pond

Sampling Date	4/91	7/91	1/92	3/92	7/92	10/92	1/93	2/93
4/91	1.000	0.679	0.948	0.950	0.943	0.956	0.923	0.977
7/91		1.000	0.817	0.851	0.870	0.772	0.841	0.803
1/92			1.000	0.994	0.982	0.996	0.995	0.983
3/92				1.000	0.996	0.984	0.988	0.991
7/92					1.000	0.967	0.976	0.991
10/92						1.000	0.990	0.978
1/93							1.000	0.972
2/93								1.000

Average r squared value = 0.933

Figure 5-55. Geochemical fingerprint for the Hycroft pregnant pond.

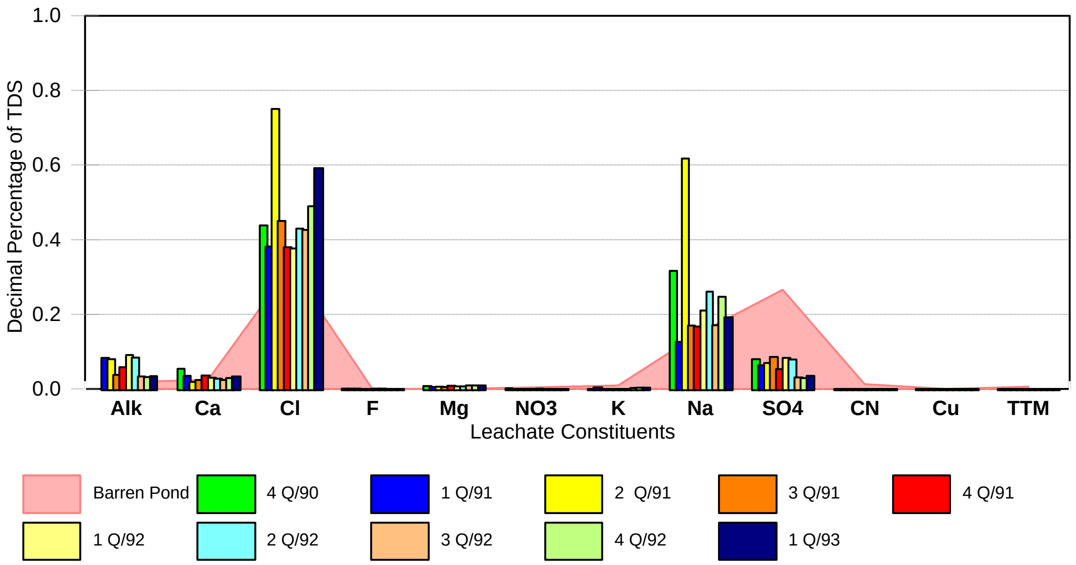


Regression analysis matrix for Hycroft barren pond

Sampling Date	4/91	7/91	1/92	3/92	7/92	10/92	1/93	2/93
4/91	1.000	0.682	0.960	0.949	0.939	0.955	0.924	0.971
7/91		1.000	0.779	0.837	0.870	0.749	0.847	0.820
1/92			1.000	0.994	0.982	0.997	0.989	0.972
3/92				1.000	0.996	0.986	0.995	0.983
7/92					1.000	0.970	0.991	0.988
10/92						1.000	0.984	0.960
1/93							1.000	0.968
2/93								1.000

Average r squared value = 0.930
Pregnant pond - barren pond comparison = 1.000

Figure 5-56. Geochemical fingerprint for the Hycroft barren pond.



Regression analysis matrix for Hycroft Make Up Water

Sampling Date	4 Q/90	1 Q/91	2 Q/91	3 Q/91	4 Q/91	1 Q/92	2 Q/92	3 Q/92	4 Q/92	1 Q/93
Barren Pond		0.688	0.584	0.747	0.684	0.719	0.693	0.642	0.625	0.622
4 Q/90										
1 Q/91		1.000	0.811	0.971	0.983	0.956	0.934	0.967	0.937	0.967
2 Q/91			1.000	0.866	0.896	0.926	0.959	0.887	0.938	0.837
3 Q/91				1.000	0.988	0.958	0.952	0.986	0.968	0.981
4 Q/91					1.000	0.979	0.975	0.991	0.983	0.978
1 Q/92						1.000	0.995	0.949	0.956	0.920
2 Q/92							1.000	0.953	0.970	0.919
3 Q/92								1.000	0.991	0.994
4 Q/92									1.000	0.973
1 Q/93										1.000

Average r squared value = 0.942
Average Make Up Water - Barren Pond comparison = 0.668

Figure 5-57. Comparison of the Hycroft process solution fingerprint with the mine make up water fingerprint.

Another result of the fingerprint comparison in Figure 5-57 is the recognition that the chloride - sulfate pattern of the barren pond is distinguishable from the chloride - sodium pattern of the make up water. Although this compositional shift is not as pronounced as that observed at other mining operations, the shift occurs consistently over the period of record. The regression analysis comparison of the make up water fingerprint with the barren pond fingerprint produced r^2 values ranging from 0.584 to 0.747 (average $r^2 = 0.668$). Thus, even with the suspect data in the second quarter 1991 data, it is possible to differentiate the barren pond fingerprint from the make up water fingerprint in every survey.

The monitoring results from the Hycroft Mine indicate that the make up water has a consistent geochemical fingerprint. The monitoring results also indicate that the process solution at the mine has a consistent geochemical fingerprint that is different from the mine make up water. Since the barren pond and the pregnant pond have a repeatable fingerprint that is consistent over time and different from the make up water fingerprint, the geochemical pattern must be a characteristic property of the process solution at this mine.

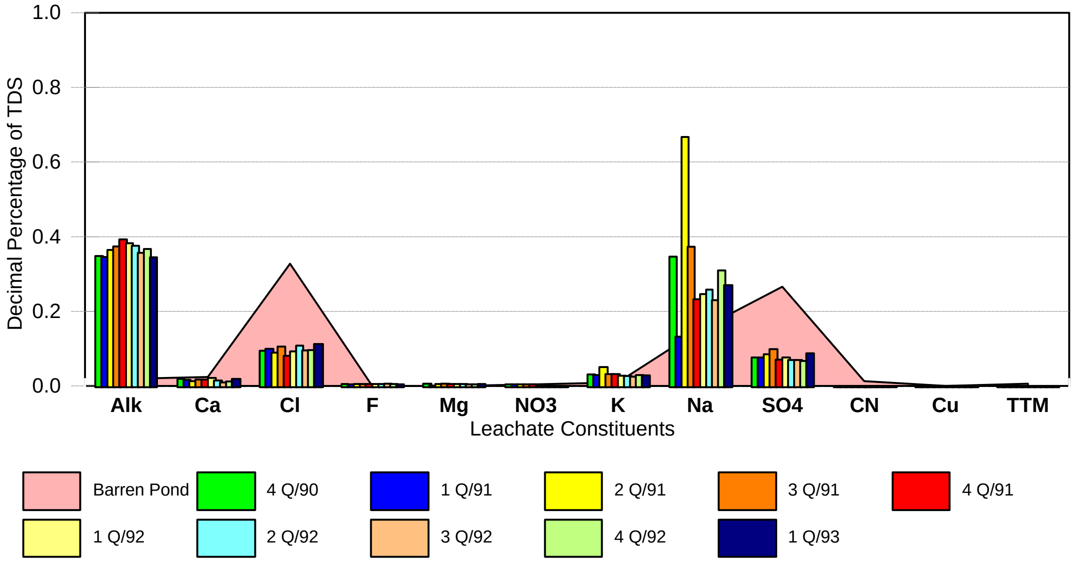
The Hycroft data file did not contain any ground-water monitoring information. Ground water was excluded from the site monitoring program because the water that is present is located at a depth greater than 500 feet. It was considered unlikely for the mining operation to impact ground water at this depth because of the high rate of evaporation in the area. However, several box springs were monitored to detect any downgradient migration of fugitive process solution that may be occurring. The monitoring results from 10 quarterly surveys at Box Springs #1 are compared with the Hycroft process solution fingerprint in Figure 5-58. The fingerprint for the box spring has a reproducible geochemical pattern ($r^2 = 0.911$) that is typical of most surface waters. More important, however, is the fact that the box springs fingerprint is characteristically different from the mine process solution fingerprint. This would indicate that the process solution from the Hycroft Mine has not impacted the box springs.

Hycroft Mine Summary

The Hycroft file contained two and one-half years of monitoring records from four locations at the mine. An evaluation of these data demonstrated several characteristics of the composition of process solutions at heap leaching facilities. These properties included a constant geochemical fingerprint at the pregnant pond, a constant barren pond fingerprint that was identical to the pregnant pond fingerprint, a process solution fingerprint that was different from the make up water fingerprint, and a process solution fingerprint that was discernably different from the box springs fingerprint. Each of these process solution characteristics have been observed in data sets from other mining operations.

The first property of significance is that the pregnant pond had a consistent geochemical fingerprint over time. The shape of this pattern was different from that observed at other mining sites. However, the same set of geochemical parameters that defined a characteristic fingerprint pattern at other mines also defined a reproducible pattern at the Hycroft Mine ($r^2 = 0.933$).

The second property of significance is that the barren pond also had a consistent geochemical fingerprint that was identical to the pregnant pond fingerprint. The estimated reproducibility of the barren pond fingerprint was 93 percent and the similarity of the barren pond and pregnant pond fingerprints was 100 percent. The importance of this observation is that these locations are part of a



Regression analysis matrix for Hycroft Box Springs #1

Sampling Date	4 Q/90	1 Q/91	2 Q/91	3 Q/91	4 Q/91	1 Q/92	2 Q/92	3 Q/92	4 Q/92	1 Q/93
Barren Pond	0.083	0.061	0.079	0.097	0.040	0.059	0.072	0.067	0.069	0.107
4 Q/90	1.000	0.786	0.893	0.999	0.921	0.942	0.956	0.942	0.990	0.975
1 Q/91		1.000	0.472	0.789	0.953	0.942	0.927	0.943	0.856	0.892
2 Q/91			1.000	0.889	0.670	0.704	0.732	0.704	0.828	0.782
3 Q/91				1.000	0.920	0.942	0.955	0.942	0.988	0.978
4 Q/91					1.000	0.997	0.990	0.995	0.963	0.970
1 Q/92						1.000	0.997	0.999	0.997	0.985
2 Q/92							1.000	0.998	0.986	0.992
3 Q/92								1.000	0.978	0.987
4 Q/92									1.000	0.991
1 Q/93										1.000

Average r squared value = 0.911
Average Box Springs #2 - Barren Pond comparison = 0.073

Figure 5-58. Comparison of the Hycroft process solution fingerprint with the geochemical fingerprint at Box Springs #1.

recirculating system and should have the same fingerprint if it is a characteristic property of the process solution.

A third property of the process solution fingerprint is that it was distinctly different from the make up water fingerprint. Since the make up water used to prepare the barren pond solution had a constant fingerprint, and the mine process solution had a consistent fingerprint that was graphically and statistically distinct from the make up water, the geochemical fingerprint of the process solution must be a characteristic feature of the heap leaching process.

Finally, a box springs located near the mine had a geochemical fingerprint that was different from the process solution pattern. Since the box springs fingerprint was consistent over time ($r^2 = 0.911$), and different from the process solution ($r^2 = 0.073$), the monitoring results suggest that the surface water is not being impacted by the mining operation. In passing, it should also be noted that the box springs fingerprint is different from the make up water fingerprint. This indicates that the make up water is being obtained from another source.

5.2.12 Paradise Peaks Mine

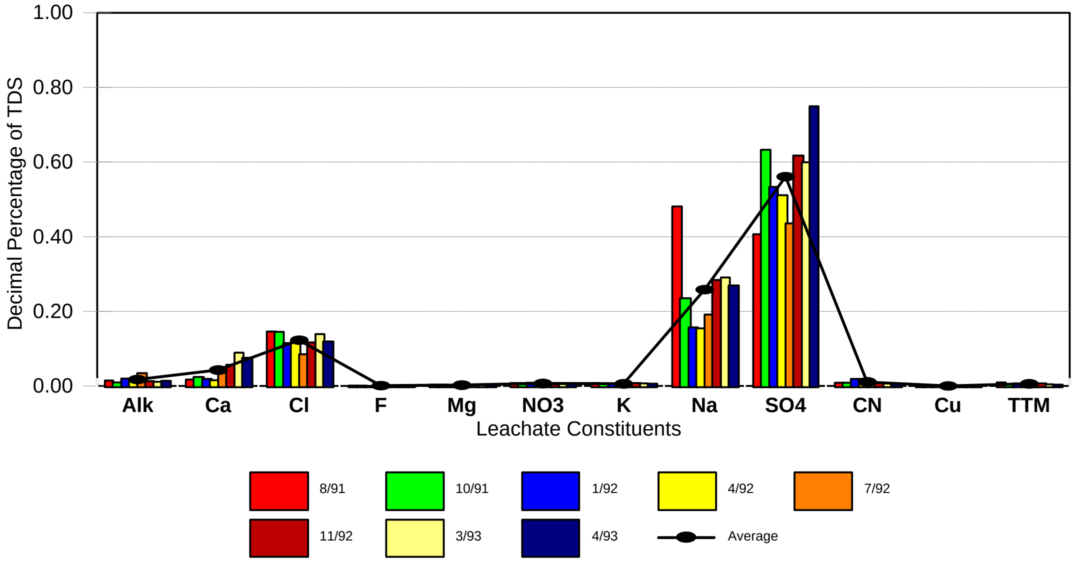
This mine is located in central Nevada and uses the conventional alkaline cyanide heap leaching procedure to recover gold from the ore being processed. The data set for the Paradise Peaks Mine included eight quarterly surveys for the pregnant and barren ponds and a limited amount of data from seven monitoring wells in the immediate vicinity of the operation.

The geochemical monitoring results for the pregnant pond at this mine are summarized in Figure 5-59. Each of the quarterly surveys define a repetitive pattern in which sulfate is the most abundant ion, sodium is the second most abundant ion, chloride is the third most abundant ion, and the remaining geochemical parameters are either minor constituents of the chemical signature or not present. The estimated reproducibility of the pregnant pond fingerprint was 91.6 percent.

An inspection of the pregnant pond data suggests that the sodium results for the August, 1991 survey are suspect. The ionic sum for this survey exceeds 115 percent of the total dissolved solids concentration and the normalized sodium concentration of 50 percent of the total dissolved solids concentration is double the sodium result for all other surveys. In addition, all of the low r^2 values for this location are associated with the August, 1991 survey (Figure 5-59). If this data set is excluded as an outlier based on data quality concerns, the reproducibility of the geochemical fingerprint in the remaining seven surveys increases from 91.6 percent to 98.4 percent.

The barren pond monitoring results from the Paradise Peaks Mine are presented in Figure 5-60. The major ions in this pattern, listed in decreasing order of abundance, are sulfate (50 percent), sodium (25 percent), and chloride (10 percent). The reproducibility of this pattern is estimated by regression analysis to be 91.7 percent. It is also important to notice that the barren pond and pregnant pond results produced an identical fingerprint. A regression analysis comparison of these two geochemical patterns produced an r^2 value of 0.999.

The barren pond data were also similar to the pregnant pond data set in another way. The August, 1991 result for sodium appears to be suspect. As with the pregnant pond data on the same date, the sodium value is double the average concentration and the ionic mass balance for the survey is biased high. If a quality assurance program consisting of mass balance and charge balance calculations had been applied to the data when they were generated, it would have been possible to identify and

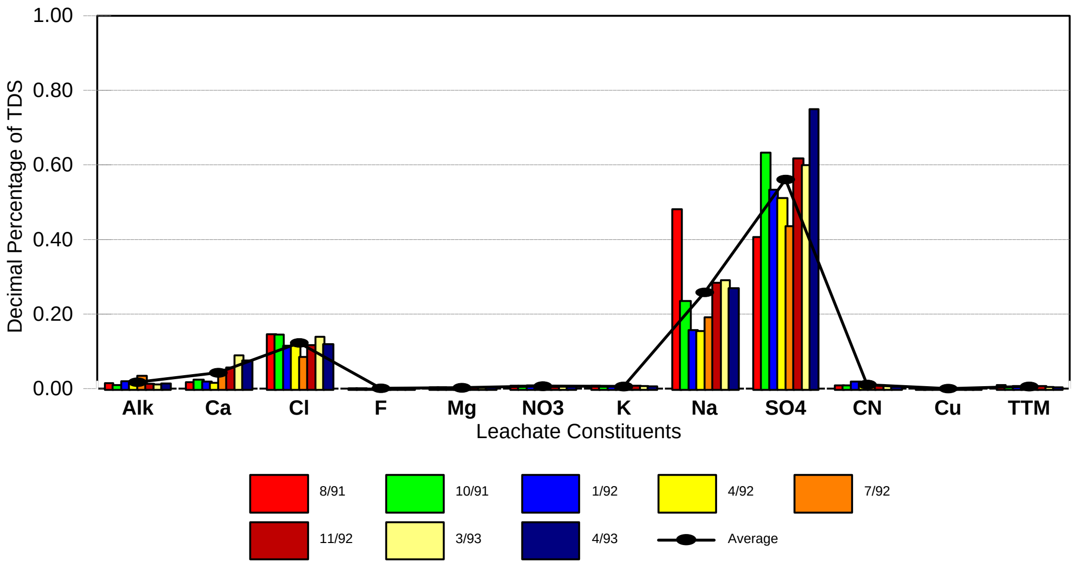


Regression analysis matrix for Paradise Peaks pregnant pond

Sampling Date	**8/91**	**10/91**	**1/92**	**4/92**	**7/92**	**11/92**	**3/93**	**4/93**
8/91	1.000	0.711	0.636	0.647	0.751	0.772	0.784	0.688
10/91		1.000	0.993	0.994	0.988	0.989	0.979	0.991
1/92			1.000	1.000	0.976	0.970	0.956	0.986
4/92				1.000	0.977	0.971	0.958	0.985
7/92					1.000	0.997	0.991	0.992
11/92						1.000	0.995	0.991
3/93							1.000	0.983
4/93								1.000

Average r squared value = 0.916

Figure 5-59. Geochemical fingerprint in the Paradise Peaks pregnant pond.



Regression analysis matrix for Paradise Peaks barren pond

Sampling Date	8/91	10/91	1/92	4/92	7/92	11/92	3/93	4/93
8/91	1.000	0.820	0.644	0.747	0.748	0.768	0.818	0.693
10/91		1.000	0.941	0.978	0.969	0.972	0.964	0.937
1/92			1.000	0.979	0.979	0.975	0.938	0.983
4/92				1.000	0.984	0.984	0.961	0.970
7/92					1.000	0.999	0.985	0.993
11/92						1.000	0.986	0.991
3/93							1.000	0.969
4/93								1.000

Average r squared value = 0.917

Figure 5-60. Barren pond fingerprint pattern at the Paradise Peaks Mine.

correct this error in a timely manner. Although the error can not be corrected at this date, the suspect data can be deleted from the data set. Removing the suspect data set increases the reproducibility of the geochemical pattern in the remaining barren pond surveys to 97.3 percent.

The data set for the Paradise Peaks Mine included limited data for seven monitoring wells. The geochemical results from each of these wells are compared to the process solution fingerprint in Figure 5-61. These ground-water results define a recurring pattern characterized by a high sulfate spike, a small sodium spike, and a minor calcium - chloride doublet. The reproducibility of this pattern at all seven monitoring wells was 89.8 percent.

A regression analysis comparison of the geochemical pattern at each of the seven monitoring wells with the Paradise Peaks process solution fingerprint produced an average r^2 value of 0.924 (a 92.4 percent match). Thus, the ground-water fingerprint was internally consistent at all locations and comparable to the process solution fingerprint. The similarity of the geochemical fingerprint at each of these locations indicate that the mine has had an impact on the local ground water.

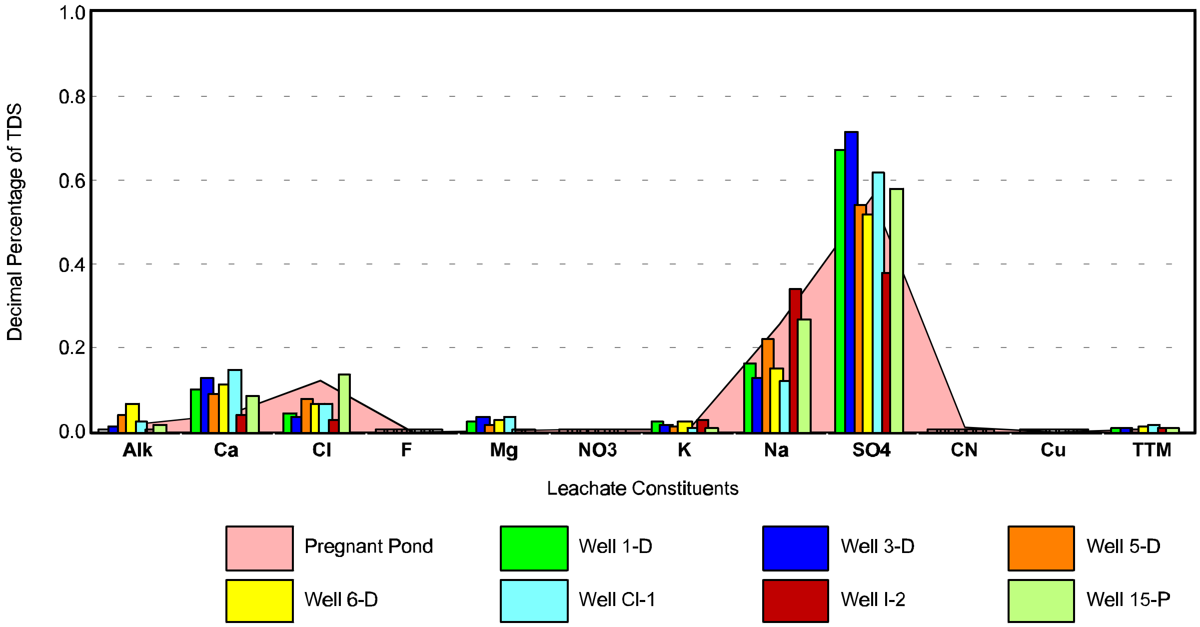
Paradise Peaks Mine Summary

The monitoring records for this mine only contained results for the process solution and several wells. Nevertheless, these limited data still demonstrated several characteristics of the composition of process solutions at a heap leaching facility. First, the geochemical data defined a sulfate-rich, alkalinity-poor pattern that has been observed at many mines. After excluding data of suspect quality, the reproducibility of this pattern over a two year period was 98.4 percent. Second, the barren pond monitoring results produced a geochemical fingerprint that was reproducible (r^2 = 0.973) and identical to the pregnant pond fingerprint (r^2 = 0.999). The fact that 16 surveys over two years from two locations in a recirculating system produce the same pattern would indicate that the geochemical fingerprint is a unique characteristic of the process solution. This condition has been observed at all the mining operations that have been previously summarized.

The limited data from this mine did not contain any information on the composition of the make up water. Therefore, it was not possible to unequivocally demonstrate that the fingerprint was a unique property of the mine process solution as was done at other sites. However, the consistent sulfate-rich, alkalinity-poor pattern in the barren pond and the pregnant pond at the Paradise Peaks Mine is not typical of most natural water systems and has been identified in the process solution at other mining operations. This implies that the Paradise Peaks fingerprint is, in fact, a characteristic of the process solution.

In some of the previous examples that have been discussed, the ground-water monitoring results produced two distinctive chemical signatures. One of these signatures was an alkalinity-rich, sulfate-poor pattern that is generally present in most natural water systems. The second signature is a sulfate-rich, alkalinity-poor pattern observed in mine process solutions. At the Paradise Peaks Mine, a different situation was encountered because all seven wells that were sampled had a ground-water fingerprint that was very similar to the process solution fingerprint (> 90 percent match). It is suggested that the ground water has been impacted by the mining operation and that the process solution fingerprint maintains its identity as it migrates away from the source. Although this assessment is tentative, and would benefit from additional spatial sampling, it is supported with the following observations:

1. The ground-water fingerprint matches the fingerprint of the process solutions at the Paradise Peaks Mine.



Regression analysis matrix for Paradise Peaks ground-water monitoring results

	Sampling Location						
	Well 1-D	**Well 3-D**	**Well 5-D**	**Well 6-D**	**Well CI-1**	**Well I-2**	**Well 15-P**
Pregnant Pond	0.925	0.886	0.982	0.932	0.885	0.863	0.995
Well 1-D	1.000	0.994	0.968	0.983	0.986	0.720	0.930
Well 3-D		1.000	0.943	0.978	0.994	0.656	0.895
Well 5-D			1.000	0.979	0.944	0.836	0.986
Well 6-D				1.000	0.982	0.730	0.942
Well CI-1					1.000	0.646	0.903
Well I-2						1.000	0.856
Well 15-P							1.000

Average r squared value = 0.898
Ground water - pregnant pond comparison = 0.924

Figure 5-61. Comparison of ground-water monitoring results with the Paradise Peaks process solution fingerprint.

2. The sulfate-rich, alkalinity-poor pattern present in the process solution and ground water has been shown to be uniquely distinctive of process solution at other heap leaching facilities.
3. The total dissolved solids concentrations for the ground water were highly variable and ranged from 900 mg/L to 3000 mg/L. Fluctuations of this magnitude do not usually occur in water that has not been impacted.

5.2.13 First Miss Getchell Gold Mine

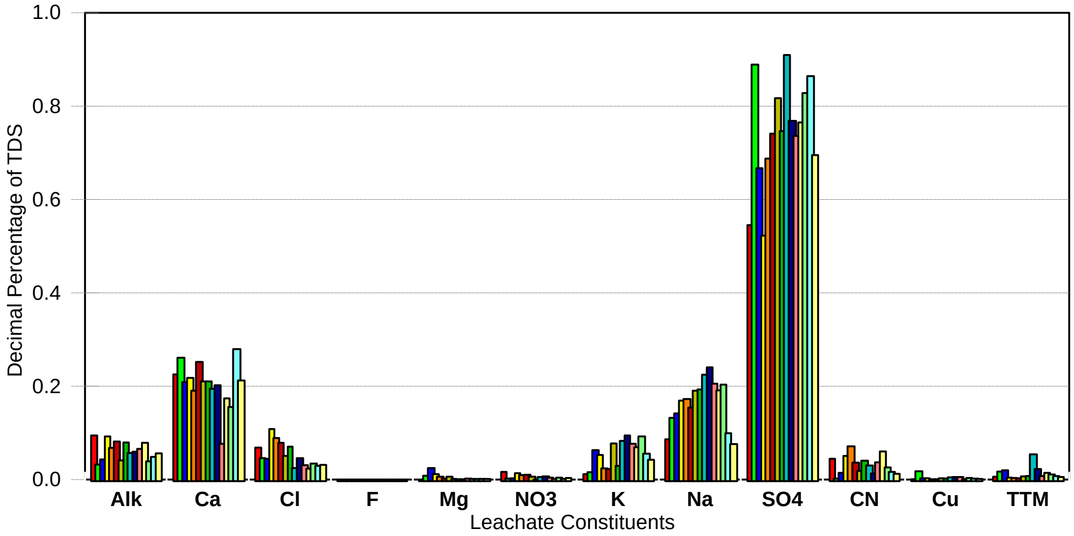
This mine is located in northern Nevada. There were no barren pond or pregnant pond results reported for this operation. However, the data file contained 15 sets of quarterly monitoring results from the tailings pond, the tailings reclaim water, and five monitoring well located around the perimeter of the tailings pond. The period of record for this site is May, 1989 through November, 1992.

The concentrations for the individual tailings pond constituents displayed considerable variability over time. For example, the total dissolved solids concentration ranged from 2187 to 3250 mg/L, sulfate ranged from 1530 to 2900 mg/L, sodium ranged from 240 to 718 mg/L, alkalinity ranged from 119 to 456 mg/L, and trace metals ranged from 8 to 59 mg/L. However, despite these fluctuations, the geochemical parameters define a constant fingerprint for the tailings water. This signature is characterized by the dominant sulfate spike (60 to 70 percent of TDS), smaller spikes for calcium and sodium (15 to 20 percent of TDS), and minor but detectable quantities of the other parameters (Figure 5-62).

An inspection of the tailings water monitoring results in Figure 5-62 suggests that there are some data quality concerns with the data. For example, there is considerable variability in the height of the sulfate spike which ranges from 50 percent to 90 percent of the total dissolved solids concentration. Also, since several of the sulfate measurements represent between 80 and 90 percent of the total dissolved solids concentration, the mass balance is biased high (either one or more of the individual analyses are high or the total dissolved solids concentration is low). However, in spite of these concerns, problems that could have been identified and corrected with a timely review of the data, the monitoring results produce a distinctive chemical signature for the tailings water. The reproducibility of this fingerprint is 96.8 percent.

The monitoring records for the First Miss Getchell Mine also included 15 sets of quarterly survey data for tailings reclaim water. These results have been presented in Figure 5-63. One point that is apparent on reviewing this information is that there is a data quality problem with some of the results. This is indicated by the variability in the reported sulfate results that approached 100 percent of the total dissolved solids concentration in one survey. There is also an apparently anomalous alkalinity result in one survey. However, in spite of the obvious data quality problems, a second point that is readily apparent on reviewing the results in Figure 5-63 is that the tailings water has a repetitive geochemical signature or fingerprint.

A comparison of the tailings water results (Figure 5-62) with the tailings reclaim water results (Figure 5-63) demonstrate that these two geochemical fingerprints are identical. A regression analysis of the two patterns produced an r^3 value of 0.997. Thus, 30 sampling events from two locations at the First Miss Getchell Mine over a four year period produced the same fingerprint pattern. This case study provides another example in which the common geochemical parameters describe a consistent chemical fingerprint that uniquely characterizes mine leachates at their source.

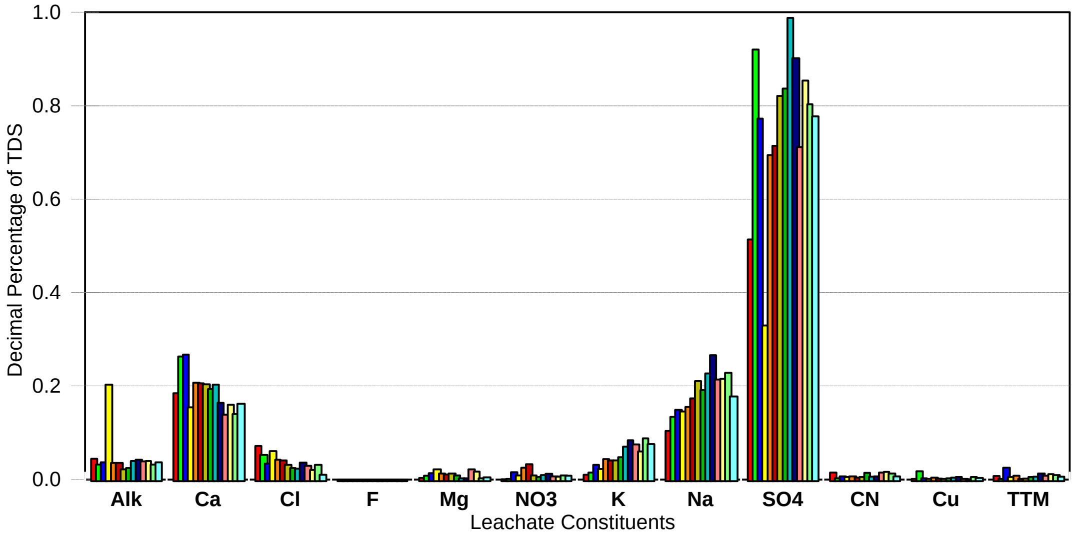


Regression analysis matrix for First Miss Getchell tailings pond

	Sampling Date														
	5/89	**7/89**	**11/89**	**2/90**	**6/90**	**8/90**	**11/90**	**2/91**	**6/91**	**8/91**	**11/91**	**2/92**	**5/92**	**8/92**	**11/92**
5/89	1.000	0.965	0.959	0.967	0.963	0.987	0.943	0.964	0.920	0.920	0.866	0.935	0.909	0.972	0.974
7/89		1.000	0.991	0.939	0.974	0.987	0.985	0.981	0.974	0.963	0.928	0.969	0.967	0.994	0.993
11/89			1.000	0.957	0.978	0.988	0.995	0.987	0.984	0.983	0.944	0.982	0.980	0.990	0.988
2/90				1.000	0.933	0.978	0.952	0.974	0.927	0.952	0.892	0.943	0.925	0.937	0.938
6/90					1.000	0.990	0.983	0.996	0.972	0.972	0.953	0.983	0.972	0.964	0.967
8/90						1.000	0.982	0.993	0.965	0.966	0.924	0.972	0.959	0.984	0.985
11/90							1.000	0.990	0.993	0.993	0.968	0.992	0.994	0.979	0.979
2/91								1.000	0.982	0.984	0.958	0.988	0.979	0.971	0.973
6/91									1.000	0.991	0.981	0.994	0.996	0.965	0.965
8/91										1.000	0.972	0.988	0.991	0.954	0.953
11/91											1.000	0.981	0.988	0.914	0.920
2/92												1.000	0.993	0.965	0.967
5/92													1.000	0.959	0.960
8/92														1.000	0.999
11/92															1.000

Average r squared value = 0.968

Figure 5-62. Composition of First Miss Getchell tailings pond water.



Regression analysis matrix for First Miss Getchell tailings reclaim water

	Sampling Date														
	5/89	**7/89**	**11/89**	**2/90**	**6/90**	**8/90**	**11/90**	**2/91**	**6/91**	**8/91**	**11/91**	**2/92**	**5/92**	**8/92**	**11/92**
5/89	1.000	0.987	0.987	0.765	0.984	0.980	0.970	0.968	0.959	0.940	0.940	0.950	0.936	0.953	0.961
7/89		1.000	0.994	0.708	0.992	0.988	0.983	0.990	0.980	0.957	0.957	0.971	0.956	0.976	0.985
11/89			1.000	0.726	0.995	0.991	0.984	0.984	0.976	0.956	0.957	0.967	0.953	0.974	0.980
2/90				1.000	0.730	0.733	0.716	0.701	0.708	0.709	0.714	0.707	0.696	0.706	0.690
6/90					1.000	0.999	0.995	0.994	0.990	0.977	0.978	0.984	0.975	0.988	0.990
8/90						1.000	0.997	0.995	0.992	0.982	0.982	0.986	0.979	0.989	0.989
11/90							1.000	0.999	0.996	0.991	0.991	0.994	0.989	0.994	0.991
2/91								1.000	0.999	0.991	0.991	0.997	0.990	0.997	0.996
6/91									1.000	0.995	0.994	0.999	0.994	0.999	0.997
8/91										1.000	0.999	0.997	0.999	0.994	0.985
11/91											1.000	0.997	0.999	0.994	0.985
2/92												1.000	0.996	0.998	0.992
5/92													1.000	0.995	0.987
8/92														1.000	0.997
11/92															1.000

Average r squared value = 0.948

Figure 5-63. Composition of tailings reclaim water at the First Miss Getchell Mine.

The fingerprint for the tailings water at the mine was compared to the ground-water monitoring results from several wells around the tailings pond. The results of this comparison at monitoring Well 2 are presented in Figure 5-64. The data clearly demonstrate that the ground water at Well 2 has a constant composition over time. The ground-water signature does not contain a dominant ion but it is still very reproducible ($r^2 = 0.976$). The important aspect of the fingerprint comparison at this location is that the ground-water fingerprint is distinguishable from the tailings water fingerprint ($r^2 = 0.238$). This would indicate that tailings water is not having an impact on this location.

The comparison of the tailings water fingerprint with the ground-water fingerprint at Well 1 leads to a different conclusion (Figure 5-65). The geochemical data define a consistent pattern at this location over time ($r^2 = 0.976$). However, a comparison of the Well 1 pattern with the Well 2 pattern indicates that the composition has been altered. This is most apparent with the large sulfate increase but there is also a smaller calcium increase and a chloride decrease. As a result of the compositional shift, the ground-water pattern at Well 1 more closely resembles the tailings water fingerprint ($r^2 = 0.846$). Thus, the monitoring results would suggest that water from the tailings pond is migrating in the direction of monitoring Well 1.

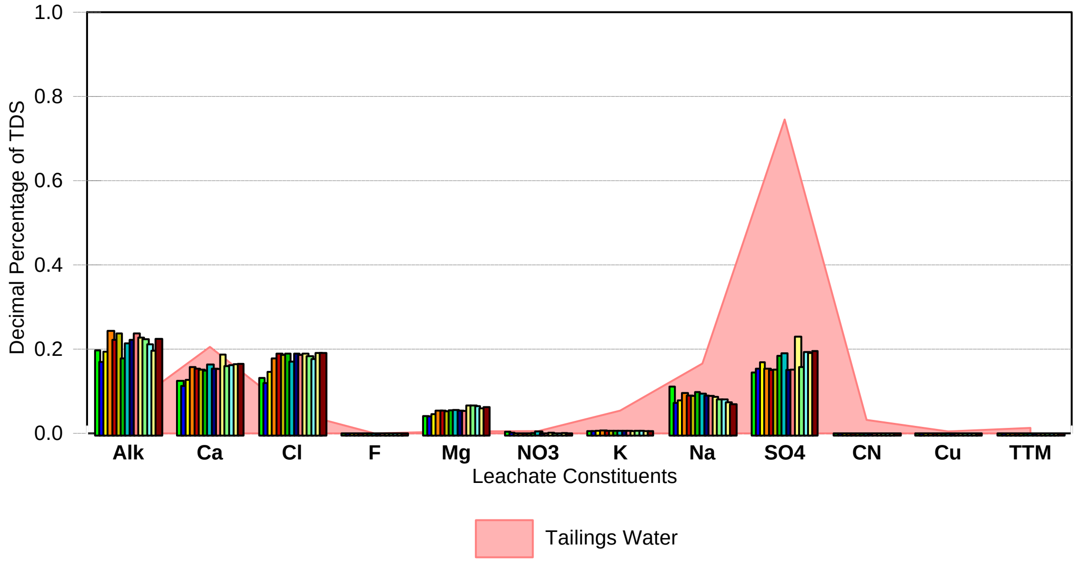
First Miss Getchell Summary

An assessment of the monitoring results for this facility demonstrated several characteristic properties of tailings water at a mining site. The single most important property is the fact that the tailings water had a constant relative composition over time. Geochemical monitoring results from 30 surveys over a four year period produced a strong, reproducible multi-ion signature or fingerprint. The fingerprint pattern was defined by 70 percent sulfate, 20 percent calcium, 15 percent sodium, and small amounts of alkalinity, chloride, and the remaining geochemical parameters. Even though the reported concentrations for each of the geochemical parameters fluctuated by more than 100 percent, and there were identifiable data quality concerns with some of the results (particularly sulfate), the reproducibility of the First Miss Getchell tailings water fingerprint pattern was estimated to be greater than 95 percent.

The same suite of geochemical parameters that defined the tailings water composition also defined a second reproducible ($r^2 = 0.976$) fingerprint pattern for the local ground water. A second important characteristic of the tailings water fingerprint is the fact that it can be distinguished from the fingerprint of the local ground water. The sulfate-rich pattern of the tailings water was graphically and statistically ($r^2 = 0.238$) distinct from the geochemical fingerprint of the ground water.

A third important characteristic of the tailings water fingerprint is that it appears to maintain its chemical identity as the mine waste leachate migrates from the source. The geochemical distribution at Well 1 has been altered and no longer resembles the local ground-water fingerprint. However, the new ionic distribution is very similar ($r^2 = 0.846$) to the tailings water fingerprint. These results suggests that the geochemical fingerprint can function as an internal tracer to identify and track the migration of mine waste leachates through the environment. This assessment is consistent with observations at several other mines, particularly the Cortez Mine, where the process solution fingerprint was identified at some distance from the mining operation.

Based on the demonstrated properties of the tailings water fingerprint, it is suggested that the geochemical parameters that define the fingerprint can be effective monitoring parameters for the mining industry. Collectively, the geochemical parameters provide a means to uniquely characterize the process solutions and tailings water at the source, to differentiate the mine leachate from ambient

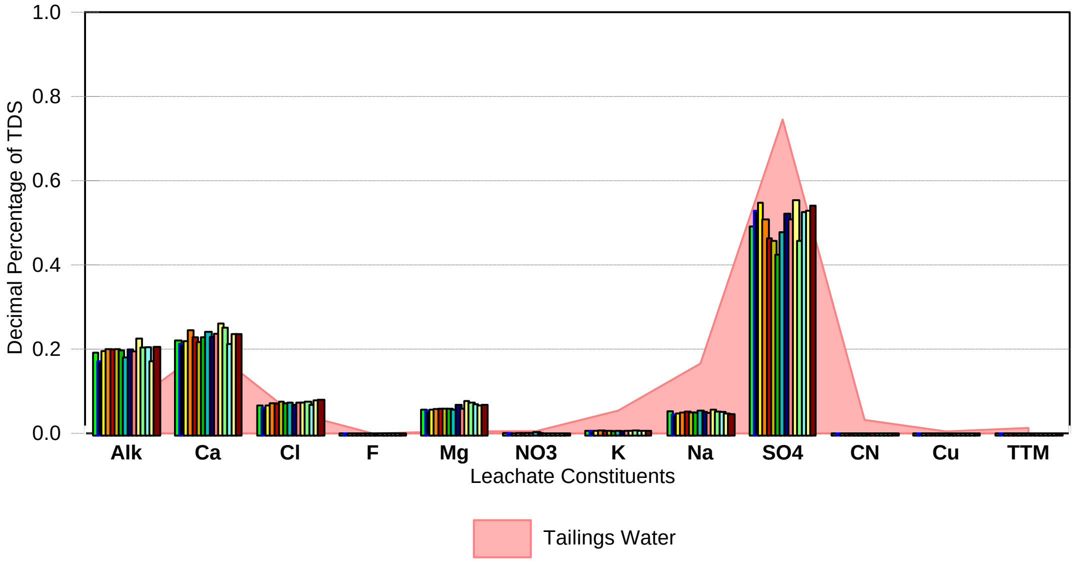


Regression analysis matrix for First Miss Getchell monitoring Well 2

	Sampling Date													
	5/89	**7/89**	**11/89**	**2/90**	**6/90**	**8/90**	**11/90**	**2/91**	**6/91**	**8/91**	**11/91**	**2/92**	**5/92**	**8/92**
Tailings Water	0.356	0.325	0.187	0.188	0.182	0.328	0.320	0.188	0.182	0.372	0.205	0.318	0.314	0.289
5/89	1.000	0.998	0.962	0.954	0.958	0.961	0.992	0.954	0.957	0.985	0.962	0.987	0.968	0.978
7/89		1.000	0.973	0.969	0.971	0.969	0.994	0.969	0.971	0.986	0.975	0.992	0.977	0.987
11/89			1.000	0.993	0.998	0.938	0.973	0.993	0.998	0.944	0.991	0.965	0.949	0.967
2/90				1.000	0.998	0.960	0.974	1.000	0.998	0.950	0.996	0.972	0.967	0.975
6/90					1.000	0.946	0.971	0.998	1.000	0.944	0.994	0.967	0.957	0.972
8/90						1.000	0.979	0.960	0.946	0.975	0.959	0.979	0.987	0.972
11/90							1.000	0.974	0.972	0.992	0.981	0.996	0.986	0.989
2/91								1.000	0.998	0.950	0.996	0.972	0.967	0.975
6/91									1.000	0.945	0.994	0.968	0.957	0.972
8/91										1.000	0.964	0.996	0.991	0.990
11/91											1.000	0.983	0.972	0.986
2/92												1.000	0.994	0.996
5/92													1.000	0.994
8/92														1.000
11/92														

Average r squared value = 0.976
Ground water vs Tailings Water = 0.238

Figure 5-64. Comparison of First Miss Getchell tailings pond fingerprint with monitoring results from Well 2.



Regression analysis matrix for First Miss Getchell monitoring Well 1

	Sampling Date														
	5/89	**7/89**	**11/89**	**2/90**	**6/90**	**8/90**	**11/90**	**2/91**	**6/91**	**8/91**	**11/91**	**2/92**	**5/92**	**8/92**	**11/92**
Tailings Water	0.889	0.875	0.841	0.822	0.820	0.791	0.845	0.855	0.859	0.835	0.792	0.856	0.875	0.851	0.879
5/89	1.000	1.000	0.992	0.986	0.986	0.974	0.990	0.996	0.994	0.991	0.975	0.996	0.997	0.996	0.886
7/89		1.000	0.994	0.990	0.991	0.979	0.991	0.998	0.996	0.994	0.978	0.998	0.996	0.998	0.867
11/89			1.000	0.999	0.998	0.995	0.999	0.998	1.000	0.999	0.994	0.994	0.995	0.998	0.860
2/90				1.000	0.999	0.998	0.997	0.992	0.998	0.989	0.997	0.993	0.990	0.996	0.832
6/90					1.000	0.997	0.995	0.996	0.998	0.998	0.995	0.994	0.989	0.996	0.832
8/90						1.000	0.994	0.989	0.993	0.994	0.999	0.984	0.981	0.988	0.821
11/90							1.000	0.996	0.998	0.997	0.995	0.990	0.995	0.995	0.872
2/91								1.000	0.999	0.999	0.989	0.999	0.996	0.999	0.861
6/91									1.000	0.999	0.992	0.996	0.996	0.999	0.869
8/91										1.000	0.995	0.996	0.993	0.998	0.850
11/91											1.000	0.983	0.983	0.988	0.836
2/92												1.000	0.993	0.998	0.850
5/92													1.000	0.997	0.899
8/92														1.000	0.865
11/92															1.000

Average r squared value = 0.976
Ground water vs Tailings Water = 0.846

Figure 5-65. Comparison of First Miss Getchell tailings pond fingerprint with monitoring results from Well 1.

ground water, and to identify any leachate that may have escaped containment and migrated away from the source.

One final issue that must be addressed briefly is that of data quality. Some of the monitoring results from the First Miss Getchell Mine are of suspect quality because the sum of the geochemical ion concentrations exceeds the reported total dissolved solids concentration (in some cases, by 30 percent or more). Since this violates the fundamental principle of mass balance, either one or more of the geochemical concentrations are erroneously high or the total dissolved solids concentration is low. In this example, it was still possible to identify the characteristic tailings water fingerprint in spite of these errors. However, if relatively simple mass balance and charge balance calculations had been performed when the data were initially generated, the errors could have been identified and corrected to produce data of higher quality.

5.2.14 Arimetco Gold Mine

This mining operation uses a heap leaching process similar to that described in Section 5.1 to recover gold from the estimated 5.5 million tons of ore that were mined in 1992. However, the Arimetco Mine uses a different leaching agent than the other heap leaching facilities that have been previously discussed. This facility uses a strongly acidic leaching solution, probably sulfuric acid, as the recirculating extraction agent. This is indicated by the low pH (pH = 2.0), the very high sulfate concentrations (56,800 mg/L), and the absence of cyanide (unionized cyanide would represent a health threat and be lost by volatilization at the reported pH). Additional properties of the Arimetco pregnant leaching solution are the very high total dissolved solids concentration (>100,000 mg/L), the extremely high concentrations for aluminum, copper, and iron (> 1,000 mg/L), and the generally high concentrations for most trace metals (Table 5-8).

The geochemical results from 10 surveys of the Arimetco pregnant leaching solution are presented in Figure 5-66. This solution has a relatively simple pattern that is dominated by the sulfate ion. A regression analysis of the monitoring results between February, 1991 and June, 1993 suggests that the reproducibility of this pattern is 97 percent. Thus, even though the Arimetco Mine uses a different leaching solution than other gold mines, the pregnant leaching solution still has a consistent fingerprint over time.

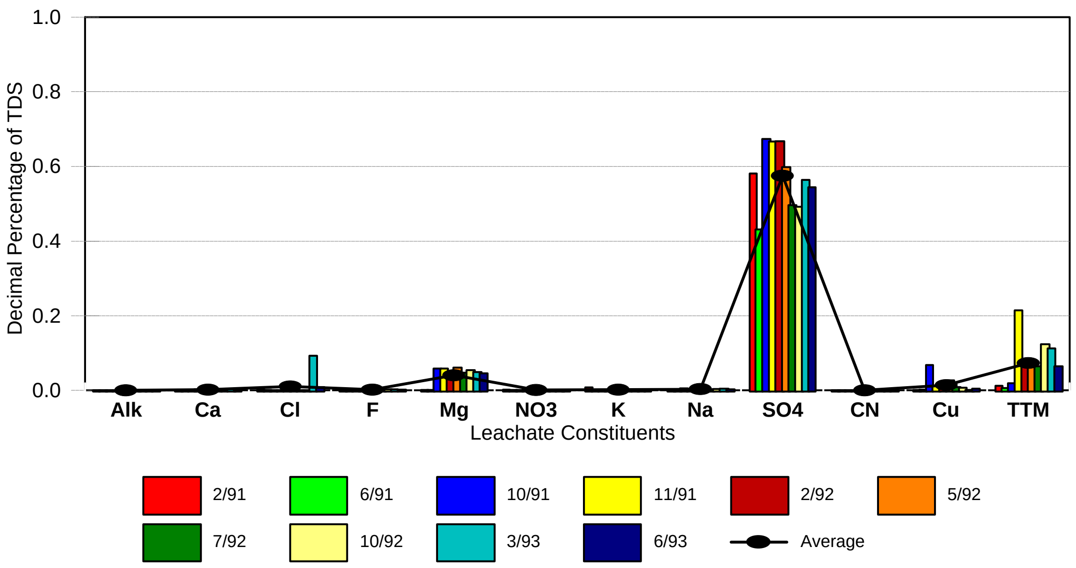
The fingerprint pattern for the Arimetco heap leaching solution is slightly different from the pregnant pond fingerprints at other gold mining operations. Specifically, although still minor, the trace metals are more apparent in the Arimetco fingerprint. Also, alkalinity and cyanide are completely absent from the fingerprint. Each of these features are related to the use of an acidic leaching solution because metals are generally more soluble at lower pH and alkalinity does not exist below a pH of approximately 4.5. However, more important than the exact shape of the fingerprint is the fact that the geochemical parameters define a consistent, reproducible pattern that characterizes the pregnant pond composition.

Ground water is used as make up water at the Arimetco Mine. The geochemical fingerprint for the make up water is contrasted with the pregnant solution fingerprint in Figure 5-67. The single dominant ion in the ground-water signature is alkalinity which is typical of most natural water systems. Except for a single anomalous value for calcium in one survey, the geochemical data define a constant multi-ion signature. The estimated reproduciblity of this signature is 93 percent.

Table 5-8. Composite monitoring results for 10 surveys of the Arimetco pregnant leaching solution.

Constituent	Mean Concentration	Standard Deviation
Alkalinity	0	0
Aluminum	6800	4774
Antimony	0.00	0.00
Arsenic	0.20	0.22
Barium	0.03	0.03
Beryllium	0.42	0.09
Bismuth	2.71	6.31
Cadmium	0.34	0.42
Calcium	216	142
Chloride	1141	2944
Chromium	2.39	0.51
Cobalt	9.09	2.48
Copper	1308	1714
Fluoride	160	142
Gallium	0.11	0.27
Iron	2610	1329
Lead	0.23	0.69
Lithium	0.96	0.60
Magnesium	4447	2243
Manganese	91	36
Mercury	0.09	0.06
Molybdenum	40.19	46.26
Nickel	6.02	1.80
Nitrate	70	92
Phosphorous	693	287
Potassium	170	242
Scandium	0.52	0.19
Selenium	0.39	1.17
Silver	0.10	0.08
Sodium	363	113
Strontium	14.03	3.37
Sulfate	56820	17884
Thallium	0.01	0.04
Tin	1.40	3.43
Titanium	4.21	2.40
Cyanide	0.00	0.00
Vanadium	7.41	3.90
Zinc	11.98	5.01
pH	2.04	0.19
TDS	109683	12762

All concentrations, except pH, expressed in units of mg/L.

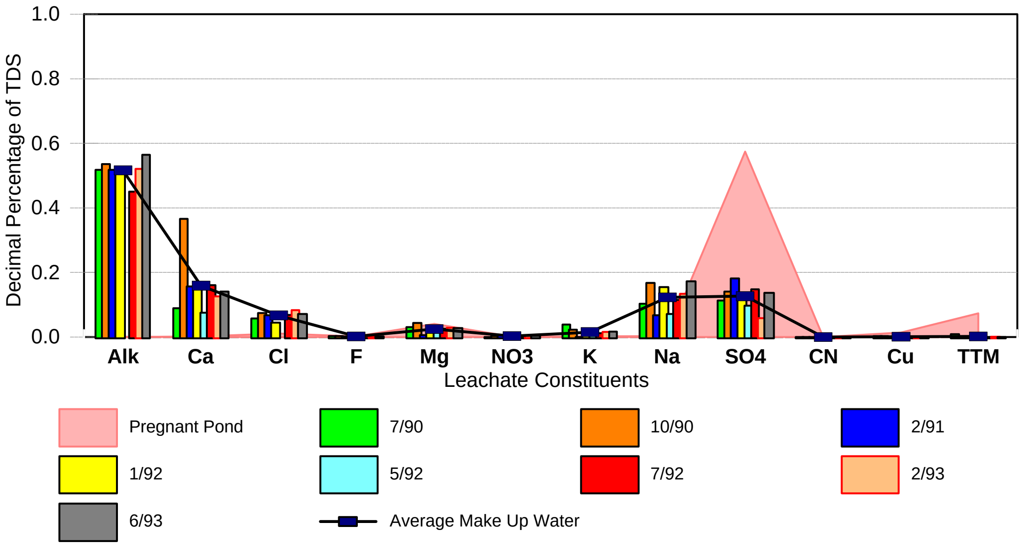


Regression Analysis Matrix for Arimetco Pregnant Pond

	Sampling Date									
	2/91	**6/91**	**10/91**	**11/91**	**2/92**	**5/92**	**7/92**	**10/92**	**3/93**	**6/93**
2/91	1.000	1.000	0.984	0.910	0.988	0.981	0.980	0.940	0.945	0.985
6/91		1.000	0.986	0.907	0.988	0.981	0.980	0.939	0.944	0.984
10/91			1.000	0.905	0.985	0.987	0.981	0.940	0.932	0.981
11/91				1.000	0.957	0.958	0.964	0.994	0.955	0.960
2/92					1.000	0.998	0.998	0.979	0.966	0.999
5/92						1.000	0.999	0.981	0.964	0.998
7/92							1.000	0.986	0.968	0.999
10/92								1.000	0.967	0.982
3/93									1.000	0.973
6/93										1.000

Average r squared value = 0.971

Figure 5-66. Fingerprint pattern for the Arimetco pregnant leaching solution.



Regression Analysis Matrix for Arimetco Make Up Water

	Sampling Date							
	7/90	**10/90**	**2/91**	**1/92**	**5/92**	**7/92**	**2/93**	**6/93**
Pregnant Pond	0.002	0.000	0.028	0.004	---	0.014	0.007	0.002
7/90	1.000	0.787	0.950	0.964	---	0.952	0.972	0.980
10/90		1.000	0.856	0.894	---	0.909	0.837	0.852
2/91			1.000	0.957	---	0.981	0.914	0.950
1/92				1.000	---	0.988	0.965	0.994
5/92					---	---	---	---
7/92						1.000	0.944	0.979
2/93							1.000	0.979
6/93								1.000

Average r squared value = 0.934
Make Up water - pregnant solution comparison = 0.008

Figure 5-67. Comparison of Arimetco pregnant leaching solution fingerprint with the mine make up water fingerprint.

The important aspect of the fingerprint comparison in Figure 5-67 is that the pregnant leaching solution has a composition that is distinctly different from the make up water. A regression analysis of the two patterns produced an r^2 value of 0.001 (less than a one percent match between the two fingerprints). The alkalinity in the make up water is lost by neutralization and the presence of the other geochemical ions are swamped out by the large increase in sulfate. The significance of this composition shift is that the resultant process solution fingerprint is not a property of the make up water and must be a unique characteristic of the pregnant leaching solution.

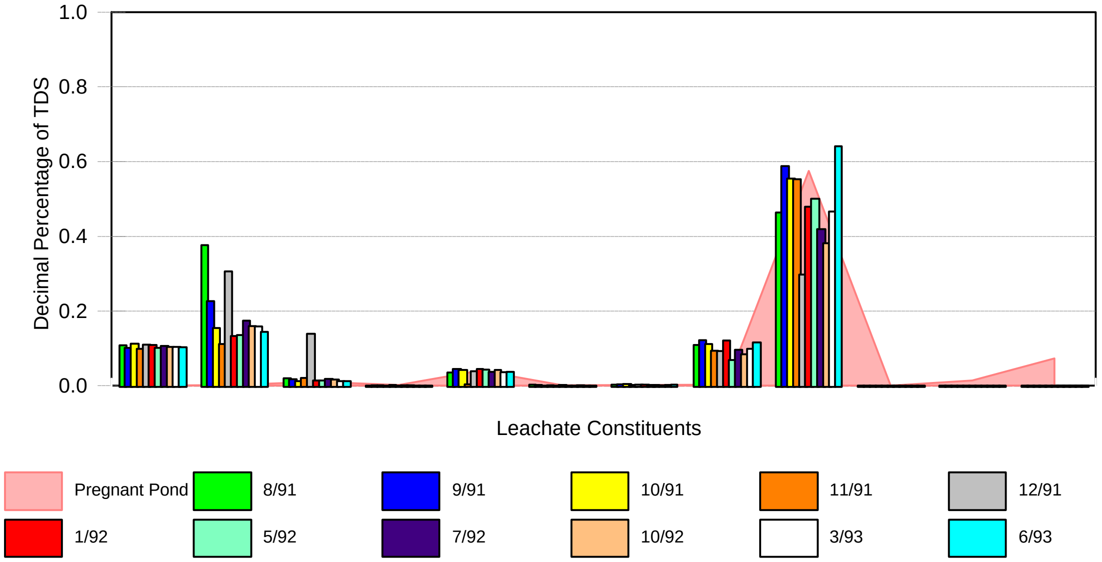
The monitoring program for this site only included a single monitoring well. The geochemical results from 10 surveys at this well are summarized in Figure 5-68. These results suggest that there is a reproducible geochemical chemical signature in the ground water at this location (r^2 = 0.971). However, this signature is distinctly different from the plant make up water that is derived from ground water (Figure 5-67). First, there is a large increase in sulfate at Well 1 (from 15 percent to more than 40 percent). Second, there is a substantial reduction in the abundance of alkalinity at Well 1 (from 50 percent to 10 percent). These simultaneous changes are consistent with a sulfate rich, alkalinity poor liquid such as Arimetco pregnant leaching solution impacting the well. A regression analysis of the Well 1 and pregnant pond fingerprints suggests that the Well 1 fingerprint bears a strong resemblance to the Arimetco pregnant leaching solution (r^2 = 0.744). The similarity of the ground water fingerprint at Well 1 and the pregnant leaching solution fingerprint provides additional evidence that mine leachate maintains its integrity as it migrates away from the source.

Although an analysis of the fingerprint patterns suggests that ground water at Well 1 has been impacted by mine process solution, the actual compositional shift for several parameters has deviated from the expected compositional shift. The observed fluctuations in relative abundance of alkalinity, calcium, sulfate, and trace metals at Well 1 deserve a brief comment:

1. Alkalinity. This parameter is absent from the pregnant leaching solution fingerprint. If the fingerprint were truly conservative, one might expect a lower alkalinity abundance at Well 1. However, the low alkalinity (0) of the process solution is due to the low pH (pH = 2). As the process solution migrates through the ground water, the pH will be quickly neutralized with a concurrent rise in pH and alkalinity. Thus, due to the reactivity of one of the process solution constituents, the actual shift in ground-water alkalinity will be less than anticipated. This was observed to be the case.

2. Calcium. This parameter is essentially absent from the mine leachate fingerprint. Therefore, one might expect the relative abundance of calcium to decline in an area impacted by mine process solution. However, the acid-base reaction that neutralizes the low pH of the original leachate as it migrates away from the source also causes an increase in the alkalinity concentration. In order to maintain the required charge balance, the concentration of one or more cations must increase to compensate for the alkalinity increase that occurred when the solution pH was neutralized. As an indirect consequence of the reactivity (low pH) of the pregnant leaching solution, the observed calcium shift was less than anticipated.

3. Sulfate. This ion is the single dominant constituent in the pregnant solution fingerprint (Figure 5-66). An increase in the relative abundance of sulfate should occur when pregnant leaching solution is present. Although a substantial sulfate increase was observed at Well 1, the actual increase was less than might be expected. In this case, the higher relative abundance of both alkalinity and calcium caused a dilution of the sulfate peak. Thus, as a result of the reactivity of the pregnant leaching solution (i.e., low pH), the sulfate shift should be lower than expected. This was observed to be the case.



Regression Analysis Matrix for Arimetco Monitoring Well 1

	Sampling Date										
	8/91	**9/91**	**10/91**	**11/91**	**12/91**	**1/92**	**5/92**	**7/92**	**10/92**	**3/93**	**6/93**
Pregnant Pond	0.499	0.793	0.841	0.881	0.318	0.818	0.866	0.747	0.743	0.802	0.881
8/91	1.000	0.881	0.807	0.747	0.886	0.799	0.799	0.894	0.893	0.852	0.766
9/91		1.000	0.988	0.965	0.703	0.982	0.982	0.993	0.990	0.995	0.976
10/91			1.000	0.989	0.623	0.997	0.996	0.982	0.980	0.996	0.996
11/91				1.000	0.569	0.983	0.987	0.952	0.947	0.977	0.996
12/91					1.000	0.621	0.617	0.733	0.733	0.673	0.576
1/92						1.000	0.987	0.981	0.978	0.994	0.990
5/92							1.000	0.975	0.975	0.990	0.993
7/92								1.000	0.999	0.994	0.962
10/92									1.000	0.993	0.953
3/93										1.000	0.985
6/93											1.000

Average r squared value = 0.971
Ground water - pregnant pond comparison = 0.744

Figure 5-68. Comparison of monitoring results at Well 1 to the Arimetco pregnant leaching solution fingerprint.

4. Trace Metals. The total trace metal concentration of the pregnant leaching solution represents approximately 10 percent of the total dissolved solids concentration. However, these constituents are essentially absent at Well 1 even though the pregnant leaching solution fingerprint is still identifiable. The lower abundance of trace metals is due to the lower solubility of most metals at higher pH and the slower migration of trace metals as a results of their chemical reactivity (greater retardation because of sorption and precipitation). The significance of this observation is that the trace metals would not be effective for detecting the early migration of mine waste leachates because they move more slowly through the subsurface environment than the geochemical parameters that define the leachate fingerprint.

Although the pregnant solution fingerprint has been distorted at Well 1, the actual changes for each of the geochemical parameters are consistent with the initial composition and reactivity of the Arimetco pregnant solution. More importantly, even with the number of parameters that have been influenced by the low pH of the pregnant solution, the original fingerprint pattern is still present and recognizable ($r^2 = 0.744$).

Arimetco Mine Summary

The composition of the Arimetco pregnant leaching solution was distinctively different from the process solutions at other gold mines that have been summarized. Some of the specific differences included a very high total dissolved solids concentration (100,000 mg/L), a very high sulfate concentration (60,000 mg/L), an exceptionally high total trace metals concentration (11,000 mg/L), a very low solution pH (pH = 2), and an absence of cyanide. By comparison, the pregnant solutions at other mines usually had a total dissolved solids concentration of 10,000 mg/L, a sulfate concentration of 5,000 mg/L, a total trace metal concentration of 1 to 10 mg/L, a solution pH of 10, and a cyanide concentration of 10 to 100 mg/L. These differences are due to the fact that the Arimetco Mine uses a strong acid solution, rather than an alkaline cyanide solution, to extract gold from the ore.

Ten sets of survey data from February, 1991 until June, 1993 were obtained for the pregnant leaching solution. The results from this monitoring program produced a consistent geochemical fingerprint that is defined by 60 percent sulfate, 10 percent total trace metals, and 5 percent magnesium ($r^2 = 0.971$). Therefore, the geochemical parameters defined a consistent, reproducible pattern for the pregnant leaching solution even though a different extraction agent was being used. This suggests that the geochemical fingerprinting concept has potential applicability to other types of mining operations other than cyanide heap leaching facilities.

The data set for this mine included two years of quarterly monitoring data for the make up water. This water had a constant relative composition that was defined by 55 percent alkalinity, 15 percent calcium, 15 percent sodium, and 15 percent sulfate. Since the make up water had a reproducible pattern over time ($r^2 = 0.934$) that was distinctively different from the pregnant leaching solution fingerprint ($r^2 = 0.008$), this indicates that the pregnant leaching solution fingerprint is a unique characteristic property of the leaching process used at the mine. This conclusion is consistent with observations at other heap leaching facilities.

The data set for this mine also included results from a single monitoring well. The geochemical parameters defined a consistent pattern for this location ($r^2 = 0.971$). However, this pattern was different from the ground water used as make up water at the plant ($r^2 = 0.118$) and more closely resembled the pregnant leaching solution fingerprint ($r^2 = 0.744$). These results suggest that process solution from the mine may be impacting ground water. The Arimetco process solution fingerprint was modified slightly by the time it reached Well 1. This change was attributed to the neutralization of the initially low solution pH which resulted in an increase in alkalinity, calcium, and a dilution of the sulfate peak. A potentially important observation is the fact that the trace metals, which constitute 10 percent of the pregnant solution fingerprint, were essentially eliminated from the ground-water fingerprint at Well 1. Since the geochemical constituents were present at Well 1 but the trace metals were not, this indicates that the trace metals migrate more slowly and monitoring for trace metals would not provide early detection of migrating mine waste leachates.

5.2.15 Nevada Goldfield Sleeper Mine

The Nevada Goldfield Sleeper Mine is located in the north-western corner of the state. The monitoring records obtained for this facility included quarterly monitoring results from five locations in the process solution (pregnant pond, barren pond, tailings reclaim water, tailings filtrate, and tailings residue), the plant make up water, and 7 monitoring wells. The period of record for this site is February, 1992 until May, 1993.

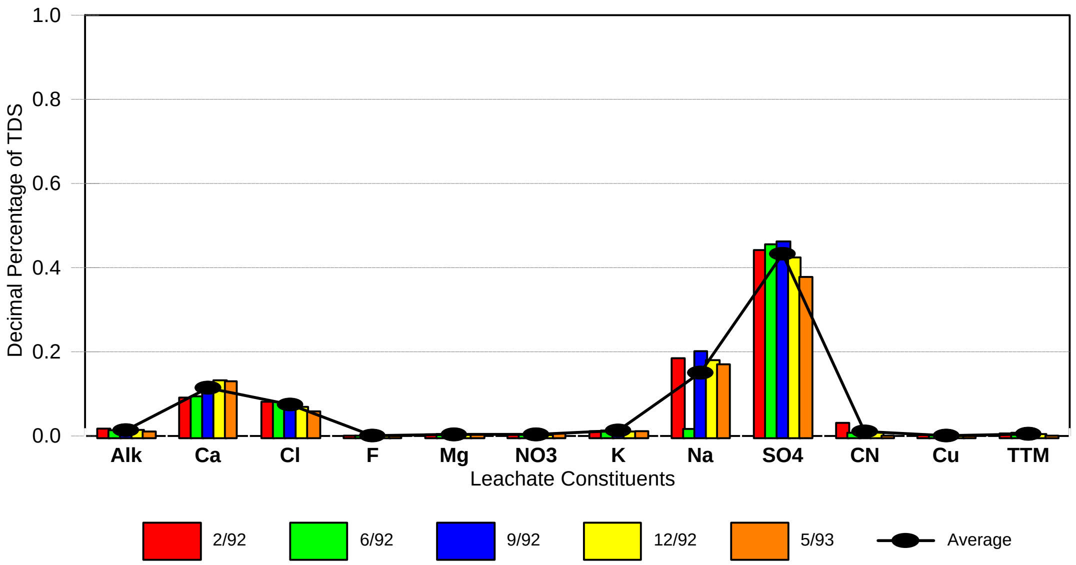
Normalized geochemical monitoring results for five quarterly surveys of the pregnant pond are presented in Figure 5-69. Each of these surveys define a repetitive geochemical fingerprint. The composition of the pregnant pond at the Nevada Goldfield Sleeper Mine is characterized by 40 percent sulfate, 15 percent sodium, 15 percent calcium, and 10 percent chloride.

A regression analysis comparison of the pregnant pond fingerprint pattern produced an r^2 value of 0.934 (a 93 percent match). Although these results suggest that the composition pattern is reproducible over time, an inspection of the results indicate that there is a data quality problem with the sodium results in the June, 1992 survey:

1. The reported sodium concentration in June, 1992 was only 50 mg/L which is considerably below the 450 to 500 mg/L reported for the pregnant pond in the other four surveys. The sodium results for June, 1992 only represented 1.6 percent of the total dissolved solids concentration compared to 15 to 20 percent in the other surveys.
2. The mass balance for the four surveys in February, 1992, September, 1992, December, 1992, and May, 1993 is in the acceptable range of 85 to 90 percent of the total dissolved solids concentration. However, the mass balance for the June, 1992 is unacceptably low at 70 percent of the total dissolved solids concentration.

The combination of factors identified above suggest that the reported sodium results for the June, 1992 survey are in error. If this type of data assessment had been performed at the time the samples were actually analyzed, it would have been possible to check for transcription errors, dilution errors, or, if necessary, reanalyze the sample. In this case, the June, 1992 data were excluded because the sodium data are suspect. A regression analysis comparison of the remaining four surveys produced an r^2 value of 0.990. That is, the reproducibility of the pregnant pond geochemical fingerprint in the remaining surveys is 99 percent.

The Nevada Goldfield Sleeper facility routinely monitors five locations in the recirculating process solution system. These locations, in addition to the pregnant pond, are the barren pond, tailings reclaim water, tailings filtrate, and tailings residue. The monitoring results from each of these locations define a similar geochemical pattern (Figure 5-70). The characteristic features of this pattern are 35 to 40 percent sulfate, 15 to 20 percent sodium, 15 percent calcium, 10 percent chloride,

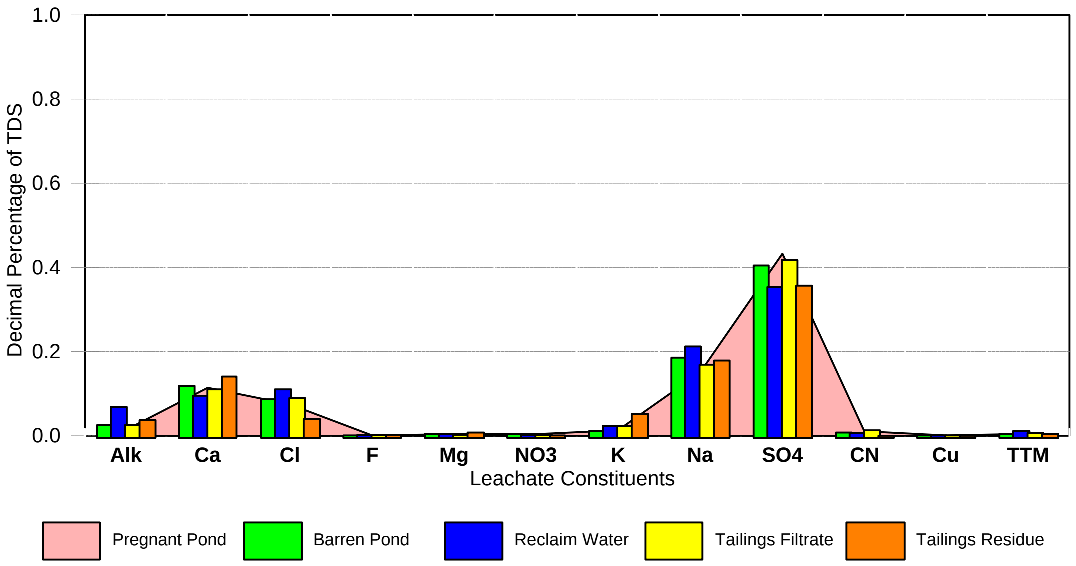


Regression analysis matrix for Nevada Goldfield Sleeper Pregnant Pond

	2/92	**6/92**	**9/92**	**12/92**	**5/93**
2/92	1.000	0.861	0.992	0.986	0.975
6/92		1.000	0.850	0.852	0.830
9/92			1.000	0.998	0.994
12/92				1.000	0.998
5/93					1.000

Average r squared value = 0.934

Figure 5-69. Geochemical fingerprint pattern at the Nevada Goldfield Sleeper Mine.



Regression analysis matrix for Nevada Goldfield Sleeper process solutions

	Barren Pond	Pregnant Pond	Reclaim Water	Filtrate	Tailings Residue
Barren Pond	1.000	0.988	0.966	0.996	0.965
Pregnant Pond		1.000	0.924	0.995	0.951
Reclaim Water			1.000	0.955	0.927
Filtrate				1.000	0.958
Tailings Residue					1.000

Average r squared value = 0.962

Figure 5-70. Comparison of process solution fingerprints at the Nevada Goldfield Sleeper Mine.

and small amounts of alkalinity and potassium. The reproducibility of this pattern, as estimated by regression analysis, is 0.962. A total of 25 surveys from five different sampling locations over a period of 16 months produced an identical fingerprint for the process solution at the Nevada Goldfield Sleeper Mine.

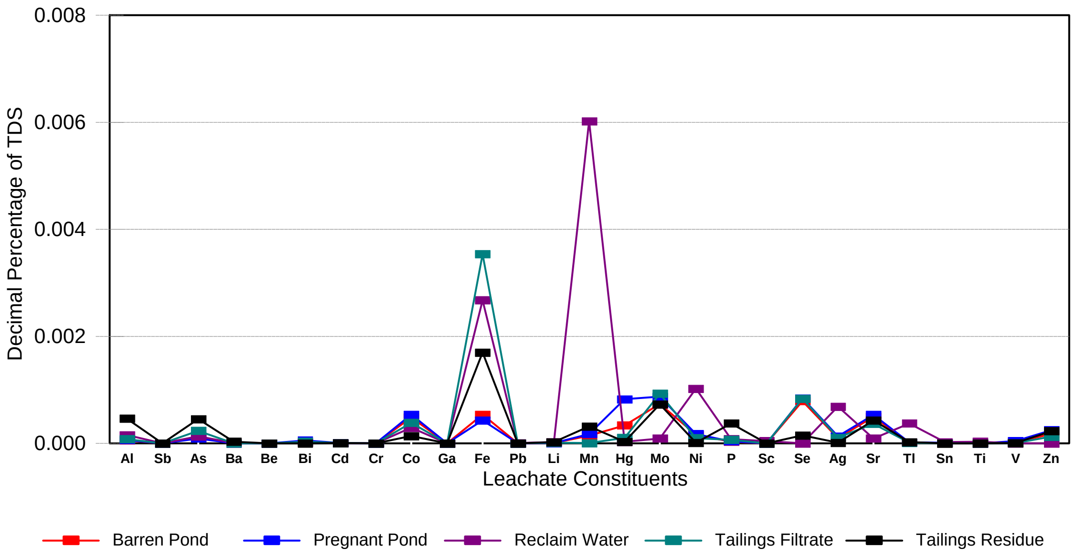
Since the geochemical monitoring results demonstrated the process solution to have a constant composition, the trace metal data were evaluated to identify possible trends with these parameters. The trace metal distribution at each of the five process solution sampling locations are summarized in Figure 5-71. These results indicate that the specific trace metals that are present and the concentrations at which they are present can vary considerably. As a result of the individual trace metal fluctuations, the regression analysis comparison of the trace metal distributions produced a low r^2 value of 0.300 (a 30 percent match between distributions). This evaluation suggests that there is not a constant trace metal fingerprint pattern in the process solution at this mine.

Geochemical monitoring results from the mine make up water are presented in Figure 5-72. These results suggest that the make up water has a constant composition over time. Using data from five quarterly surveys, the reproducibility of this pattern is 87 percent. However, if the March, 1993 data set is excluded because of data quality concerns (chloride and sulfate are biased low, the mass balance for the survey is only 56 percent of the total dissolved solids concentration, and the charge balance is off by 101 percent), the reproducibility of the make up water fingerprint increases to more than 98 percent ($r^2 = 0.987$). Thus, the make up water also has a unique chemical signature or fingerprint.

The make up water fingerprint is distinctively different from the process solution fingerprint at the mine. The make up water has a higher relative abundance of alkalinity, chloride, and sodium and a lower relative abundance of calcium and sulfate (Figure 5-72). Based on these consistent differences, the composition of the make up water is altered after it is used in the leaching process and the resultant fingerprint pattern is a characteristic property of the process solution.

The Nevada Goldfield Sleeper process solution fingerprint is compared to ground-water monitoring results from Well OH-36M in Figure 5-73. The ground water at OH-36M has a reproducible geochemical pattern ($r^2 = 0.907$) that has a higher abundance of alkalinity, chloride, and sodium than the process solution and a lower abundance of calcium and sulfate than the process solution. These compositional differences are identical to those identified when comparing the plant make up water to the process solution (Figure 5-72). In fact, the ground-water fingerprint is an identical match to the make up water fingerprint ($r^2 = 0.980$) and distinguishable from the process solution fingerprint ($r^2 = 0.310$). These results suggest that ground water similar to that at Well OH-36M is used as plant make up water and that the ground water in the vicinity of Well OH-36M has not been impacted by process solution fingerprint.

Ground-water monitoring results from five of the wells at Nevada Goldfield Sleeper are similar to those presented in Figure 5-73. The geochemical pattern is similar to the make up water fingerprint and unlike the process solution fingerprint. These observations support the conclusion that ground water at these locations has not been impacted by operations at the mine. However, at two monitoring wells, a shift in the ground-water composition has occurred. The ground-water fingerprint at Well EP-1 has a lower abundance of alkalinity than the make up water, a lower abundance of sodium than the make up water, and a higher abundance of sulfate than the make up water (Figure 5-74). As a result of this compositional shift, the ground water fingerprint at Well EP1 has a reduced similarity to the make up water ($r^2 = 0.688$) and an increased comparability to the

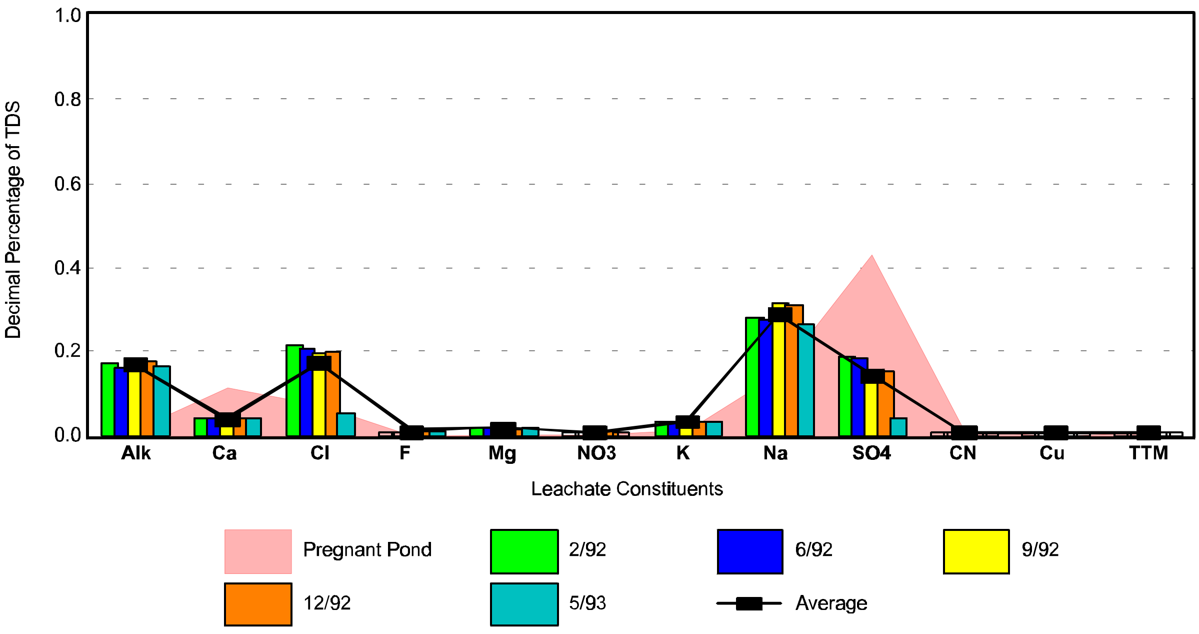


Regression analysis matrix for Nevada Goldfield Sleeper trace metal results

	Barren Pond	Pregnant Pond	Reclaim Water	Filtrate	Tailings Residue
Barren Pond	1.000	0.889	0.016	0.386	0.299
Pregnant Pond		1.000	0.004	0.198	0.154
Reclaim Water			1.000	0.094	0.152
Filtrate				1.000	0.813
Tailings Residue					1.000

Average r squared value = 0.300

Figure 5-71. Trace metal distributions in Nevada Goldfield Sleeper process solutions.

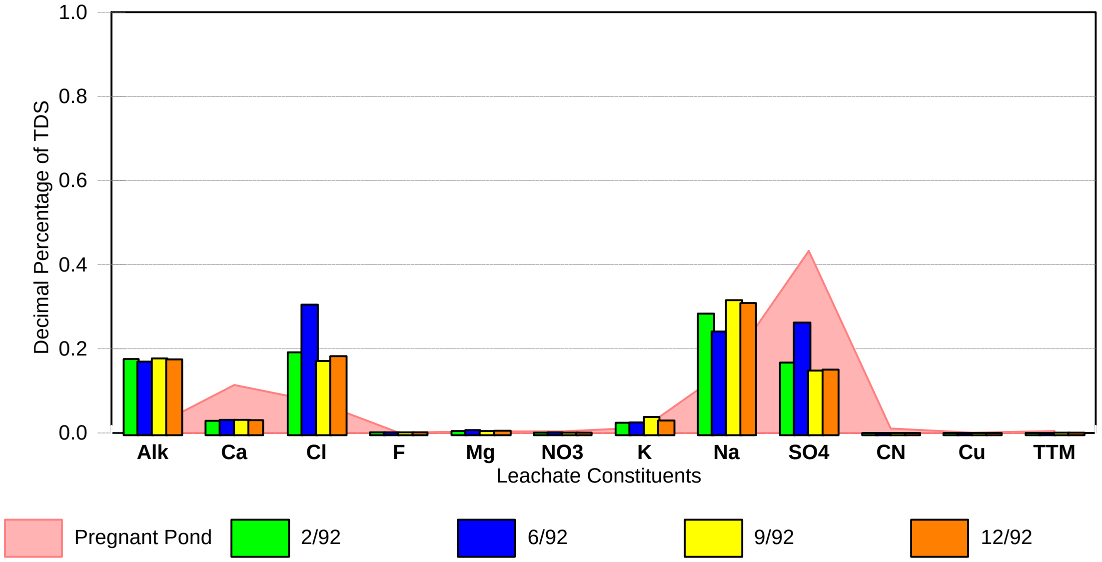


Regression analysis matrix for Nevada Goldfield Sleeper make up water

	2/92	6/92	9/92	12/92	5/93
Pregnant Pond	0.324	0.333	0.249	0.240	0.048
2/92	1.000	0.999	0.982	0.982	0.654
6/92		1.000	0.981	0.981	0.644
9/92			1.000	0.999	0.760
12/92				1.000	0.761
5/93					1.000

Average r squared value = 0.874
Pregnant pond - make up water comparison = 0.239

Figure 5-72. Comparison of the Nevada Goldfield Sleeper process solution fingerprint to the make up water fingerprint.

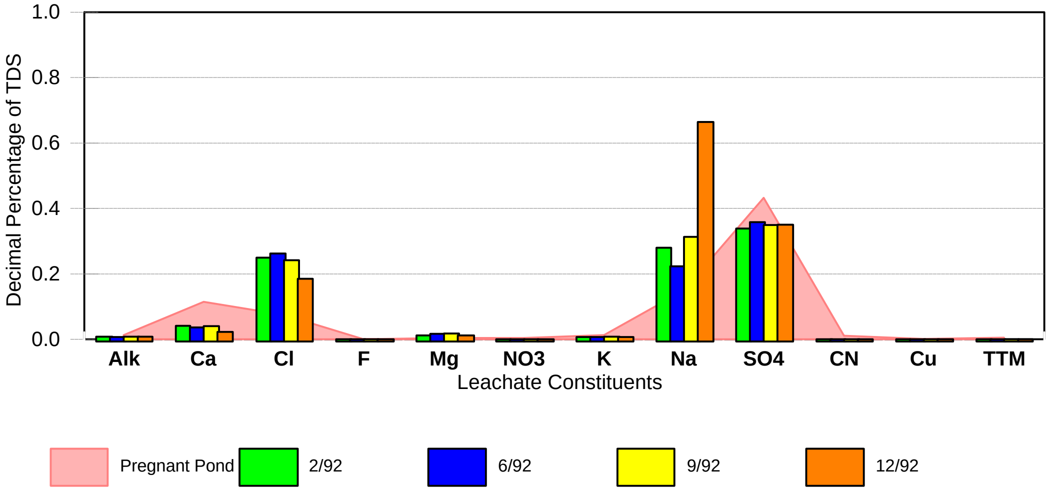


Regression analysis matrix for Sleeper Well OH-36M

	Sampling Date			
	2/92	**6/92**	**9/92**	**12/92**
2/92	1.000	0.873	0.984	0.992
6/92		1.000	0.783	0.812
9/92			1.000	0.998
12/92				1.000

Average r squared value = 0.907
Ground water - pregnant pond comparison = 0.310
Ground water - make up water comparison = 0.980

Figure 5-73. Comparison of monitoring results from Well OH-36M to the Nevada Goldfield Sleeper process solution.



Regression analysis matrix for Sleeper Well EP-1

	Sampling Date			
	2/92	**6/92**	**9/92**	**12/92**
2/92	1.000	0.980	0.996	0.749
6/92		1.000	0.961	0.621
9/92			1.000	0.799
12/92				1.000

Average r squared value = 0.851
Ground water - pregnant pond comparison = 0.637
Ground water - make up water comparison = 0.688

Figure 5-74. Comparison of monitoring results at Well EP1 to the Nevada Goldfield Sleeper process solution fingerprint.

process solution fingerprint ($r^2 = 0.637$). Although the transition has not been complete, the characteristic changes that have occurred suggest that the ground water in the vicinity of Well EP1 has been impacted.

Nevada Goldfield Sleeper Summary

The monitoring records from this site provide another positive example of the potential to use geochemical parameters to fingerprint the composition of process solution at heap leaching facilities. Geochemical monitoring results from 25 sampling events, five surveys at each of five separate sampling locations, produced an identical fingerprint pattern with a reproducibility of 96 percent. The characteristic features of this fingerprint were 40 percent sulfate, 15 to 20 percent sodium, 15 percent calcium, and 10 percent sodium.

The site monitoring data from this mine also illustrated three characteristics of the process solution composition. First, the trace metal content of the solution was highly variable. As a result, it was not possible to define a trace metal fingerprint. Second, the geochemical fingerprint of the process solution was different from the fingerprint for plant make up water and ground water. Consequently, the geochemical fingerprint pattern can be used to differentiate process solution from other water supplies. Third, the data from two wells suggests that the process solution fingerprint remains intact as the mine waste leachate migrates from the source. Therefore, the fingerprint provides a means to monitor the migration of mine waste leachates. Each of these properties of the process solution fingerprint have been observed in data sets from other mines.

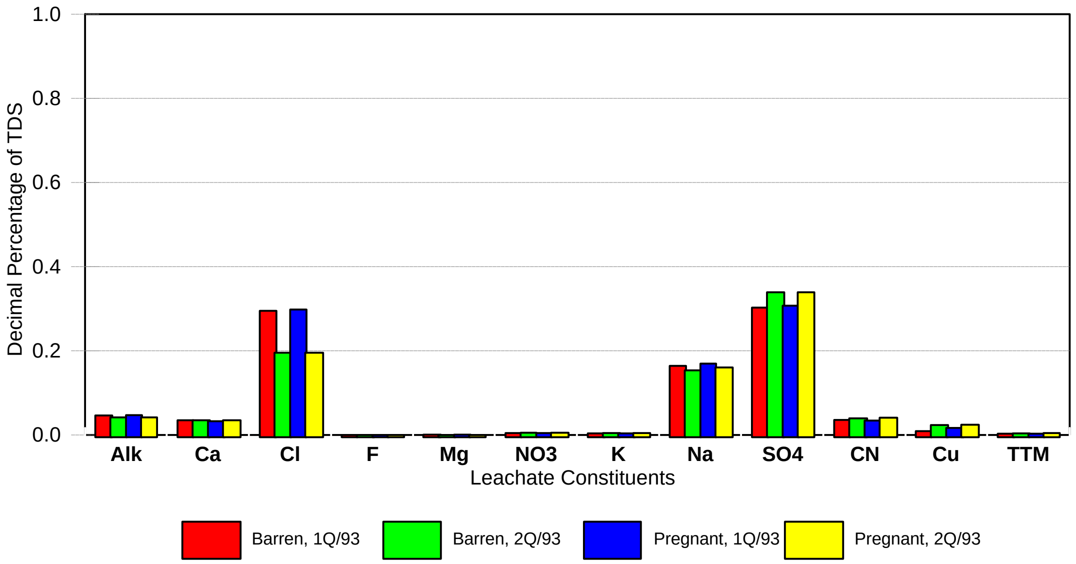
Another feature of the fingerprinting concept that was illustrated with this example was the built in quality control checks on the data. Since the geochemical ions represent essentially all of the total dissolved solids in solution, two effective checks are to compare the sum of the ions with the total dissolved solids concentration and to compare the sum of the cations (in meq/L) with the sum of the anions (in meq/L). In this case, the data evaluation identified anomalous results for chloride and sulfate in the make up water. When these data were excluded because of data quality concerns, a regression analysis of the remaining data demonstrated the make up water to have a characteristic, reproducible fingerprint that was different from the mine process solution.

5.2.16 Corona Gold Mine

The search of monitoring records produced a small amount of information for this heap leaching facility located in western Nevada. The data set for the Corona Mine consists of two quarters of monitoring results for the barren pond and the pregnant pond and two quarters of data from two monitoring wells.

Four sets of monitoring results for the Corona process solution have been summarized in Figure 5-75. Although there is a little uncertainty associated with the height of the chloride peak, these results suggest that this process solution has a consistent ionic composition. The pattern is characterized by 30 to 35 percent sulfate, 20 to 25 percent chloride, 15 percent sodium, and less than five percent each of alkalinity, calcium, cyanide, and copper. The estimated reproducibility of this fingerprint is 94.8 percent.

The data set for this mine is small and the period of record is very short. Therefore, it could be argued that the high degree of reproducibility in the geochemical pattern is an artifact of the limited amount of data. However, when viewed from the larger perspective that the same set of geochemical



Regression analysis matrix for geochemical parameters in Corona Process water

	Barren Pond 1	Barrren Pond 2	Pregnant Pond 1	Pregnant Pond 2
Barren Pond 1	1.000	0.922	1.000	0.922
Barren Pond 2		1.000	0.923	1.000
Pregnant Pond 1			1.000	0.923
Pregnant Pond 2				1.000

Average r squared value = 0.948

Figure 5-75. Geochemical fingerprint pattern for process solution at the Corona Gold Mine.

parameters defined a reproducible ionic pattern at all 15 mines that have previously been evaluated, these results provide additional evidence that heap leaching process solutions can be uniquely characterized at their source based on their ionic composition.

Monitoring results from the two Corona wells have been summarized in Figure 5-76. These data suggest that the ground water has a characteristic geochemical pattern in which alkalinity is the most abundant ion. The estimated reproducibility of the ground water fingerprint is 91 percent (r^2 = 0.914).

There are several differences between the ground-water and Corona process solution fingerprints. As indicated in Figure 5-76, the ground water consistently has a higher relative abundance of alkalinity and a lower abundance of chloride, sodium, and sulfate. Based on these differences, there is a low degree of similarity between these two fingerprints (r^2 = 0.291) which should make it feasible to use the geochemical fingerprint to detect and monitor the migration of mine process solution through the environment. However, at this time, neither ground-water monitoring location appears to be impacted by the nearby mine.

Corona Gold Mine Summary

The data file for this mine only contained a limited amount of information. However, these data still demonstrated two useful properties of heap leaching process solution fingerprints that have been observed at other sites. First, the geochemical parameters defined a characteristic composition pattern for the process solution. The reproducibility of this fingerprint was estimated to be 94.8 percent. Second, the ground water in the vicinity of the mining operation had a distinctive but different fingerprint. The characteristic differences in composition should make it possible to unequivocally identify any process solution that may be spilled or escape containment at the mine.

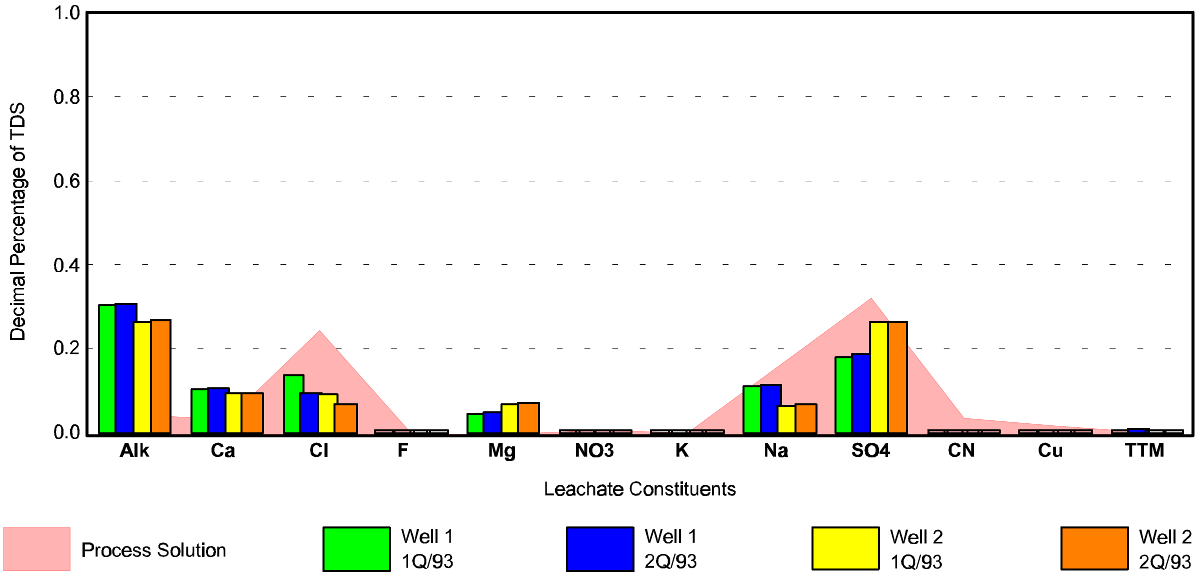
5.2.17 Bullfrog Gold Mine

This mine is located in west-central Nevada. The monitoring records include data for tailings water, tailings residual, plant make up water, and two monitoring wells. However, the period of record is short and consists of only two sets of quarterly monitoring data.

The geochemical monitoring results for the Bullfrog tailings water are presented as modified Stiff Diagrams or histograms in Figure 5-77. These data demonstrate that the tailings water at this facility has a constant composition in which sodium and sulfate represent 75 to 80 percent of the total dissolved solids concentration. The reproducibility of this fingerprint pattern is 98.8 percent.

The exact shape of the process solution and tailings water fingerprint may vary from mine to mine. For example, the Bullfrog tailings water fingerprint is very similar to the pregnant pond fingerprint at the Alligator Ridge Mine (Figure 5-12) but it is very different from the Lone Pine pregnant pond fingerprint (Figure 5-2). Although all mine leachates do not share the same fingerprint pattern, it is important to recognize that the same set of geochemical parameters (alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, and sulfate) has defined a unique multi-ion pattern that characterized the process solutions at each mine with a high level of reproducibility (generally greater than 90 percent).

The fingerprint for the water supply wells at the Bullfrog Mine is presented in Figure 5-78. Each of these wells must withdraw water from the same aquifer because the geochemical pattern is identical

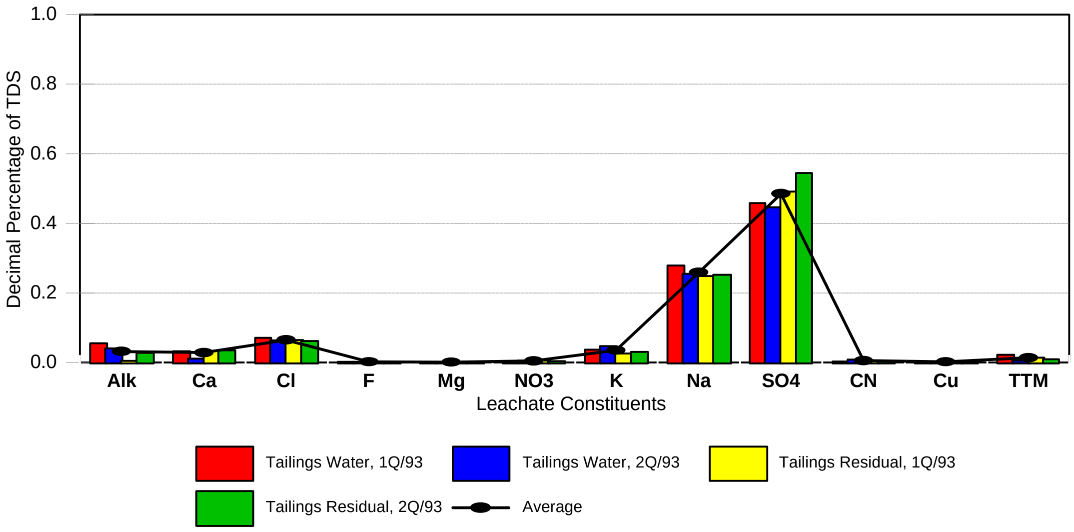


Regression analysis matrix for Corona ground water.

	Well 1 1Q/93	Well 1 2Q/93	Well 2 1Q/93	Well 2 2Q/93
Pregnant Solution	0.279	0.225	0.353	0.306
Well 1 1Q/93	1.000	0.981	0.867	0.851
Well 1 2Q/93		1.000	0.893	0.894
Well 2 1Q/93			1.000	0.995
Well 2 2Q/93				1.000

Average r squared value = 0.914
Ground water - process solution comparison = 0.291

Figure 5-76. Comparison of ground-water monitoring results to the Corona process solution fingerprint pattern.

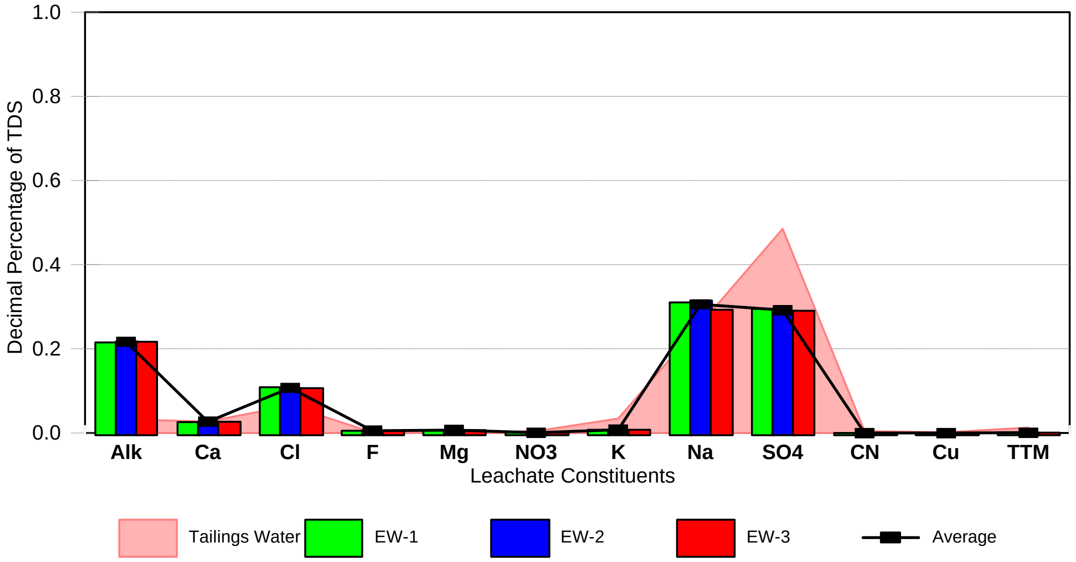


Regression analysis matrix for Bullfrog Tailings Water

Sampling Location & Date		Tailings Water 1Q/93	Tailings Water 2Q/93	Tailings Residue 1Q/93	Tailings Residue 2Q/93
Tailings Water	**1 Q/93**	1.000	0.995	0.983	0.981
Tailings Water	**2 Q/93**		1.000	0.987	0.986
Tailings Residue	**1 Q/93**			1.000	0.996
Tailings Residue	**2 Q/93**				1.000

Average r squared value = 0.988

Figure 5-77. Geochemical fingerprint pattern for tailings water at the Bullfrog Mine.



Regression analysis matrix for Bullfrog make up water

	Sampling Location		
	Well EW-1	**Well EW-2**	**Well EW-3**
Tailings Water	0.684	0.671	0.681
Well EW-1	1.000	1.000	0.999
Well EW-2		1.000	0.998
Well EW-3			1.000

Average r squared value = 0.999
Make up water - tailings water comparison = 0.679

Figure 5-78. Comparison of the water supply fingerprint to the tailings water fingerprint at the Bullfrog Mine.

($r^2 = 0.999$). The dominant ions of the water supply fingerprint are alkalinity, sodium, and sulfate that represent 80 percent of the total dissolved solids concentration.

The differences between the water supply fingerprint and the tailings water fingerprint are not as dramatic or pronounced as they were at other mining sites. This is due to the fact that sodium and sulfate are major ions in both fingerprints. However, these two patterns can still be distinguished from each other by regression analysis because the degree of similarity is only 68 percent (Figure 5-78).

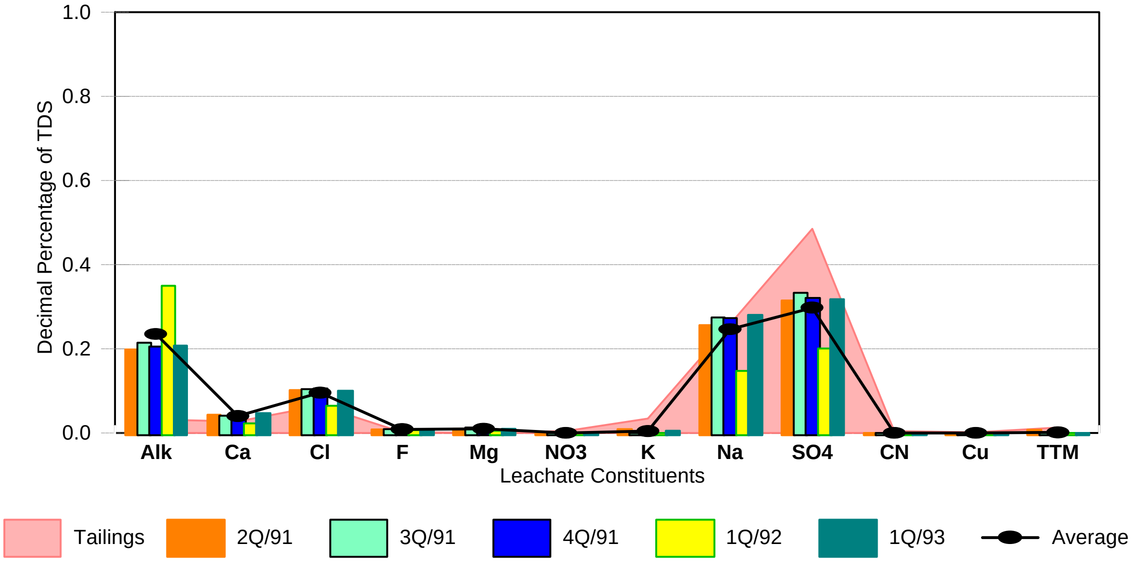
Geochemical monitoring results from Bullfrog Well 1 are compared to the tailings water fingerprint in Figure 5-79. This comparison is very similar to the water supply - tailings water comparison in Figure 5-78. The ground water at Well 1 has the same three principle components as the water supply wells (alkalinity, sodium, and sulfate). The similarity of the ground water and water supply fingerprints is estimated to be almost 93 percent ($r^2 = 0.926$). In contrast, the similarity of the ground-water fingerprint at Well 1 to the tailings water fingerprint is only 65 percent. The analysis of fingerprint patterns suggests that Well 1 has not been impacted by tailings water from the Bullfrog Mine.

All of the Well 1 monitoring results were used in the fingerprint assessment summarized above. However, an inspection of the results from the first quarter, 1992 survey suggest that these data may be suspect. The following factors indicate one or more data quality problems with this survey:

1. The alkalinity is reported as 653 mg/L compared to a range of 219 to 230 mg/L in the other four surveys. This would explain the apparently anomalous alkalinity spike in the first quarter, 1992 fingerprint (Figure 5-79).
2. The reported total dissolved solids concentration was 1140 mg/L which is outside the range of 650 to 706 mg/L reported in the other four surveys. Since the fingerprint in Figure 5-79 is based on normalized concentrations (actual concentrations divided by total dissolved solids concentration), a total dissolved solids concentration that is biased high would explain the apparently low results for both sodium and sulfate in the first quarter, 1992 fingerprint.
3. A mass balance of the first quarter, 1992 survey indicates that the sum of the ions only represents 79 percent of the total dissolved solids concentration. Although this is only marginally outside reasonable data quality limits of 80 to 120 percent, it indicates that one or more of the analyses are low or the total dissolved solids concentration is high.
4. Finally, an anion - cation balance using the first quarter, 1992 results indicates that the charge balance is off by - 39 percent (i.e., an excess of anions over cations). An erroneously high alkalinity concentration would explain this charge imbalance which is outside reasonable data quality limits of -20 to +20 percent.

The combination of a high alkalinity result and a high total dissolved solids concentration would explain the distortions of the ground-water fingerprint in the first quarter, 1992 survey, the low mass balance, and the charge imbalance.

An active quality assurance program could identify and correct the cause of the erroneous data. Since this is not feasible with three year old data, the first quarter, 1992 survey was excluded to examine the effect of removing suspect data on the fingerprint recognition process. After deleting the first quarter 1992 survey, the reproducibility of the geochemical fingerprint defined in the



Regression analysis matrix for Bullfrog Well 1

	Sampling Date				
	2Q/91	**3Q/91**	**4Q/91**	**1Q/92**	**1Q/93**
Tailings Water	0.760	0.750	0.750	249.000	0.741
Make up Water	0.980	0.982	0.985	0.692	0.989
2Q/91	1.000	0.999	0.999	0.686	0.998
3Q/91		1.000	0.999	0.696	0.998
4Q/91			1.000	0.685	0.999
1Q/92				1.000	0.686
1Q/93					1.000

Average r squared value = 0.841
Ground water - tailings water comparison = 0.650
Ground water - make up water comparison = 0.926

Figure 5-79. Comparison of monitoring results at Well 1 to the Bullfrog tailings water fingerprint.

remaining four surveys increases from 89 percent to 99 percent. Also, the match between the ground-water pattern at Well 1 and the plant water supply increases from 92 percent to 98 percent. The remaining data sets still indicate that there is a reproducible ground-water fingerprint at Well 1 that matches the plant make up water fingerprint. However, the exclusion of suspect data produces an improved resolution of the fingerprint pattern and an assessment of its comparability to other sources.

Bullfrog Gold Mine Summary

The monitoring data from this facility demonstrated two properties of the process solution fingerprint that have been observed at other sites. First, the common geochemical parameters defined a characteristic pattern with a high degree of reproducibility (98 percent). The tailings water fingerprint at the Bullfrog Mine consisted of 50 percent sulfate, 25 to 30 percent sodium, and small amounts of the remaining geochemical parameters. Second, the plant make up water and local ground water also had a characteristic geochemical fingerprint that could be graphically and statistically differentiated from the tailings water fingerprint. Based on a fingerprint assessment, ground water is not being impacted by operations at the Bullfrog Mine.

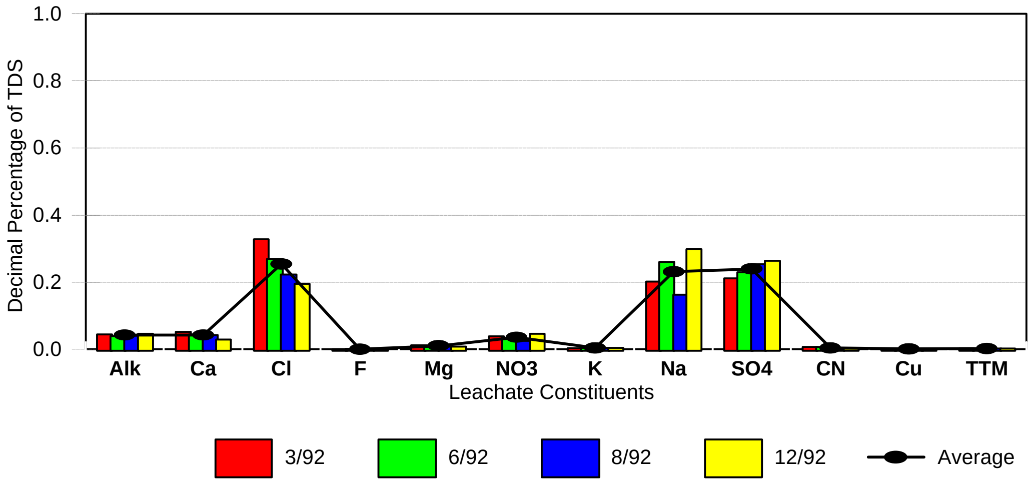
The primary objective of this investigation was to identify a set of parameters that can be used for monitoring of mining sites. Each of the data sets that have been reviewed suggest that the common geochemical parameters can be used for this purpose. The geochemical parameters define a distinctive fingerprint that characterizes mine leachates at the source, retains its chemical identity as the leachates migrate, and differentiates mine leachates from regional ground water. In addition, the geochemical parameters can fulfill a second function by providing a method to assess and control the quality of the monitoring results. This added benefit is possible because the sum of the geochemical ions must equal the total dissolved solids concentration and the sum of the cations must equal the sum of the anions. As shown with the Bullfrog example, it was possible to use the concepts of mass balance and charge balance to identify and flag data of suspect quality. The subsequent evaluation of acceptable quality data produced a more precise estimate of the fingerprint pattern.

5.2.18 Marigold Gold Mine

The Marigold Mine is a northern Nevada heap leaching facility. The required monitoring being conducted at this facility includes quarterly monitoring at several process solution locations (pregnant pond, barren pond, and tailings reclaim water), three water supply wells, and 15 locations around the heap leaching pad and the tailings disposal basin. Unfortunately, most of the wells were reported as dry and ground-water data are only reported for a single location.

The site file contained four surveys of the pregnant pond. These results are presented in Figure 5-80. As has been observed at other heap leaching facilities, the geochemical parameters define a recurring pattern for this solution. The three most abundant ions are chloride, sulfate, and sodium and the reproducibility of this signature is estimated to be almost 90 percent ($r^2 = 0.897$).

The Marigold file also contained four sets of quarterly survey results for the barren pond. The geochemical data from these surveys are compared to the pregnant pond fingerprint in Figure 5-81. These results also describe a repetitious pattern in which chloride, sodium, and sulfate are the dominant ions. The reproducibility of the barren pond fingerprint is 91 percent. More importantly, except for small fluctuations in the height of the sodium peak, the barren pond fingerprint is identical to the pregnant pond fingerprint ($r^2 = .916$). Thus, the Marigold Mine provides another example for

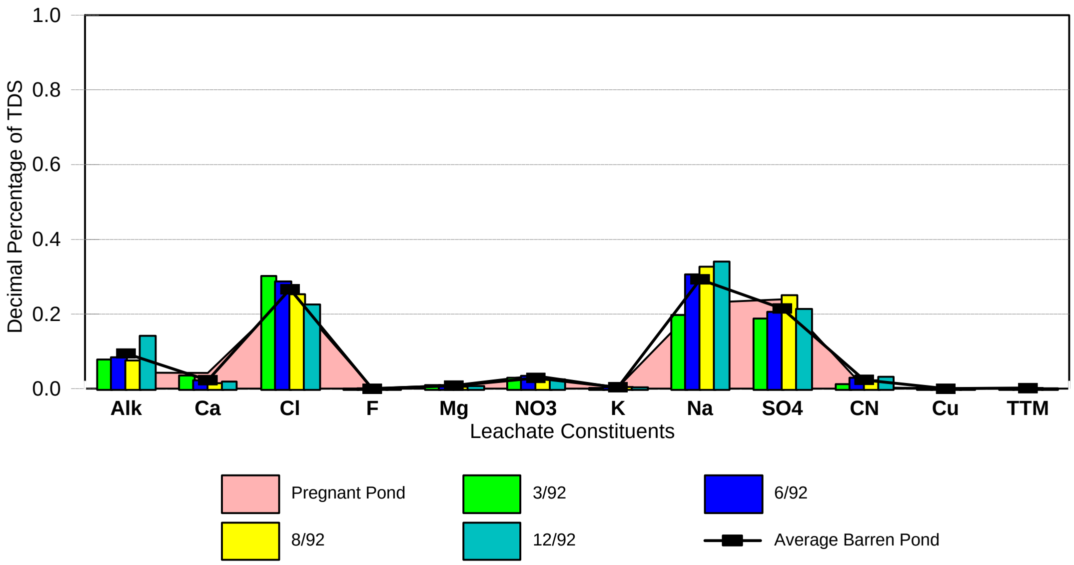


Regression analysis matrix for Marigold pregnant pond

	Sampling Date			
	3/92	**6/92**	**8/92**	**12/92**
3/92	1.000	0.945	0.912	0.787
6/92		1.000	0.928	0.937
8/92			1.000	0.872
12/92				1.000

Average r squared value = 0.897

Figure 5-80. Geochemical fingerprint pattern for the Marigold Mine pregnant pond solution.



Regression analysis matrix for Marigold barren pond

	Sampling Date			
	3/92	**6/92**	**8/92**	**12/92**
3/92	1.000	0.930	0.871	0.802
6/92		1.000	0.977	0.945
8/92			1.000	0.958
12/92				1.000

Average r squared value = 0.914
Pregnant pond barren pond comparison = 0.916

Figure 5-81. Comparison of barren pond monitoring results to the Marigold pregnant pond fingerprint pattern.

which the geochemical monitoring parameters define a consistent fingerprint pattern for the facility process solution.

The Marigold make up water is derived from three wells. Monitoring results from two annual sampling events at each of these locations are compared with the process solution fingerprint in Figure 5-82, These results illustrate two important points. First, the make up water has a distinctive fingerprint pattern. This alkalinity-rich pattern, which is common for most natural water systems, has a reproducibility of 95 percent. Second, the process solution is distinctly different from the make up water fingerprint. The similarity of the two fingerprints is less than 15 percent ($r^2 = 0.147$).

The monitoring results summarized in Figure 5-82 indicate that the make up water added to the barren pond has a constant composition over time. However, since the mine process solution also has a constant composition that is discernably different from the make up water composition, the preparation of the barren solution and the heap leaching process itself must cause a distinctive shift in composition. Consequently, the resultant process solution fingerprint must be a unique property of the leaching solution.

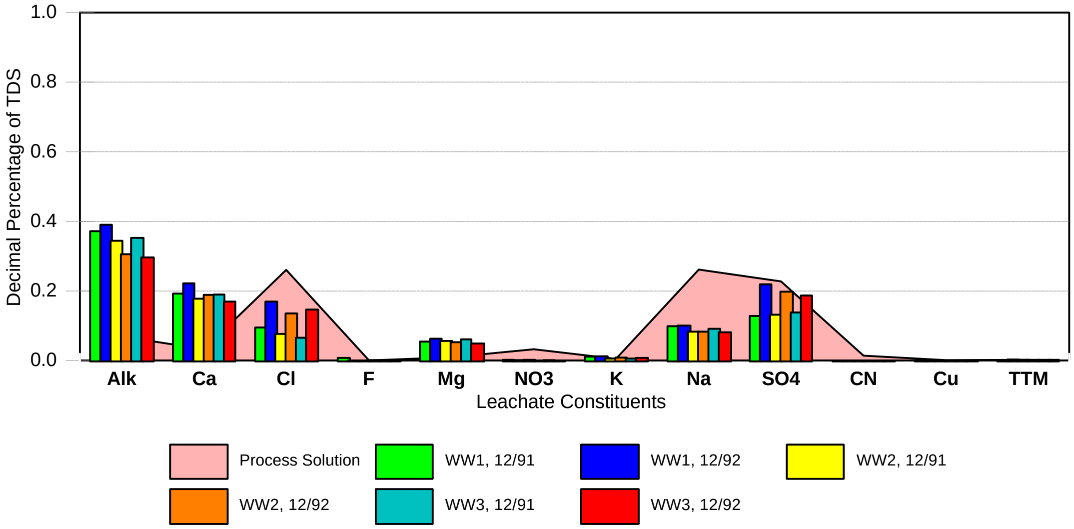
Geochemical monitoring results from a single well in the vicinity of the tailings pond are compared to the process solution fingerprint in Figure 5-83. The ground water at Well MMCPZ5 has a reproducible signature ($r^2 = 0.944$). However, when compared to the make up water fingerprint, the abundance of several geochemical parameters have been altered at Well MMCPZ5. The alkalinity peak has been lost and the calcium peak has been reduced while the chloride peak is up substantially and the sodium and sulfate peaks are up slightly. As a results of these changes, the ground water at Well MMCPZ5 does not resemble the ground water used as make up water ($r^2 = 0.105$) but has an increased comparability to the process solution fingerprint (0.714). This assessment suggests that tailings leachate is impacting the ground water in the vicinity of the monitoring well.

Marigold Gold Mine Summary

The historical records from this mine provided another small set of data to characterize the process solutions at a heap leaching facility. The geochemical data from eight surveys of the pregnant pond and barren pond defined a similar chemical signature characterized by 30 percent chloride, 30 percent sodium, and 20 percent sulfate. The reproducibility of this pattern was estimated by regression analysis to by 91 percent ($r^2 = 0.916$). Marigold process solution was distinguishable from both plant make up water and local ground water based on the fingerprint pattern defined by the common geochemical parameters. In addition, the monitoring results from Well MMCPZ5 suggest that the process solution can maintain its chemical identity as it migrates through the subsurface environment. These properties suggest that the geochemical fingerprints can be useful for uniquely characterizing the composition of mine process solutions at their source and monitoring their movement following an accidental spill or leakage event.

5.2.19 Chimney Creek Gold Mine

The Chimney Creek Gold Mine is another heap leaching facility located in northern Nevada. The data set for this facility did not contain any monitoring data for the pregnant pond or barren pond. However, the data set included five quarterly surveys for tailings water, five surveys of tailings reclaim water, five surveys of fresh water (assumed to be plant make up water), and five surveys at each of three monitoring wells. The period of record for this mine is late 1989 until early 1992.

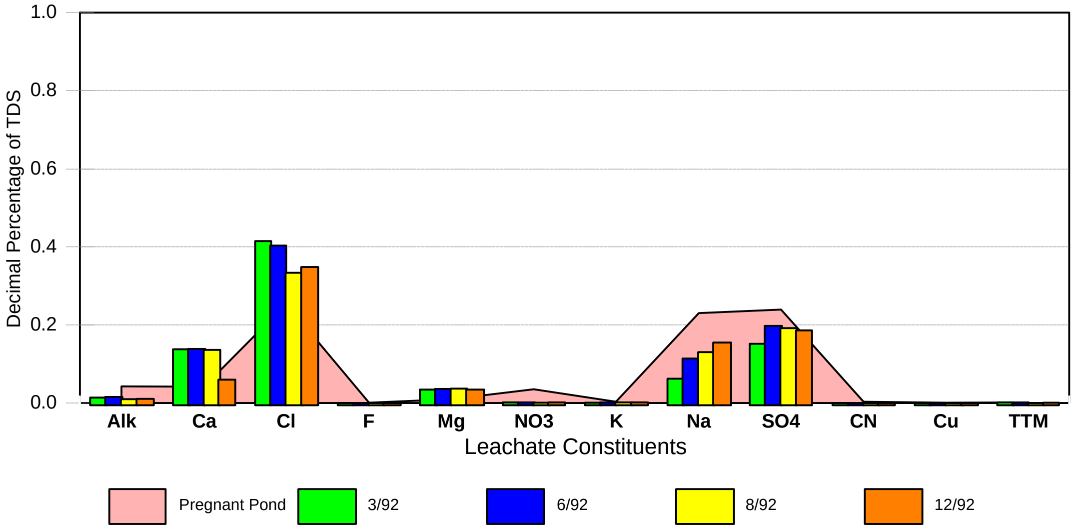


Regression analysis matrix for Marigold make up water

	Sampling Location and Date					
	WW1 12/91	**WW1 12/92**	**WW2 12/91**	**WW2 12/92**	**WW3 12/91**	**WW3 12/92**
Pregnant Pond	0.089	0.192	0.081	0.211	0.074	0.236
WW1 12/91	1.000	0.945	0.996	0.918	0.992	0.911
WW1 12/92		1.000	0.949	0.995	0.936	0.995
WW2 12/91			1.000	0.927	0.998	0.916
WW2 12/92				1.000	0.916	0.996
WW3 12/91					1.000	0.901
WW3 12/92						1.000

Average r squared value = 0.953
Make up water - pregnant pond comparison = 0.147

Figure 5-82. Comparison of the make up water composition to the Marigold Mine process solution fingerprint.



Regression analysis matrix for Marigold Well MMCPZ5

	Sampling Date			
	3/92	**6/92**	**8/92**	**12/92**
Pregnant Pond	0.560	0.703	0.767	0.846
Make up Water	0.097	0.116	0.126	0.082
3/92	1.000	0.975	0.929	0.878
6/92		1.000	0.986	0.946
8/92			1.000	0.951
12/92				1.000

Average r squared value = 0.944
Well MMCPZ5 - pregnant pond comparison = 0.714
Well MMCPZ5 - make up water comparison = 0.105

Figure 5-83. Comparison of monitoring results from Well MMCPZ5 to the Marigold process solution fingerprint.

The geochemical results from five surveys of the tailings water are summarized in Figure 5-84. This pattern is similar to the process solution fingerprint at the Rabbit Creek Mine (Figure 5-27) and the Alta Gold Mine (Figure 5-51). However, the fingerprint at the Chimney Creek Mine is more variable as indicated by the average regression coefficient r^2 value of only 0.645.

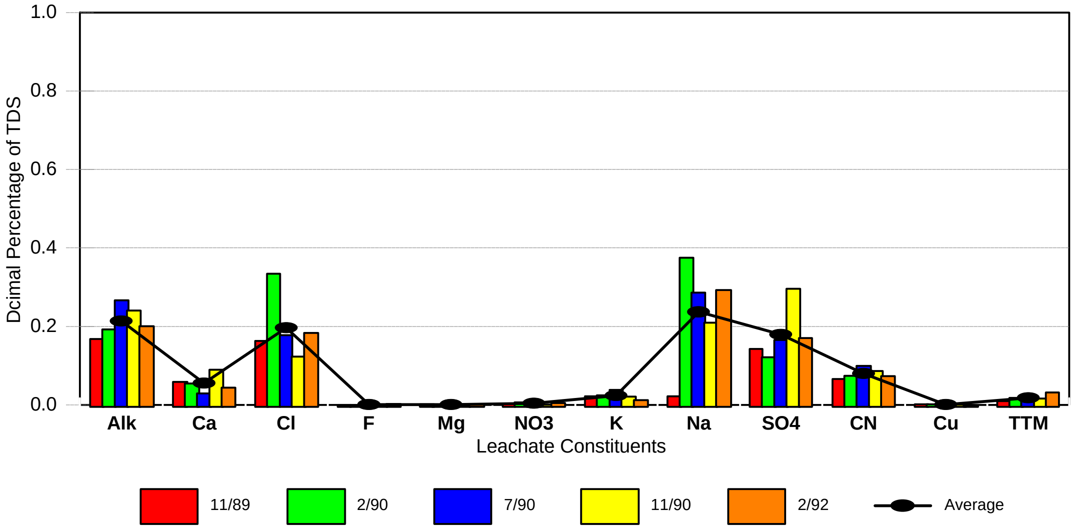
The probable cause for the low reproducibility of the Chimney Creek tailings water fingerprint is that the data are of suspect quality. The following observations support this assessment:

1. The mass balance for the December, 1989 survey is only 66 percent which is outside project data quality objective limits of 80 percent to 120 percent. An inspection of the normalized data in Figure 5-84 suggests that the reported sodium value is in error. The December, 1989 value represents less than five percent of the total dissolved solids concentration whereas sodium represents approximately 30 percent of the total dissolved solids concentration in all other surveys.
2. The charge balance for the December, 1989 survey is -78 percent (i.e., an excess of anions over cations). This is consistent with the low sodium value reported for the sampling event.
3. The mass balance for the February, 1990 survey is 120 percent of the total dissolved solids concentration. Analysis that appear to be biased high are sodium and chloride. Although the mass balance is within the project data quality objective range of 80 percent to 120 percent, it contrasts with the low recovery in the previous survey and increases inter-survey variability.
4. The sulfate result in the October, 1990 survey is approximately double the reported concentration in other surveys.

The suspect data could have been flagged sooner and corrected if routine mass balance and mass balance calculations had been applied when the samples were first analyzed.

The geochemical data for the tailings reclaim water are compared to the Chimney Creek tailings water fingerprint in Figure 5-85. These data suggest a repetitive composition pattern in which sodium is the most abundant constituent (30 percent), chloride and sulfate are the second most abundant constituents (20 percent), and alkalinity is the third most abundant constituent (15 percent). This pattern is similar to the tailings water fingerprint but the regression analysis comparison ($r^2 = 0.746$) is smaller than that calculated at other mining sites. Again, the causative factor appears to be data of suspect quality:

1. Data quality problems create uncertainty in the average values for the tailings water fingerprint.
2. The mass balance for the December, 1989 survey is only 78 percent which is outside project data quality objective limits of 80 percent to 120 percent.
3. The mass balance for the February, 1990 and February, 1992 surveys are 116 percent and 119 percent, respectively. Although these results are in the acceptable range, they contribute to inter-survey variability.
4. The charge balance for the December, 1989 survey is +39 percent which indicates an excess of cations over anions. The low alkalinity value in this survey would explain the charge imbalance and the low mass balance.

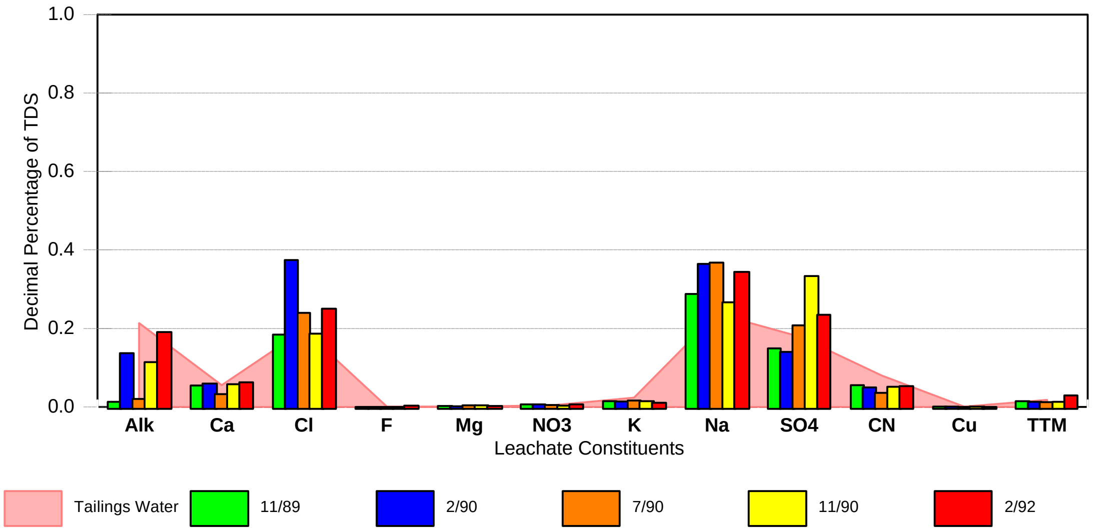


Regression analysis matrix for Chimney Creek Tailings Water

	Sampling Date				
	11/89	**2/90**	**7/90**	**11/90**	**2/92**
11/89	1.000	0.331	0.475	0.603	0.411
2/90		1.000	0.796	0.469	0.877
7/90			1.000	0.770	0.095
11/90				1.000	0.762
2/92					1.000

Average r squared value = 0.645

Figure 5-84. Tailings water fingerprint at the Chimney Creek Mine.



Regression analysis matrix for Chimney Creek Tailings Reclaim Water

	Sampling Date				
	11/89	**2/90**	**7/90**	**11/90**	**2/92**
Tailings Water	0.625	0.77	0.641	0.759	0.936
11/89	1.000	0.833	0.989	0.736	0.816
2/90		1.000	0.839	0.608	0.866
7/90			1.000	0.776	0.842
11/90				1.000	0.859
2/92					1.000

Average r squared value = 0.815
Tailings water - Reclaim water comparison = 0.746

Figure 5-85. Comparison of tailings reclaim data to the Chimney Creek tailings water fingerprint.

The monitoring results suggest that the tailings water and the tailings reclaim water at the Chimney Creek Mine have the same qualitative fingerprint. This agrees with observations at other mining sites that process solutions (pregnant pond, barren pond, tailings water, and tailings reclaim water) have a consistent geochemical signature. However, the quantitative estimate of the reproducibility of the Chimney Creek pattern is lower than other mines due to identifiable data quality concerns.

Monitoring results from the Chimney Creek fresh water source are contrasted with the tailings water fingerprint in Figure 5-86. This information displays two points that have been observed at other heap leaching facilities. The first point is that the fresh water has its own fingerprint pattern defined by 30 percent alkalinity, 15 percent sodium, 10 percent calcium, and small amounts of other geochemical constituents. The reproducibility of this pattern is estimated to be 99 percent. The second point is that the tailings water fingerprint can be differentiated, both graphically and statistically, from the fresh water fingerprint. The importance of these two points is that the uniform make up water undergoes a shift in composition after it is used in the leaching process and the resulting geochemical fingerprint is a characteristic property of the mine process solution.

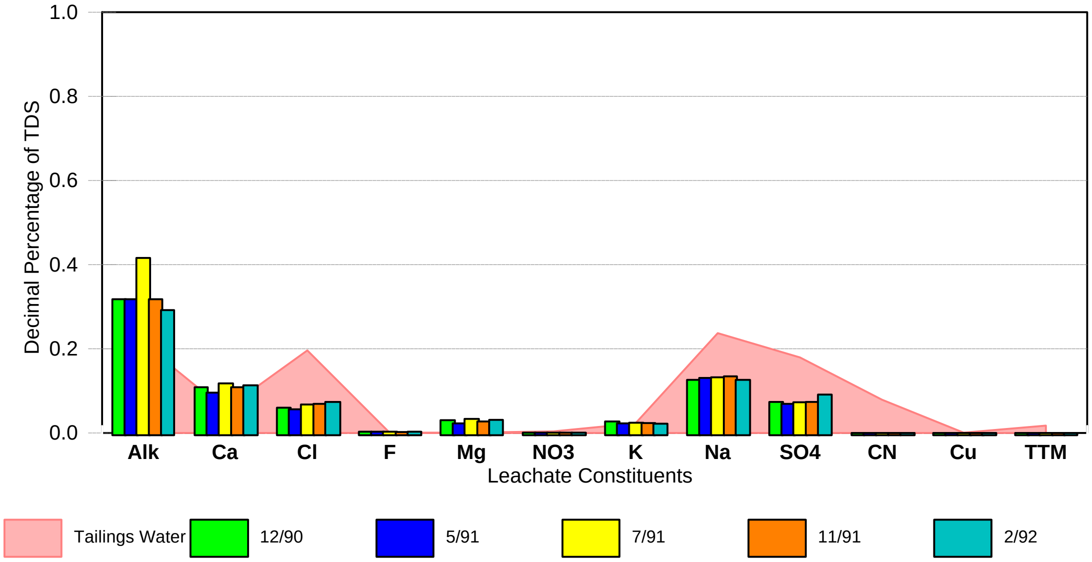
Although the make up water monitoring results define a consistent compositional pattern, it must be pointed out that these data are also of suspect quality. The problems with the make up water data are less obvious because the relative abundance of each geochemical constituent, with the possible exception of alkalinity in the July, 1991 survey, are consistent over the period of record. However, the sum of the ions only averages 77 percent of the total dissolved solids concentration for the five surveys and the charge balance is a - 30 percent (an excess of anions or a deficiency of cations). Both of these values are outside project data quality assurance acceptance limits of 80 percent to 120 percent for total dissolved solids and - 20 percent to + 20 percent for the charge balance. Thus, even though the compositional trends are encouraging and consistent with assessments at other mines, the Chimney Creek results should be used cautiously because of data quality concerns.

The site monitoring program at the Chimney Creek Mine also included three monitoring wells. Results from Well 1, a location adjacent to the heap leaching pad, are compared to the fingerprint pattern for tailings water in Figure 5-87. This comparison demonstrates three properties of the ground water fingerprint.

1. The ground-water fingerprint is similar to the make up water fingerprint shown in Figure 5-86. This would indicate that local ground water is used at the mine as make up water. Also, since the ground-water monitoring results are of acceptable quality (the mass balance and the charge balance are in the acceptable range), these results suggest that the make up water fingerprint in Figure 5-86 has not been significantly distorted by the identified data quality problems.
2. The ground-water fingerprint is reproducible over the period of record. The match between eight survey fingerprints at Well 1 was estimated as 99.3 percent.
3. The ground-water fingerprint at Well 1 was distinctly different from the tailings water fingerprint. The r^2 value for this comparison was 0.464 compared to 0.500 for the make up water - tailings water comparison. This suggests that tailings water from the mine has not impacted the ground water at this location.

Chimney Creek Mine Summary

Monitoring results for this mine provided five sets of quarterly data for several locations at the facility. However, the results for the tailings water, the tailings reclaim water, and the plant make up

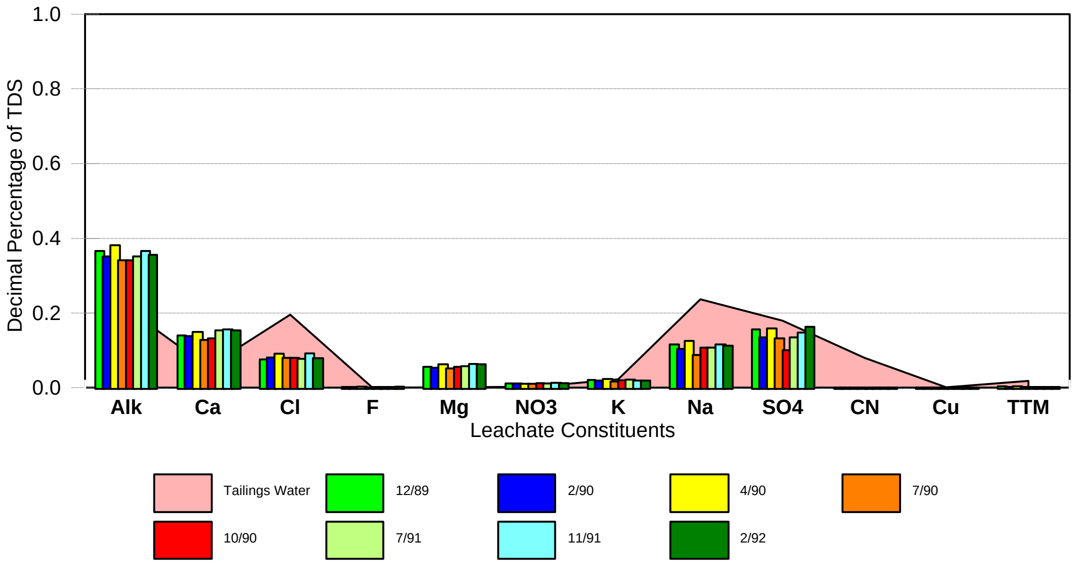


Regression analysis matrix for Chimney Creek make up water

	Sampling Date				
	12/90	**5/91**	**7/91**	**11/91**	**2/92**
Tailings Water	0.489	0.502	0.433	0.521	0.553
12/90	1.000	0.998	0.991	0.998	0.990
5/91		1.000	0.991	0.997	0.984
7/91			1.000	0.986	0.968
11/91				1.000	0.993
2/92					1.000

Average r squared value = 0.990
Make up water - tailings water comparison = 0.500

Figure 5-86. Comparison of make up water composition to the Chimney Creek tailings water fingerprint.



Regression analysis matrix for ground water at Chimney Creek Well 1

	Sampling Date							
	12/89	**2/90**	**4/90**	**7/90**	**10/90**	**7/91**	**11/91**	**2/92**
Tailings Water	0.434	0.468	0.497	0.456	0.453	0.451	0.480	0.474
12/89	1.000	0.997	0.999	0.995	0.981	0.994	0.995	0.997
2/90		1.000	0.998	0.998	0.991	0.998	0.998	0.994
4/90			1.000	0.995	0.986	0.996	0.998	0.996
7/90				1.000	0.986	0.994	0.995	0.992
10/90					1.000	0.990	0.988	0.974
7/91						1.000	0.998	0.995
11/91							1.000	0.996
2/92								1.000

Average r squared value = 0.993
Tailings water - ground water comparison = 0.464

Figure 5-87. Comparison of ground-water monitoring results at Well 1 to the Chimney Creek tailings water fingerprint.

water were limited by data quality problems. Employing the same set of geochemical parameters used to fingerprint process solutions at other heap leaching facilities, suspect data were identified because they failed to achieve acceptable levels of mass balance or charge balance. The errors that contributed to these problems, whether they were clerical errors, dilution errors, instrument calibration errors, or analytical errors, could have been identified and corrected if the data had been subjected to a quality assurance assessment at the time they were initially generated.

Despite the data quality problems, the monitoring results from this site support two important trends observed at other mining operations. First, the geochemical parameters define a distinctive fingerprint pattern for the tailings water and reclaim water. The reproducibility of this pattern was lower than at other mining facilities (0.645 to 0.815) due to data quality problems. However, it was still possible to identify the major components of the fingerprint, estimate their relative abundance, and compare the fingerprints at two locations. Second, the make up water and local ground water also had a distinctive fingerprint that was different from the tailings water fingerprint. Thus, even with data of suspect quality, the fingerprint patterns are so unique and characteristic that they can qualitatively differentiate tailings water from ground water.

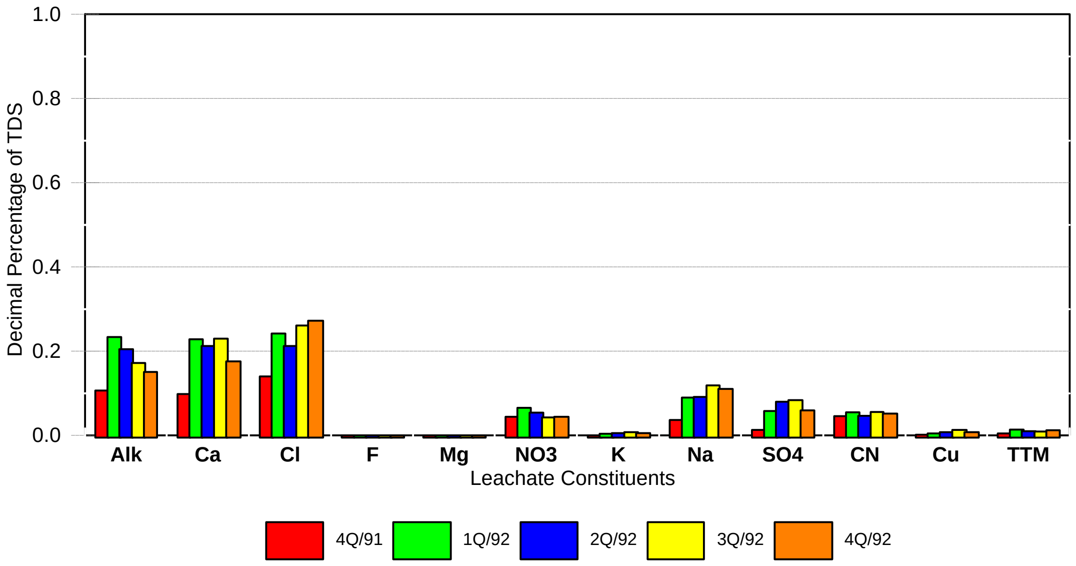
5.2.20 Bald Mountain Gold Mine

Monitoring results from five quarterly surveys of the Bald Mountain pregnant pond II, a northern Nevada heap leaching facility, are presented in Figure 5-88. These data suggest that the process solution at this mine has a characteristic geochemical fingerprint defined by an alkalinity - calcium - chloride triplet and smaller but reproducible quantities of the other parameters. Even though there are apparent data quality problems with the reported total dissolved solids concentration for the fourth quarter, 1991 survey, the reproducibility of the fingerprint was estimated at 92.8 percent.

The following observations suggest that the reported fourth quarter, 1991 total dissolved solids concentration is in error. First, the fourth quarter, 1991 results are approximately double the concentrations in the other surveys. Second, the mass balance for the fourth quarter survey is less than 50 percent of the total dissolved solids concentration but the other surveys are in the 85 to 90 percent range. This would indicate that one or more of the individual analyses are biased low or the total dissolved solids concentration is biased high. Third, the charge balance for the fourth quarter, 1991 survey is in the acceptable range. Since it is unlikely that all of the individual geochemical analyses would be biased to the same extent, the most likely cause for the distorted fourth quarter, 1991 fingerprint is an erroneous total dissolved solids concentration.

Data from barren pond II at the facility are compared to the pregnant pond II fingerprint in Figure 5-89. These data suggest that the barren pond has a reproducible geochemical fingerprint ($r^2 = 0.973$) that is identical to the pregnant pond II fingerprint ($r^2 = 0.973$). The existence of a similar fingerprint pattern at the pregnant pond and the barren pond of this mine is consistent with data assessments at other facilities.

The Bald Mountain Mine was somewhat unusual in that the data file contained results for two pregnant ponds and two barren ponds. Average results for five surveys at these four monitoring locations are presented in Figure 5-90. The data from the pregnant pond I - barren pond I circuit produce an identical signature ($r^2 = 0.990$) and the data from the pregnant pond II - barren pond II circuit also produce an identical signature ($r^2 = 0.996$). However, each circuit has a different pattern with the result that the comparability between the two process solutions is only 61.9 percent.

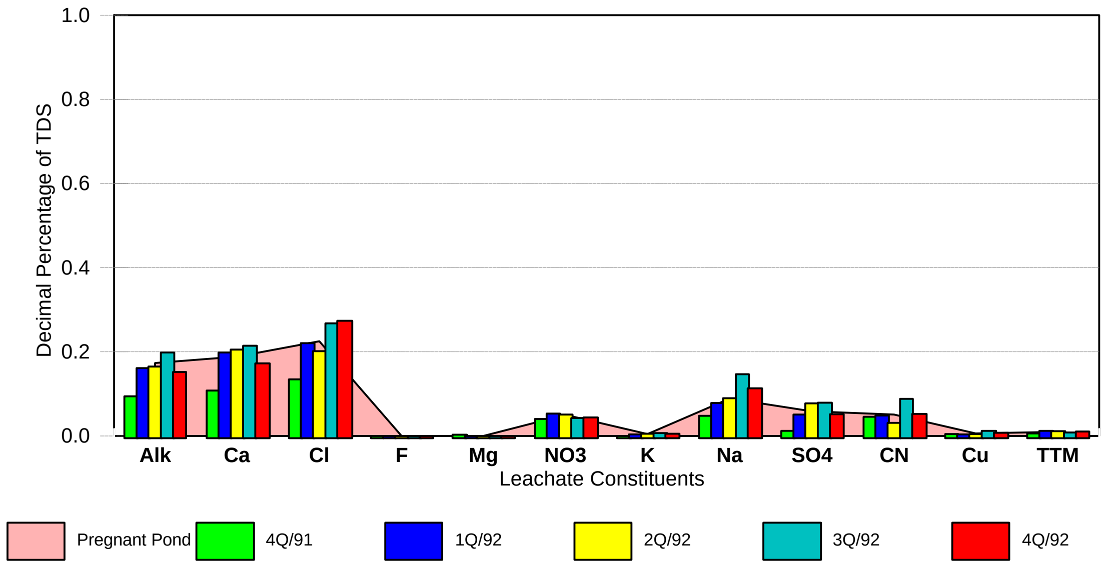


Regression analysis matrix for Bald Mountain pregnant pond II

	Sampling Date				
	4Q/91	**1Q/92**	**2Q/92**	**3Q/92**	**4Q/92**
4Q/91	1.000	0.942	0.898	0.884	0.911
1Q/92		1.000	0.988	0.938	0.898
2Q/92			1.000	0.959	0.897
3Q/92				1.000	0.967
4Q/92					1.000

Average r squared value = 0.928

Figure 5-88. Geochemical fingerprint pattern for pregnant pond II at the Bald Mountain Mine.

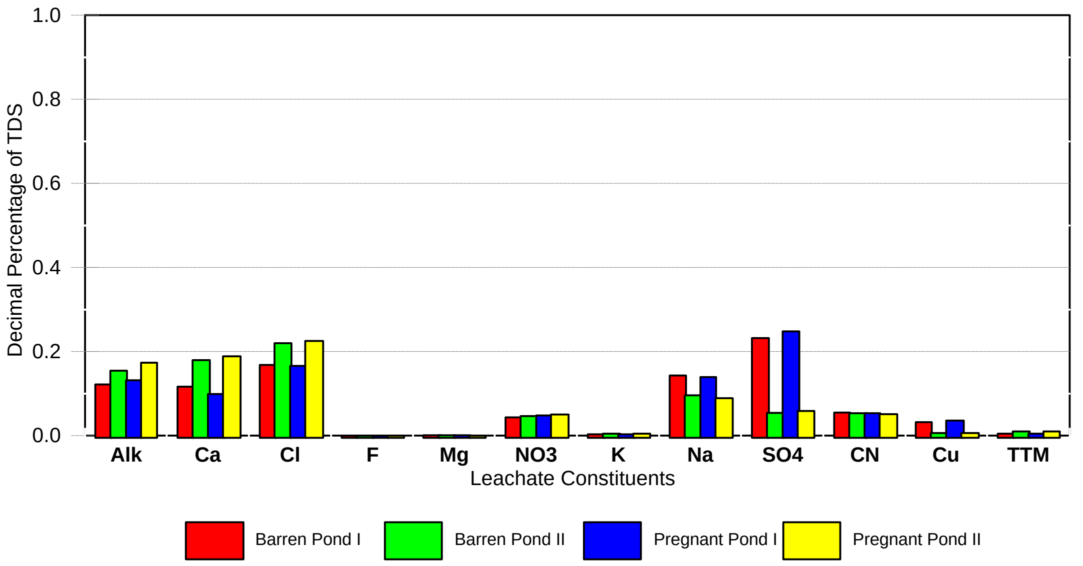


Regression analysis matrix for Bald Mountain barren pond II

	Sampling Date				
	4Q/91	**1Q/92**	**2Q/92**	**3Q/92**	**4Q/92**
Pregnant Pond II	0.961	0.995	0.977	0.972	0.959
4Q/91	1.000	0.966	0.901	0.934	0.940
1Q/92		1.000	0.978	0.954	0.947
2Q/92			1.000	0.939	0.906
3Q/92				1.000	0.961
4Q/92					1.000

Average r squared value = 0.973
Barren Pond II - Pregnant Pond II comparison = 0.973

Figure 5-89. Comparison of barren pond II monitoring results with the Bald Mountain pregnant pond II fingerprint.



Regression analysis matrix for Bald Mountain process solution

	Sampling Location			
	Barren Pond I	**Barren Pond II**	**Pregnant Pond I**	**Pregnant Pond II**
Barren Pond I	1.000	0.468	0.990	0.460
Barren Pond II		1.000	0.401	0.996
Pregnant Pond I			1.000	0.398
Pregnant Pond II				1.000

Average r squared value = 0.619

Figure 5-90. Comparison of geochemical fingerprint patterns for Bald Mountain process solutions.

A comparison of the monitoring data from the two circuits demonstrated that process solution II consistently had a lower total dissolved solids concentration (800 mg/L vs 1150 mg/L), a lower sulfate concentration (45 mg/L vs 275 mg/L), a lower sodium concentration (70 mg/L vs 150 mg/L), a lower cyanide concentration (40 mg/L vs 60 mg/L), and a lower copper concentration (5 mg/L vs 40 mg/L). Concentration differences of this magnitude are easily measurable with current techniques and were repeatedly seen in all five quarterly surveys. Therefore, it is unlikely that the differences are due to analytical error. Although no explanations were given, it is plausible that the two fingerprints are due to the processing of different ores or the use of a differently formulated process solution. The important feature of this example is that the process solution fingerprint is so distinctive that it can differentiate two sources at the same facility.

The site monitoring program at the Bald Mountain Mine was limited to two monitoring wells. Geochemical results from these locations are compared to process solution fingerprint II in Figure 5-91. This comparison illustrates three characteristics of the fingerprinting concept that have been observed at other mining operations. First, the ground-water data from both wells define a repeatable pattern in which alkalinity is the most abundant ion. Second, the ground-water pattern has a high degree of consistency and reproducibility ($r^2 = 0.941$). Third, and most important, the ground-water fingerprint is different from the process solution I fingerprint ($r^2 = 0.201$) and the process solution II fingerprint ($r^2 = 0.529$). Based on these properties, it should be possible to detect and identify Bald Mountain process solution if it were to enter the local aquifer.

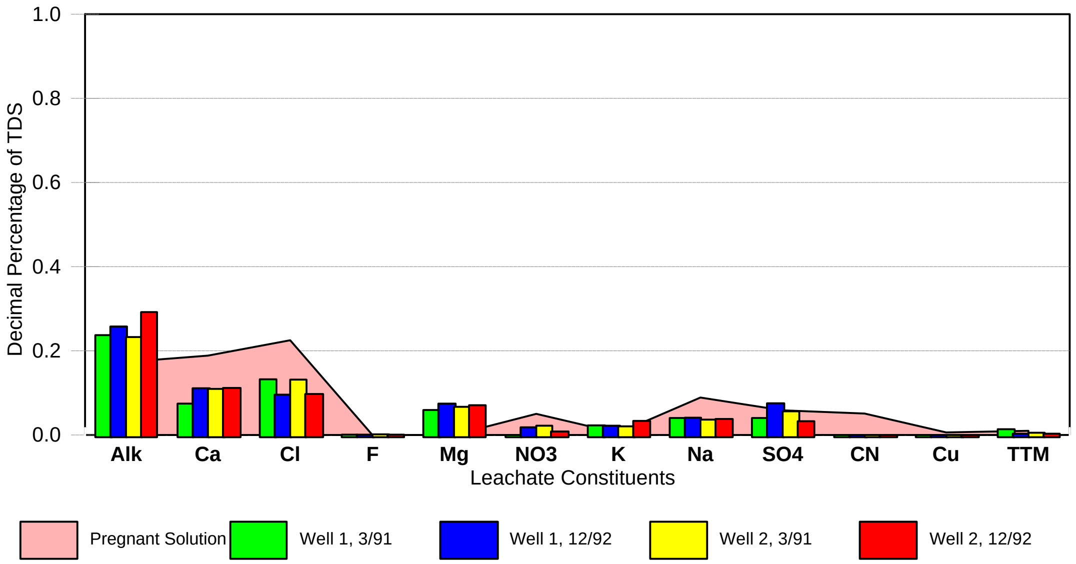
The trends identified in the Bald Mountain ground-water data are encouraging and consistent with trends observed at other sites. However, this specific example should be used with caution because the ground-water data are of suspect quality. The calculated ionic sum for the geochemical parameters are only in the range of 62 to 69 percent which is below the project lower data quality acceptance limit of 80 percent of the total dissolved solids concentration. In addition, the charge balance for these data sets are off by + 40 percent (i.e., an excess of cations or a deficiency of anions) and outside the project data quality acceptance range of - 20 percent to + 20 percent. The monitoring results clearly indicate that there is a consistent compositional difference between the process solution and the ground water but better quality data are needed to verify the absolute difference in composition.

Bald Mountain Mine Summary

This site was unusual in that monitoring results from two separate process systems were reported. However, five sets of quarterly monitoring data produced a distinctive fingerprint pattern for each location. The reproducibility of each fingerprint was on the order of 92 to 99 percent. The ability to characterize the process solutions at this mine based on the relative abundance of geochemical constituents is consistent with similar observations at other sites.

The monitoring records included annual results from two wells on the property. The geochemical results from these surveys defined a consistent pattern in which alkalinity was the single most abundant constituent. Based on the different fingerprint patterns, it was concluded that the ground water at these two monitoring locations has not been impacted by process solution from the Bald Mountain Mine.

An assessment of the Bald Mountain monitoring records demonstrates that the geochemical parameters can be used to define a multi-ion chemical signature or fingerprint that differentiates mine process solutions from ground water. In addition, the collective use of the geochemical parameters



Regression analysis matrix for ground water at Bald Mountain Mine

		Sampling Location and Date			
		Well 1 3/91	**Well 1 12/92**	**Well 2 3/91**	**Well 2 12/92**
Pregnant Pond I		0.207	0.241	0.220	0.136
Pregnant Pond II		0.558	0.492	0.608	0.479
Well 1	**3/91**	1.000	0.927	0.945	0.918
Well 1	**12/92**		1.000	0.952	0.960
Well 2	**3/91**			1.000	0.944
Well 2	**12/92**				1.000

Average r squared value = 0.941
Ground water - pregnant pond I comparison = 0.201
Ground water - pregnant pond II comparison = 0.529

Figure 5-91. Comparison of ground-water monitoring results to the Bald Mountain process solution II fingerprint.

also provides independent checks on the quality of data produced by a monitoring program at a mining facility. These two checks on internal data consistency are a mass balance and an anion - cation charge balance. These checks suggest that the process solution results are of acceptable quality but the ground-water results are of suspect quality because the mass balance is low by more than 30 percent and the charge balance is high by + 40 percent. The active application of these data quality checks can insure the production of valid monitoring data to characterize conditions at mining sites.

5.2.21 American Eagle Flowery Mine

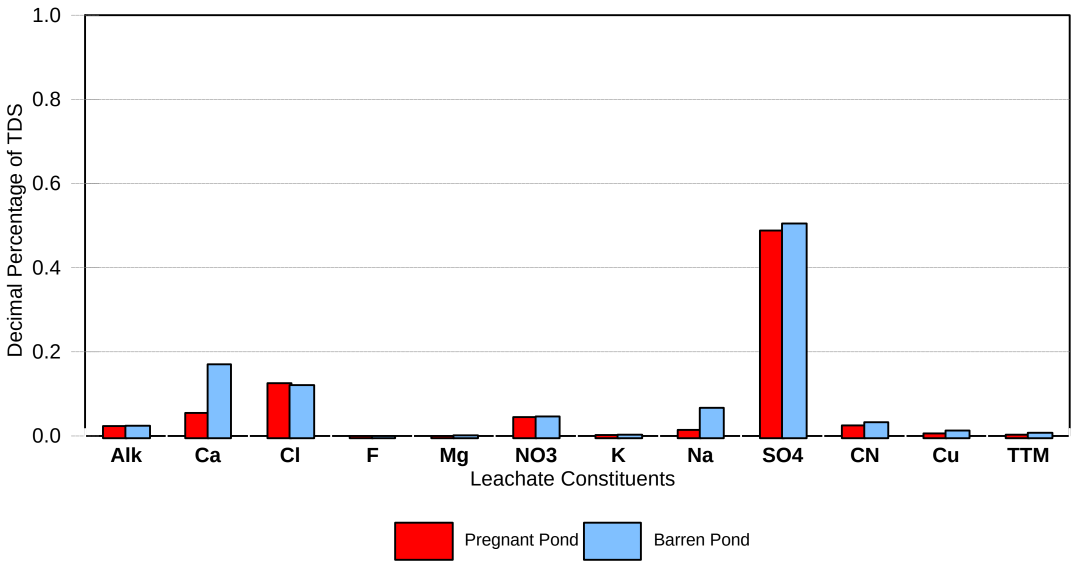
This site is located in western Nevada. The records for this mine included single surveys of the pregnant pond, the barren pond, the plant make up water, and five quarterly surveys at seven monitoring wells installed on the property. The period of record for these results is 1990 - 1991.

The monitoring results for the two process pond surveys at the American Eagle Flowery Mine are presented in Figure 5-92. The geochemical parameters define a repetitive pattern at these two locations in which sulfate is the single dominant ion. Although there is some variability associated with the small calcium peak, the reproducibility of this sulfate-rich pattern was estimated to be 94 percent.

The American Eagle Flowery process solution fingerprint is compared to the plant make up water fingerprint in Figure 5-93. The make up pattern has a slightly lower sulfate content and a higher alkalinity content. A regression analysis of the two patterns suggests that there is a 73 percent match between the two fingerprints. The compositional shift between the process solution and the make up water is smaller at this mine than has been observed at other sites. This small change could be due to the fact that the background ground-water conditions are fortuitously similar to the process solution composition or the production well may have been impacted by past mining activities on site.

The ground-water monitoring data for this mine defined two geochemical patterns. One of these patterns was characterized by 40 percent sulfate, 20 percent alkalinity, and a relatively low total dissolved solids concentration of 750 - 800 mg/L. This pattern bears a strong resemblance to the make up water fingerprint shown in Figure 5-93. The second ground-water pattern was characterized by 60 percent sulfate, a very low alkalinity content (< 5 percent), and an elevated total dissolved solids concentration of 2500 mg/L. This pattern was identified at five of seven ground-water monitoring locations including Well MH10 which is less than 100 feet from the pregnant pond and the heap leaching pad. The reproducibility of the ground-water fingerprint at Well MH10 was 99.6 percent and the match with the process solution fingerprint was 93 percent (Figure 5-94). The identification of the process solution fingerprint at five monitoring locations suggests that this particular mine has had an impact on the local ground water.

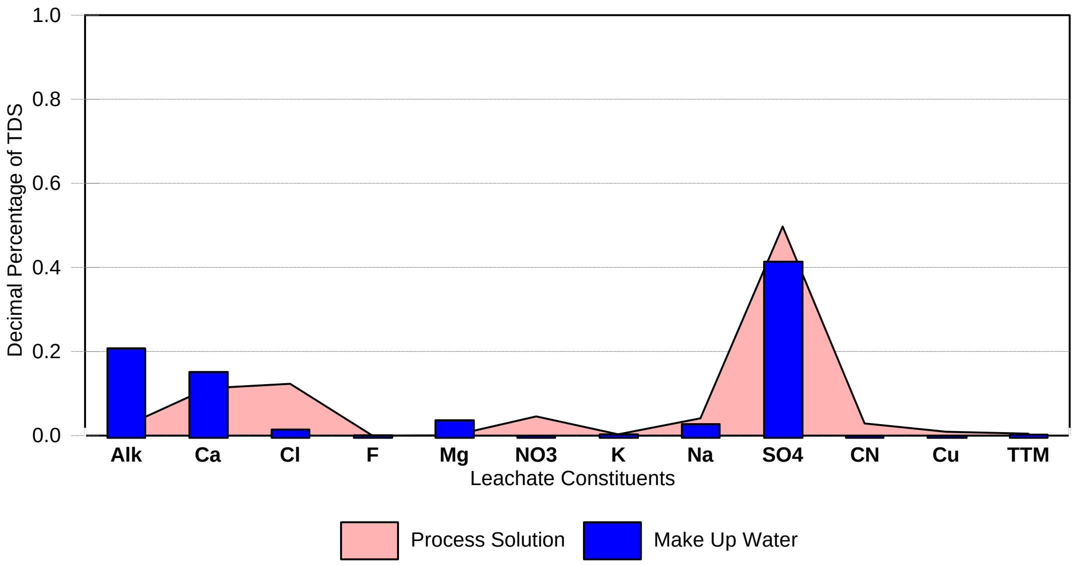
A second important observation concerning ground-water conditions at the American Eagle Flowery Mine is the fact that the process solution fingerprint was identified at a well (MH5) more than one-half mile downgradient from the facility. This suggests that the distinctive geochemical fingerprint pattern, that can be used to characterize the process solution at its source, maintains its chemical integrity as it migrates through the subsurface. Thus, as has been shown at other sites, the fingerprint can also be used to detect and identify mine leachate following an accidental spillage or leakage event.



Regression analysis matrix for American Eagle process solution

Pregnant pond - barren pond comparison = 0.941

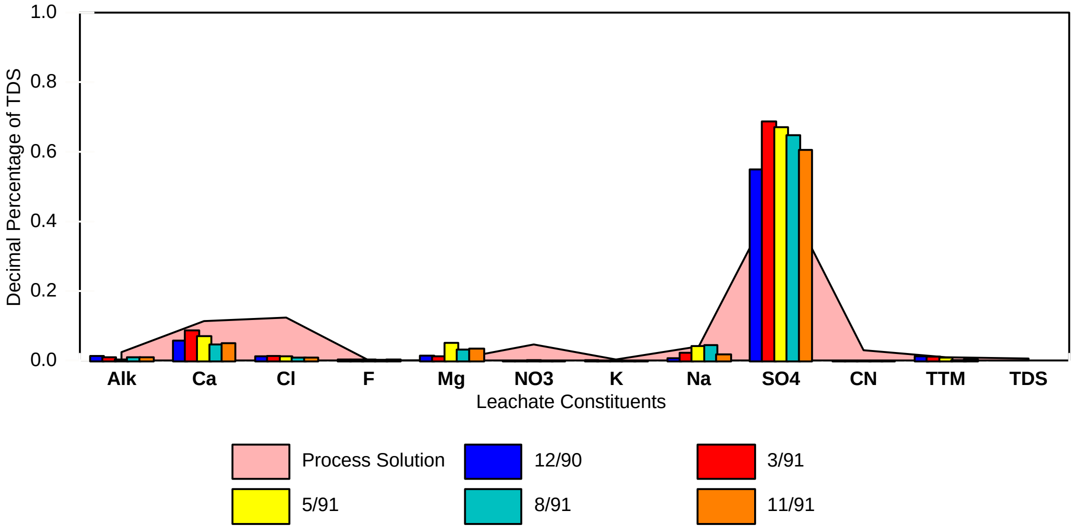
Figure 5-92. Process solution fingerprint at the American Eagle Flowery Mine.



Regression analysis matrix for American Eagle make up water

Process solution-make up water comparison = 0.730

Figure 5-93. Comparison of make up water composition to the American Eagle Flowery process solution fingerprint.



Regression analysis matrix for American Eagle Well MH10

	Sampling Date				
	12/90	**3/91**	**5/91**	**8/91**	**11/91**
Process Solution	0.937	0.942	0.926	0.924	0.927
12/90	1.000	0.999	0.994	0.994	0.998
3/91		1.000	0.995	0.994	0.996
5/91			1.000	0.998	0.998
8/91				1.000	0.998
11/91					1.000

Average r squared value = 0.996
Well MH10 - process solution comparison = 0.931

Figure 5-94. Comparison of ground-water monitoring results at MH10 to the American Eagle Flowery process solution fingerprint.

American Eagle Flowery Summary

This example provided a small amount of data for a gold heap leaching facility in western Nevada. An evaluation of this information reinforced four characteristic trends of process solutions and mine waste leachates that were observed at other sites.

1. The subset of geochemical parameters defined a fingerprint pattern that characterized the composition of the process solution. The absolute shape of this fingerprint varied from that observed at other mines but the same set of parameters were useful for creating the compositional pattern. The reproducibility of the American Eagle Flowery pattern was estimated by regression analysis to be 94 percent.
2. The process solution fingerprint could be differentiated from the plant make up water fingerprint. Although the compositional shift was not as pronounced as at other mines, the process solution has a reduced relative abundance of alkalinity, an increased relative abundance of sulfate, and an increase in total dissolved solids. The resulting shift in composition can be used to characterize the process solution.
3. The process solution fingerprint was identified in ground water more than one-half mile from the heap leaching operations. This indicates that the fingerprint maintains its identity as the solution migrates through the subsurface.
4. An evaluation of the monitoring data identified the process solution fingerprint in five of seven monitoring wells. This suggests that the fingerprint can be used as an internal tracer to delineate ground-water areas impacted by a mining operation.

5.2.22 Other Heap Leaching Sites

During the project data collection efforts, monitoring results from several additional gold mines were obtained from the Nevada Department of Environmental Protection. These sites were not included as case studies for one of the following reasons.

> <u>Limited Data</u>. Some of the facility files had a small amount of monitoring data. For example, the records may have contained a single survey for a pregnant pond but no information on the plant make up water or ground water. Since this information is not sufficient to assess the reproducibility of a fingerprint pattern or conduct a case study, it was not used in the preparation of this report. Possible reasons for the limited data are (1) the mine was just beginning operations when data were being collected or (2) the data were being used at the time site files were being reviewed.
>
> <u>Site in closure</u>. Several of the mining operations were inactive or in closure. Conditions that may have contributed to this status are (1) the ore supply was not economically viable at that time, (2) some mines were inactive because of necessary construction or repair activities, or (3) the mine ore supply was exhausted. These sites were also excluded from the case study section.
>
> <u>Data Quality Problems</u>. As the data were being tabulated and reviewed, they were subjected to internal data quality checks based on fundamental considerations of mass balance and electrical charge balance. When the data quality objectives of the project were not met, the data were flagged as suspect. These data were discussed in the individual case studies to demonstrate that the geochemical monitoring data could be used to assess the acceptability of the data as well as

define a characteristic fingerprint pattern for the mine process solutions. However, at a couple of sites the monitoring data were judged to be of very poor quality and were not used as a case study.

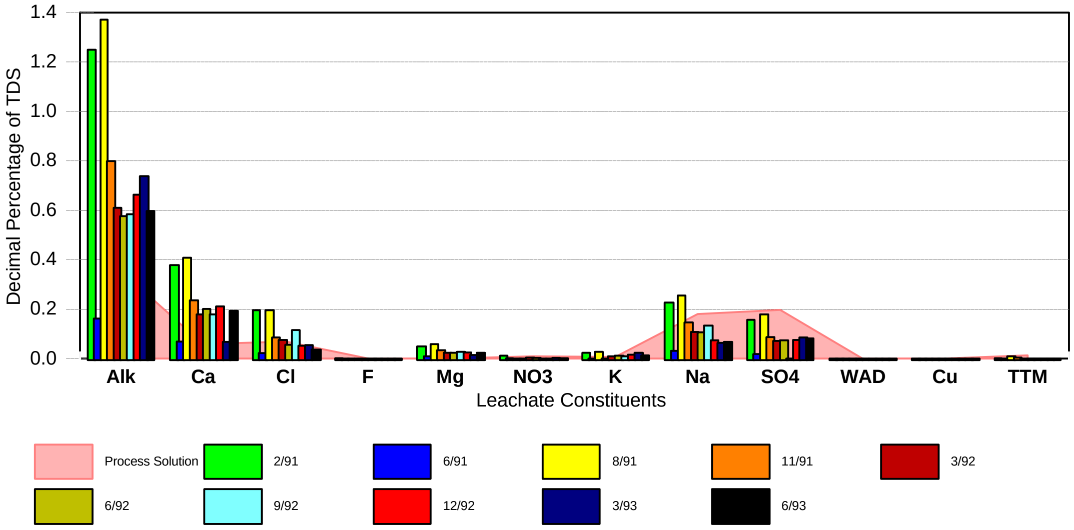
An example of this type of data from monitoring Well 1 at the Atlas Gold Mine is shown in Figure 5-95. Data quality problems are evident because the alkalinity result, by itself, represents more than 100 percent of the total dissolved solids concentration in several surveys. Also, over the three year period of record, the mass balance fluctuates from a low of 25 percent to a high of 181 percent (project limits were 80 percent to 120 percent). In addition, the anion - cation balance fluctuates from -30 percent to +70 percent and each set of data is outside the project data quality acceptance limits of -20 percent to +20 percent. There are problems with the total dissolved solids results, particularly in the first three surveys, but there also has to be error associated with one or more of the individual geochemical analyses because of the anion - cation imbalance.

Even though these data are not of acceptable quality, this set still illustrates two potential benefits of monitoring for the geochemical parameters. The first benefit is that they offer two internal checks on data quality. Since the geochemical ions represent essentially all of the total dissolved solids concentration in ground water and mine waste leachates, the sum of the ions must equal the total dissolved solids concentration and the sum of the positively charged ions (cations) must equal the sum of the negatively charged ions (anions). When both of these checks are satisfied, the data can be considered acceptable for use. However, when either of these checks are not satisfied, as in this example, the data are not of acceptable quality and appropriate actions can be initiated to correct the problem (i.e., check the sample paper work for possible transcription or dilution errors, reanalyze the sample if possible, and resample if necessary). In either case, these data quality checks can be performed on a real time basis without the need for extensive replicate analysis or statistical assessment of the data. The second benefit of geochemical monitoring is that these results can be used to fingerprint the composition of the mine process solution and differentiate it from adjacent ground water. Despite the data quality problems, the monitoring results from Atlas Well 1 still provide a strong qualitative indication of a reproducible geochemical pattern (Figure 5-95).

5.3 Discussion of Heap Leaching Case Studies

The primary objective of the project was to identify an appropriate set of parameters that could be used in monitoring programs at mining sites. In order to insure that the project results were representative of the mining industry and could be extrapolated to a general site, monitoring records from 26 gold mining operations were tabulated and evaluated. These sites represent approximately 25 percent of the heap leaching facilities in Nevada and 10 percent of the facilities in the United States.

The extensive inorganic analyses that have been composited define the compositional characteristics of process solutions and tailings water at heap leaching facilities. These characteristics include (1) common geochemical ions such as sodium, calcium, magnesium, alkalinity, chloride, and sulfate are repeatedly present as the most abundant constituents, (2) individual trace metals may be present at concentrations ranging from 1 to more than 100 mg/L, (3) more than 20 leachate constituents, including geochemical ions, trace metals, and cyanide, may be present at concentrations that could degrade environmental conditions in the vicinity of a mine, and (4) the concentration of each leachate constituent varies considerably at a site and between sites.



Regression analysis matrix for Atlas Gold Mine Monitoring Well 1

	Sampling Date									
	2/91	**6/91**	**8/91**	**11/91**	**3/92**	**6/92**	**9/92**	**12/92**	**3/93**	**6/93**
Process Solution	0.753	0.700	0.760	0.743	0.750	0.740	0.677	0.703	0.737	0.713
2/91	1.000	0.984	0.999	0.997	0.999	0.994	0.979	0.989	0.947	0.986
6/91		1.000	0.983	0.984	0.983	0.992	0.968	0.981	0.886	0.979
8/91			1.000	0.998	0.999	0.995	0.976	0.990	0.950	0.987
11/91				1.000	0.999	0.997	0.976	0.992	0.949	0.990
3/92					1.000	0.996	0.976	0.993	0.953	0.990
6/92						1.000	0.967	0.994	0.930	0.994
9/92							1.000	0.959	0.908	0.946
12/92								1.000	0.948	0.999
3/93									1.000	0.945
6/93										1.000

Average r squared value = 0.975
Process solution - monitoring well comparison = 0.727

Figure 5-95. Monitoring data from Atlas Gold Mine Well 1.

The one identified process solution property of greatest initial concern was the highly variable concentrations observed for each constituent. This condition was of concern because it may indicate that the data, which were produced by multiple laboratories, were of poor quality. Fortunately, since the State of Nevada requires essentially complete analysis on collected samples, this concern could be evaluated by calculating the mass balance and the charge balance on each sample. The vast majority of the individual geochemical data sets were shown to be of acceptable quality. Anomalous values were occasionally encountered, as discussed in the case studies, but most of the compiled information could be used as intended.

Once it was determined that the highly variable concentrations were a characteristic of mine waste leachates and not an a priori indication of poor data quality, the data sets were examined for a recurring trend or pattern. One obvious change in every set was the large total dissolved solids increase in the process solution that ranged from 3 to 10 times the total dissolved solids concentration of make up water. Although total dissolved solids itself is not a unique indicator of mining wastes, the possibility of using the geochemical distribution that defined the total dissolved solids concentration was explored. This approach was taken because ionic distribution has previously been used to successfully fingerprint brine solutions, ground water, landfill leachates, and municipal waste ash leachates (Stiff, 1951; Davis and DeWiest, 1966; Tonjes, et al, 1995; and Plumb and Engelmann, 1991).

Monitoring results for the individual geochemical parameters were divided by the total dissolved solids concentration of the sample. In addition to reducing the effect of concentration variability, this data normalization process offered two benefits that aided in the identification of recurring trends. The first benefit of this data transformation is that it defined a common y-axis that allowed a direct comparison of geochemical histograms from different times at the same location or different sampling locations at the site. The second benefit of this transformation is that it provided a rapid means to assess the acceptability or usability of the data. Since the sum of the individual ions must be less than the total dissolved solids concentration for the sample, a rapid visual inspection of the histograms flagged data sets in which one ion exceeded the reported total dissolved solids concentration or the ionic sum was less than 80 percent or more than 120 percent of the total dissolved solids concentration. The flagged data sets were then inspected for possible transcription or data entry errors.

One of the first steps in the investigation was to compare the reproducibility of results from a single location. Monitoring results from successive quarterly surveys at the same location were used for this purpose because replicate analyses were not reported in the monitoring programs at mining sites. This assessment provided an estimate of the reproducibility of the fingerprint patterns over time and was conducted with data from the pregnant pond which is the location at which ore pile leachate is collected and processed to recover gold and other metals that have been extracted (Figure 5-1).

The monitoring results from each pregnant pond, which generally consisted of 3 to 16 sets of quarterly data, were used to construct geochemical fingerprints for each facility. These fingerprints were subjected to regression analysis to determine the similarity or reproducibility of each pattern. As indicated in Table 5-9, the reproducibility of the geochemical fingerprints ranged from 0.703 at Bald Mountain Mine I to 0.980 at the Cortex Mine with an average reproducibility of 0.902. That is, the average reproducibility of the pregnant pond geochemical fingerprint based on more than 100 sampling events over four years at 21 heap leaching facilities is 90.3 percent. (In reviewing the Case Studies and compiling Table 5-9, surveys that contained suspect quality data were excluded from this tabulation. A total of 10 quarterly surveys were deleted for this reason. Data sets that were affected by this decision are indicated with brackets in Table 5-9.)

Table 5-9. Summary of Nevada gold mine process solution fingerprint analyses.

Gold Mine	Pregnant Pond	Barren Pond	Process Solution	Make Up Water	Ground Water Impact
Lone Tree	[0.817]	[0.792]	0.995	0.035	(+)
Green Springs		0.944		0.000	0
Alligator Ridge	0.920	0.907	0.989	0.052	+
Oliver Hills	0.865	0.843	0.972	0.538	0
Barrick	0.970	0.970	0.989		+
Rabbit Creek	0.857	[0.802]	0.888	0.318	0
Aurora	0.879	0.810	0.977	0.257	0
Cortez	0.980	0.986	0.983	0.211	+
Florida Canyon	[0.963]	[0.982]	0.998	0.140	(+)
Alta	[0.908]	[0.908]	0.922	0.046	
Hycroft	0.933	0.930	1.000	0.668	0
Paradise Peaks	[0.984]	[0.973]	0.999		(+)
First Miss Getchell			0.968	0.238	+
Arimetco	0.971			0.008	+
Nevada Goldfield	0.934	0.942	0.988	0.239	(+)
Corona	0.922	0.923	0.948		0
Bullfrog			0.988	0.679	0
Marigold	0.897	0.914	0.916	0.147	+
Chimney Creek			0.746	0.500	0
Bald Mountain I	0.703	0.688	0.990		0
Bald Mountain II	0.928	0.973	0.996		0
American Eagle			0.941	0.730	
Atlas			0.910		+
Dee Gold	0.921	0.987	0.959		
Candelaria			0.990	0.957	+
Buckskin			0.720	0.111	0
Average	0.908	0.904	0.949	0.309	

[ ] = One or more data sets excluded because of identified data quality problems.
\+ = Mine process solution detected in ground water.
(+) = Possible evidence of process solution present in ground water.
0 = Mine process solution not detected in ground water.

The geochemical fingerprint pattern varied from site to site. For example, sulfate is the dominant component in the fingerprint at the Alligator Ridge Mine, the Barrick Mine, the Paradise Peaks Mine, and the Arimetco Mine, but chloride is the dominant component in the geochemical fingerprint at the Florida Canyon Mine, and several components are equally abundant in the fingerprint at the Lone Tree and Green Springs Mines. These differences are influenced by the ore that is being mined, the leaching process that is used, and the composition of the make up water itself. However, it is important to recognize that all pregnant pond fingerprints share three important features. The first is that the same small set of geochemical parameters (alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, and sulfate) define a consistent pattern at each mine. The second point is that the pattern is highly reproducible at each mine (generally greater than 90 percent). The third point is that cyanide and trace metals, even though they are constituents of greatest regulatory concern, do not contribute substantially to the definition of the pregnant pond fingerprints.

The hypothesis that geochemical parameters define a consistent fingerprint pattern was examined further by evaluating monitoring results from other process solution locations at each mine. Since heap leaching facilities utilize a recirculating system to extract gold from the ore, locations such as the barren pond should have a consistent ionic composition that is similar to the pregnant pond fingerprint. As shown in summary Table 5-9, the reproducibility of the barren pond fingerprints ranged from a low of 68.8 percent at the Bald Mountain Mine I to a high of 98.7 percent at the Dee Gold Mine and averaged 90.4 percent across all sites. More importantly, the average comparability, or match, between the pregnant pond fingerprints and the barren pond fingerprints for 24 sites selected at random from the files of the Nevada Department of Environmental Protection was 94.9 percent. By comparison, the reproducibility of the trace metal fingerprints ranged from 16.2 percent to 58.6 percent with an average value of 28.6 percent.

The process solution geochemical fingerprint comparison exceeded 95 percent at 16 sites and exceeded 90 percent at 21 of 24 sites. Since the pregnant pond at 24 sites had a reproducible geochemical signature (> 90 percent), the barren pond at the same facilities also had a reproducible geochemical signature (> 90 percent), and these two signatures were identical (95 percent match), the project results demonstrate that heap leaching process solutions (pregnant pond, barren pond, tailings water) have a distinctive ionic composition or fingerprint that is defined by the relative abundance of the common geochemical parameters.

In order to demonstrate that the identified fingerprint patterns were a characteristic property of the process solutions and not an artifact of the plant make up water, the process water and make up water fingerprint patterns were compared for each mine. The resultant regression analysis comparisons from 19 sites have been summarized in the Make Up Water column of Table 5-9. These values ranged from a low of 0 percent at the Green Springs Mine to a high of 95.7 percent at the Candelaria Mine. The average process solution - make up water fingerprint match at 19 mines was 31 percent ($r^2 = 0.397$). These results suggest that the ore leaching process causes a distinctive shift in the composition of the make up water. Since the make up water used at each mine had a constant geochemical fingerprint, and the process solution at each mine had a fingerprint pattern that was consistently different from the make up water, the process solution fingerprint must be a distinctive property of the leaching solutions. Therefore, the geochemical fingerprints provide a technique to uniquely characterize process solutions at their source.

The majority of the process water - make up water fingerprint comparisons produced regression analysis r^2 values of less than 0.300 (Table 5-9). That is, the ore leaching process caused a significant and distinctive shift in the ionic composition of the make up water. However, four mines had relatively high fingerprint comparison values ranging from 0.661 to 0.957. There are at least two explanations for these sites.

1. It could be fortuitous that the natural ground water had a fingerprint pattern similar to the mine process solution. For those sites with an r^2 value that is less than 0.70 - 0.75, it should still be possible to statistically differentiate process solution from make up water.
2. A second possibility is that past operations at a mine had already impacted the plant water supply. This is a likely possibility at the Dee Gold Mine where the fingerprint match exceeded 95 percent but the ground-water fingerprint at other monitoring locations is distinctly different from the process solution fingerprint.

Detailed site investigations would be required to explore these possibilities in more detail.

One objective of selecting monitoring parameters is to be able to identify mining sites at which fugitive process solution or tailings pond leachate is impacting ground water. This issue was addressed by comparing the characteristic fingerprint pattern of a mine process solution with the ground-water pattern at adjacent monitoring wells. In making these comparisons, the following conventions were used:

1. If a regression analysis of the ground-water and process solution fingerprints produced an r^2 value of 0.800 or greater at one or more well (an 80 percent match), the ground water was considered impacted and a "+" was entered into the Ground Water Impact column of Table 5-9.
2. If a regression analysis of the ground-water and process solution fingerprints indicated a shift away from the ground-water pattern and towards the process solution pattern, but the resulting r^2 value was less than 0.800, a "[+]" was entered into the Ground Water Impact column of Table 5-9.
3. If a regression analysis of the ground-water and process solution fingerprints produced an r^2 value of 0.200 or less, a "0" was entered into the Ground Water Impact column of Table 5-9.

Of the 23 sites where this assessment was attempted, a strong, positive process solution fingerprint ($r^2 > 0.800$) was identified in the ground water at eight mines (35 percent). In addition, a tentative identification of process solution was made in the ground water at another three sites. Thus, based on fingerprint analysis, ground water has been impacted at 48 percent of the gold mining sites reviewed in this study.

A process solution fingerprint was not detected in the ground water at 11 mines. However, one can not conclude that the ground water has not been impacted at these sites. The reason for this caution is that the site monitoring program at several mines is limited to three wells or less. Thus, it is possible that some mines may be having a localized impact on ground water but the impact is not being detected because of limited spatial sampling. Consequently, the most appropriate conclusion is that at least 48 percent of the heap leaching sites that have been reviewed are having a localized impact on ground water.

The statement that a large percentage of heap leaching facilities are having an impact on local ground water is based solely on the identification of the characteristic process solution fingerprint at one or more monitoring locations. This determination is not concerned with whether the impacts are adversely affecting ground-water quality or whether the impacted water is moving off site but simply that fugitive mine waste leachates have been detected at some distance from the source. In general, it is not possible to use the existing datasets to track the off site migration of mine waste leachates because of the limited spatial sampling (some site programs only required monitoring at three wells or less which is not sufficient to define the area that has been impacted). However, it would be a relatively simple matter to return to a site and conduct more extensive monitoring to determine the extent of leachate migration or associated water quality problems after the process solution or tailings leachate have been detected in ground water.

The assessment of ground water monitoring results from Nevada heap leaching facilities offered additional insight into two properties of the process solution fingerprints. First, the mine leachates maintained their ionic composition as they migrated through the ground water. Thus, the same fingerprint patterns that can be used to uniquely characterize process solutions at their source can also be used as an internal tracer to detect fugitive process solutions and tailings leachate in the environment. Second, the individual site assessments suggest that the common geochemical parameters that define the process solution fingerprints will migrate faster than the trace metals present in process solution. This was best demonstrated with the Cortez data set in which the process solution fingerprint was identified at more than 10 monitoring wells but the trace metal pattern at each location was identical to background ground-water conditions. The significance of this observation is that the trace metals in process solution, that had concentrations too variable to define a characteristic fingerprint pattern at the source, would not be effective monitoring parameters for the early detection of fugitive process solution because of their slower rate of migration.

5.4 Heap Leaching Summary

Site monitoring records from 26 gold mining operations across the State of Nevada were compiled to characterize the process solutions and tailings leachates at heap leaching facilities. The resulting data set provided up to four years of information that described the occurrence and distribution of 39 inorganic parameters and cyanide in mine waste leachates. The project database was reviewed and evaluated to identify trends that would provide a basis for selecting monitoring parameters that could be incorporated into an effective monitoring strategy for mining sites.

An assessment of the composited monitoring data demonstrated that a small set of geochemical parameters, alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, and sulfate, were the most abundant constituents in process solutions and tailings leachates. Collectively, these ions generally represented more than 90 percent of the total dissolved solids concentration of the mine waste leachates. Although the actual concentration for each of the geochemical parameters was highly variable, the normalized concentrations (actual concentration/total dissolved solids concentration) were observed to be constant. The normalized geochemical concentrations defined a multiple ion signature or chemical fingerprint that characterized the process solutions and tailings leachates at heap leaching facilities.

The properties of the process solution fingerprints were evaluated in a series of 21 case studies. The fingerprint patterns were shown to display the following attributes:

1. The fingerprint at a single process solution monitoring location was constant over time. Based on the results from 3 to 16 quarterly surveys, the reproducibility of the patterns was estimated by regression analysis to be greater than 90 percent.

2. The process solution fingerprint at each mine was spatially consistent. The reproducibility of the geochemical pattern between different locations in the recirculating process solution, the pregnant pond, the barren pond, tailings water, and tailings reclaim water, was estimated by regression analysis to be almost 95 percent. The spatial comparability of the process solution fingerprints exceeded 90 percent at 21 of 24 mines.
3. The process solution fingerprint at each mine was visually and statistically distinct from the plant make up water fingerprint. The average comparability of the two patterns was only 30.9 percent. Based on the distinctive shift in composition that occurs, the geochemical pattern provides a unique mechanism to identify mine waste leachates.
4. The mine process solution fingerprint is distinctly different from the background ground water fingerprint in the vicinity of a mine. The most frequently encountered scenario is that background ground water has a low total dissolved solids concentration and a fingerprint that would be characterized as being alkalinity-rich and sulfate poor (alkalinity generally represents more than 50 percent of the total dissolved solids concentration). By comparison, process solutions have a high to very high total dissolved solids concentration and a fingerprint that would be characterized as being sulfate-rich and alkalinity-poor (sulfate represents more than 50 percent of the total dissolved solids concentration).
5. Fugitive process solution maintains its chemical identity as it migrates through the subsurface environment. Thus, the geochemical fingerprint functions as an internal tracer that can be used to detect mine waste leachates. Process solution fingerprints were identified in the ground water at 48 percent of the case studies.
6. The geochemical parameters appear to migrate faster through the subsurface environment than trace metals present in the process solution at a mine. This is indicated by the fact that the geochemical fingerprint has been detected in one or more wells at 48 percent of the case studies but elevated trace metal concentrations have not been detected.

An evaluation of monitoring records from Nevada heap leaching facilities has demonstrated that the process solution and tailings leachates at these mines have a characteristic geochemical fingerprint. This fingerprint reproducibly characterizes the mine waste leachates at the source, differentiates mine waste leachates from plant make up water and regional ground water, and can detect and identify the leachates as they migrate away from the source following a spill or leakage event. It is suggested that the individual geochemical parameters that define the process solution fingerprints would be an effective set of monitoring parameters for heap leaching facilities.

The composited monitoring data were also reviewed to identify possible trends in the trace metal data. However, although 18 different metals were present at concentrations that exceeded screening criteria and represent a potential environmental risk, no useful characteristic trends were identified:

1. The individual trace metal concentrations were highly variable and most of the data sets were non-normally distributed.
2. There was no indication of a reproducible trace metal pattern either at one location over time or at different sampling locations in the recirculating process solution. The average reproducibility of the trace metal pattern, as estimated by regression analysis, was only 28.6 percent.
3. The trace metal component of the process solutions and tailings leachates do not appear to migrate through the subsurface environment as rapidly as the geochemical parameters in the

ground water at 48 percent of the sites, the trace metal distribution at these impacted locations was still similar to background conditions.

4. Because the trace metals represent such a small percentage of the total dissolved solids concentration of the mine waste leachates (generally less than 5 percent), there are no internal data quality checks that can be used to independently verify data quality or detect suspect quality data.

Trace metals would not be effective primary monitoring parameters because they are not uniquely characteristic of process solutions and tailings leachates and they migrate too slowly to provide early detection of fugitive mine waste leachates.

Section 6

Assessment of Monitoring Results From Tailings Basins at Arizona Copper Mines

The initial objective of the project was to be able to characterize process solutions at heap leaching facilities in order to identify appropriate monitoring parameters for this sector of the mining industry. The original scope was expanded to include tailings basins at southwest copper mines when the initial results began to suggest that the tailings basin leachates at Nevada gold mining facilities had a reproducible geochemical fingerprint. The data used in this portion of the study were obtained from the files of the Arizona Department of Environmental Quality.

Comprehensive inorganic analyses were tabulated for the tailings basin and several adjacent monitoring wells at each mine. A review of this information indicated that the same set of geochemical parameters that defined the composition of process solutions and tailings leachate at heap leaching facilities were also the most abundant constituents in tailings leachate at Arizona copper mines (Table 3-4). Therefore, each of the data sets were evaluated to determine whether the geochemical parameters could also be used to fingerprint the composition of tailings leachates at copper mines. These results are presented in a series of case studies.

6.1 Twin Butte Copper Mine

The Twin Butte Mine is located in southern Arizona. It is a former open pit copper mine that is presently in closure. A schematic of the mine is presented in Figure 6-1. The mine used a flotation process to recover copper from sulfide ore from 1969 to mid 1975 and 1976 until 1985. A second process that used a sulfuric acid leaching procedure to recover copper from oxide ores was operated between 1975 and 1983. Tailings Dam 3, which covers an area of approximately 2 square miles, received 82,000,000 tons of tailings between 1977 and 1985 (Anamax Mining Company, 1985). The smaller Tailings Dam 2 (1.1 square miles) received 84,000,000 tons of tailings between 1969 and 1985.

The monitoring records for this facility contained a considerable amount of data. This information included the following:

1. Analytical results for five types of tailings slurries from different phases of the plant operation. These included sulfide tailings, oxide tailings, mixed tailings, a laboratory leachate, and an estimated leachate composition used in modeling studies.
2. Five years of field monitoring data from Tailings Dam 3.
3. Five years of monitoring results from two wells located upgradient (west) of the Tailings Dams.

4. Five years of monitoring data from more than a dozen wells located downgradient (east) of the Tailings Dam.
5. The results of a detailed laboratory study that was conducted to characterize the composition and behavior of tailings leachate constituents under controlled conditions.

The collected samples in each of the data subsets identified above were analyzed for nine geochemical parameters, 17 trace metals, pH, and total dissolved solids.

6.1.1 Tailings Leachate Characterization

The Twin Butte file contained five sets of data that described the composition of tailings leachate at this mine (Table 6-1). The sulfide tailings were produced when a flotation process was used to recover copper from a sulfide ore. This leachate had a low total dissolved solids concentration, a neutral pH, and a relatively low total trace metals concentration. The oxide tailings were produced when sulfuric acid was used to extract copper from oxide ores. By comparison, the leachate from these tailings had a very high total dissolved solids concentration, a very low pH, and an extremely high total trace metals concentration. When both processes were being used, the tailings were combined to produce a mixed tailings slurry. The site file also described a tailings leachate used in a series of laboratory column studies. Based on the low pH and high total dissolved solids concentration, this leachate was produced with oxide ores. Finally, the file contained an "estimated" leachate that was used in some computer modeling studies.

These data demonstrate the variable concentrations that have been reported for constituents in tailings leachate at the Twin Butte Mine. Some of the examples include magnesium fluctuating between 2 mg/L and 2800 mg/L, sulfate fluctuating between 500 mg/L and 20,000 mg/L, total dissolved solids fluctuating between 1000 mg/L and 30,000 mg/L, pH fluctuating between 1.6 and 8.0, and total trace metals fluctuating between 2.63 mg/L and 1963 mg/L (Table 6-1).

Each of the constituent concentrations in Table 6-1 were normalized to the leachate total dissolved solids concentration as had been done at each of the heap leaching facilities. These results are presented as a series of histograms in Figure 6-2. Although there is some uncertainty regarding the actual height of each peak, the geochemical data defined a characteristic, repeatable pattern for the Twin Butte tailings leachates. The reproducibility of the sulfate-rich, alkalinity-poor fingerprint pattern at this mine was estimated by regression analysis to be 91 percent ($r^2 = 0.907$). Thus, despite the variable concentrations, which ranged over an order of magnitude or more for many leachate constituents, the tailings leachates at this mine had a constant multi-ion signature.

The normalized trace metal data for the tailings leachates are presented in Figure 6-3. The trace metal distribution in the mixed tailings leachate and the sulfide tailings leachate is distinctly different from the distribution in the oxide tailings leachate and the laboratory leachate. A major factor which contributes to this variability is pH which is neutral for the sulfide tailings (pH = 7.5 - 8.0) and very acidic in the oxide tailings (pH = 1.6 - 2.0). However, although the oxide tailings leachate and the laboratory leachates have similar distribution, the oxide tailings leachate is missing the aluminum peak. The estimated reproducibility of the trace metal distributions in the Twin Butte tailings leachates was only 17.3 percent. Similar results, in which the geochemical parameters in mine leachates defined a fingerprint with a reproducibility greater than 90 percent but the trace metals defined a fingerprint with a reproducibility less than 30 percent, was observed at the Nevada heap leaching facilities.

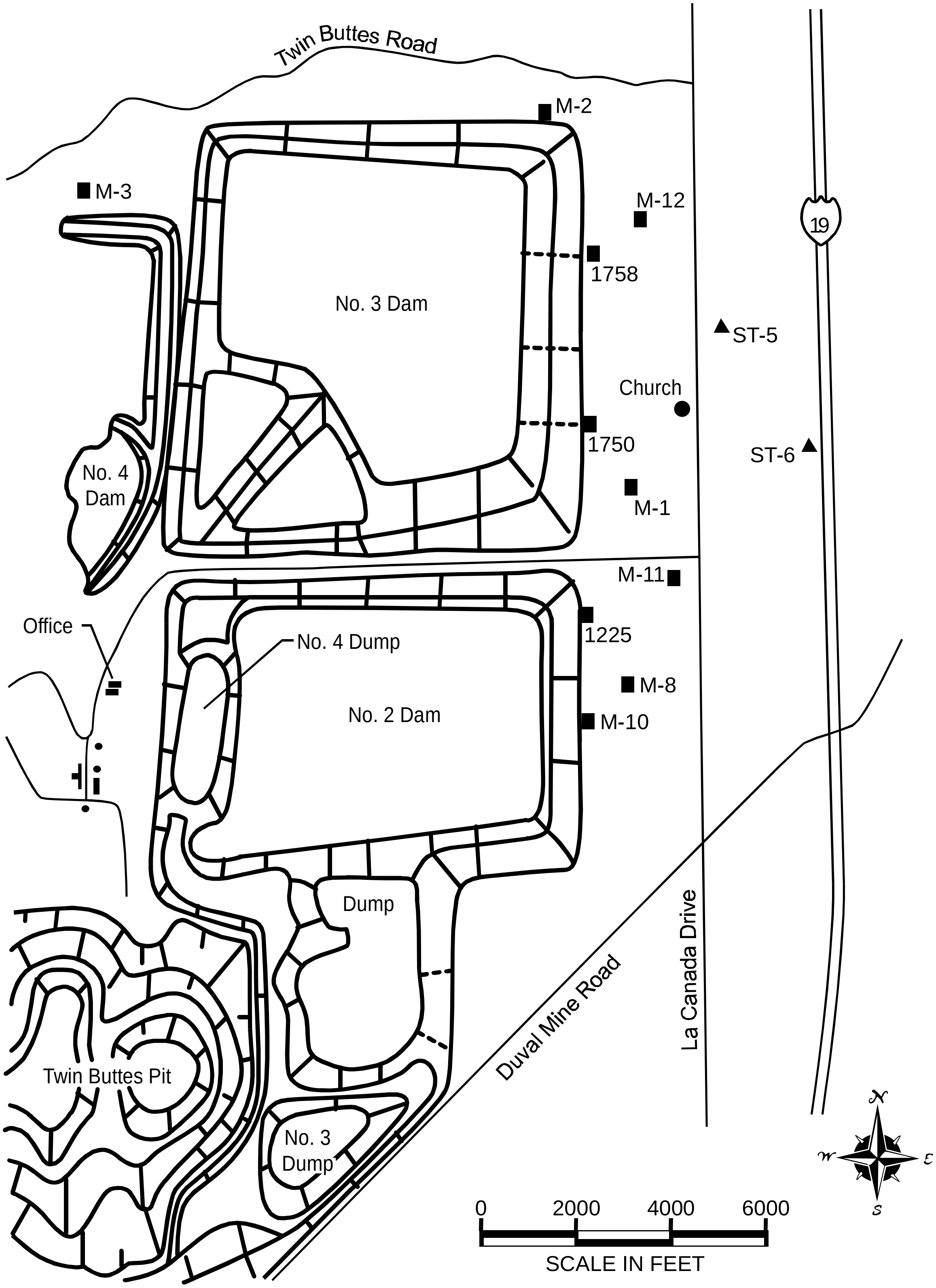
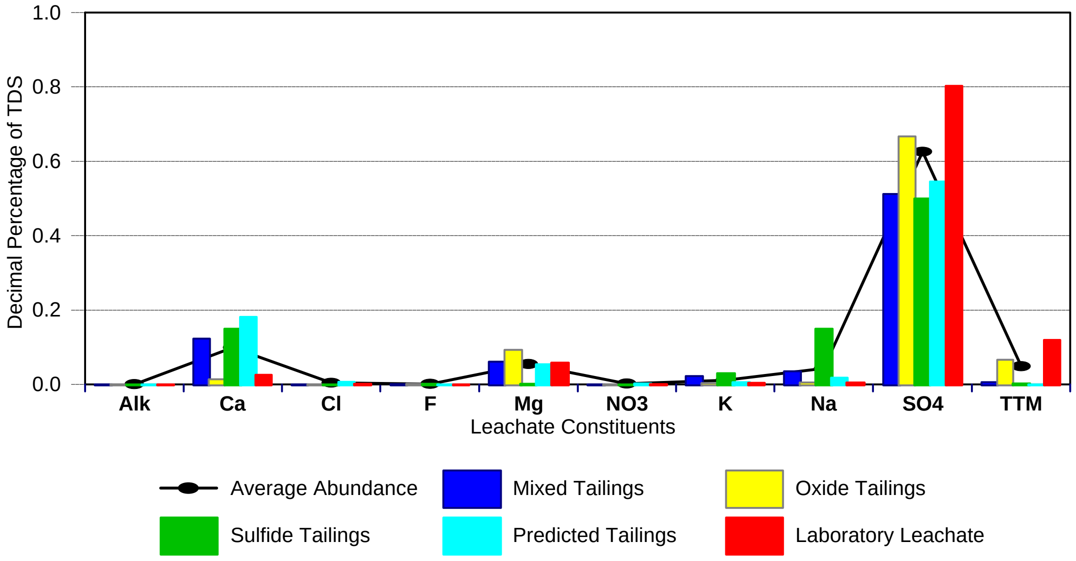


Figure 6-1. Schematic of the Twin Butte tailings disposal area.

Table 6-1. Reported composition of Twin Butte tailings leachates.

Constituents	Sulfide Tailings	Oxide Tailings	Mixed Tailings	Estimated Leachate	Laboratory Leachate	Average Concentration	Standard Deviation
Alkalinity		0		0	0	0	0
Calcium	150	400	600	1000	560	542	278
Chloride				35	38	37	2
Fluoride	2	40	3	1		11	16
Magnesium	2	2800	300	300	1310	942	1029
Nitrate				15	15	15	0
Potassium	30	100	55	30	85	60	28
Sodium	150	150	170	100	112	136	26
Sulfate	500	20000	3000	3000	17925	8885	8305
TTM	2.6	1963	29.4	1.03	2652	930	1146
TDS	1000	30000	4900	5500	22300	12740	11323
pH	8.00	2.00	7.50		1.61	4.78	2.98
Iron	0.20	750	15.	0.10	690	291	351
Manganese	0.15	600		0.50	650	313	313
Copper	0.20	200	2.0	0.01	194	79	96
Zinc	0.05	400	10.	0.02	285	139	170
Arsenic	0.01	0.20	0.10	<0.005	0.13	0.09	0.08
Cadmium		2.0	0.30		1.95	1.42	0.79
Chromium	0.01	5.0		<0.01	6.80	2.95	3.02
Lead	0.01	1.2		<0.05	1.93	0.79	0.82
Beryllium		0.3		<0.01	0.50	0.27	0.21
Nickel		2.0		<0.01	2.20	1.40	0.99
Molybdenum	2.00	0.20	2.00	0.10	<0.10	0.86	0.93
Aluminum					780	780	0.00
Phosphorous					34	34	0.00
Cobalt		2.00		<0.02	5.16	2.39	2.12
Cyanide	0.001	0.01	0.01			0.01	0.00

All results, except pH, expressed in units of mg/L.

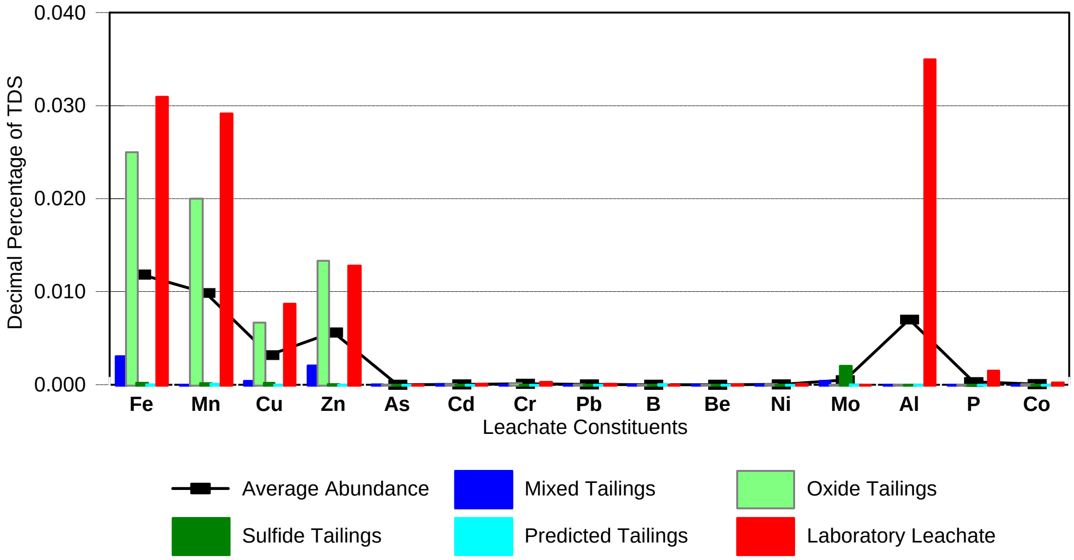


Regression analysis matrix for Twin Butte tailings leachate

	Mixed Tailings	Oxide Tailings	Sulfide Tailings	Predicted Tailings	Laboratory Leachate
Mixed Tailings	1.000	0.936	0.925	0.987	0.927
Oxide Tailings		1.000	0.809	0.885	0.992
Sulfide Tailings			1.000	0.912	0.817
Predicted Tailings				1.000	0.880
Laboratory Leachate					1.000

Average r squared value = 0.907

Figure 6-2. Geochemical fingerprint pattern for Twin Butte tailings leachate.



Regression analysis matrix for Twin Butte trace metal fingerprints

	Mixed Tailings	Oxide Tailings	Sulfide Tailings	Predicted Tailings	Laboratory Leachate
Mixed Tailings	1.000	0.584	0.008	0.000	0.221
Oxide Tailings		1.000	0.001	0.247	0.507
Sulfide Tailings			1.000	0.012	0.007
Predicted Tailings				1.000	0.142
Laboratory Leachate					1.000

Average r squared value = 0.173

Figure 6-3. Trace metal fingerprint pattern for Twin Butte tailings leachate.

6.1.2 Laboratory Column Studies

The Twin Butte file also contained the results of a column migration study. This study was originally performed to determine retardation or attenuation coefficients for each of the tailings leachate constituents. However, because of the extensive analyses that were reported, the results also provide insight into the behavior of mine leachate fingerprints under controlled conditions.

A series of six columns (61 cm high x 13.33 cm diameter) were packed with approximately 8500 cc of alluvial soil collected near the mine. A laboratory leachate (Table 6-1) was applied to the top of the column at a rate of 2 - 3 ml/min and allowed to percolate through the soil column. A total of four pore volumes of eluate were collected over time from each column. Each of the collected samples were analyzed for eight geochemical parameters, 15 trace metals, pH, and total dissolved solids.

The calculated attenuation coefficients for each of the tailings leachate constituents are presented as a histogram in Figure 6-4a. These values ranged from 0 to 6500 (the larger the coefficient, the greater the constituent attenuation and the slower it migrates). An inspection of these results shows that all of the high attenuation coefficients are associated with trace metals and iron, copper, and zinc are the only parameters with an attenuation coefficient greater than 1000. At this scale, the attenuation coefficients of the geochemical parameters are not evident.

The same set of calculated attenuation coefficients are replotted on an expanded vertical scale in Figure 6-4b. At a scale expansion of 200:1, it is apparent that the attenuation coefficients for the individual geochemical parameters are in the range of 0 to 2. These values are below the attenuation coefficients for all of the trace metals. The significance of these results is that the individual geochemical parameters would be expected to migrate faster through the environment because they have lower attenuation coefficients than each of the trace metals in the tailings leachates.

Since the Twin Butte tailings leachate was shown to have a constant geochemical fingerprint and the column study provided complete geochemical analyses for the column eluants, the results were used to evaluate the behavior of the leachate fingerprint as it migrated through the column (Figure 6-5). The first fraction shows some distortion of the fingerprint (higher calcium, lower sulfate) which is probably the result of a pH interaction with the column (initial leachate pH = 1.61). However, the match between the first pore volume sample and the original leachate fingerprint was still 90 percent. With subsequent column eluant samples, the match between the two fingerprints continued to improve until it reached 99 percent by the fourth pore volume. Similar results were observed in all six columns. That is, the tailings leachate fingerprint migrated through the soil column with minimal or no distortion of the pattern and it migrated rapidly because it was identifiable in the first eluants collected from the soil columns.

The trace metal distributions in the eluant samples were also compared to the trace metal distribution of the tailings leachate applied to the column (Figure 6-6). These results show that the trace metals display a different behavior than the geochemical parameters. First, in agreement with the higher attenuation coefficients, the trace metals are essentially absent from the first eluant samples. Even though the tailings leachate has migrated through the column and is identifiable by the geochemical fingerprint (Figure 6-5), the trace metals have not yet transited the column. Second, the trace metal patterns present in the eluant samples are more variable and not similar to the trace metal distribution of the leachate applied to the column. Aluminum and iron have been eliminated from the pattern, while manganese and zinc have a higher relative abundance in the eluants than in the tailings leachate. As a consequence of these distortions, there is less than a 25 percent match between the eluant patterns and the leachate fingerprint. Thus, unlike the geochemical results, there is essentially no relationship between the trace metal fingerprint in the column eluants and the fingerprint in the initial tailings leachate.

The column study results demonstrate three of the characteristic properties of mine waste leachate constituents. First, the set of geochemical parameters have attenuation coefficients that are 5 to 7000 times smaller than the trace metals. One consequence of the lower attenuation coefficients is that the geochemical parameters would be expected to migrate more rapidly through the environment than the trace metals. Second, the column study demonstrated that the geochemical fingerprint for the mine waste leachate maintained its chemical identity as it migrated through the soli column. Thus, the same set of parameters that can be used to uniquely fingerprint mine waste leachate at the source can also be used to detect and identify mine waste leachate as it migrates away from the source. Third, the trace metal distribution pattern in the column eluants is distorted compared to the original tailings leachate pattern. Since the trace metals migrate more slowly than the geochemical parameters, and their original distribution is altered on migrating through a soil column, the results suggest that trace metals would not be effective for early detection of mine waste leachate migration.

6.1.3 Field Monitoring Results

Tailings Dam 3

The Twin Butte data file contained the results from 19 surveys at Tailings Dam 3. The results of these sampling efforts are presented as an area plot in Figure 6-7. This information illustrates the following characteristics of the tailings leachate:

1. Sulfate has always been the most abundant ion in the leachate. However, between June, 1983 and August, 1985, its relative abundance has increased.
2. Between December, 1980 and June, 1983, the tailings leachate had a stable relative composition.
3. In June, 1983, the composition of the leachate was modified with the introduction of oxide tailings. The sulfuric acid used in processing oxide ore lowered the pH drastically (from 8.0 to 2.0), alkalinity was depleted (by operational definition, alkalinity does not exist below a pH of 4.5), and the abundance of sulfate was increased. Trace metals are more apparent in the area plot after June, 1983. This is due to the higher solubilities of trace metals at lower pH and the fact that trace metal analyses were not reported prior to June, 1983.

The geochemical monitoring results from the Twin Butte Tailings Dam 3, conducted between December, 1980 and August, 1985, are presented as a series of histograms in Figure 6-8 (five sets of data were considered suspect and deleted from the presentation because the mass balance for the results exceed 130 percent of the total dissolved solids concentration). Each of the remaining surveys define a consistent pattern in which sulfate represents 55 - 60 percent of the total dissolved solids concentration, calcium represents 15 percent of the total dissolved solids concentration, and magnesium represents 10 percent of the total dissolved solids concentration. The estimated reproducibility of the geochemical fingerprint pattern in the Twin Butte tailings pond was 97 percent ($r^2 = 0.970$). A comparison of the individual survey fingerprints with the laboratory fingerprint described in Figure 6-3 produced regression coefficient values that ranged from 0.967 to 0.991. Thus, both the field monitoring results and the laboratory studies at this copper mine demonstrate that the tailings leachate had a constant geochemical fingerprint.

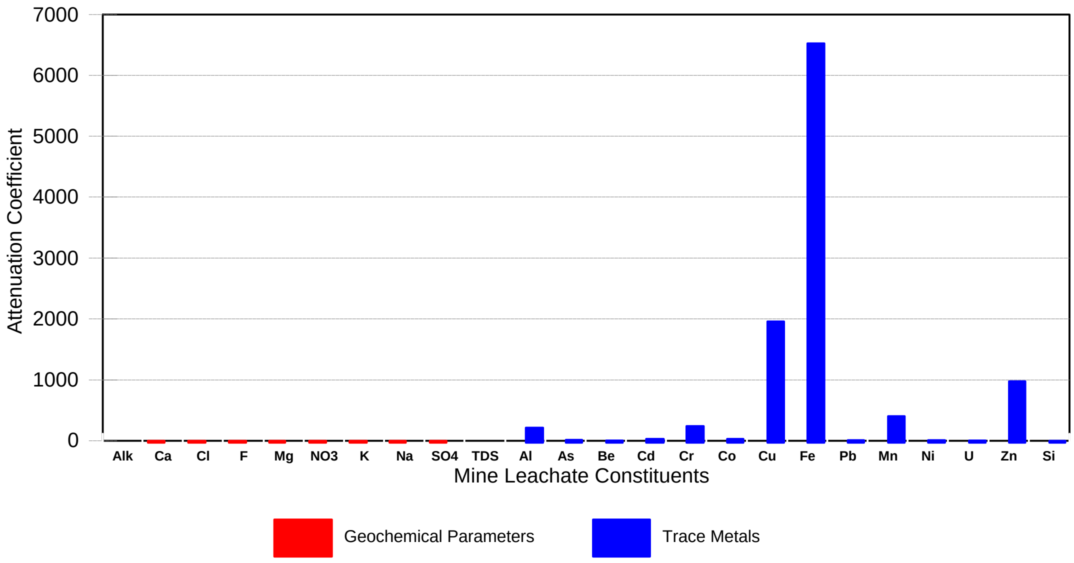


Figure 6-4a. Attenuation coefficients for Twin Butte tailings leachate constituents.

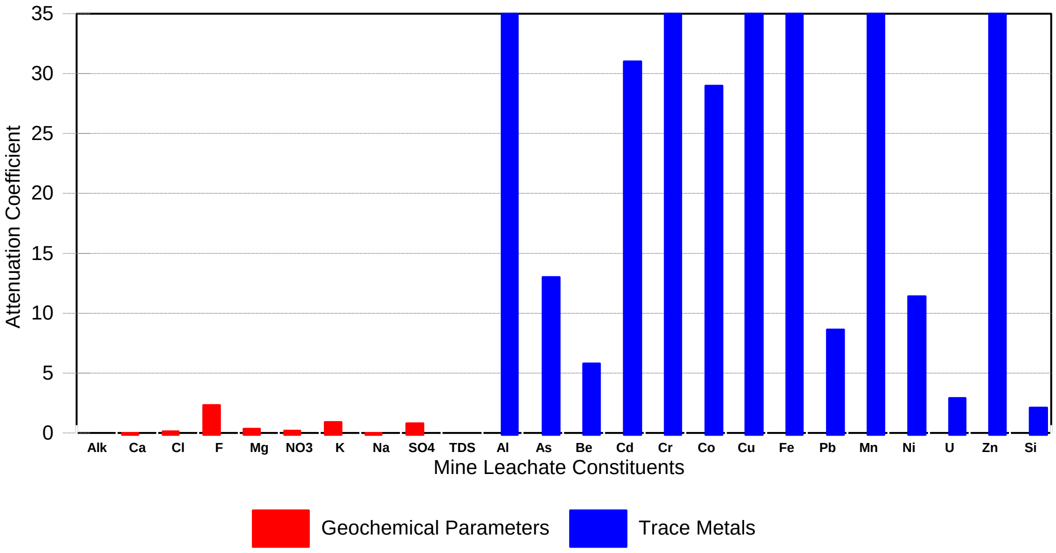
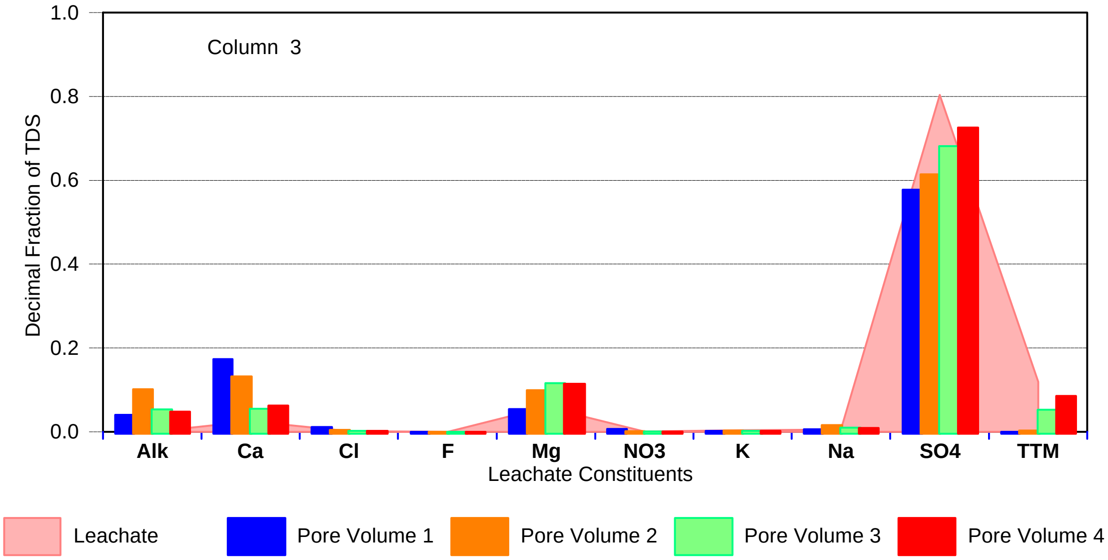


Figure 6-4b. Attenuation coefficients for Twin Butte tailings constituents (200:1 expanded scale).



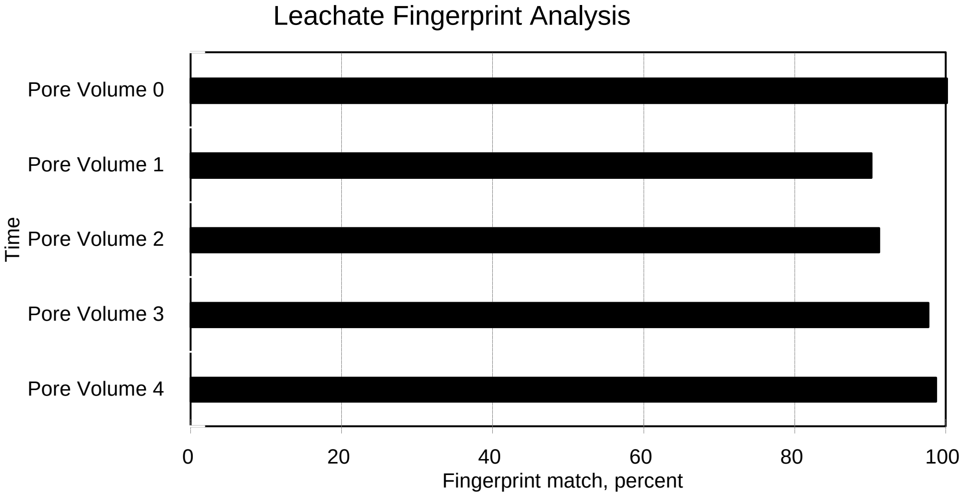


Figure 6-5. Geochemical fingerprint in Twin Butte column eluant samples.

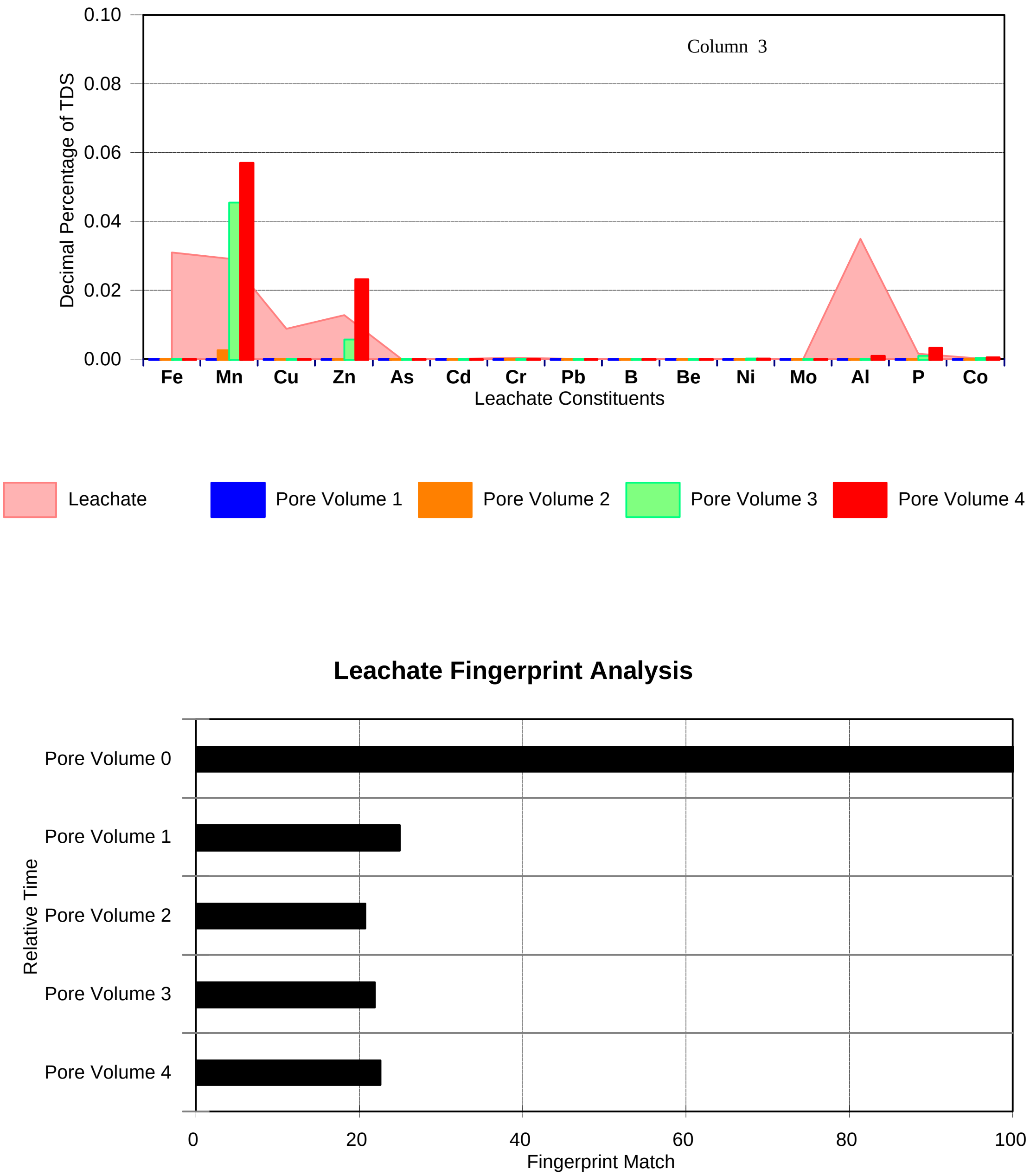


Figure 6-6. Trace metal fingerprint patterns in Twin Butte column eluant samples.

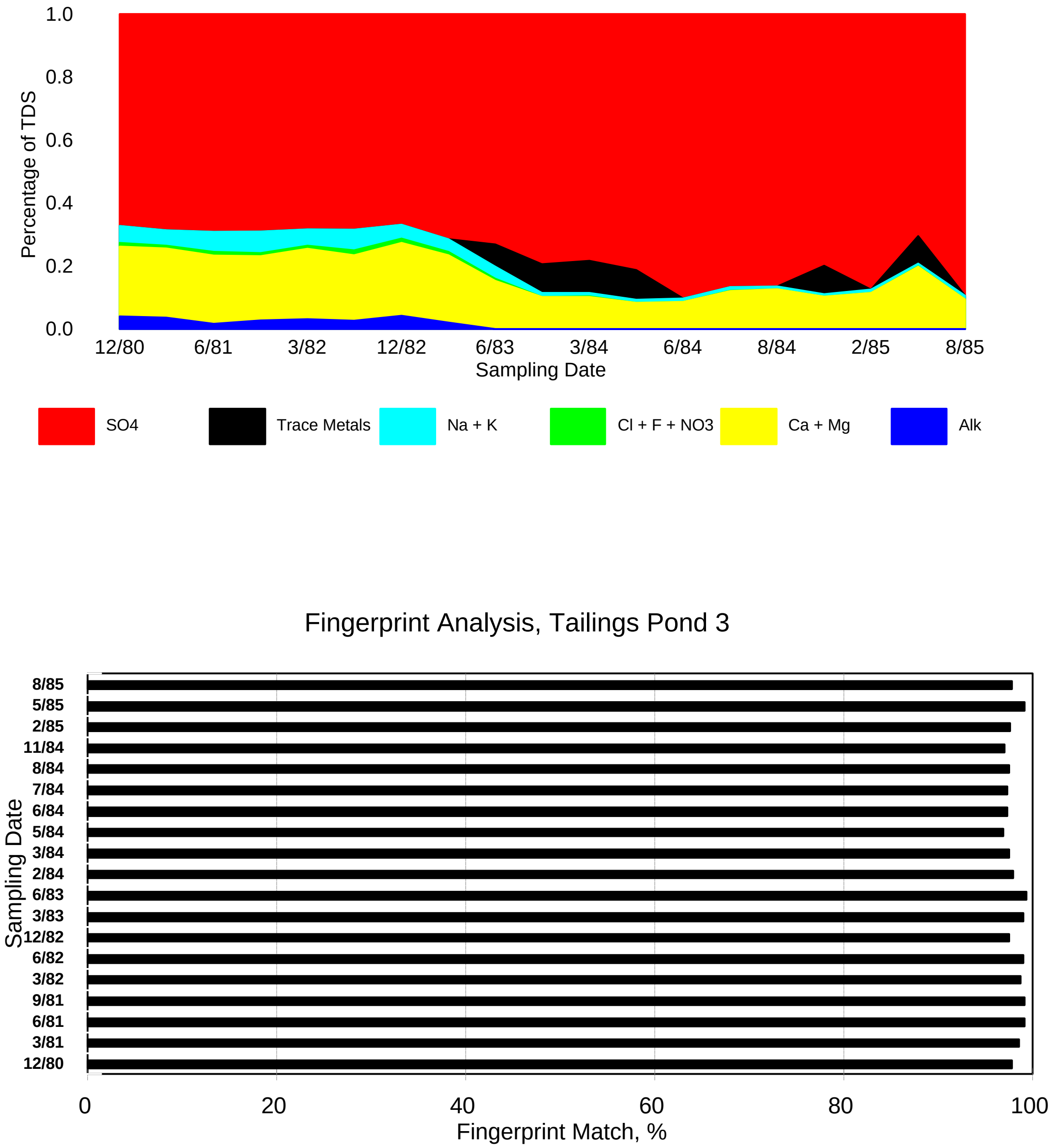
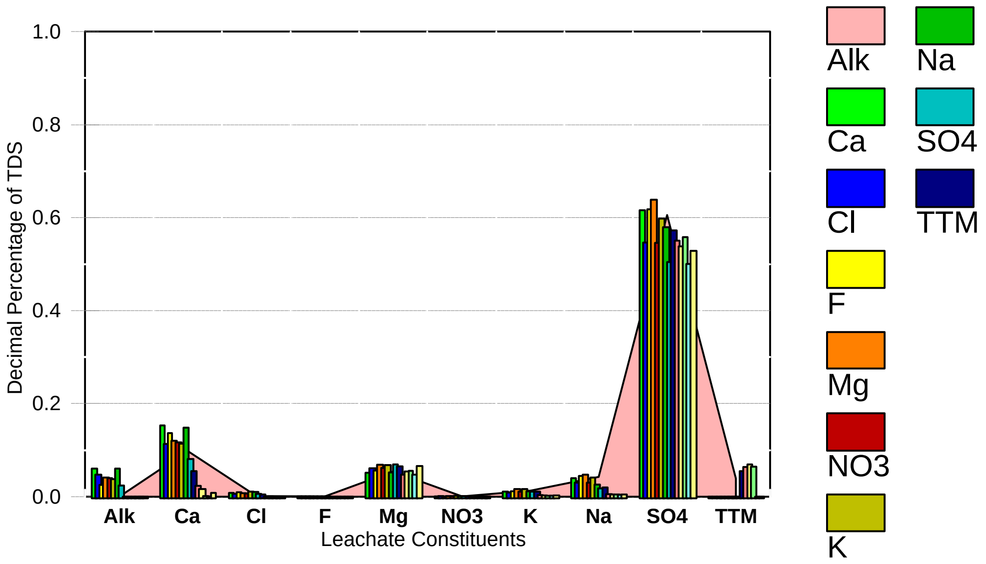


Figure 6-7. Tailings leachate composition over time at Twin Butte Tailings Pond 3.



Regression analysis matrix for Twin Butte Tailings Pond 3 monitoring results

	Tailings Pond 3 Sampling Date													
	12/80	**3/81**	**6/81**	**9/81**	**3/82**	**6/82**	**12/82**	**3/83**	**6/83**	**2/84**	**3/84**	**5/84**	**6/84**	**7/84**
12/80	1.000	0.997	0.995	0.994	0.997	0.994	0.999	0.985	0.952	0.929	0.919	0.911	0.936	0.937
3/81		1.000	0.996	0.998	1.000	0.998	0.996	0.995	0.967	0.947	0.939	0.933	0.957	0.959
6/81			1.000	0.998	0.998	0.998	0.984	0.992	0.968	0.946	0.936	0.929	0.953	0.954
9/81				1.000	0.999	1.000	0.992	0.996	0.973	0.954	0.946	0.941	0.965	0.967
3/82					1.000	0.999	0.996	0.995	0.967	0.947	0.938	0.932	0.956	0.958
6/82						1.000	0.992	0.997	0.974	0.954	0.946	0.941	0.965	0.968
12/82							1.000	0.984	0.949	0.926	0.916	0.908	0.933	0.935
3/83								1.000	0.981	0.964	0.958	0.954	0.976	0.980
6/83									1.000	0.996	0.994	0.991	0.986	0.986
2/84										1.000	0.999	0.998	0.986	0.984
3/84											1.000	0.999	0.983	0.982
5/84												1.000	0.986	0.985
6/84													1.000	0.999
7/84														1.000

Average r squared value = 0.970

Figure 6-8. Geochemical fingerprint pattern in Twin Butte Tailings Pond 3.

The trace metal data from tailings dam 3 are presented in histogram format in Figure 6-9. The four metals that are repeatedly present are copper, iron, manganese, and zinc. The average match between these patterns is 0.800. However, there is a significant change over time. The match between the trace metal pattern from the June, 1983 survey and the remainder of the surveys is only 41 percent but the match between all surveys after February, 1984 is 99 percent.

The reproducibility of the trace metal distribution after that date is due to the disposal of oxide tailings that lowered the leachate pH to approximately 2.0.

Upgradient Monitoring Wells

Monitoring Well M-3 is located approximately one-half mile west (upgradient) of Tailings Dam 3 (Figure 6-1). The geochemical monitoring results from 13 surveys at this well are contrasted with the tailings leachate fingerprint in Figure 6-10. Each of the surveys demonstrate that alkalinity is the dominant ion in ground water upgradient of the tailings disposal area and represents 35 - 40 percent of the total dissolved solids concentration. The reproducibility of the upgradient ground-water pattern between August, 1980 and May, 1985 was 93 percent. However, the similarity between the alkalinity-rich, sulfate-poor fingerprint of upgradient ground water and the sulfate-rich, alkalinity-poor fingerprint of the tailings leachate was only 1.6 percent.

The trace metal distribution at Well M-3 is compared to the trace metal distribution in tailings leachate in Figure 6-11. The reproducibility of the trace metal fingerprint at this upgradient location was estimated by regression analysis to be 87 percent ($r^2 = 0.867$). This pattern was distinctly different from the trace metal pattern for tailings leachate ($r^2 = 0.113$).

The compositional fingerprints for geochemical parameters and trace metals that were described for Well M-3 were also observed at Well M-4 (approximately one mile west of Well M-3). Since the ground water upgradient of the Twin Butte Mine has a reproducible fingerprint that is characteristically different from the tailings leachate, these patterns should be useful for detecting and identifying any leachate that is migrating away from the tailings disposal area.

Downgradient Monitoring Wells

Monitoring Well M-1 is located approximately 2000 feet downgradient from the south-east corner of Tailings Dame 3 (Figure 6-1). The geochemical results from this well are presented as a series of histograms and compared to the tailings leachate fingerprint in Figure 6-12. The ground water has undergone a compositional shift when compared to upgradient Well M-3 (Figure 6-8). The data show that the ground water at Well M-1 consists of 45 percent sulfate, 15 percent calcium, and 10 - 15 percent alkalinity. This sulfate-rich, alkalinity-poor pattern has a reproducibility of 99 percent and a strong resemblance (86 percent match) to the tailings leachate fingerprint. Based on the geochemical fingerprint comparison, the monitoring results clearly demonstrate that tailings leachate has impacted the ground water in the vicinity of Well M-1 for several years.

The composition of the tailings leachate that has migrated to Well M-1 has been altered slightly. The ground water has an increased abundance of both alkalinity and calcium. This is undoubtedly due to a simple and rapid neutralization of the initial leachate with calcium carbonate in the alluvial soils. The acid-base reaction would increase the solution pH, increase alkalinity (bicarbonate) in the solution, and increase the calcium to maintain the mass balance. Another change that has occurred is the reduction in total trace metals. These parameters collectively represent 5 - 10 percent of the leachate fingerprint but are essentially absent from Well M-1. Each of these changes were observed in the column attenuation study. These results demonstrate that the environmental behavior of the leachate is consistent with its behavior under controlled conditions in the laboratory and that the geochemical fingerprint of the leachate can still be identified after it migrates some distance from the source.

The trace metal results from Well M-1 are presented graphically in Figure 6-13. Each of these surveys indicate that small amounts of iron and zinc are consistently present at this location. However, although the geochemical results indicate that this well has been impacted by leachate for several years, this fingerprint is a poor match for tailings leachate ($r^2 = 0.437$). These field results are consistent with the column study that demonstrated the trace metal fingerprint will be altered as leachate migrates away from the source.

A second downgradient monitoring location at the Twin Butte site is Well M-2 which is located at the north-east corner of Tailings Dam 3 (Figure 6-1). The normalized geochemical monitoring results from this well are compared to the tailings leachate fingerprint in Figure 6-14. These results appear to be more variable than those at Well M-1 because the reproducibility of the pattern is only 77 percent and the match with the leachate fingerprint is only 27 percent. However, a closer inspection of the data suggests that temporal charges are occurring at this well because the relative abundance of alkalinity is decreasing and the relative abundance of sulfate is increasing with time.

Geochemical monitoring results were used to construct an area plot to illustrate the compositional shift that has occurred at Well M-2 (Figure 6-15). Between August, 1980 and December, 1981, the results from this location defined a fingerprint that is identical to the alkalinity-rich, sulfate-poor fingerprint at upgradient Well M-3 (Figure 6-10). Six surveys produced a geochemical fingerprint that had a 97 percent match with upgradient conditions. This pattern also had less than a one percent match with the tailings leachate fingerprint.

A series of systematic changes began to occur at Well M-2 in 1982 and 1983. These changes included a decrease in the relative abundance of alkalinity and an increase in the relative abundance of sulfate. Although not shown, there was also a simultaneous increase in the total dissolved solids concentration. As a result of this compositional shift, the similarity between ground water at Well M-2 and the tailings leachate increased from less than 10 percent to 90 percent. Since 1984, the fingerprint comparison has stabilized in the 85 to 90 percent range. Each of the identified changes could only have been caused by the migration of fugitive tailings leachate migrating to and past Well M-2.

Another important observation illustrated in Figure 6-15 is that the trace metals at Well M-2 did not show any appreciable change over time. Even though trace metals represent five to ten percent of the total dissolved solids concentration of tailings leachate, and leachate caused a significant shift in ground-water composition at Well M-2, there was no notable increase in trace metals prior to, during, or after the transition. These field monitoring results, which are consistent with the column migration study, suggest that trace metals would not be effective parameters to detect the early migration of tailings leachate.

Downgradient Well 1225 is located on the north-east corner of Tailings Dam 2 (Figure 6-1). Fifteen years of monitoring data for the geochemical parameters have been summarized as an area plot in Figure 6-16. These results illustrate the same trends that were identified and discussed for Well M-2:

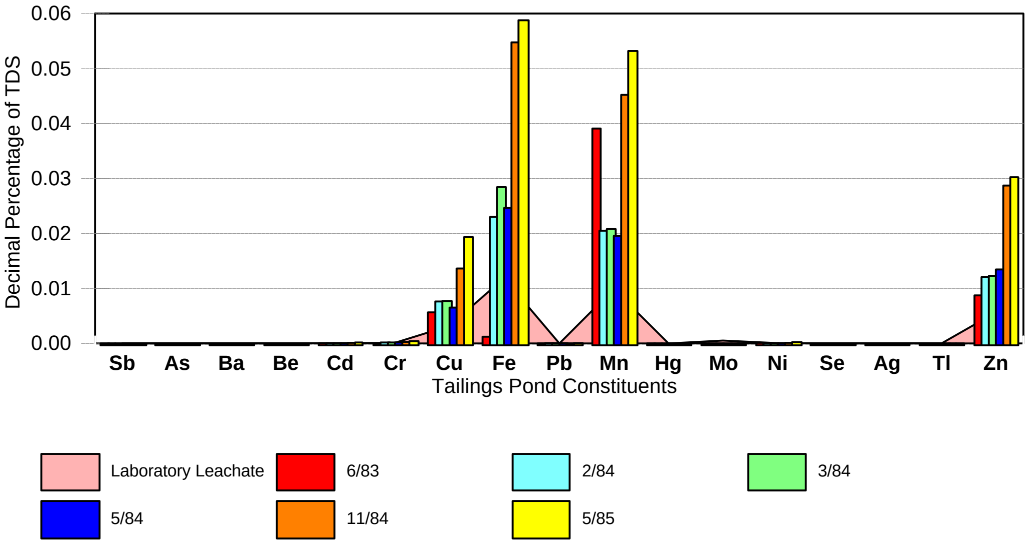
1. Between June, 1970 and July, 1976, the ground water at this location had a composition that can be described as alkalinity-rich and sulfate-poor. This geochemical fingerprint, which is identical to that observed at upgradient Wells M-3 and M-4 and at downgradient Well M-2 prior to the detection of tailings leachate, only had a 5 percent match with the tailings leachate fingerprint.
2. The composition of ground water at Well 1225 was altered between 1976 and 1980. These changes included an increase in the total dissolved solids concentration, a large increase in the relative abundance of sulfate, and a decrease in the relative abundance of alkalinity. As a result of these changes, the similarity between the geochemical fingerprint at this well and tailings leachate increased from 5 percent to 80 percent.
3. As tailings leachate began impacting the ground-water composition at Well 1225, the relative abundance of trace metals was not affected. This observation is consistent with field observations at Well M-2 and the laboratory column studies.
4. The ground-water composition stabilized between 1983 and 1984. The final geochemical fingerprint has a 90 percent match with tailings leachate. The fingerprint comparison is identical to that observed in the column studies (86 percent) and at Well M-2 (85 to 90 percent).

The assessment of monitoring results from the Twin Butte tailings basin (Figure 6-8) and the laboratory studies (Figure 6-2) showed that the leachate had a constant geochemical fingerprint. The monitoring data from Well 1225 illustrate the environmental behavior of the fingerprint. First, the geochemical fingerprint remains in tact as the leachate migrates from the source. As a result of this characteristic, a series of simultaneous changes uniquely identify the occurrence of leachate at a monitoring well.

These changes include an increase in total dissolved solids, an increase in the relative abundance of sulfate, a decrease in the relative abundance of alkalinity, and an improved fingerprint match at the monitoring location. Second, the trace metal component of the fingerprint does not migrate as rapidly as the geochemical components. The higher attenuation coefficients and the lower solubilities at neutral pH contribute to the slower movement of the trace metals. The field data indicate that trace metals would not be useful for early detection of leachate migration because the geochemical composition shift occurs before any changes in trace metal abundance.

Monitoring results from Well M-7, located approximately 1000 feet south of Well M-10 (Figure 6-1), are presented as an area plot in Figure 6-17. The initial sampling at this well in July, 1981 was not sufficient to establish background conditions. However, it is apparent that the relative abundance of alkalinity declined during 1981 and 1982 and the relative abundance of sulfate increased from 20 percent to 60 percent of the total dissolved solids. Over the same period, the fingerprint match between the ground water and the tailings leachate increased from 20 percent to 95 percent. Thus, the data from this station provide another example of mine tailings leachate retaining its geochemical fingerprint as it migrates through the subsurface environment.

It is worth noting that the trace metal component of the leachate fingerprint are not present at Well M-7. Even though trace metals represent five to ten percent of the total dissolved solids concentration of the leachate (Figure 6-8), and leachate has been present at Well M-7 for four years, there has been no change in the trace metal abundance over time. These monitoring results provide additional evidence that the trace metals will migrate slower than the leachate.

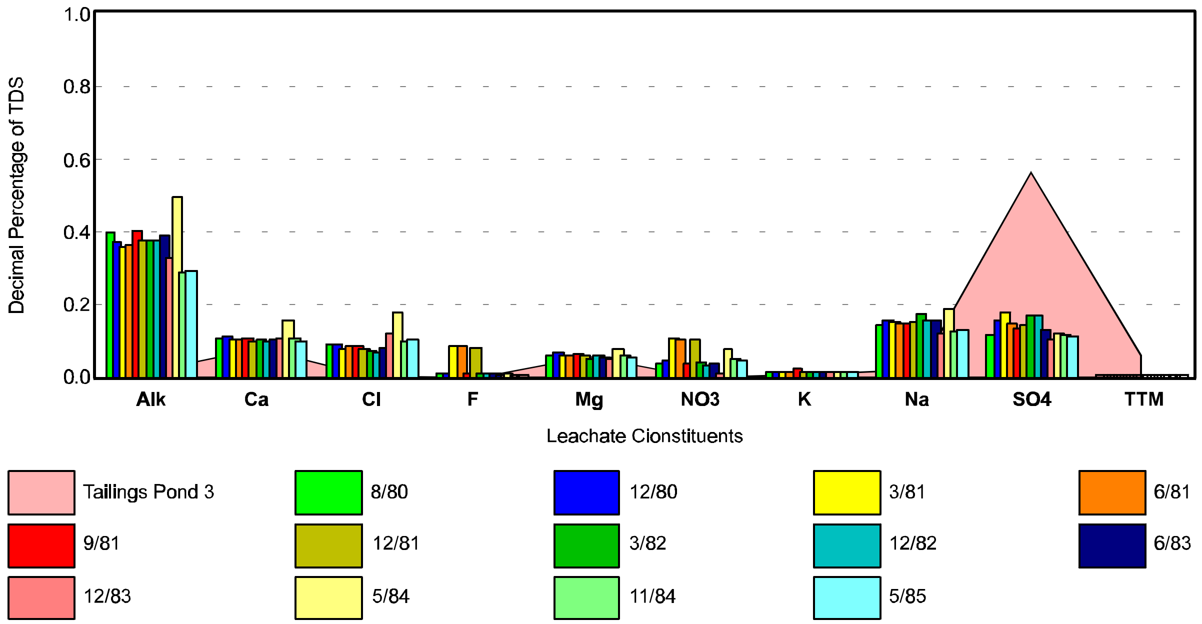


Regression analysis matrix for trace metal fingerprint in tailings dam 3

	6/83	2/84	3/84	5/84	11/84	5/85
Laboratory Leachate	0.415	0.996	0.994	0.995	0.997	0.996
6/83	1.000	0.447	0.351	0.387	0.408	0.455
2/84		1.000	0.988	0.993	0.995	1.000
3/84			1.000	0.992	0.993	0.987
5/84				1.000	0.999	0.992
11/84					1.000	0.995
5/85						1.000

Average r squared value = 0.800
Average r squared value for 6/83 survey = 0.410
Average r squared value for all surveys after 2/84 = 0.993

Figure 6-9. Trace metal fingerprint pattern in Twin Butte Tailings Pond 3.

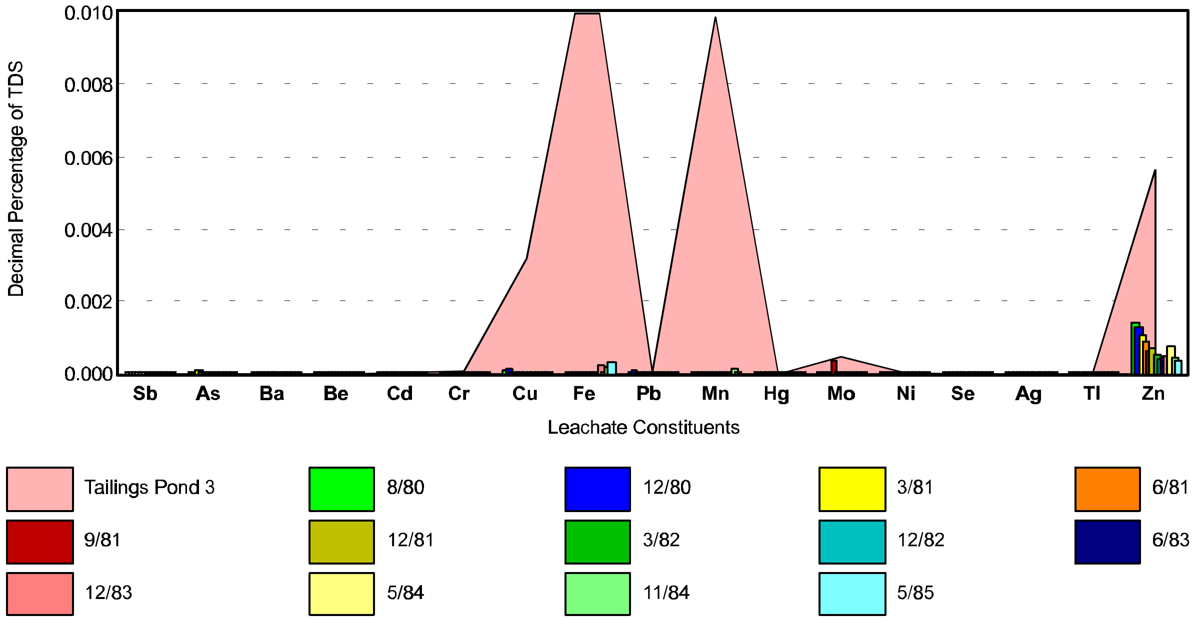


Regression analysis matrix for the geochemical fingerprint at Twin Butte Tailings Monitoring Well M-3

	Sampling Date												
	8/80	**12/80**	**3/81**	**6/81**	**9/81**	**12/81**	**3/82**	**12/82**	**6/83**	**12/83**	**5/84**	**11/84**	**5/85**
Tailings Pond 3	0.002	0.026	0.032	0.008	0.007	0.005	0.038	0.042	0.006	0.003	0.020	0.010	0.008
8/80	1.000	0.981	0.889	0.945	0.998	0.923	0.963	0.967	0.996	0.970	0.969	0.971	0.974
12/80		1.000	0.916	0.919	0.989	0.922	0.993	0.993	0.991	0.954	0.938	0.982	0.982
3/81			1.000	0.990	0.904	0.986	0.923	0.924	0.908	0.817	0.833	0.878	0.875
6/81				1.000	0.920	0.998	0.916	0.916	0.925	0.850	0.878	0.896	0.896
9/81					1.000	0.928	0.976	0.981	0.998	0.963	0.954	0.971	0.973
12/81						1.000	0.920	0.921	0.933	0.849	0.882	0.895	0.895
3/82							1.000	0.997	0.982	0.925	0.901	0.958	0.960
12/82								1.000	0.982	0.925	0.897	0.953	0.953
6/83									1.000	0.961	0.956	0.975	0.976
12/83										1.000	0.974	0.973	0.980
5/84											1.000	0.971	0.976
11/84												1.000	0.996
5/85													1.000

Average r squared value for ground-water data = 0.931
Average ground water tailings pond comparison = 0.016

Figure 6-10. Geochemical fingerprint at upgradient Well M-3.



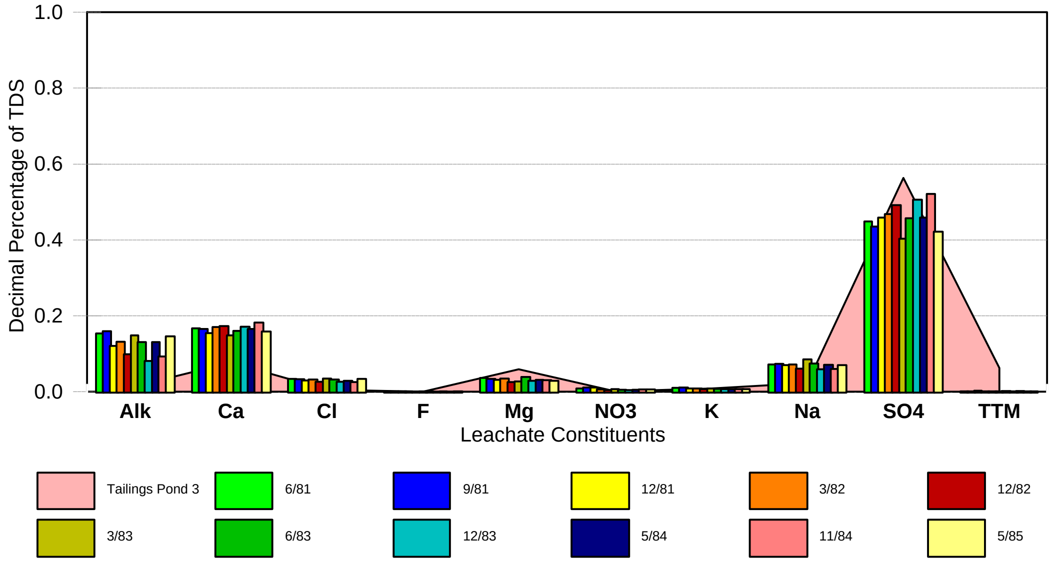
Regression analysis matrix for the trace metal fingerprint at Twin Butte Tailings Monitoring Well M-3

	Sampling Date												
	8/80	**12/80**	**3/81**	**6/81**	**9/81**	**12/81**	**3/82**	**12/82**	**6/83**	**12/83**	**5/84**	**11/84**	**5/85**
Tailings Pond 3	0.070	0.070	0.067	0.069	0.038	0.069	0.069	0.069	0.069	0.256	0.069	0.370	0.446
8/80	1.000	0.998	0.999	1.000	0.771	1.000	1.000	1.000	1.000	0.862	1.000	0.845	0.555
12/80		1.000	0.995	0.997	0.765	0.997	0.997	0.997	0.997	0.857	0.997	0.838	0.550
3/81			1.000	0.999	0.770	0.999	0.999	0.999	0.999	0.861	0.999	0.844	0.555
6/81				1.000	0.772	1.000	1.000	1.000	1.000	0.863	1.000	0.847	0.557
9/81					1.000	0.772	0.772	0.772	0.772	0.648	0.772	0.625	0.403
12/81						1.000	1.000	1.000	1.000	0.863	1.000	0.847	0.557
3/82							1.000	1.000	1.000	0.863	1.000	0.847	0.557
12/82								1.000	1.000	0.863	1.000	0.847	0.557
6/83									1.000	0.863	1.000	0.847	0.557
12/83										1.000	0.863	0.948	0.883
5/84											1.000	0.847	0.557
11/84												1.000	0.811
5/85													1.000

Average r squared value for ground-water data = 0.867

Average ground water tailings pond comparison = 0.133

Figure 6-11. Trace metal distribution at upgradient Well M-3.

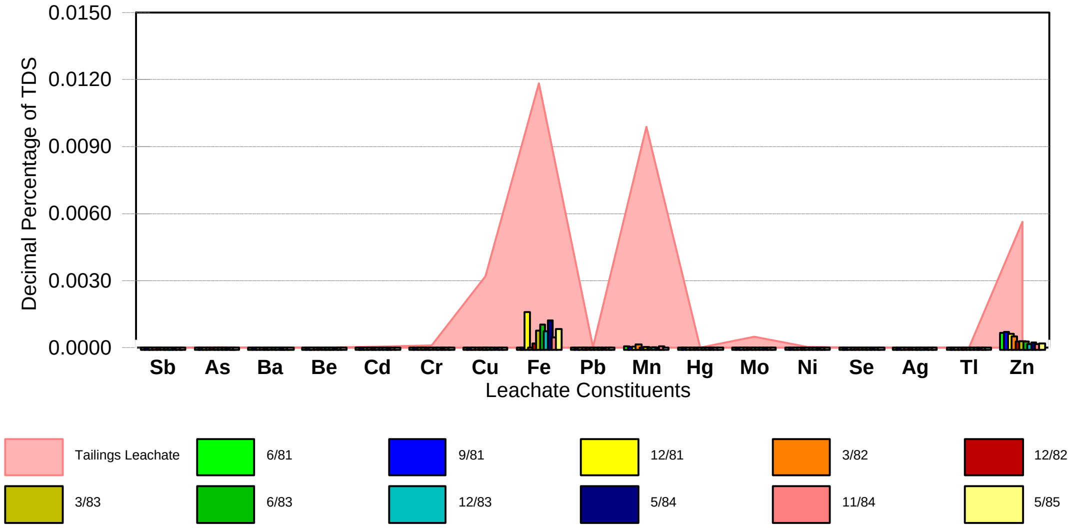


Regression analysis matrix for the geochemical fingerprint at Twin Butte Tailings Monitoring Well M-1

	Sampling Date										
	6/81	**9/81**	**12/81**	**3/82**	**12/82**	**3/83**	**6/83**	**12/83**	**5/84**	**11/84**	**5/85**
Tailings Pond 3	0.835	0.819	0.883	0.864	0.900	0.810	0.869	0.917	0.865	0.909	0.828
Upgradient ground water	0.147	0.163	0.141	0.110	0.065	0.172	0.114	0.047	0.112	0.054	0.151
6/81	1.000	0.999	0.993	0.997	0.982	0.996	0.997	0.970	0.997	0.975	1.000
9/81		1.000	0.989	0.994	0.975	0.997	0.994	0.961	0.994	0.967	0.999
12/81			1.000	0.999	0.995	0.987	0.999	0.989	0.999	0.992	0.992
3/82				1.000	0.993	0.991	1.000	0.985	1.000	0.989	0.996
12/82					1.000	0.970	0.992	0.998	0.993	0.999	0.980
3/83						1.000	0.992	0.956	0.991	0.961	0.997
6/83							1.000	0.984	1.000	0.987	0.996
12/83								1.000	0.985	1.000	0.967
5/84									1.000	0.989	0.996
11/84										1.000	0.973
5/85											1.000

Average r squared value for ground-water data = 0.989
Average ground water tailings pond comparison = 0.863
Upgradient - Well 1 comparison = 0.116

Figure 6-12. Geochemical fingerprint at downgradient Well M-1.

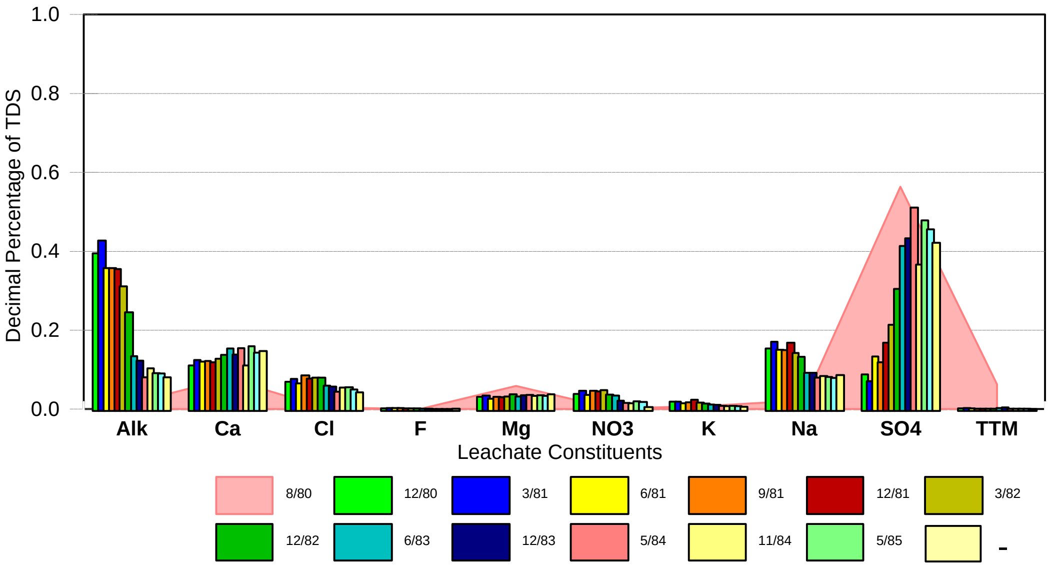


Regression analysis matrix for the trace metal fingerprint at Twin Butte Tailings Monitoring Well M-1

	Sampling Date										
	6/81	**9/81**	**12/81**	**3/82**	**12/82**	**3/83**	**6/83**	**12/83**	**5/84**	**11/84**	**5/85**
Tailings Pond 3	0.093	0.083	0.591	0.164	0.389	0.608	0.558	0.559	0.543	0.664	0.551
Upgradient ground water	0.990	0.993	0.132	0.927	0.722	0.130	0.066	0.043	0.036	0.099	0.050
6/81	1.000	0.999	0.091	0.963	0.658	0.091	0.037	0.021	0.016	0.067	0.025
9/81		1.000	0.092	0.951	0.662	0.092	0.038	0.021	0.016	0.066	0.026
12/81			1.000	0.081	0.639	1.000	0.987	0.974	0.967	0.990	0.978
3/82				1.000	0.604	0.082	0.030	0.016	0.012	0.067	0.020
12/82					1.000	0.636	0.529	0.479	0.461	0.583	0.496
3/83						1.000	0.986	0.974	0.967	0.993	0.978
6/83							1.000	0.997	0.995	0.985	0.999
12/83								1.000	1.000	0.979	1.000
5/84									1.000	0.972	0.999
11/84										1.000	0.980
5/85											1.000

Average r squared value for ground-water data = 0.552
Average ground water tailings pond comparison = 0.437
Upgradient - Well 1 comparison = 0.381

Figure 6-13. Trace metal distribution at downgradient Well M-1.



Regression analysis matrix for the geochemical fingerprint at Twin Butte Tailings Monitoring Well M-2

	Sampling Date													
	8/80	**12/80**	**3/81**	**6/81**	**9/81**	**12/81**	**3/82**	**12/82**	**6/83**	**12/83**	**5/84**	**11/84**	**5/85**	—
Tailings Pond 3	0.151	0.008	0.152	0.001	0.009	0.048	0.190	0.428	0.458	0.599	0.335	0.494	0.468	0.510
Upgradient ground water	0.964	0.953	0.981	0.984	0.983	0.971	0.569	0.643	0.619	0.477	0.728	0.577	0.603	0.567
8/80	1.000	0.994	0.989	0.992	0.979	0.928	0.767	0.513	0.487	0.345	0.610	0.445	0.473	0.433
12/80		1.000	0.974	0.984	0.959	0.898	0.726	0.466	0.438	0.300	0.557	0.397	0.423	0.388
3/81			1.000	0.996	0.997	0.972	0.849	0.618	0.592	0.448	0.709	0.551	0.579	0.539
6/81				1.000	0.991	0.960	0.825	0.584	0.557	0.413	0.674	0.516	0.542	0.502
9/81					1.000	0.982	0.873	0.649	0.625	0.481	0.740	0.583	0.611	0.570
12/81						1.000	0.946	0.768	0.745	0.609	0.843	0.708	0.732	0.694
3/82							1.000	0.927	0.913	0.816	0.964	0.888	0.903	0.879
12/82								1.000	0.997	0.970	0.983	0.995	0.996	0.990
6/83									1.000	0.978	0.981	0.997	0.999	0.994
12/83										1.000	0.922	0.988	0.981	0.990
5/84											1.000	0.968	0.978	0.958
11/84												1.000	0.999	0.997
5/85													1.000	0.994
—														1.000

Average r squared value for ground-water data = 0.768
Average ground water tailings pond comparison = 0.275
Upgradient - Well 1 comparison = 0.780

Figure 6-14. Geochemical fingerprint pattern at Well M-2.

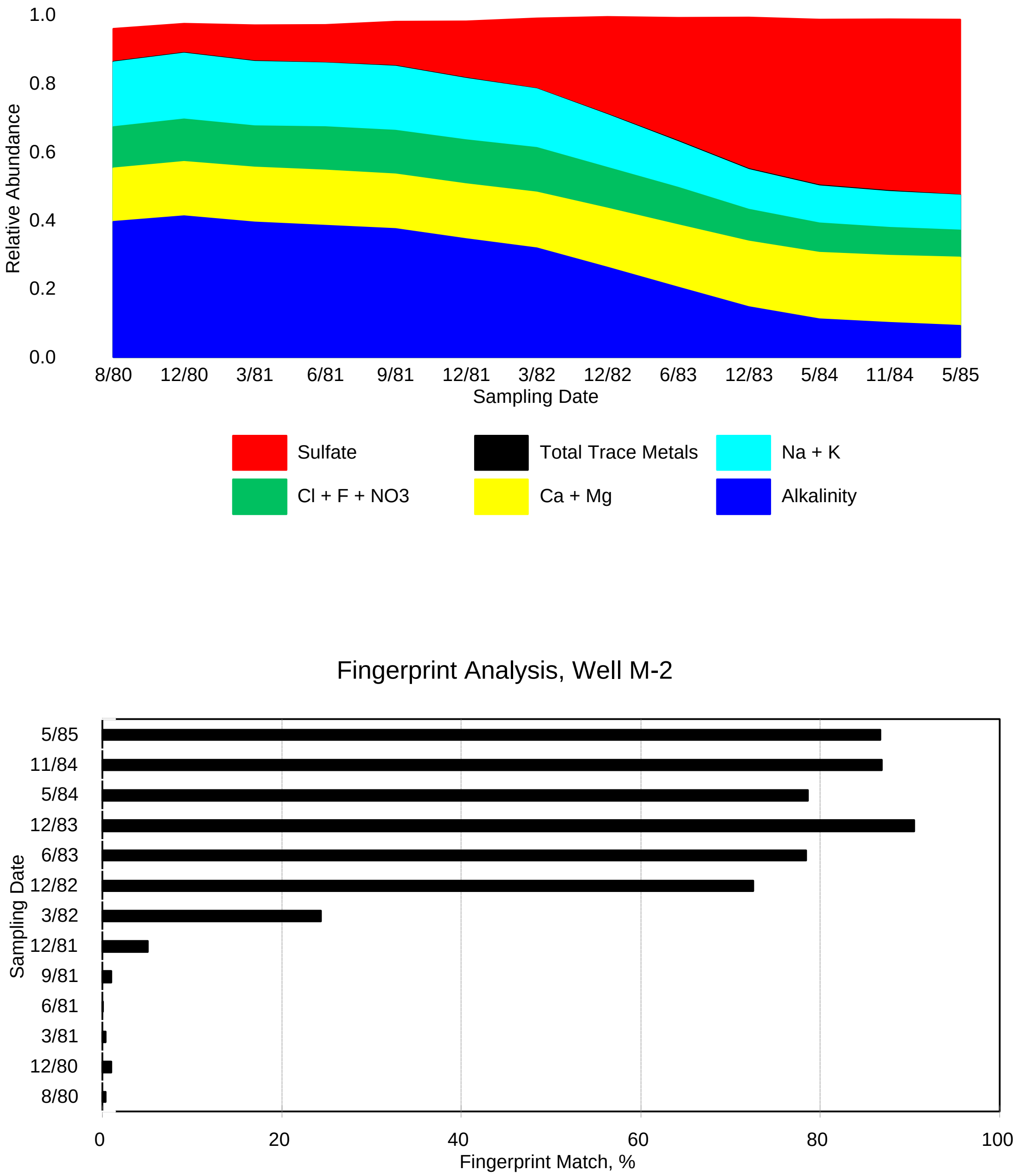


Figure 6-15. Area plot of monitoring results at Well M-2.

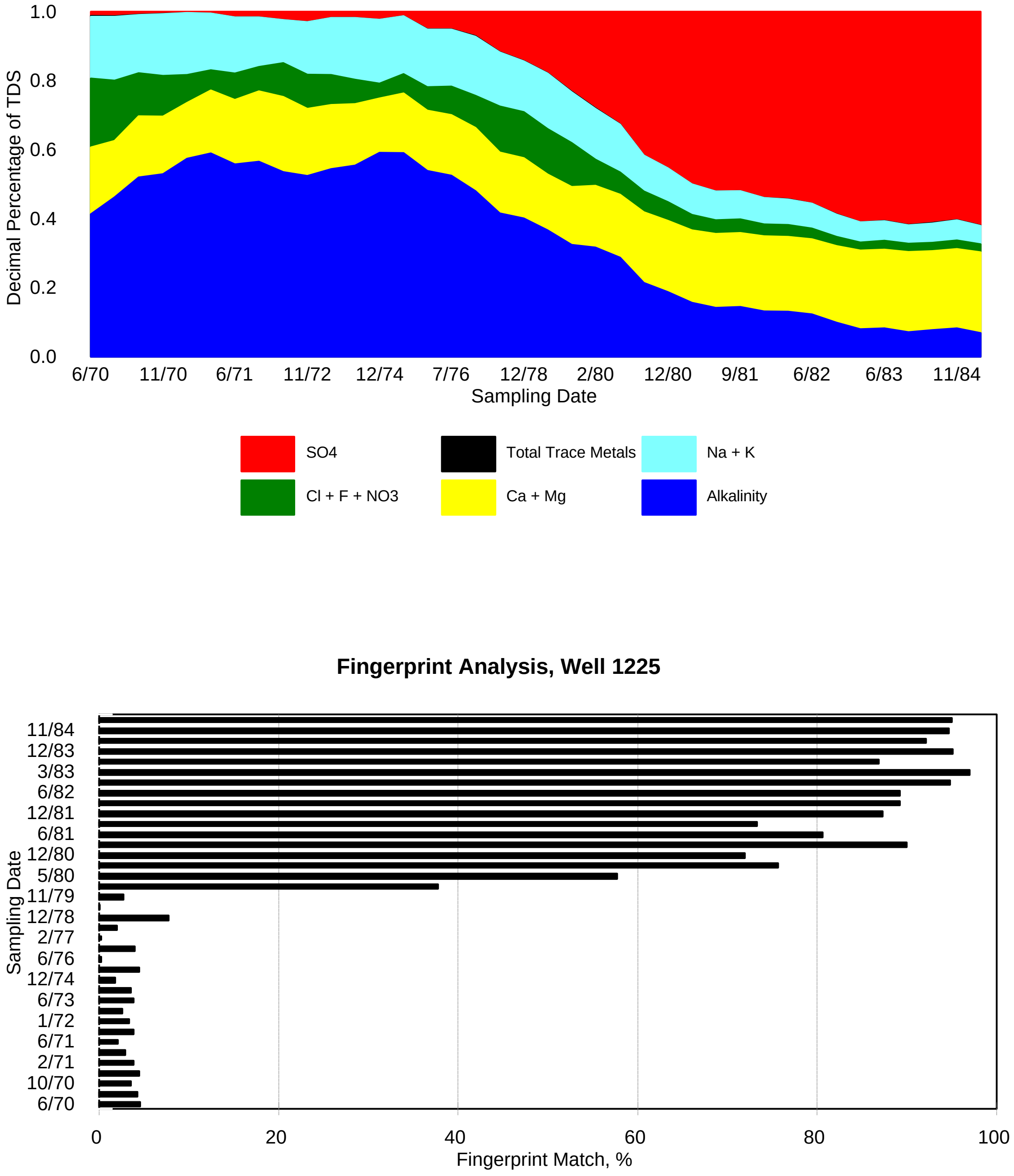
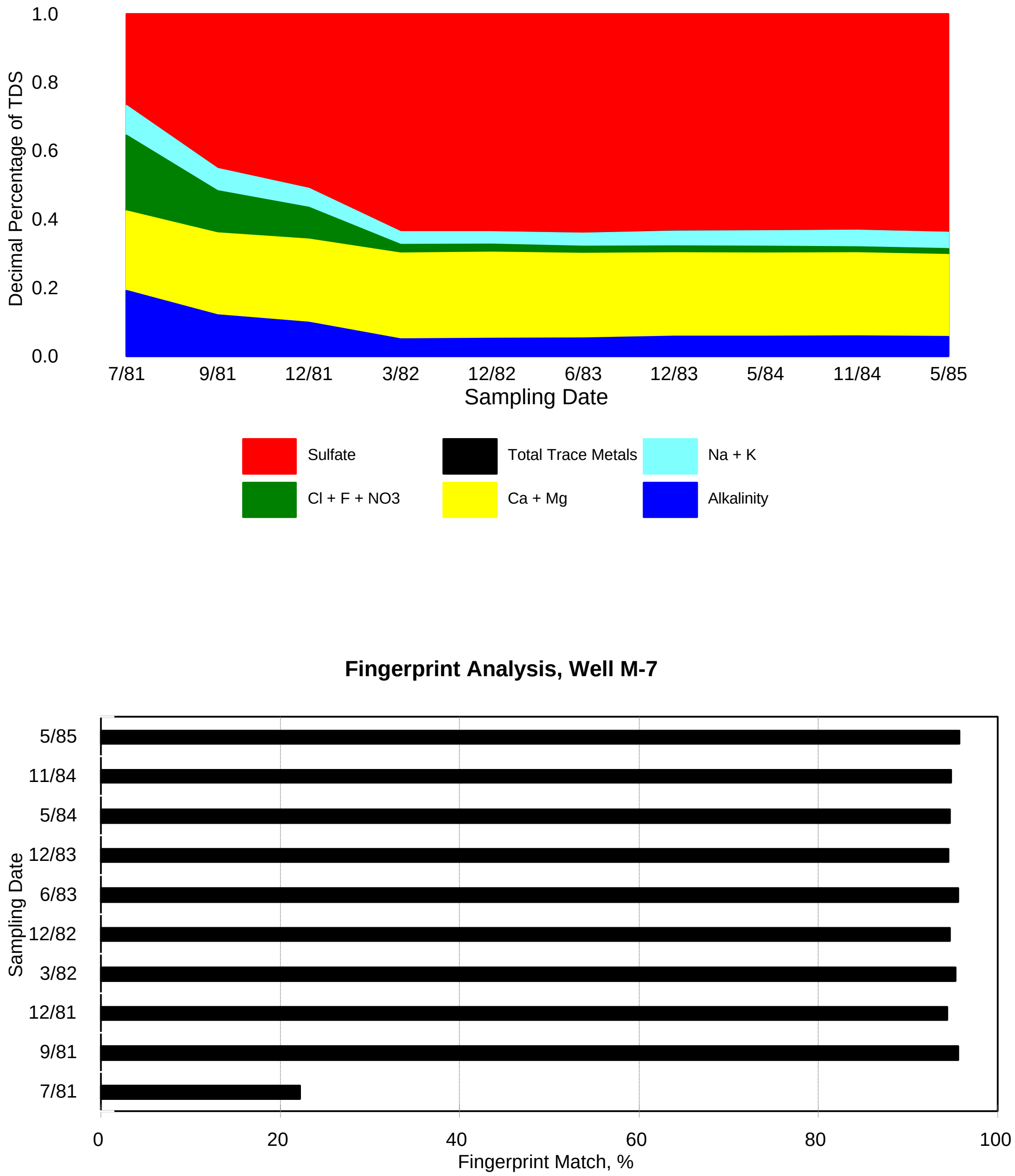


Figure 6-16. Monitoring results from downgradient Well 1225.



Fingerprint Analysis, Well M-7

Figure 6-17. Monitoring results from downgradient Well M-7.

Monitoring results from downgradient Well M-5, located 1000 feet north of Well 1225 (Figure 6-1), are presented in Figure 6-18. These data indicate that alkalinity-rich, sulfate-poor conditions typical of upgradient background conditions were present at this location from August, 1980 until early 1982. Between 1982 and 1985, there was a gradual intrusion of tailings leachate. Over this period, the total dissolved solids concentration increased and the relative abundance of sulfate increased from 10 percent to 50 percent while the relative abundance of alkalinity decreased from 50 percent to 25 percent. As a result of this compositional shift, the similarity between the ground-water fingerprint and tailings leachate increased from less than 1 percent to 80 percent.

Geochemical monitoring results from Well 1758 are presented in Figure 6-19. These data produce a constant alkalinity-rich, sulfate-poor fingerprint that is identical to the ground water at upgradient Wells M-3 and M-4. A comparison of this fingerprint with tailings leachate produced low r^2 values of 0.010. Thus, despite the proximity of the tailings basin to this location, leachate has not impacted the ground water at Well 1758.

The monitoring data from one final downgradient well have been summarized in Figure 6-20. These data also define a constant alkalinity-rich, sulfate-poor pattern that has been identified at upgradient locations and downgradient locations not impacted by fugitive tailings leachate. The similarity between this ground-water fingerprint and the tailings leachate is less than 1 percent. The results from this location are similar to the characteristics of the regional ground-water fingerprint and demonstrate that tailings leachate has not migrated the one-half mile between the tailings basin and the Church well.

6.1.4 Twin Butte Summary

This mine is more complicated than the other facilities that have been reviewed because two types of ore were processed and two different extraction techniques were used. However, despite these factors, the various tailings leachates from this mine had a very similar geochemical fingerprint. This fingerprint was defined by 60 percent sulfate, 15 percent calcium, and 10 percent magnesium and had a reproducibility of 97 percent over time.

Monitoring results upgradient of the tailings basin demonstrated the local ground water to have a characteristic alkalinity-rich, sulfate-poor fingerprint that was graphically and statistically distinct from Twin Butte tailings leachate. By comparison, the data from downgradient monitoring locations produced one of three patterns:

1. Ground water from the Well 1258 and the Church well had a low total dissolved solids concentration and a geochemical fingerprint defined by relatively high alkalinity and relatively low sulfate. This pattern is identical to ground water upgradient of the tailings basin and indicates that tailings leachate has not impacted there areas.
2. Ground water from Wells M-1, M-6, and RT-1 consistently had a high total dissolved solids concentration and a geochemical fingerprint defined by relatively high sulfate and relatively low alkalinity. This pattern had a 90 percent match with tailings leachate and only a 10 percent match with background ground water. These results demonstrate that tailings leachate will maintain its chemical identity as it migrates through the environment and that these areas have been impacted by leachate from the Twin Butte tailings basin over the entire period of record.
3. The ground-water composition was more variable at Wells M-2, M-5, M-7, and 1225 than at other wells. The reason for the increased variability at these locations is that the earliest data

from these wells represented unimpacted background conditions and the latest data represented ground water that had been impacted by fugitive tailings leachate. The monitoring records from these locations illustrate the systematic compositional shift that occurs when tailings leachate infiltrates into an area. These results also conclusively demonstrate that the geochemical fingerprint of tailings leachate remains intact as it migrates through the subsurface environment. These data sets also verify that trace metals are not present when a tailings leachate plume first enters an area.

The Twin Butte data file also contained a very useful column migration study that described the behavior of mine waste leachate under controlled conditions. This study demonstrated that the geochemical fingerprint of tailings leachate retains its identity as it migrates through a soil column. There was some distortion of the geochemical fingerprint in the initial column eluant because of an acid-base reaction but the geochemical pattern was still identifiable (90% match). In subsequent column eluants, the fingerprint match increased to 95 to 99%. Thus, the laboratory and field results from the Twin Butte Mine verify that the geochemical fingerprint can be used to identify mine waste leachate at some distance from the source.

Another important outcome of the Twin Butte column study is the assessment of trace metal mobility. The results indicated that each of the trace metals have a higher attenuation coefficient than the geochemical parameters. Therefore, the metals would be expected to migrate more slowly than the parameters that define the leachate fingerprint. This laboratory observation was verified with field data from Wells M-2, M-5, M-7, and 1225 that showed the migration of tailings leachate into these areas even though there was no measurable change in trace metal abundance.

6.2 Phelps-Dodge Tailings Disposal Area

This tailings disposal area is located in central Arizona along the north bank of the Verde River. The tailings ponds cover an area of approximately 0.26 square miles (4300 feet x 1700 feet). As shown in Figure 6-21, the monitoring program for this site consists of 14 monitoring wells and 2 sampling locations in the Verde River.

The data that were compiled and reviewed for the Phelps-Dodge site are the result of 10 quarterly surveys conducted between May, 1991 and March, 1994. The samples were collected from the following locations identified in Figure 6-21:

1. Two upgradient wells (Wells G1 and G2).
2. Six wells located within the boundaries of the tailings disposal area (Wells G3, G4, G5, G6, G7, and G8).
3. Six wells located downgradient of the tailings disposal area (Wells G9, G10, G11, G12, G13, and G14).
4. Two surface water sampling stations in the Verde River. Station S1 is located upstream of the tailings disposal area and station S2 is located downstream of the tailings disposal area.

Each of the collected samples were analyzed for calcium, magnesium, sodium, potassium, alkalinity, chloride, fluoride, and sulfate, collectively referred to as the geochemical parameters, total dissolved solids, pH, and a variable number of trace metals. The ground water samples were analyzed for 12 trace metals including silver, arsenic, barium, cadmium, copper, chromium, iron, mercury, lead, manganese, selenium, and zinc. However, the only trace metals reported for the surface water samples were copper and iron.

6.2.1 Characterization of Phelps-Dodge Tailings Leachate

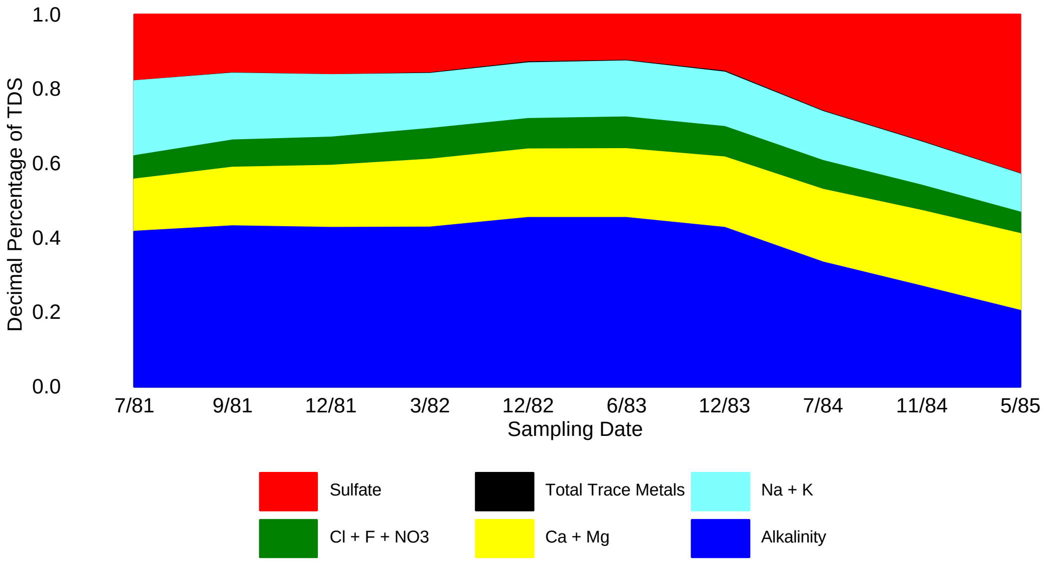
Well G3 is located in the northwest corner of the tailings disposal area (Figure 6-21). Monitoring results from 10 quarterly surveys at this location have been summarized in Table 6-2. An inspection of this information shows the Phelps-Dodge tailings leachate to have a high and variable total dissolved solids concentration over time (3800 to 8600 mg/L), a high and variable sulfate concentration (2500 to 4800 mg/L), and elevated concentrations of iron and manganese that exceed established water quality criteria. Also, except for the December, 1991 survey, the mass balance for the each data set is in the range of 0.887 to 1.011 which is an indication of acceptable quality data.

In order to determine whether the Phelps-Dodge tailings leachate had a consistent geochemical fingerprint, the results presented in Table 6-2 were normalized to the reported total dissolved solids concentration. The transformed data are presented as a series of bar charts in Figure 6-22. These results indicate that the tailings leachate has a reproducible geochemical fingerprint that is defined by 60 percent sulfate, 15 percent magnesium, 8 percent calcium, and minor amounts of alkalinity, chloride, and sodium. This pattern had an average regression analysis r^2 value of 0.999. That is, despite the observed variability for total dissolved solids and sulfate, the reproducibility of the geochemical fingerprint between 1991 and 1994 was 99.9 percent.

Monitoring results from a second location in the Phelps-Dodge tailings disposal area are presented in Figure 6-23. There is an obvious data quality problem in the March, 1994 survey at Well G7 because the reported sulfate value represents more than 120 percent of the total dissolved solids concentration. Since the alkalinity-TDS, calcium-TDS, and magnesium-TDS ratios are all consistent with previous surveys, the total dissolved concentration is probably acceptable and the sulfate concentration is erroneously high. The remaining nine surveys at this location define a repeatable pattern in which sulfate accounts for 60 percent of the total dissolved solids concentration, magnesium accounts for 15 percent of the total dissolved solids concentration, alkalinity accounts for 10 percent of the total dissolved solids concentration, and calcium accounts for 7 percent of the total dissolved solids concentration. This pattern has an estimated reproducibility of 99 percent and is identical to the geochemical fingerprint at Well G3 ($r^2 = 0.990$).

Geochemical fingerprint patterns constructed with monitoring data from each of the six wells in the Phelps-Dodge tailings disposal area are compared in Figure 6-24. Each data set defines a similar pattern in which sulfate is the single most abundant ion. The comparability of this multi-ion pattern at different locations in the tailings disposal area was estimated by regression analysis to be 98.9 percent.

The monitoring results summarized in Figures 6-22, 6-23, and 6-24 illustrate two characteristics of Phelps-Dodge tailings leachate composition. First, the relative composition is constant across the site because data from six locations within the boundary of the tailings disposal area produce an identical pattern. Second, the relative composition is constant over time because 10 sets of data over three years from two different location also produce the same pattern. This combination of observations suggests that the geochemical fingerprint pattern defined by 60 percent sulfate, 15 percent magnesium, 10 percent calcium, and 5 percent alkalinity is a characteristic property of tailings leachate at this site.



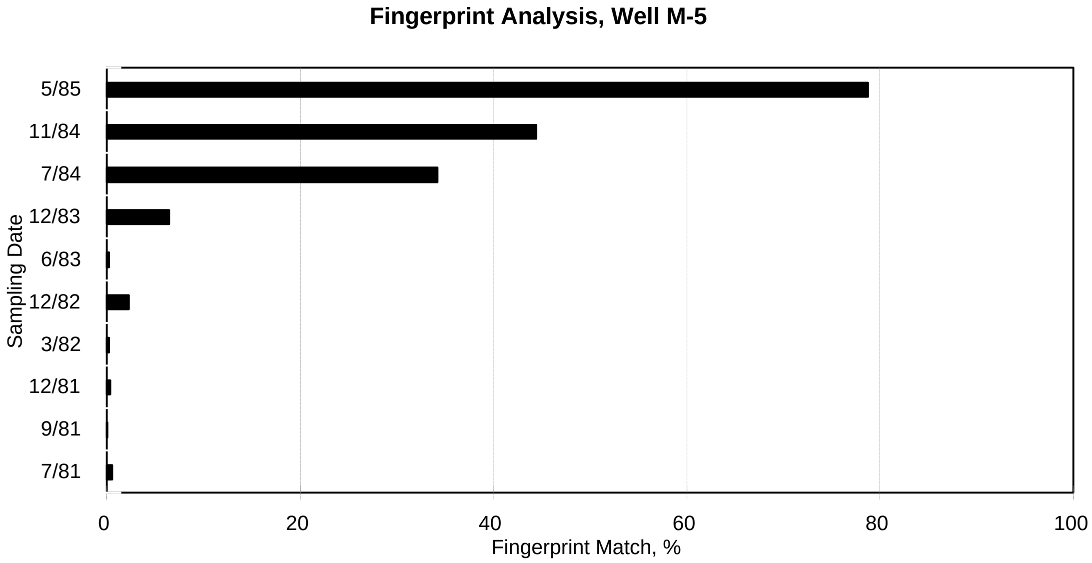


Figure 6-18. Monitoring results from downgradient Well M-5.

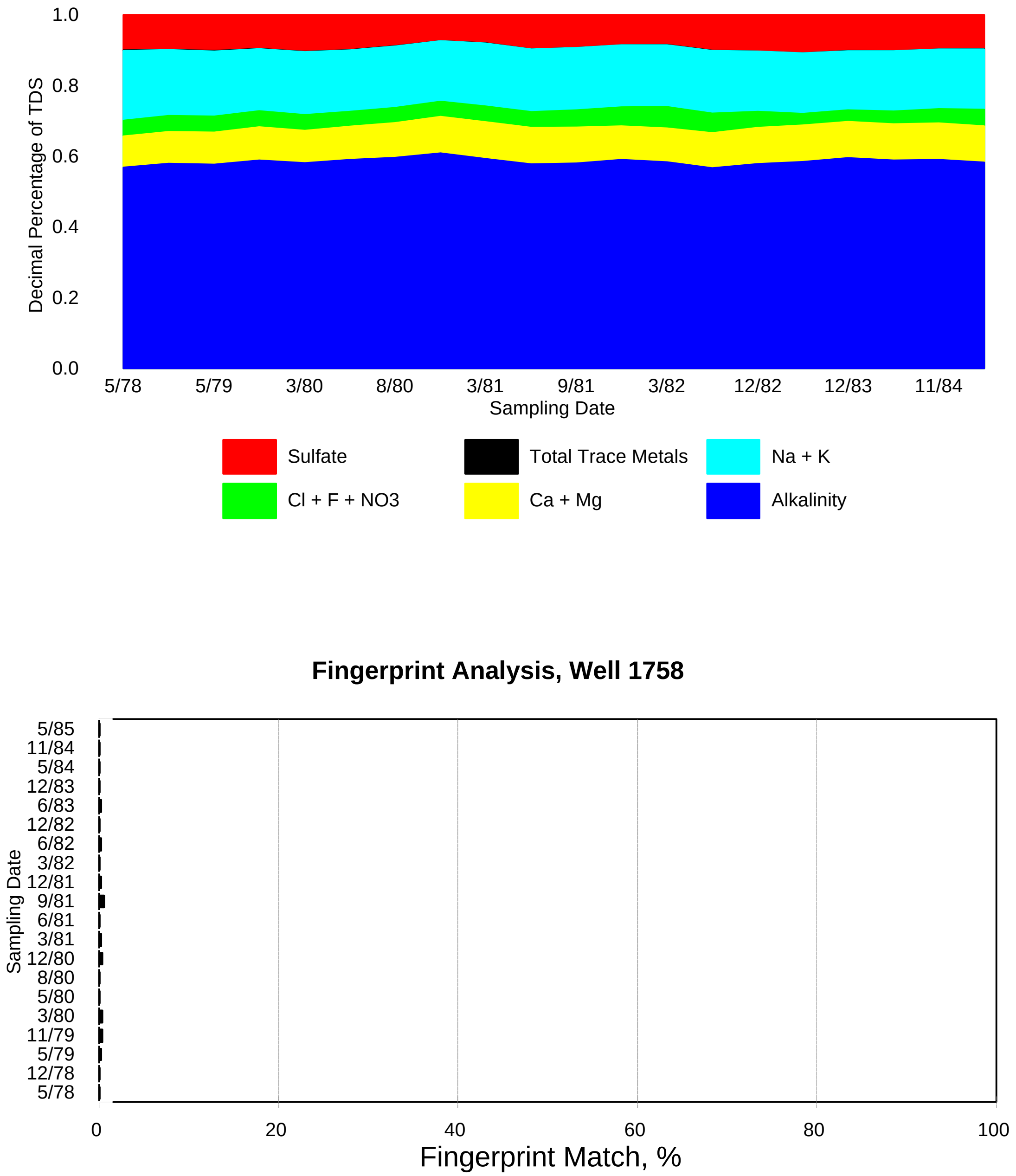
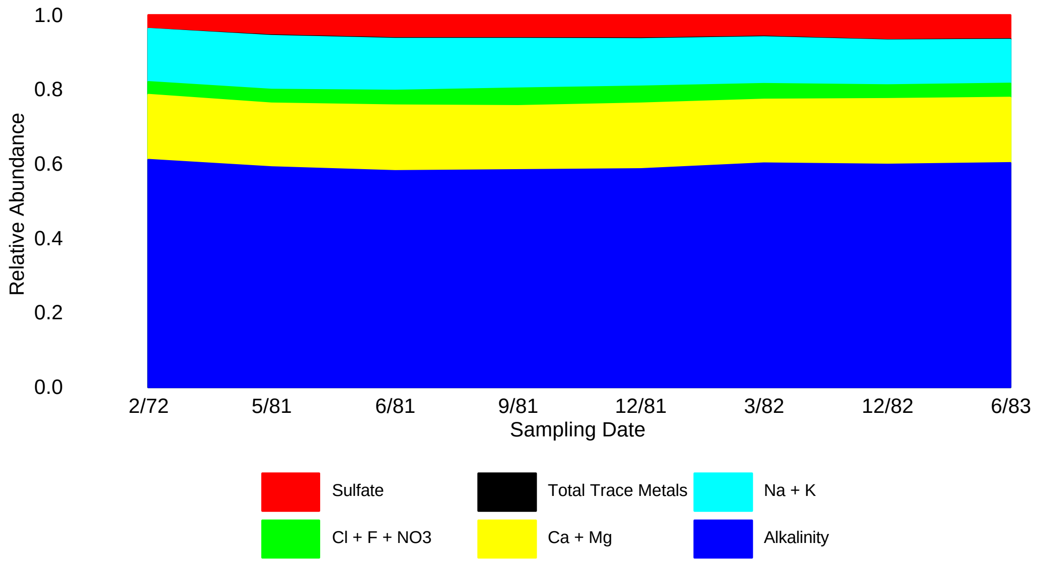


Figure 6-19. Monitoring results from downgradient Well 1758.



Fingerprint Analysis, Church Well

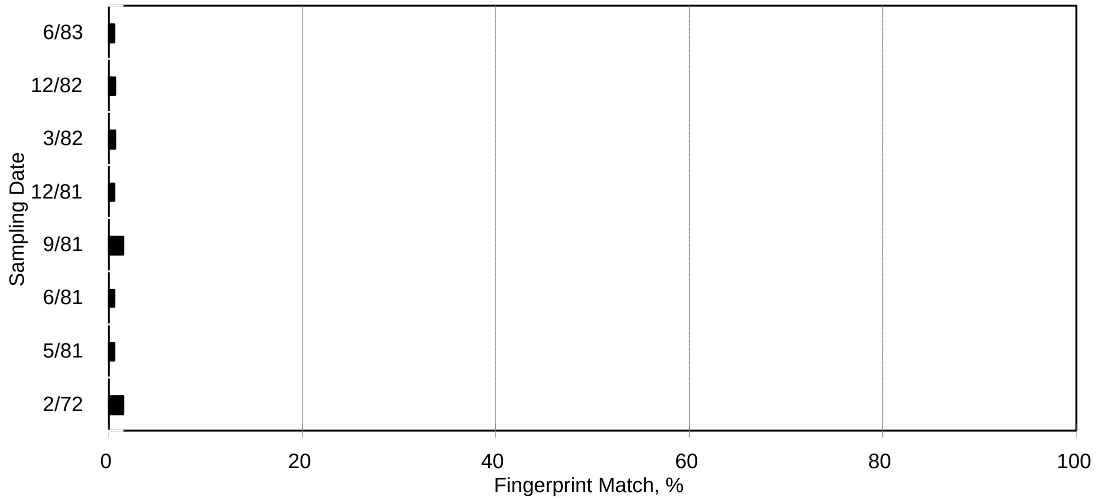


Figure 6-20. Monitoring results from the Church well downgradient of Twin Butte Tailings Pond 3.

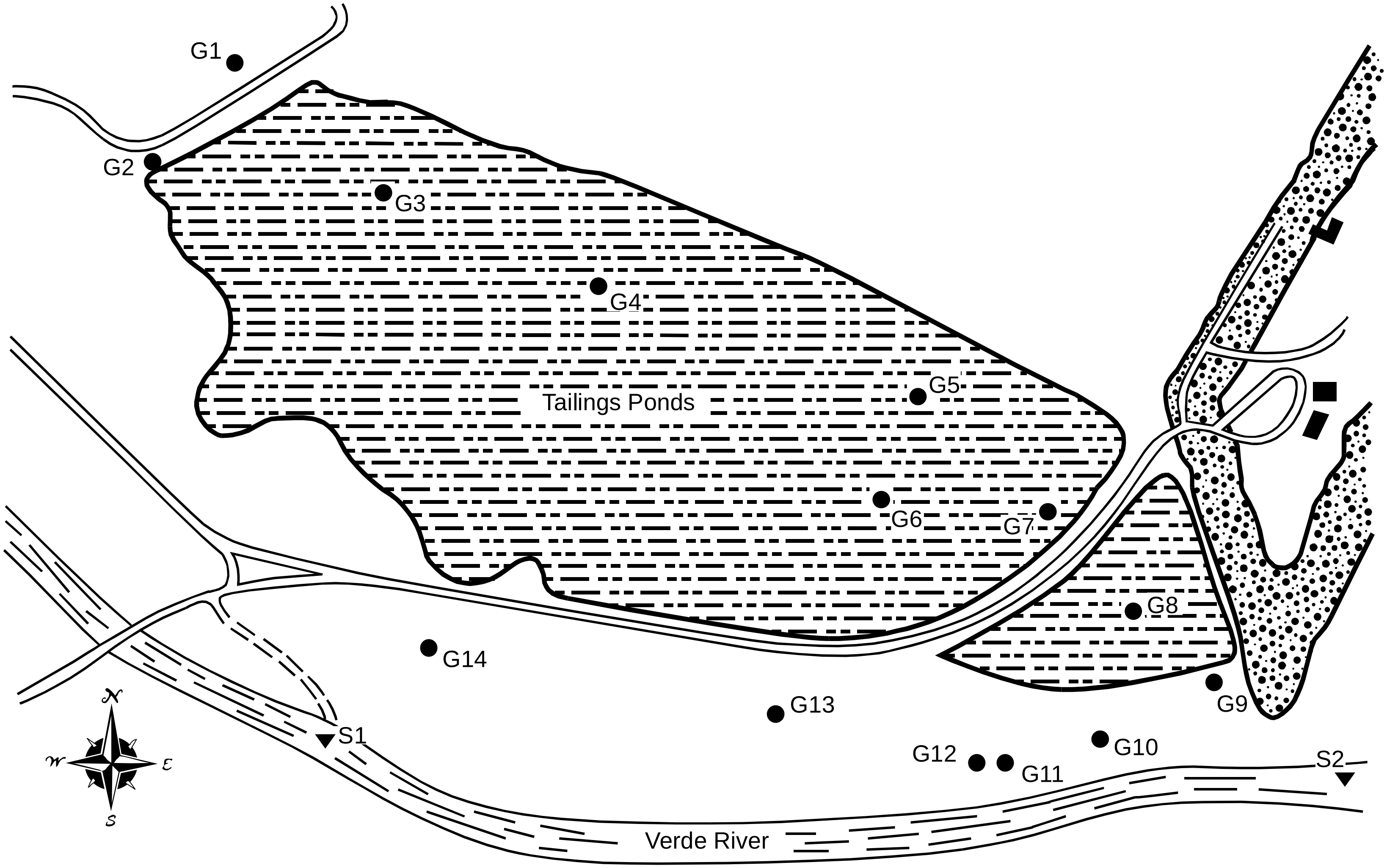
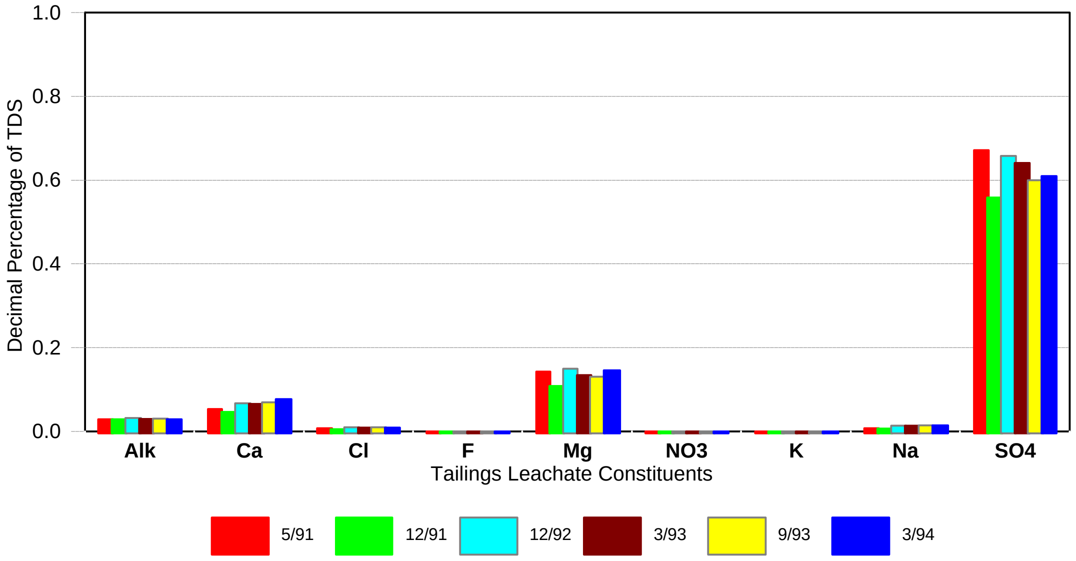


Figure 6-21. Site map for the Phelps-Dodge tailings disposal area.

Table 6-2. Monitoring results from Well G3 in the Phelps-Dodge tailings disposal area.

	Sampling Date										Average Concentration	Standard Deviation
	5/2/91	7/5/91	12/6/91	8/27/92	1/26/93	3/22/93	6/10/93	9/15/93	12/15/93	3/30/94		
Alkalinity	300	273	301	288	340	307	304	319	289	299	302	17
Calcium	341	380	404	456	254	257	304	278	291	314	328	63
Chloride	48	47	46	42	35	35	36	39	42	37	41	5
Fluoride	1.14	1.15	1.04	1.02	1.17	1.00	1.00	0.25	1.04	1.04	0.99	0.25
Magnesium	912	885	926	826	568	523	595	524	631	600	699	159
Nitrate	<0.06	0.06	0.08	<0.06	<0.06	<0.06	<0.06	<0.06	<0.6	<0.06	0.01	0.03
Potassium												
Sodium	48	59	58	53	49	55	56	57	58	59	55	4
Sulfate	4300	4600	4800	3700	2500	2500	2900	2400	3000	2500	3320	899
Total Dissolved Solids	6400	7100	8600	5800	3800	3900	4300	4000	4300	4100	5230	1577
Silver	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
Arsenic	0.04	0.05	0.05	0.05	0.06	0.06	0.07	0.05	0.07	0.07	0.06	0.01
Barium	0.02	0.02	0.02	0.02	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.00
Cadmium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.00	0.00
Chromium	<0.1	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00
Copper	0.01	0.03	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01
Iron	41	52	61	51	22	26	33	23	34	35	38	12
Mercury	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.00	0.00
Manganese	1.07	1.24	1.32	1.26	0.64	0.78	0.85	0.71	0.80	0.85	0.95	0.24
Lead	0.00	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.00	0.00
Selenium	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.00	0.00
Zinc	0.04	0.03	0.03	0.11	0.07	0.03	0.03	0.04	0.07	0.09	0.05	0.03
Sum of Ions/TDS	0.94	0.89	0.77	0.93	0.99	0.95	0.98	0.91	1.01	0.94	0.93	0.07

All concentrations except pH and sum of Ions/TDS expressed in mg/L.
pH expressed in standard units.
Sum of Ions/TDS expressed as a decimal percentage of TDS.

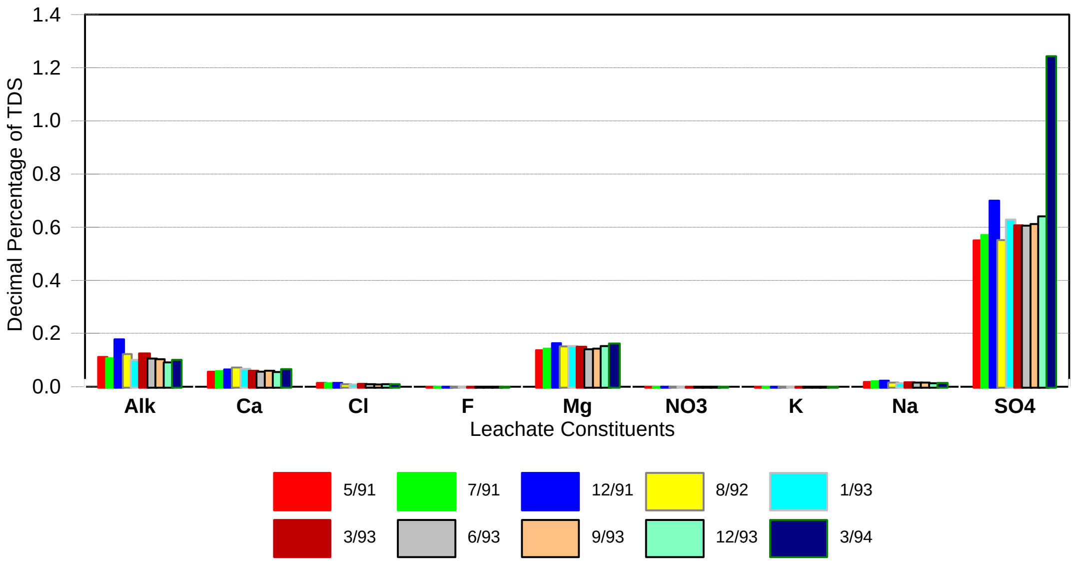


Regression analysis matrix for Well G3 in Phelps-Dodge tailings disposal area

	Sampling Date									
	5/91	**7/91**	**12/91**	**8/92**	**1/93**	**3/93**	**6/93**	**9/93**	**12/93**	**3/94**
5/91	1.000	1.000	0.999	0.998	0.999	0.999	0.999	0.999	1.000	0.998
7/91		1.000	1.000	0.998	0.999	0.999	0.999	0.999	1.000	0.997
12/91			1.000	0.998	0.999	0.999	0.999	0.999	0.999	0.996
8/92				1.000	0.999	0.999	0.999	1.000	0.999	1.000
1/93					1.000	1.000	0.999	1.000	1.000	0.999
3/93						1.000	1.000	1.000	1.000	0.999
6/93							1.000	1.000	1.000	0.999
9/93								1.000	1.000	0.999
12/93									1.000	0.999
3/94										1.000

Average r squared value = 0.999

Figure 6-22. Geochemical fingerprint at Phelps-Dodge Well G3.

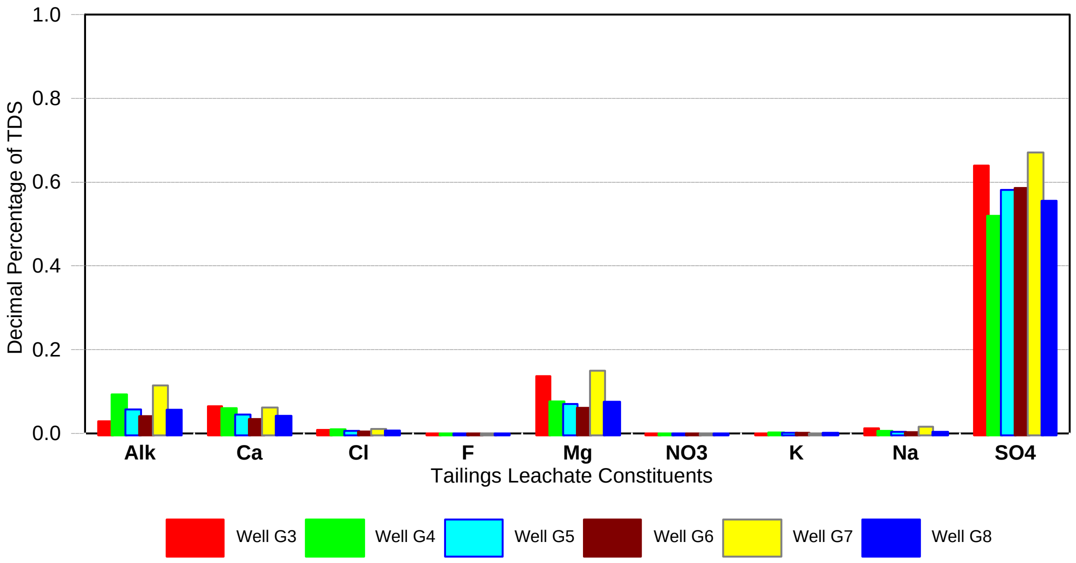


Regression analysis matrix for Well G7 in Phelps-Dodge tailings disposal area

	Sampling Date									
	5/91	**7/91**	**12/91**	**8/92**	**1/93**	**3/93**	**6/93**	**9/93**	**12/93**	**3/94**
5/91	1.000	1.000	0.996	0.998	0.998	1.000	0.999	0.999	0.996	0.976
7/91		1.000	0.994	0.998	0.999	0.999	1.000	1.000	0.998	0.971
12/91			1.000	0.995	0.989	0.997	0.993	0.992	0.987	0.965
8/92				1.000	0.996	0.998	0.996	0.996	0.992	0.964
1/93					1.000	0.998	0.999	1.000	0.999	0.983
3/93						1.000	0.999	0.999	0.996	0.976
6/93							1.000	1.000	0.999	0.984
9/93								1.000	0.999	0.984
12/93									1.000	0.986
3/94										1.000

Average r squared value = 0.993

Figure 6-23. Geochemical fingerprint at Phelps-Dodge Well G7.



Regression analysis matrix for Phelps-Dodge tailings disposal area

	Sampling Location					
	Well 3	**Well 4**	**Well 5**	**Well 6**	**Well 7**	**Well 8**
Well 3	1.000	0.974	0.986	0.985	0.983	0.989
Well 4		1.000	0.993	0.987	0.992	0.993
Well 5			1.000	0.999	0.986	1.000
Well 6				1.000	0.979	0.998
Well 7					1.000	0.989
Well 8						1.000

Average r squared value = 0.989

Figure 6-24. Comparison of the geochemical fingerprint from 6 wells in the Phelps-Dodge tailings disposal area.

6.2.2 Assessment of Ground-Water Conditions

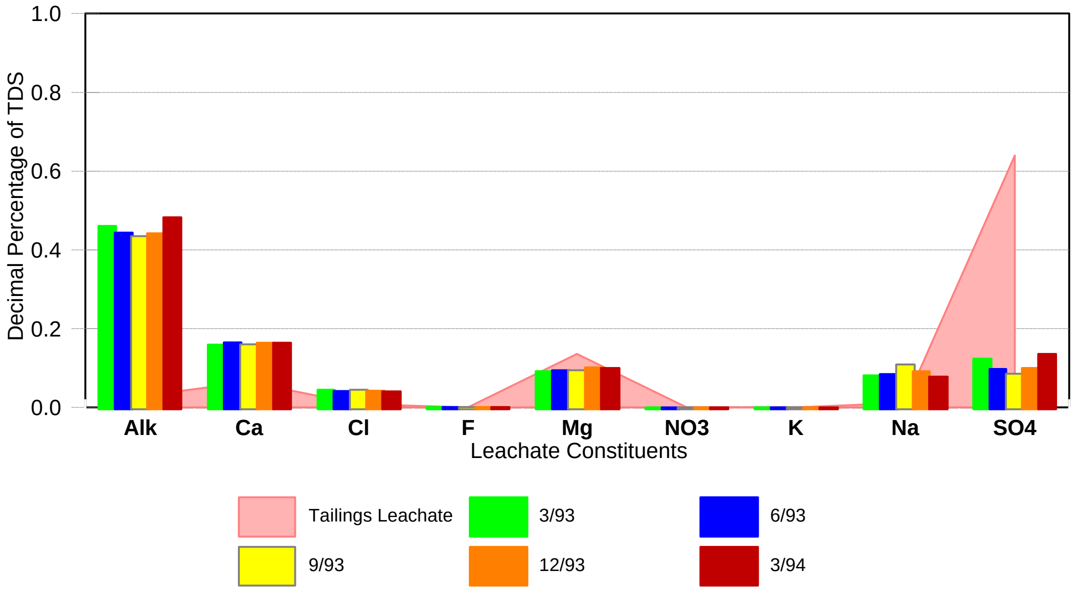
Monitoring data from Well G2, located west-northwest and upgradient of the tailings disposal area, are presented in Figure 6-25. These results indicate that alkalinity (bicarbonate and carbonate) is the dominant ion in the ground water upgradient of the tailings basin. The ground-water composition in this area consists of 45 percent alkalinity, 15 percent calcium, 10 percent magnesium, 10 percent sodium, and 10 percent sulfate. The geochemical fingerprint for ground water upgradient of the tailings disposal area has a reproducibility of 99.3 percent.

The upgradient ground-water fingerprint is contrasted with the tailings leachate fingerprint in Figure 6-25 to illustrate two points. First, the results from five quarterly surveys at this location produced a consistent geochemical fingerprint. The calcium bicarbonate pattern, which is typical of most natural water systems, had a reproducibility of 99 percent over time. Second, the alkalinity-rich, sulfate-poor pattern for upgradient ground water is distinctively different from the sulfate-rich, alkalinity-poor fingerprint of the tailings leachate. A regression analysis of the two fingerprints indicates that the similarity between the patterns is less than one percent ($r^2 = 0.004$). This difference reinforces the earlier statement that the sulfate-rich, alkalinity-poor fingerprint is a characteristic property of the tailings leachate at the Phelps-Dodge facility.

The site monitoring program at this facility includes six wells that are located downgradient of the tailings disposal area (Wells G9, G10, G11, G12, G13, and G14 in Figure 6-21). The normalized geochemical monitoring results from Wells G9, G13, and G14 are compared to the tailings leachate fingerprint in Figure 6-26. The ground-water signature at each of these locations is dominated by a major peak for alkalinity (35 percent of the total dissolved solids concentration), small peaks for calcium and magnesium (10 percent of the total dissolved solids concentration), and very small amounts of chloride, sodium, and sulfate. This pattern is highly reproducible at the three monitoring locations ($r^2 = 0.998$), very similar to the ground-water fingerprint at upgradient Well G2 (Figure 6-25), and distinctly different from the tailings leachate fingerprint ($r^2 = 0.000$). Although these data must be used cautiously because of data quality concerns, the results suggest that tailings leachate is not impacting the ground water at G9, G13, and G14. [The quality of the data sets from these three wells are considered to be suspect because the geochemical mass balance represents less than 60 percent of the total dissolved solids concentration. Based on the reproducibility of the geochemical pattern, the most likely error is a high bias in the total dissolved solids results.]

The monitoring results from downgradient Wells G10, G11, and G12 are compared to the tailings leachate fingerprint in Figure 6-27. The reproducible chemical signature ($r^2 = 0.984$) at each of these locations is characterized by a major sulfate peak (55-60 percent of the total dissolved solids concentration), minor peaks for alkalinity, calcium, and magnesium (5-15 percent of the total dissolved solids concentration), and negligible amounts of the other geochemical parameters. The geochemical fingerprint at Wells G10, G11, and G12 is visually distinct ($r^2 = 0.016$) from the characteristic pattern at upgradient Well G2 (Figure 6-25) and identical ($r^2 = 0.986$) to the ground-water fingerprint repeatedly observed within the boundary of the tailings disposal area (Figure 6-24). Based on the fingerprint comparisons and the location of the monitoring wells, tailings leachate has migrated beyond the limits of the tailings disposal area in a southeasterly direction towards the Verde River. This case study provides another demonstration that mine waste leachate maintains its chemical identity as it migrates away from the source.

Downgradient Well G11 was sampled on 10 occasions between May, 1991 and March, 1994. As can be seen from an inspection of the summarized data in Figure 6-28, each set of quarterly monitoring



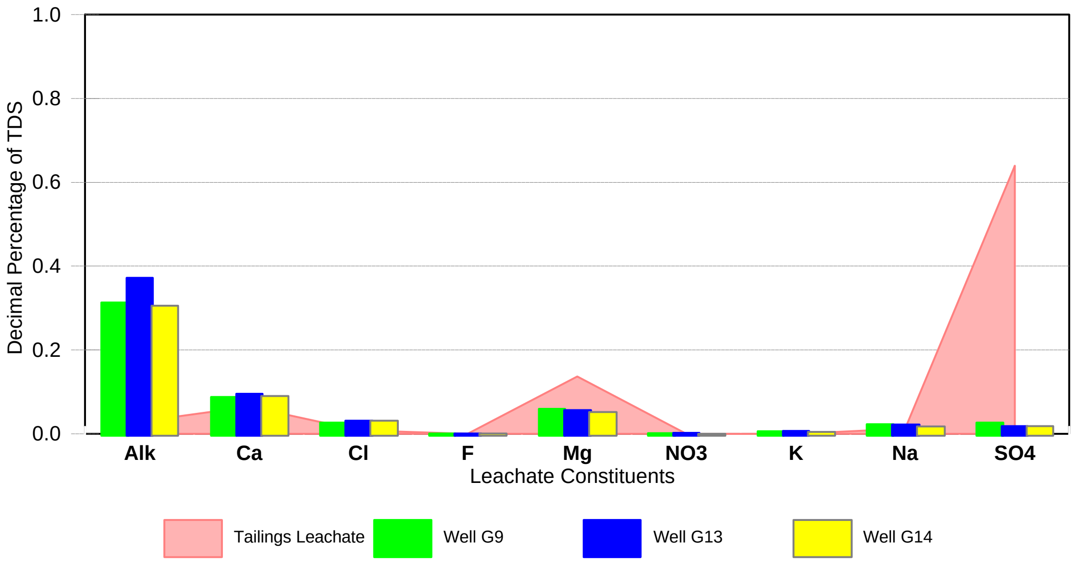
Regression analysis matrix for Phelps-Dodge upgradient Well G2

	Sampling Date				
	3/93	**6/93**	**9/93**	**12/93**	**3/94**
Tailings leachate	0.008	0.001	0.000	0.002	0.012
3/93	1.000	0.996	0.985	0.995	0.999
6/93		1.000	0.995	0.999	0.993
9/93			1.000	0.996	0.979
12/93				1.000	0.992
3/94					1.000

Average r squared value = 0.993

Ground water - tailings leachate comparison = 0.004

Figure 6-25. Comparison of the upgradient geochemical fingerprint with the Phelps-Dodge tailings leachate fingerprint.



Regression analysis matrix for unimpacted downgradient wells

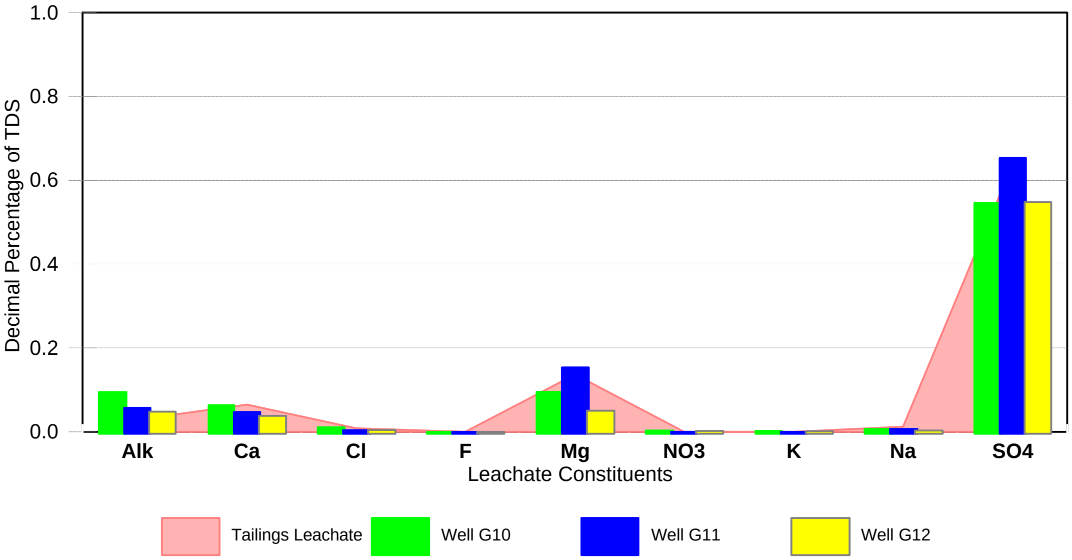
	Sampling Location		
	Well 9	**Well 13**	**Well 14**
Tailings leachate	0.001	0.000	0.000
Background GW	0.961	0.946	0.951
Well 9	1.000	0.997	0.998
Well 13		1.000	0.998
Well 14			1.000

Average r squared value = 0.998

Downgradient-upgradient comparison = 0.953

Downgradient-leachate comparison = 0.000

Figure 6-26. Geochemical fingerprint at Wells G9, G13, and G14 downgradient of the tailings disposal area.

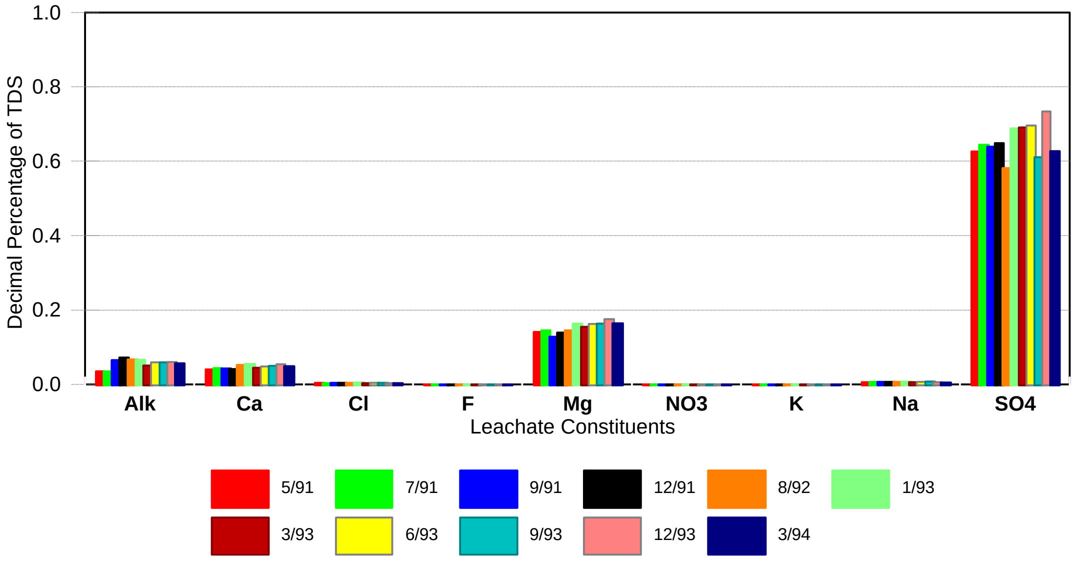


Regression analysis matrix for impacted downgradient wells

	Sampling Location		
	Well 10	**Well 11**	**Well 12**
Tailings Leachate	0.980	0.996	0.981
Background GW	0.032	0.008	0.009
Well 10	1.000	0.986	0.988
Well 11		1.000	0.979
Well 12			1.000

Average r squared value = 0.984
Downgradient-upgradient comparison = 0.016
Downgradient-leachate comparison = 0.986

Figure 6-27. Geochemical fingerprint at Wells G10, G11, and G12 downgradient of the tailings disposal area.



Regression analysis matrix for Well G11 downgradient of tailings disposal area

	Sampling Date										
	5/91	**7/91**	**9/91**	**12/91**	**8/92**	**1/93**	**3/93**	**6/93**	**9/93**	**12/93**	**3/94**
5/91	1.000	1.000	0.997	0.997	0.996	0.998	1.000	0.999	0.997	0.999	0.998
7/91		1.000	0.997	0.996	0.996	0.998	1.000	0.999	0.997	0.999	0.998
9/91			1.000	1.000	0.997	0.998	0.998	0.999	0.995	0.998	0.996
12/91				1.000	0.998	0.999	0.999	0.999	0.997	0.998	0.997
8/92					1.000	0.999	0.998	0.999	0.999	0.999	0.999
1/93						1.000	0.999	1.000	0.999	1.000	0.999
3/93							1.000	1.000	0.998	1.000	0.998
6/93								1.000	0.999	1.000	0.999
9/93									1.000	0.999	1.000
12/93										1.000	0.999
3/94											1.000

Average r squared value = 0.998

Figure 6-28. Temporal monitoring results at Well G11 downgradient of the tailings disposal area.

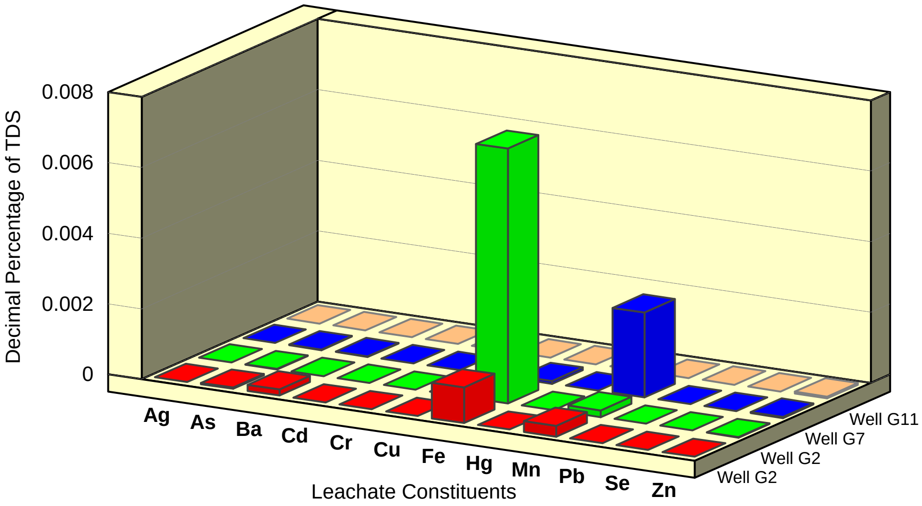
results at this location produced a similar geochemical signature ($r^2 = 0.998$). Specifically, sulfate was the single dominant ion in the fingerprint (60-65 percent of the total dissolved solids concentration), magnesium was a minor constituent (15 percent of the total dissolved solids concentration), while calcium, chloride, alkalinity, and sodium were present as trace constituents (< 5 percent of the total dissolved solids concentration). The ground-water fingerprint at Well G11 has been consistent over the period of record, it is comparable to that at adjacent Wells G10 and G12, it is identical to the geochemical fingerprint repeatedly observed at all six locations within the tailings disposal area, and it is distinctively different from the ground-water fingerprint at upgradient Wells G1 and G2. These results demonstrate that tailings leachate has been migrating in a southeasterly direction towards the river for at least the three years for which monitoring data are available.

Trace metal data from four locations in the Phelps-Dodge monitoring program are compared in Figure 6-29. The first set of data, from upgradient Well G2, is devoid of any characteristic features. The second set of data from Well G3, at the northwest end of the tailings basin, shows elevated levels of both iron and manganese. The third set of data from Well G7, at the southeast end of the tailings basin, also shows elevated levels of iron and manganese. However, the relative abundance has been altered and manganese is now the most abundant trace metal. Finally, the fourth set of data summarizes the trace metal distribution at down gradient Well G11. Although geochemical fingerprint analysis suggests that Well G11 has been impacted by tailings leachate for at least three years, the trace metals associated with the leachate are not in evidence at this location.

The assessment of monitoring results from the Phelps-Dodge site illustrates two important attributes of trace metals in mine waste leachates. First, the abundance of trace metals is more variable than the geochemical parameters. The trace metal distribution varied by location within the tailings disposal area even though geochemical monitoring results from six tailings basin locations over ten quarterly surveys defined a consistent fingerprint with a high level of reproducibility ($r^2 = 0.989$). This condition suggests that it would be difficult to uniquely characterize the composition of mine waste leachates with trace metals.

A second important attribute of trace metals is that they appear to migrate more slowly than the geochemical parameters that define the tailings leachate fingerprint. Although tailings leachate has continually been present at downgradient Wells G10, G11, and G12 for a period of three years, the most abundant trace metals in the leachate have not been detected at levels above background. The significance of this observation is that trace metals would not be effective for early detection of fugitive mine waste leachate since they have a lower environmental mobility than the geochemical ions that define the leachate fingerprint.

The monitoring results from six wells located downgradient of the Phelps-Dodge tailings disposal area produced two distinctive chemical signatures. The data from Wells G9, G13, and G14 produced an alkalinity-rich, sulfate-poor fingerprint that is identical to that shown to be present at upgradient Wells G1 and G2. The similarity of these patterns ($r^2 = 0.953$) supports the conclusion that tailings leachate has not impacted these wells. The data from Wells G10, G11, and G12 defined a sulfate-rich, alkalinity-poor fingerprint that is constant over time and identical ($r^2 = 0.986$) to that shown to be present at Wells G3, G4, G5, G6, G7, and G8 within the tailings disposal area. The similarity of the ground-water fingerprints at Wells G10, G11, and G12 with the tailings leachate fingerprint, and the proximity of these locations to the downgradient boundary of the tailings disposal area, supports the conclusion that tailings leachate has migrated in a southeasterly direction towards the nearby river. The migration of leachate has been occurring for some time because the characteristic fingerprint has been identified at Well G11 during each quarterly survey between May, 1991 and



Regression analysis matrix for Phelps-Dodge trace metal data

	Sampling Location			
	Well 2	**Well 3**	**Well 7**	**Well 11**
Well 2	1.000	0.910	0.045	0.007
Well 3		1.000	0.001	0.003
Well 7			1.000	0.005
Well 11				1.000

Average r squared value = 0.162

Figure 6-29. Spatial monitoring results for trace metals at the Phelps-Dodge tailings disposal area.

March, 1994. An equally important observation is that the geochemical leachate fingerprint retained its chemical identity as it migrated away from the source. Therefore, the geochemical parameters can be used to uniquely characterize mine waste leachate at its source and to detect its movement following accidental spill or leakage events.

6.2.3 Assessment of Surface Water Conditions

The monitoring records for this site included ten sets of quarterly data for two surface water stations in the Verde River. Since the ground water data assessment indicated that tailings leachate had been migrating in the direction of the river for several years, the surface water data were evaluated to identify possible changes due to the mining operation. The monitoring data suggest that elevated concentrations of sulfate, magnesium, and total dissolved solids are present at Station S2 downstream of the tailings disposal area (Table 6-3). However, even though the high concentrations of these parameters in tailings leachate could account for these changes, the upstream - downstream concentration differences were not significantly different when analyzed with a Students t Test (p = 0.05, 18 df).

Table 6-3. Comparison of Verde River monitoring results.

Constituent	Upstream (S1)			Downstream (S2)			Difference*
Alkalinity	211.8	+/-	45.8	213.1	+/-	46.6	No
Calcium	48.0	+/-	7.7	50.7	+/-	8.4	No
Chloride	12.7	+/-	3.6	12.9	+/-	3.5	No
Magnesium	25.2	+/-	7.2	34.3	+/-	16.5	No
Sulfate	27.7	+/-	12.2	67.4	+/-	60.7	No
TDS	274	+/-	49	345	+/-	138	No
Copper	0.003	+/-	0.006	0.002	+/-	0.006	No
Iron	0.665	+/-	0.802	0.575	+/-	0.722	No

All concentrations expressed in units of mg/L.

The estimated error is one standard deviation based on 10 surveys conducted between May, 1991 and March, 1994.

* Significant difference using the Student's t Test (p = 0.05, 18 df).

Monitoring results were used to prepare graphical fingerprints of the Verde River (Figure 6-30). The data from each survey, at both upstream and downstream locations, produced histograms in which alkalinity is the single dominant ion, calcium is the second most abundant ion, and chloride, magnesium, and sulfate are trace constituents of the fingerprint. This chemical signature is very similar to that observed at wells located upgradient of the tailings disposal area.

The distinctive fingerprint that has been defined for Phelps-Dodge tailings leachate is not readily apparent at the downstream monitoring location. However, a closer inspection of the upstream - downstream differences suggests that a subtle but constant compositional shift is occurring downstream of the tailings disposal area. Specifically, when the surface water monitoring results are expressed as a percentage of the total dissolved solids concentration, the downstream alkalinity results are always lower, the downstream sulfate results are always higher, and the downstream magnesium results are always higher. These compositional shifts, which occurred in all 10 surveys,

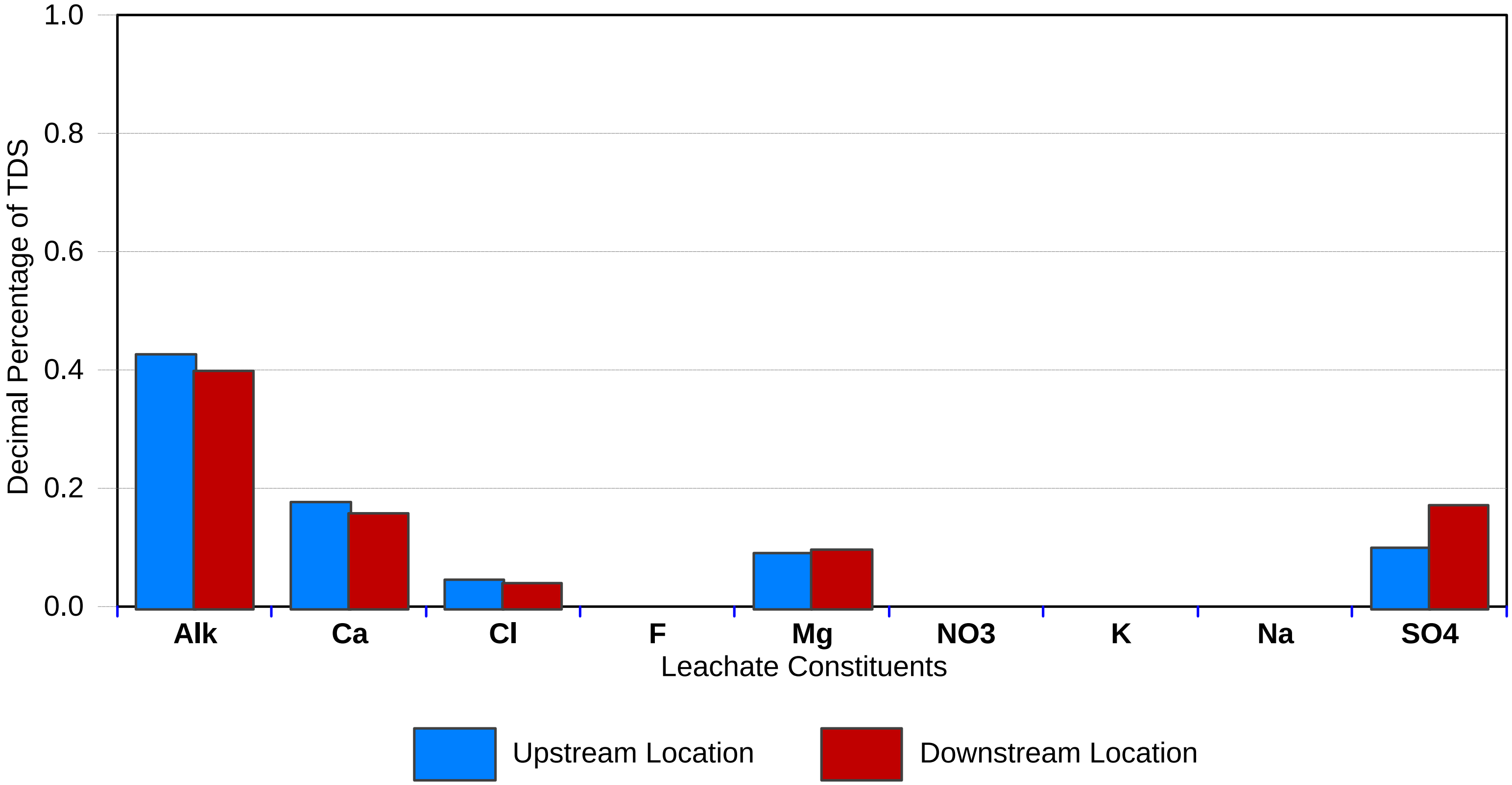


Figure 6-30. Monitoring results upstream and downstream of the Phelps-Dodge tailings disposal facility.

are consistent with an alkalinity-poor, sulfate-rich source, such as tailings leachate from the tailings disposal area of the copper mining facility, entering the Verde River between the two sampling locations.

In order to further investigate the possibility of contaminated ground water entering the river, expected downstream concentrations were calculated on the assumption that leachate was entering the river. Because the actual rate of dilution is not known, estimated downstream concentrations were calculated for a range of dilutions of contaminated ground water (Well G11) with upstream river water (S1). This produced a series of simultaneous conditions that should be observed at the downstream location because the leachate had a constant ionic composition over time, each leachate constituent travels the same distance in the river to sampling station S2, and is subjected to the same degree of dilution.

The results of these calculations suggest that total dissolved solids, sulfate, and magnesium would be expected to show the largest concentration increases downstream of the tailings disposal area. The magnitude of the downstream increase would be dependent on the actual rate of dilution (Table 6-4). For example, if ground water represented five percent of the flow at Station S2, the expected alkalinity concentration would be 227 mg/L and the expected sulfate concentration would be 310 mg/L. However, if ground water only represented two percent of the flow at Station S2, the expected alkalinity concentration would only be 218 mg/L and the expected sulfate concentration would only be 141 mg/L. A comparison of the calculated values (Table 6-4) with the actual stream concentrations (Table 6-3) strongly suggests that tailings leachate represents 0.5 percent of the Verde River flow at station S2. The values calculated for each leachate parameter at an assumed dilution of 200 to 1 are very reasonable approximations to the actual river conditions and within the estimated confidence limits for each parameter.

Table 6-4. Calculated downstream Verde River concentrations based on assumed mixing of upstream river water and tailings leachate from the Phelps-Dodge tailings disposal area.

	Assumed percentage of upstream river water						
Parameter	**100**	**99.5**	**99.0**	**98.5**	**98.0**	**97.5**	**95.0**
Alkalinity	211.8	213.5	214.9	216.5	218.1	219.6	227.4
Calcium	48.0	49.8	51.6	53.4	55.2	57.0	66.1
Chloride	12.7	12.8	12.9	12.0	12.1	12.2	13.7
Magnesium	25.2	31.8	38.3	44.9	51.9	57.9	90.7
Sulfate	27.7	55.9	84.1	112.4	140.6	168.8	309.9
TDS	274	316	358	400	442	484	693
Copper	0.003	0.003	0.003	0.003	0.003	0.003	0.003
Iron	0.665	0.662	0.659	0.655	0.652	0.649	0.633

All concentrations expressed in units of mg/L.

Calculated concentrations for each assumed dilution of tailings leachate with upstream Verde River water were normalized to the total dissolved solids concentration. These transformed data are presented in Table 6-5 and represent the ionic composition that would be expected at Station S2 if leachate were present at the assumed rate of dilution. For example, alkalinity should decrease from 47 percent of the total dissolved solids concentration to 20 percent of the total dissolved solids concentration as leachate from the tailings disposal area increases from 0 percent to 5 percent of the flow. Concurrently, the percentage of magnesium should increase from 9.2 percent to 13.1 percent and sulfate should increase from 10 percent to 45 percent.

Table 6-5. Estimated composition of downstream Verde River water for various dilutions of Phelps-Dodge tailings leachate.

	Assumed percentage of upstream river water						
Parameter	**100**	**99.5**	**99.0**	**98.5**	**98.0**	**97.5**	**95.0**
Alkalinity	47.2	41.2	36.6	33.0	30.1	27.7	20.0
Calcium	17.5	15.8	14.4	13.4	12.5	11.8	9.5
Chloride	4.6	4.1	3.6	3.2	3.0	2.7	2.0
Magnesium	9.2	10.1	10.7	11.2	11.6	12.0	13.1
Sulfate	10.1	17.7	23.5	28.1	31.8	34.9	44.9
Copper	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Iron	0.24	0.21	0.18	0.16	0.15	0.13	0.09

All concentrations expressed in units of mg/L.

The difference between the calculated ionic composition at Station S2 and the actual ionic composition at Station S1 provides an estimate of the compositional shift that should occur in the Verde River for various dilutions of tailings leachate. These values are presented in Table 6-6. Thus, if the tailings leachate is not entering the river, there should be no change in the composition (100 percent upstream river water) and if tailings leachate represents five percent of the flow, alkalinity should decrease in relative abundance by 44 percent, calcium should decrease in relative abundance by 8 percent, and sulfate should increase in relative abundance by 35 percent (95 percent upstream river water). For larger dilutions of the tailings leachate, these values would be proportionately reduced.

Table 6-6. Calculated compositional shifts in the Verde River (downstream - upstream) for various assumed dilutions of Phelps-Dodge tailings leachate.

	Assumed percentage of upstream river water						
Parameter	**100**	**99.5**	**99.0**	**98.5**	**98.0**	**97.5**	**95.0**
Alkalinity	0.0	-9.7	-17.0	-23.0	-28.0	-32.0	-44.0
Calcium	0.0	-1.7	-3.1	-4.2	-5.0	-5.7	-8.0
Chloride	0.0	-0.6	-1.0	-1.4	-1.7	-1.9	-2.7
Magnesium	0.0	0.8	1.5	2.0	2.4	2.8	3.9
Sulfate	0.0	7.6	13.4	18.0	21.4	24.8	34.6
Copper	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Iron	0.24	0.21	0.18	0.16	0.15	0.13	0.09

All concentrations expressed as a percentage of the total dissolved solids concentration (Table 6-4).

The anticipated compositional shifts that should occur at Station S2 for a 200:1 dilution of tailings leachate with upstream Verde River water are compared with the observed compositional shifts in Table 6-7. An inspection of these results strongly suggests that a 200:1 dilution (99.5 percent upstream river water) of tailings leachate would account for the observed changes in the Verde River composition between the two sampling locations:

1. An assumed 200:1 dilution of tailings leachate with upstream river water leads to a correct estimation of the direction of the compositional shift for each major constituent in the tailings leachate fingerprint (alkalinity, calcium, and chloride decreased in relative abundance and magnesium and sulfate increased in relative abundance).
2. An assumed 200:1 dilution of tailings leachate with upstream river water leads to a correct estimation of the magnitude of the compositional shift for each major constituent in the fingerprint.
3. The relative compositional shifts observed at downstream station S2 would have been substantially different for one or more of the tailings leachate fingerprints if another source was responsible for the changes.

Table 6-7. Comparison of actual compositional shifts in the Verde River with estimated compositional shifts based on an assumed 200:1 dilution (99.5%) of tailings leachate with upstream river water.

Constituent	Observed Changes	Calculated Changes
Alkalinity	-11.6	-9.7
Calcium	-1.9	-1.7
Chloride	-0.6	-0.6
Magnesium	0.6	0.8
Sulfate	7.2	7.6
Copper	0.00	0.00
Iron	0.00	0.00

Values are downstream minus upstream differences expressed as a percentage of the total dissolved solids concentration.

The evaluation of monitoring results from the Phelps-Dodge tailings disposal area demonstrated that the tailings leachate had a characteristic ionic signature or fingerprint. The fingerprint was useful for differentiating tailings leachate from adjacent ground water and tracking its movement in a southeasterly direction beyond the perimeter of the disposal area and towards the Verde River. Based on the characteristic geochemical fingerprints for tailings leachate and the Verde River, the observed compositional shifts in the river were used to estimate the occurrence of tailings leachate in the river. These results suggest that leachate from the tailings disposal area represents 0.5 percent of the river flow at the downstream monitoring location.

6.2.4 Phelps-Dodge Tailings Disposal Area Summary

Geochemical monitoring results from six wells within the Phelps-Dodge tailings disposal area produced a characteristic fingerprint in which sulfate was the single dominant ion. The reproducibility of this pattern was estimated by regression analysis to be almost 99 percent (r^2 = 0.989). The sulfate-rich, alkalinity-poor signature was shown to be graphically and statistically distinct from the alkalinity-rich, sulfate-poor fingerprint of ground water upgradient of the tailings disposal area.

An assessment of the ground-water monitoring results from six wells located downgradient of the tailings disposal area defined two geochemical fingerprints. The data from three wells produced an alkalinity-rich, sulfate-poor fingerprint that was identical to conditions at the upgradient wells (r^2 = 0.953) and unlike the tailings fingerprint (r^2 = 0.000). These results suggest that tailings leachate is not present in these areas. However, the monitoring results from the remaining three wells, each of which had a concurrent increase in total dissolved solids, defined a multi-ion signature that matched the tailings leachate fingerprint (r^2 = 0.986) and did not match the upgradient fingerprint (r^2 = 0.016). An important observation concerning the composition and behavior of tailings leachate is that the distinctive fingerprint remained intact and identifiable as the leachate migrated away from the source. Based on the fingerprint comparison, tailings leachate is migrating from the disposal area in a southeasterly direction towards the Verde River (Wells G10, G11, and G12).

Although the distinctive tailings leachate fingerprint has been present at three downgradient locations for at least three years (1991-1994), the trace metal distribution at these wells does not match the trace metal distribution of tailings leachate and the most abundant metals in the leachate are not in evidence at Wells G10, G11, and G12. These conditions suggest that the trace metal constituents of tailings leachate do not migrate as rapidly as the geochemical constituents. One consequence of their slower movement is that trace metal monitoring would not provide for early detection of mine waste leachate migration.

The ground-water monitoring results indicated that leachate from the tailings basin was migrating towards the Verde River. The tailings leachate fingerprint was not readily identifiable in the river. However, based on the constant composition of the leachate and the upstream water, it was possible to estimate the dilution of leachate with river water. An assumed dilution of 200:1 led to a correct estimation of the direction of the compositional shift and the magnitude of the compositional shift that occurred for each leachate parameter at the downstream monitoring location.

6.3 Cyprus Sierrita Copper Mine

The Cyprus Sierrita mine is located in southern Arizona adjacent to the Twin Butte copper mine (Section 6.1). The tailings impoundment at this facility covers slightly more than 3 square miles (14,000 ft x 6400 ft). As shown in Figure 6-31, the downgradient monitoring wells are located along the eastern and southern perimeter of the tailings basin. The data set from this mine consisted of six estimates for the tailings leachate composition and nine sets of quarterly monitoring data from the downgradient wells (August, 1990 - September, 1993).

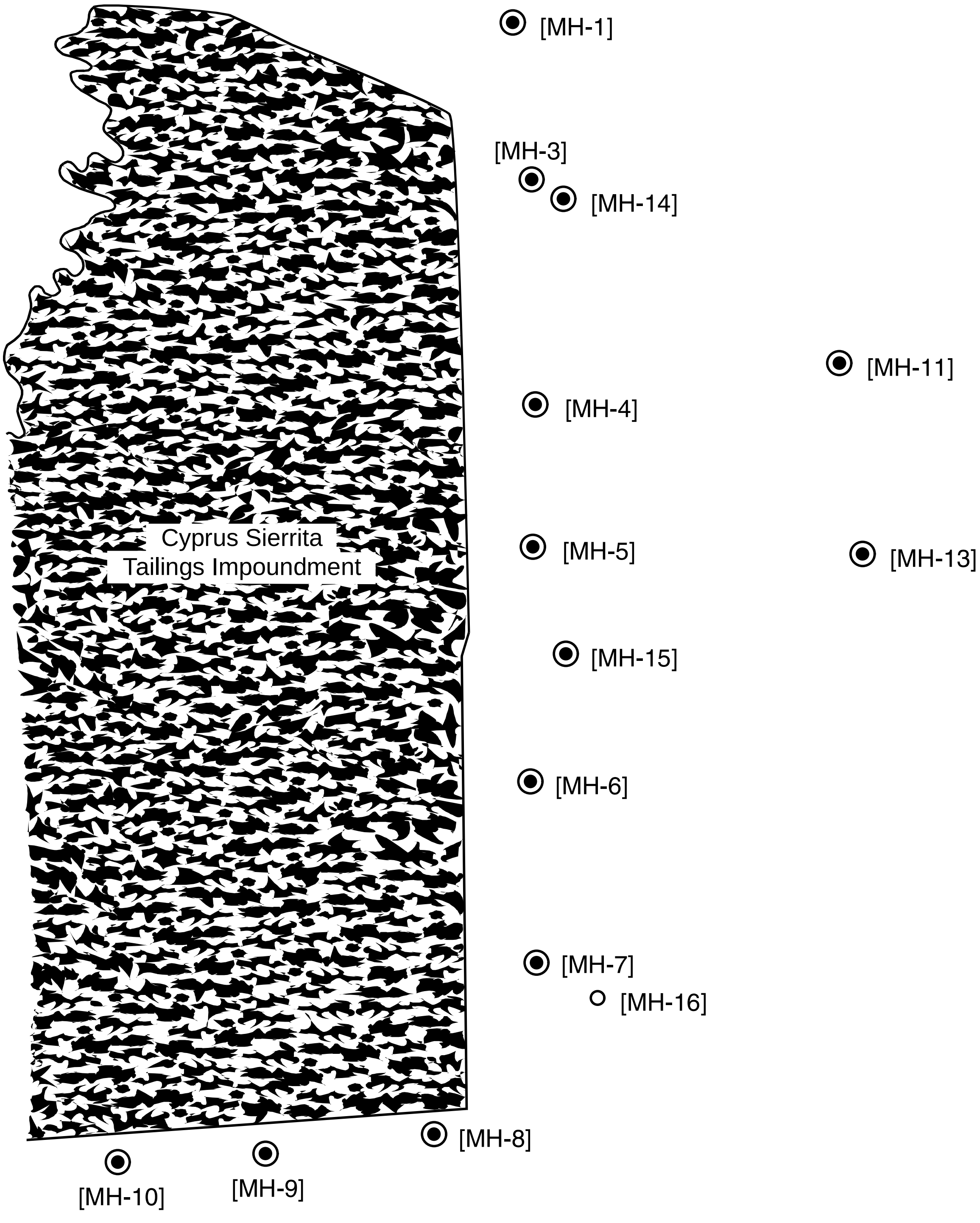


Figure 6-31. Ground-water monitoring locations in the vicinity of the Cyprus Sierrita tailings impoundment.

6.3.1 Tailings Leachate Characterization

The tailings leachate samples that were analyzed included the raffinate pond, the tailings slurry, the tailings reclaim water, a seepage pond, and two Headwall samples. The fingerprint patterns prepared with the geochemical data from these samples are compared in Figure 6-32. Each set of data defined a fingerprint in which sulfate was the single dominate ion that represented 50 - 60 percent of the total dissolved solids concentration of the tailings leachate.

The geochemical fingerprint for the Cyprus Sierrita tailings leachate was very similar to the tailings leachate fingerprint at the nearby Twin Butte Mine (Figure 6-2). Although there was some variability associated with the small calcium and chloride peaks in the fingerprint, this pattern had a reproducibility of 89 percent ($r^2 = 0.887$).

6.3.2 Ground-Water Monitoring Results

The data file for this mine did not contain any results for a monitoring well upgradient of the tailings basin. However, because of the proximity of the Twin Butte Mine, the results from Twin Butte upgradient Well M-3 were used as a reasonable approximation of background conditions at the Cyprus Sierrita Mine. Based on this assumption, ground water upgradient of the Cyprus Sierrita tailings impoundment would be expected to have an alkalinity-rich, sulfate-poor fingerprint similar to that shown in Figure 6-10.

Monitoring Well MH-14 is located approximately 1500 feet east of the northeast corner of the tailings impoundment. The geochemical monitoring results from eight surveys over three years at this well have been summarized in a series of histograms in Figure 6-33. Each of these data sets define a reproducible pattern in which sulfate is the most abundant ion (55 - 60 percent of the total dissolved solids concentration), calcium is the second most abundant ion (20 percent of the total dissolved solids concentration), and the remaining ions are minor components of the fingerprint.

There are four specific observations that can be drawn regarding the ground-water conditions at Well MH-14.

1. The ground-water composition is distinctly different from the alkalinity-rich, sulfate-poor distribution upgradient of the Twin Butte mine assumed to be present upgradient of the tailings impoundment.
2. The ground-water composition at Well MH-14 is identical to the tailings leachate fingerprint at the Cyprus Sierrita mine. A regression analysis of the two patterns produced an r^2 value of 0.967 (a 97 percent match).
3. The results from this location provide another example to demonstrate that a tailings leachate retains its distinctive geochemical identity as it migrates through the environment.
4. The trace metal component of the tailings fingerprint has been deleted at Well MW-14. Since the well has apparently been impacted by tailings leachate for at least three years and trace metal increases are still not in evidence, this is another indication that the trace metals in mine waste leachate will not migrate as rapidly as the geochemical constituents.

Monitoring Well MH-15 is located approximately 1500 feet east of the tailings impoundment perimeter. The geochemical monitoring data from nine surveys at this location define a reproducible pattern in which sulfate is the most abundant ion and calcium is the second most abundant ion (Figure 6-34). This pattern has a reproducibility of 99 percent over time and is an identical match for the tailings leachate fingerprint (98 percent match).

The data from this well reinforce each of the observations that were made at Well MH-14. The most important observation is that the geochemical fingerprint remains intact as tailings leachate migrates away from the impoundment. This permits the leachate to be unequivocally identified as the causative factor for the changing ground water conditions at the well. A second important observation is that the trace metals, which represent five percent of the total dissolved solids concentration of tailings leachate, are essentially absent from the fingerprint at Well MH-15. This data set provides another demonstration that the trace metals in tailings leachate do not migrate as rapidly as the geochemical constituents.

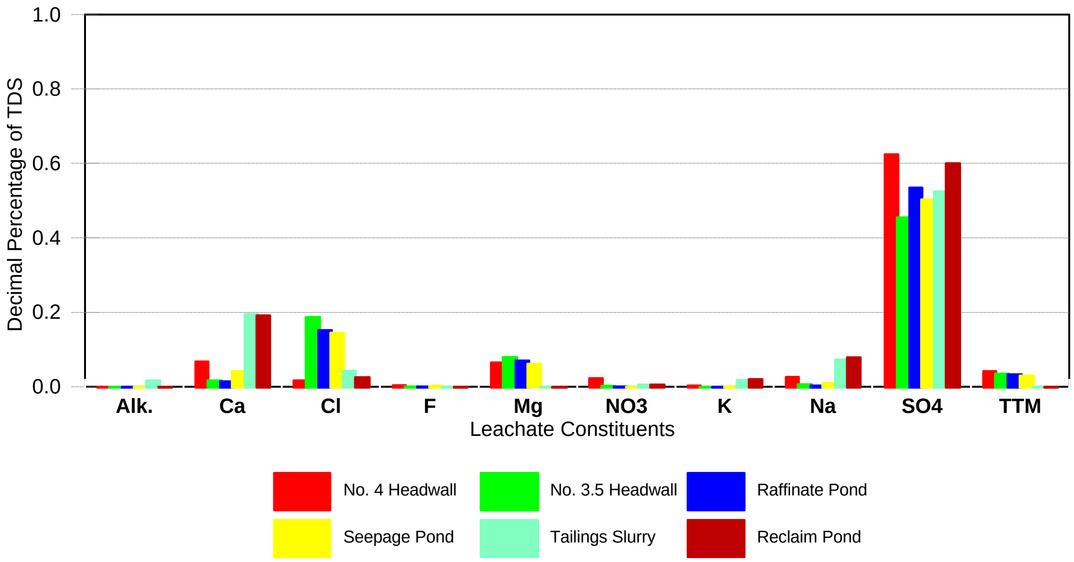
The data from one final Cyprus Sierrita well have been summarized in Figure 6-35. Well MH-16 is located east of the southeast corner of the tailings impoundment (Figure 6-30). The two surveys completed in 1990 suggest that this well may have been impacted by tailings leachate at one time because the relative abundance of alkalinity was lower, the relative abundance of sulfate was higher, and the geochemical fingerprint was somewhat similar to the tailings leachate fingerprint (75 to 57 percent match). However, since the middle of 1992, the relative abundance of alkalinity has increased, the relative abundance of sulfate has decreased, and the similarity to the tailings leachate has dropped to only 10 percent. The existing conditions (35 percent alkalinity, 15 percent sulfate, and 15 percent calcium) are very similar to ground-water conditions upgradient of the Twin Butte Mine (Figure 6-10) and assumed to be upgradient of the Cyprus Sierrita Mine.

The monitoring records from Well MH-16 indicate that it had been impacted by tailings leachate prior to 1990. Since that time, the presence of leachate has been decreasing at this well. Based on the similarity of the current geochemical fingerprint at Well MH-16 with assumed upgradient conditions, it appears that the fugitive leachate is being flushed from the system with upgradient water.

6.3.3 Cyprus Sierrita Summary

The available data set for this mine was not as extensive as those at the Twin Butte Mine or the Phelps-Dodge Mine. However, the data from six different monitoring locations demonstrated that the tailings leachate at this mine had a constant relative composition defined by 55 - 60 percent sulfate, 20 percent calcium, and 10 percent sodium. The geochemical fingerprint had a reproducibility of 89 percent and was very similar to the copper tailings leachate fingerprint at the Twin Butte Mine (Section 6.1) and the Phelps-Dodge tailings disposal area (Section 6.2).

The site monitoring data from wells downgradient of the tailings impoundment defined two distinctive geochemical fingerprints. The results from 1992 and later at Well MH-16 produced an alkalinity-rich, sulfate-poor fingerprint that was a match for the ground water assumed to be upgradient of the facility. The similarity of these patterns suggests that this area is not being impacted by tailings leachate. However, the results from Wells MH-14 and MH-15 produced a sulfate-rich, alkalinity-poor pattern that had a 90 percent match with the tailings leachate fingerprint. These results suggest that the ground water east and north of the tailings impoundment are being impacted by fugitive tailings leachate. This example demonstrates again that mine leachates maintain their ionic composition as they migrate and the geochemical fingerprint can be used to detect and identify them at some distance from the source.

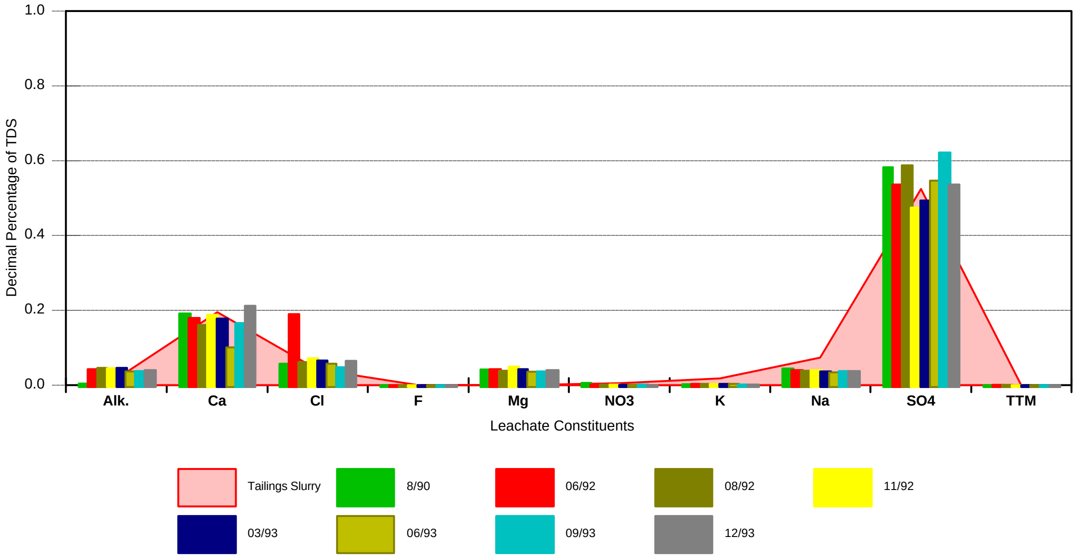


Regression Analysis Matrix for Cyprus Sierrita Tailings Leachates

	Headwall #4	Headwall #3.5	Raffinate	Seepage Pond	Reclaim Pond	Tailings Slurry
Headwall #4	1.000	0.839	0.915	0.922	0.924	0.896
Headwall #3.5		1.000	0.985	0.980	0.728	0.717
Raffinate Pond			1.000	0.997	0.804	0.787
Seepage Pond				1.000	0.838	0.825
Reclaim Pond					1.000	0.996
Tailings Slurry						1.000

Average r squared value = 0.877

Figure 6-32. Geochemical fingerprint pattern for Cyprus Sierrita tailings leachate.

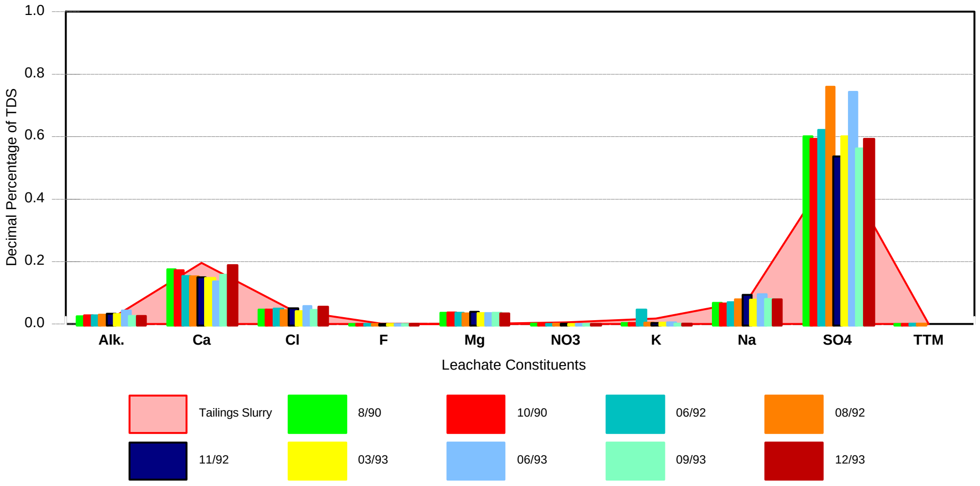


Regression Analysis Matrix for the Geochemical Fingerprint at Cyprus Sierrita Well MH-14.

	Sampling Date							
	8/90	**6/92**	**8/92**	**11/92**	**3/93**	**6/93**	**9/93**	**12/93**
Tailings Slurry	0.986	0.908	0.975	0.976	0.979	0.950	0.977	0.983
8/90	1.000	0.933	0.990	0.988	0.991	0.973	0.992	0.991
6/92		1.000	0.938	0.949	0.948	0.926	0.926	0.939
8/92			1.000	0.984	0.993	0.992	0.999	0.985
11/92				1.000	0.998	0.956	0.981	0.998
3/93					1.000	0.970	0.990	0.998
6/93						1.000	0.991	0.956
9/93							1.000	0.984
12/93								1.000

Average r squared value = 0.974
Ground water - tailings slurry comparison = 0.967

Figure 6-33. Geochemical monitoring results from Cyprus Sierrita downgradient monitoring Well MH-14.

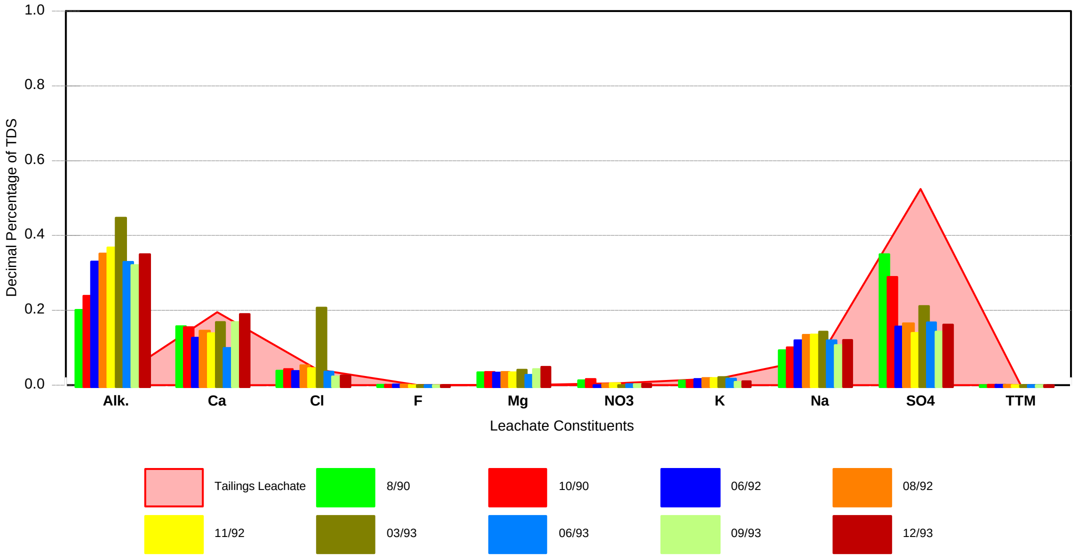


Regression Analysis Matrix for the Geochemical Fingerprint at Cyprus Sierrita Well MH-15

	Sampling Date								
	8/90	**10/90**	**6/92**	**8/92**	**11/92**	**3/93**	**6/93**	**9/93**	**12/93**
Tailings Slurry	0.988	0.987	0.976	0.967	0.981	0.978	0.959	0.985	0.992
8/90	1.000	1.000	0.992	0.992	0.996	0.997	0.987	0.999	0.999
10/90		1.000	0.992	0.992	0.995	0.997	0.987	0.999	0.998
6/92			1.000	0.994	0.988	0.994	0.991	0.991	0.988
8/92				1.000	0.990	0.998	0.998	0.992	0.986
11/92					1.000	0.997	0.990	0.999	0.996
3/93						1.000	0.996	0.998	0.994
6/93							1.000	0.989	0.981
9/93								1.000	0.998
12/93									1.000

Average r squared value = 0.994
Ground water - tailings slurry comparison = 0.979

Figure 6-34. Geochemical monitoring results from Cyprus Sierrita downgradient Well MH-15.



Regression Analysis Matrix for the Geochemical Fingerprint at Cyprus Sierrita Well MH-16

	Sampling Date								
	8/90	**10/90**	**6/92**	**8/92**	**11/92**	**3/93**	**6/93**	**9/93**	**12/93**
Tailings Leachate	0.753	0.573	0.108	0.105	0.059	0.086	0.117	0.106	0.115
8/90	1.000	0.961	0.560	0.553	0.469	0.473	0.576	0.546	0.559
10/90		1.000	0.745	0.740	0.663	0.642	0.754	0.731	0.742
6/92			1.000	0.998	0.990	0.876	0.992	0.974	0.971
8/92				1.000	0.992	0.893	0.985	0.976	0.974
11/92					1.000	0.878	0.976	0.969	0.964
3/93						1.000	0.871	0.824	0.819
6/93							1.000	0.941	0.936
9/93								1.000	1.000
12/93									1.000

Average r squared value = 0.820
Ground water - tailings leachate comparison = 0.225

Figure 6-35. Geochemical monitoring results from Cyprus Sierrita downgradient Well MH-16.

The assessment of the monitoring data from the Cyprus Sierrita Mine also provided another example in which the trace metal components migrated more slowly than the geochemical fingerprint. Although tailings leachate was present at Wells MH-14 and MH-15 for more than three years, as indicated by the geochemical fingerprint, the higher trace metal concentrations associated with the leachate were not in evidence. The significance of this observation is that trace metals would not be suitable monitoring parameters for early detection of tailings leachate migration.

6.4 Zonia Copper Mine

The final Arizona copper mining facility to be summarized is the Zonia Mine. The data set that was reviewed was incomplete because it did not contain any monitoring results for the tailings basin and the data were further limited by some readily identifiable data quality concerns. However, the ground-water monitoring data from this site still illustrate the potential of using geochemical monitoring results to fingerprint mine leachates.

A site map for the Zonia Mine is shown in Figure 6-36. The site monitoring program includes at least one well upgradient of the leaching basins (Well A-16), a series of wells that are east and downgradient of the leaching basins (Well Z-601, cabin well, Well Z-602, and Well Z-605), and several additional on-site wells. Each location was sampled on 10 occasions between 1993 and 1994 and the collected samples were analyzed for most of the common geochemical parameters, pH, total dissolved solids, and 11 trace metals for which drinking water criteria have been established.

6.4.1 Background Ground-Water Conditions

The geochemical monitoring results from upgradient Well A-16 are summarized in Figure 6-37. These data define a pattern in which alkalinity is the most abundant constituent and calcium and sulfate are the second most abundant constituents. This fingerprint, which is similar to that observed upgradient of other copper mines, had a reproducibility of 76 percent.

6.4.2 Downgradient Ground-Water Conditions

The geochemical monitoring results from Well Z601, a location approximately 1500 feet northeast of the ore processing facility, are presented in Figure 6-38. The geochemical fingerprint at this location is defined by 50 percent alkalinity, 20 percent sulfate, and small quantities of the other geochemical parameters. This pattern had a reproducibility of 94 percent. The similarity of this pattern with that at upgradient Well A-16, a 74 percent match, suggests that mine waste leachate has not impacted this location.

Data from the Old Mill well at this site have been summarized in Figure 6-39. There is an obvious data quality problem with the December, 1994 survey because the ionic sum equals more than 140 percent of the total dissolved solids concentration. However, except for the variability associated with the small calcium peak, these results define a repetitious pattern in which sulfate is the single dominant peak. The reproducibility of this pattern was estimated by regression analysis to be 86 percent.

The geochemical fingerprint at the Old Mill well represents a distinctive shift from the observed pattern at Well A-16. The sulfate-rich, alkalinity-poor pattern at the Old Mill well is only a 12 percent match for the alkalinity-rich, sulfate-poor pattern at the upgradient well. Although the data file for this mine did not contain any information on the raffinate pond or the tailings ponds, these results suggest that the ground water has been impacted by mine waste leachate because the geochemical fingerprint at the Old Mill well is similar to tailings leachate fingerprints at other copper mines (Figure 6-2, Figure 6-22, and Figure 6-32) and the fact that this pattern represents a characteristic shift from background conditions upgradient of the site.

Well A-14 is an on-site well located approximately 500 feet east of the raffinate ponds. Normalized geochemical monitoring results from this well define a consistent pattern in which sulfate is the most abundant ion, calcium is the second most abundant ion, and alkalinity is the third most abundant ion (Figure 6-40). This pattern had a reproducibility of 85 percent based on the results of 11 surveys conducted between March, 1993 and December, 1994. The sulfate-rich geochemical fingerprint at Well A-14 is very similar to the geochemical fingerprint at the Old Mill well but only has a 22 percent match with the upgradient fingerprint at Well A-16. These results also suggest that ground water at the site has been impacted by mine waste leachate.

Well Z605 is located approximately 1000 feet from an existing leach basin and close to the southern boundary of the Zonia Mine (Figure 6-36. The geochemical results from this well define a consistent, repetitive pattern in which sulfate represents approximately 60 percent of the total dissolved solids concentration (Figure 6-41). The reproducibility of the geochemical fingerprint was estimated by regression analysis to be 93 percent.

The geochemical fingerprint at Well Z605 is identical to that observed at the Old Mill well (Figure 6-39) and Well A-14 (Figure 6-40) but different from the alkalinity-rich, sulfate-poor pattern observed at upgradient Well A-16 and Well Z601. On the assumption that this pattern is indicative of copper mine waste leachate (Figure 6-2, Figure 6-22, and Figure 6-32), these results indicate that fugitive emissions from the Zonia Mine have impacted the ground water. More importantly, this set of data provides another indication that a mine waste leachate fingerprint can and will maintain its chemical identity as it migrates away from the source.

The results from one final ground-water monitoring location at the Zonia Mine are summarized in Figure 6-42. This particular set of data is presented because it illustrates the data quality problems that were present and the ability of this approach to detect them. An inspection of the results from Well Z603 indicates that sulfate represented more than 150 percent of the total dissolved solids concentration in two surveys, that total trace metals represented 50 percent of the total dissolved solids concentration in the same surveys, and calcium and sulfate each represented 100 percent of the total dissolved solids concentration in another survey. Since these conditions are not possible because the sum of the ions must equal the total dissolved solids concentration, the individual analyses are biased high and/or the total dissolved solids concentrations are biased low. If this assessment technique were applied as the data were being produced, it would be a relatively simple matter to identify the source of the error and institute corrective action in order to produce data of acceptable quality. When the flagged data are omitted, the remaining results at Well Z603 define a sulfate-rich, alkalinity-poor pattern that is similar to that at the Old Mill well and has a reproducibility of 94 percent.

6.4.3 Zonia Summary

Despite the limitations due to data quality, the monitoring results from 11 locations at the Zonia Mine only describe two geochemical fingerprints. The ground water at upgradient Well A-16 has a low total dissolved solids concentration and a fingerprint pattern that is characterized by a high relative abundance of alkalinity and a low relative abundance of sulfate. The ground water at four other wells also has a low total dissolved solids concentration and an alkalinity-rich, sulfate-poor fingerprint that is a fair to good match for the upgradient conditions (Table 6-8). However, ground water from three locations near the mine operation (Old Mill well, Instrument Shack well, and Well A-14) have elevated levels of total dissolved solids and a sulfate-rich, alkalinity-poor fingerprint that is not similar to upgradient conditions (Table 6-8). Although monitoring results for the Zonia raffinate pond or tailings ponds were not recovered during the records search, this geochemical fingerprint is identical to the characteristic tailings leachate fingerprint observed at three other Arizona copper mines. These results suggest that fugitive mine waste leachate is responsible for the altered ground-water composition at these locations.

Ground water at three locations downgradient of the mine (Well Z602, Well Z603, and Well Z605) has total dissolved solids concentrations above background levels and a consistent alkalinity-poor, sulfate-rich composition (Table 6-8). Since these conditions are a poor match for the ground water upgradient of the mine (8 to 24 percent match) but very similar to ground water conditions at the mine site (Old Mill well, Instrument Shack well, and Well A-14), the geochemical fingerprint analysis suggests that these areas have also been impacted by mine waste leachate. In addition, because these monitoring wells are located approximately 1000 feet from the ore processing facilities, these results provide further evidence that mine waste leachates maintain their characteristic geochemical identity as they migrate away from the source.

This case study also demonstrated the ability to identify suspect quality monitoring data with the geochemical fingerprint analysis technique. The highly variable concentrations in mine tailings leachates can complicate any attempt to assess data quality using conventional techniques. However, since the sum of the individual geochemical ions must be less than or equal to the total dissolved solids concentration, the ratio of concentration to total dissolved solids must be less than 1.0 for each geochemical parameter and the sum of the normalized values must be within prescribed limits (the data quality objective used during this project was that the sum of the ions should represent at least 80 percent but no more than 120 percent of the total dissolved solids concentration). An inspection of the graphical fingerprints readily identifies data sets that fail to meet these objectives without the need for extensive replicate analysis of samples or complicated statistical analysis of the results.

6.5 Discussion of Copper Mine Case Studies

The initial objective of this project was to identify appropriate monitoring parameters for cyanide heap leaching facilities. As the initial results began to indicate that geochemical parameters could be used to fingerprint the process solutions and tailings leachates at gold mines, the scope of the project was expanded to include copper mines. The data used in this study were provided by the Arizona Department of Environmental Quality.

The monitoring results from the individual mines were compiled to characterize the composition of tailings leachates at copper mines (Chapter 3). This information indicated that copper tailings leachates shared many of the same properties as process solutions and tailings leachates at heap leaching facilities. Specifically, (1) the concentrations for each constituent were highly variable and most were non-normally distributed, (2) the total dissolved solids concentration for tailings leachates were very high and averaged 10,000 mg/L, (3) a small number of common geochemical ions were repeatedly present as the most abundant constituents in the leachates, and (4) at least 15 constituents are present at concentrations that could potentially degrade water environmental conditions in the vicinity of a mine.

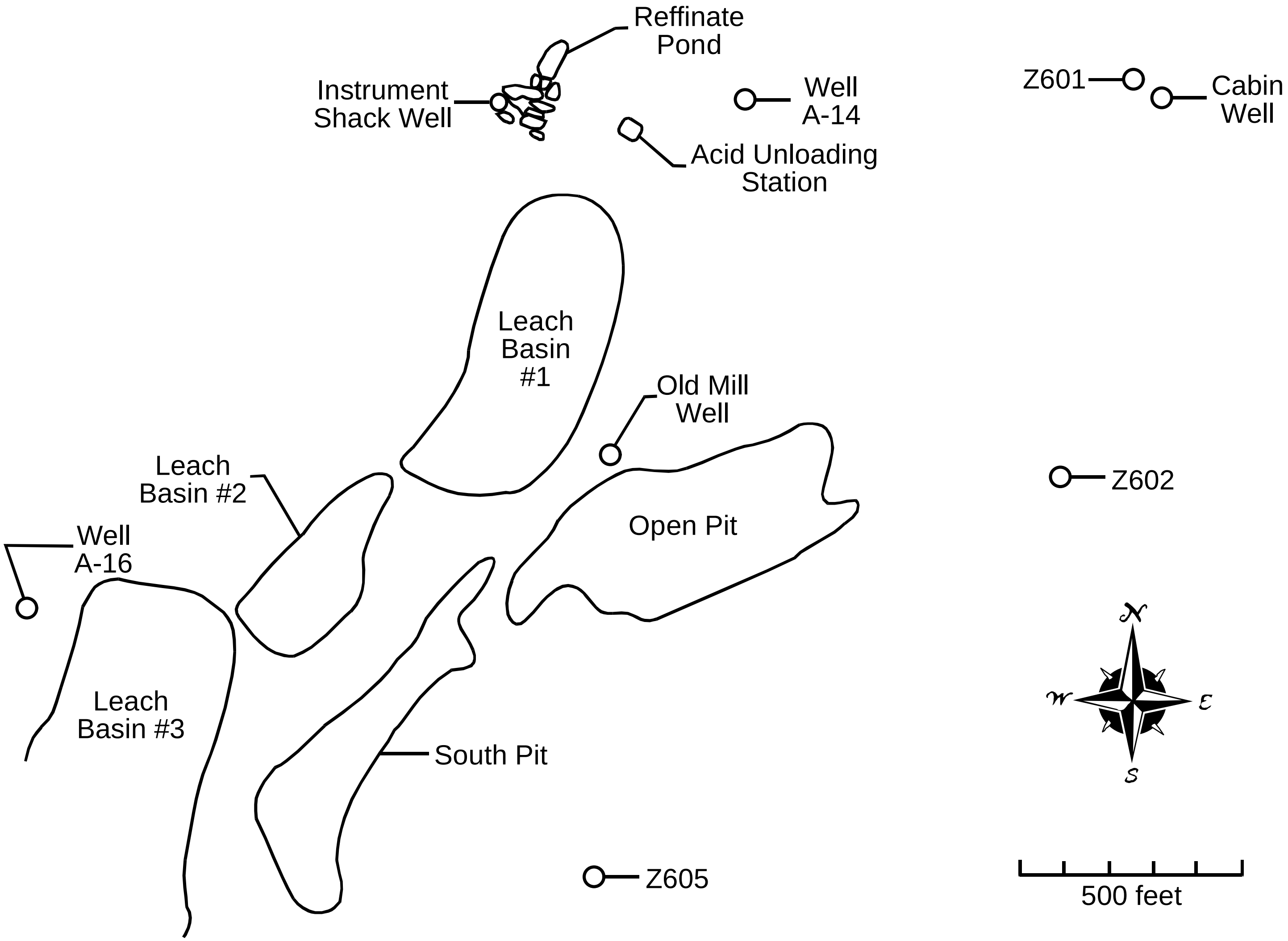


Figure 6-36. Site map for the Zonia Copper Mine.

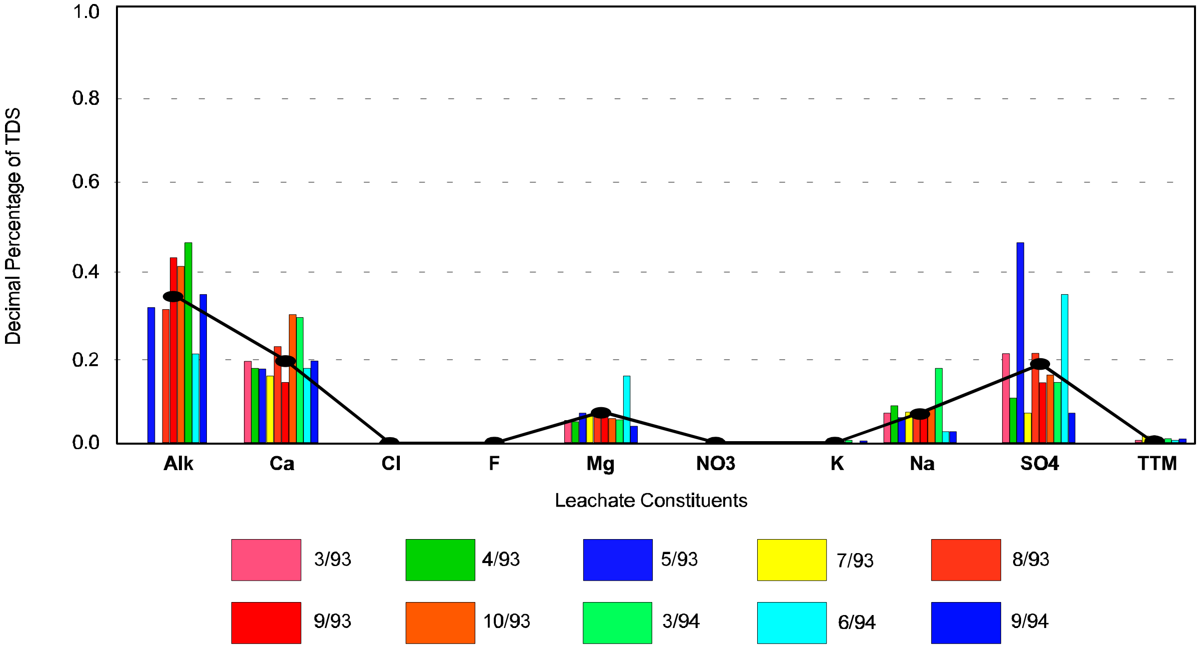


Figure 6-37. Geochemical fingerprint at upgradient Well A-16.

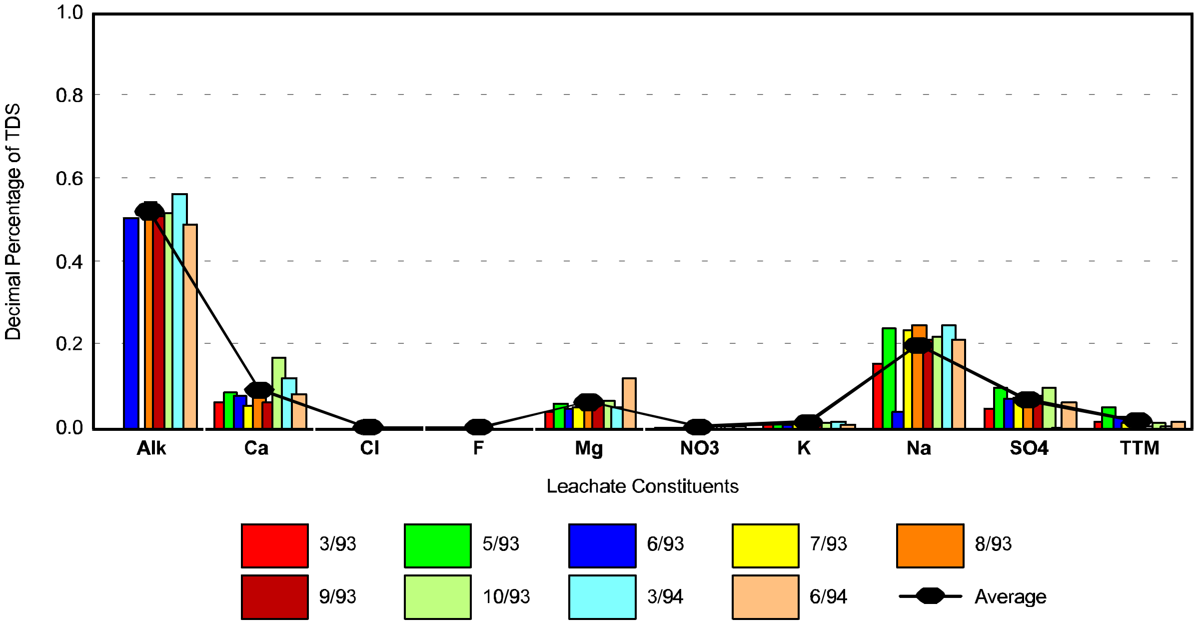


Figure 6-38. Geochemical fingerprint at downgradient Well Z601.

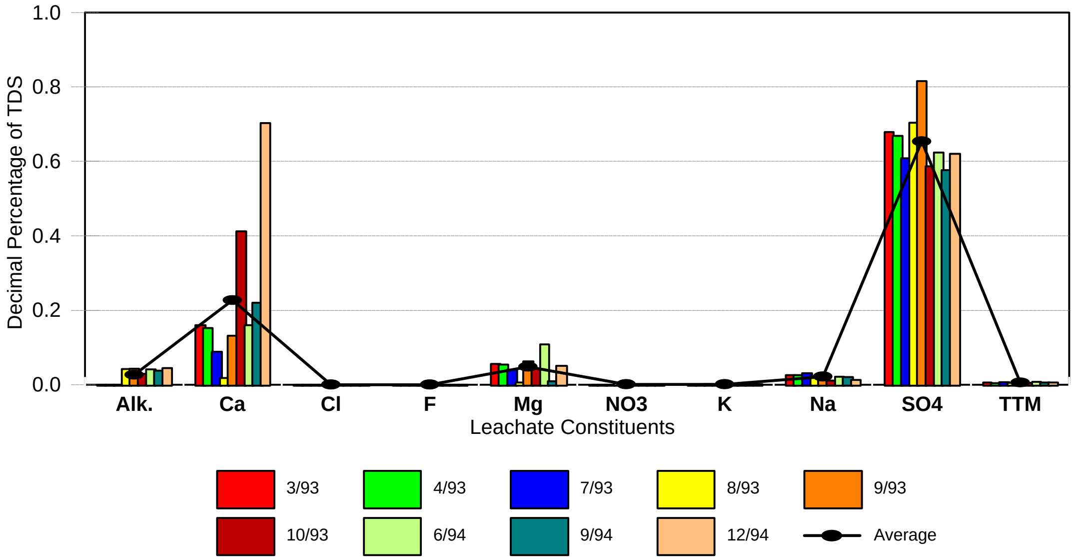


Figure 6-39. Geochemical monitoring results at the Old Mill well.

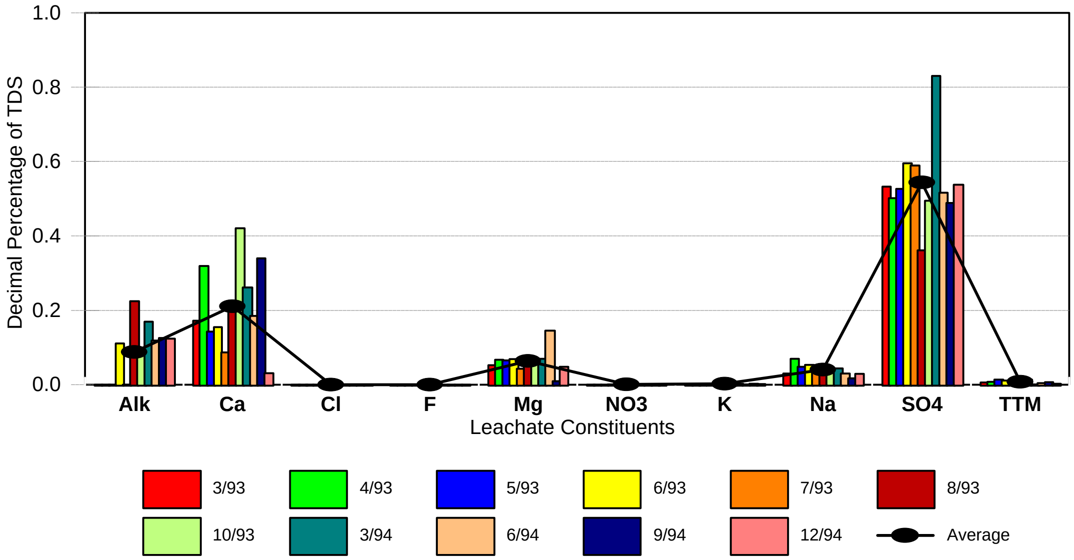


Figure 6-40. Geochemical monitoring results at Well A-14.

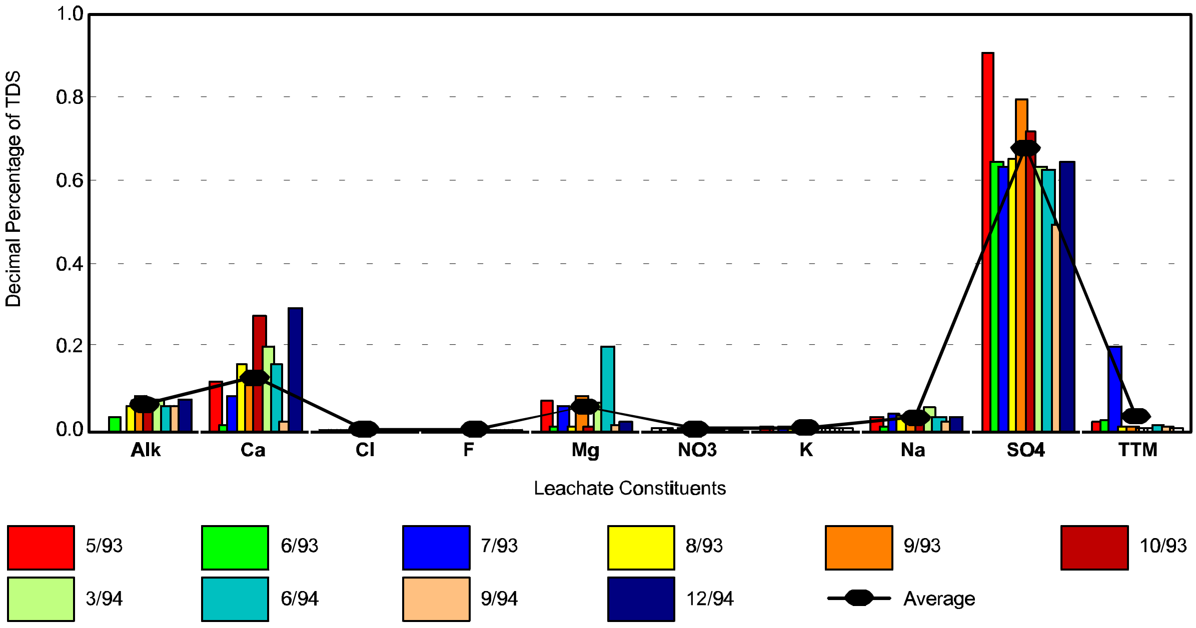


Figure 6-41. Geochemical monitoring results at Well Z605.

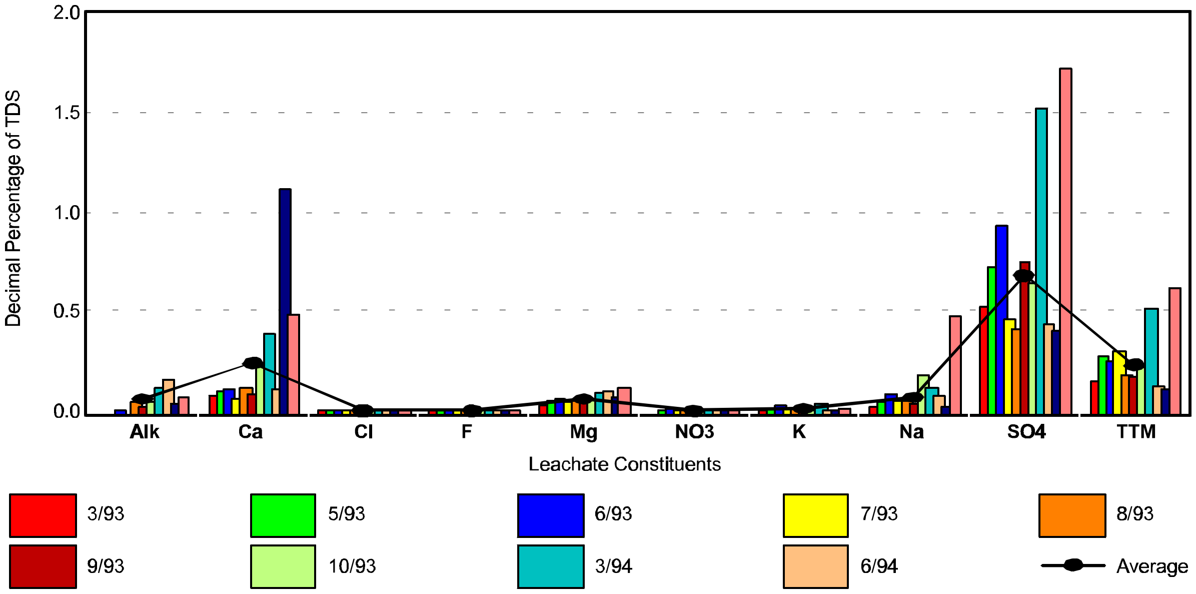


Figure 6-42. Geochemical monitoring results at Well Z603.

Table 6-8. Assessment of the ground-water monitoring results from the Zonia Copper Mine.

Location	Geochemical Pattern	TDS[1]	Reproducibility[2,3]	Upgradient Match[2,3]
Well A-16	Alk-rich, SO_4-poor	300-800	76.3 (15)	—
Well Z601	Alk-rich, SO_4-poor	300-500	94.0 (21)	74.2 (7)
Well Z607	Alk-rich, SO_4-poor	200-600	69.8 (15)	49.7 (6)
Cabin Well	Alk-rich, SO_4-poor	300-500	79.8 (6)	73.1 (4)
Cuprite Well	Alk-rich, SO_4-poor	200-300	94.0 (28)	94.4 (8)
Old Mill Well	SO_4-rich, Alk-poor	2800-3300	85.6 (36)	11.6 (9)
Instrument Shack	SO_4-rich, Alk-poor	1300-2300	83.9 (55)	20.9 (11)
Well A-14	SO_4-rich, Alk-poor	1800-3000	84.9 (55)	22.1 (11)
Well Z602	SO_4-rich, Alk-poor	1400-1900	91.1 (28)	24.5 (8)
Well Z603	SO_4-rich, Alk-poor	1000-4000	94.3 (6)	8.5 (4)
Well Z605	SO_4-rich, Alk-poor	1600-1900	93.1 (28)	12.7 (8)

[1] Total dissolved solids concentration expressed in mg/L.

[2] Listed value is the average regression analysis r^2 value times 100.

[3] Value in parenthesis is the number of regression analysis performed.

The same graphical fingerprinting technique that was used at ash monofills and heap leaching facilities was applied to the copper mine data. The concentration for each constituent was divided by the total dissolved solids concentration of the tailings leachate. This data normalization process reduced the effect of concentration variability between surveys and provided a rapid method to assess data quality. The resultant fingerprint patterns were compared visually and statistically using regression analysis.

The monitoring records for the individual copper mines did not contain results from multiple locations in a recirculating process solution as was the case with the heap leaching facilities. However, each mine generally contained several years of monitoring data for their tailings basin. These data were used to develop geochemical fingerprints for the tailings leachates and to evaluate their reproducibility over time.

1. The Twin Butte tailings leachate had a sulfate-rich, alkalinity-poor fingerprint. The reproducibility of this pattern during 14 surveys over 5 years was 97 percent.
2. Leachate in the Phelps-Dodge tailings disposal area had a sulfate-rich, alkalinity-poor geochemical fingerprint. Based on 10 quarterly surveys at six wells in the tailings disposal area, the reproducibility of the Phelps-Dodge fingerprint was 99 percent.
3. Tailings leachate at the Cyprus Sierrita Mine had a sulfate-rich, alkalinity-poor fingerprint. The reproducibility of this pattern based on sampling results from six locations in the tailings disposal area was estimated to be 88 percent.
4. The Zonia file did not contain any information on the tailings pond composition. However, ground-water monitoring results from several wells near the mill site produced geochemical fingerprints that were sulfate-rich and alkalinity-poor and had reproducibilities ranging from 83 to 86 percent. This pattern is very similar to the tailings leachate fingerprint observed at the Twin Butte, Phelps-Dodge, and Cyprus Sierrita copper mines.

At each of the copper mines, the geochemical monitoring results defined a consistent and reproducible pattern for the tailings leachate. However, unlike the heap leaching facilities, the geochemical fingerprint for copper tailings leachates was nearly identical at all sites. This was undoubtedly influenced by the fact that each mine uses a sulfuric acid based raffinate to extract copper from the ore being processed (sulfate is the dominant ion, leachate pH is approximately 2).

The next step in evaluating the composition of copper tailings leachates was to demonstrate that the identified tailings leachate fingerprints were different from background conditions at each mine. Since there was no information on make up water used at each of the copper mines, the tailings leachate fingerprints were compared to geochemical fingerprints for ground water upgradient of the mine. In each of the case studies, the upgradient ground water was characterized by relatively high levels of alkalinity (40 to 50 percent of the total dissolved solids concentration) and relatively low levels of sulfate (10 to 20 percent of the total dissolved solids concentration). The geochemical fingerprint for tailings leachate was visually and statistically distinct from the background fingerprint at each mine.

The final step in the site assessment was to contrast the tailings leachate fingerprint with the geochemical fingerprint in ground water downgradient of the tailings disposal areas. In each of the case studies, two distinctive geochemical fingerprints were present in the ground water downgradient of the tailings basins. One of the patterns was an alkalinity-rich, sulfate-poor fingerprint that was identical to conditions upgradient of the tailings basin. The similarity of these fingerprint indicates that mining activities have not had an impact on the ground water in these areas. However, the second pattern identified at downgradient monitoring locations was a sulfate-rich, alkalinity-poor fingerprint that was very similar to the tailings leachate fingerprint (85 to 99 percent match). These results clearly identify areas that have been impacted by fugitive tailings leachate.

The evaluation of monitoring records from the Arizona copper mines demonstrated that tailings leachates have a characteristic ionic fingerprint and this distinctive geochemical signature will retain its identity as the leachate migrates through the subsurface environment. Both of these properties of mine waste leachates were also observed at the Nevada heap leaching sites.

Although the primary objective of the data collection phase of the project was to obtain field monitoring results that could be used to characterize mine waste leachates and environmental conditions in the vicinity of mining operations, the individual site files were also reviewed for additional information on the composition or behavior of mine waste leachates. One very beneficial study recovered during the course of this project was a laboratory column study performed on behalf of the Twin Butte Mine. This particular study was initially performed to determine the attenuation coefficients of individual tailings leachate constituents. However, because complete sample analyses were performed, it was possible to use this study to evaluate the behavior of the tailings leachate fingerprint under controlled laboratory conditions.

The solution applied to the laboratory soil columns had a geochemical fingerprint that was identical to the Twin Butte tailings leachate. The initial eluant samples collected from the soil columns had geochemical fingerprints that produced a 90 percent match with the original leachate fingerprint. Subsequent eluant samples collected from the soil columns had a 95 to 99 percent match with the tailings leachate fingerprint. The results of this study demonstrate that the geochemical fingerprint will remain intact as tailings leachates migrate through a soil column. As a consequence, the geochemical fingerprint functions as an internal tracer that can be used to detect and identify tailings leachate at some distance from the source. This characteristic verifies the identification of tailings fingerprints at monitoring locations downgradient of each copper mine.

The Twin Butte column study was also useful for assessing the relative mobility of tailings leachate constituents. As discussed above and shown in Figure 6-43, the geochemical fingerprint transited the soil column immediately and with minimal distortion. However, the trace metals, that collectively represented 11.9 percent of the total dissolved solids concentration of the leachate applied to the column, were not present in the collected eluant samples. While it would have been interesting and informative if the column study had been run for a longer period of time, the results demonstrate that the trace metals in leachate will migrate more slowly than the individual geochemical parameters and the geochemical fingerprint.

The Twin Butte site monitoring data provided corroboration of the slower mobility of trace metals in tailings leachate. Specifically, the monitoring results for Well M-2 (Figure 6-16), Well 1225 (Figure 6-16), and Well M-7 (Figure 6-17) graphically depict tailings leachate migrating past these station. In each example, the ground water composition under went a systematic change from an alkalinity-rich, sulfate-poor fingerprint to a sulfate-rich, alkalinity-poor fingerprint that resembled the tailings leachate fingerprint. Even though trace metals represent more than five percent of the total dissolved solids concentration in leachate, trace metal increases were not detected at the monitoring stations before, during, or after the detection of the tailings leachate geochemical fingerprint. The significance of this observation is that monitoring for trace metals would not provide an early warning or detection of mine waste leachate migration because of their slower rate of movement.

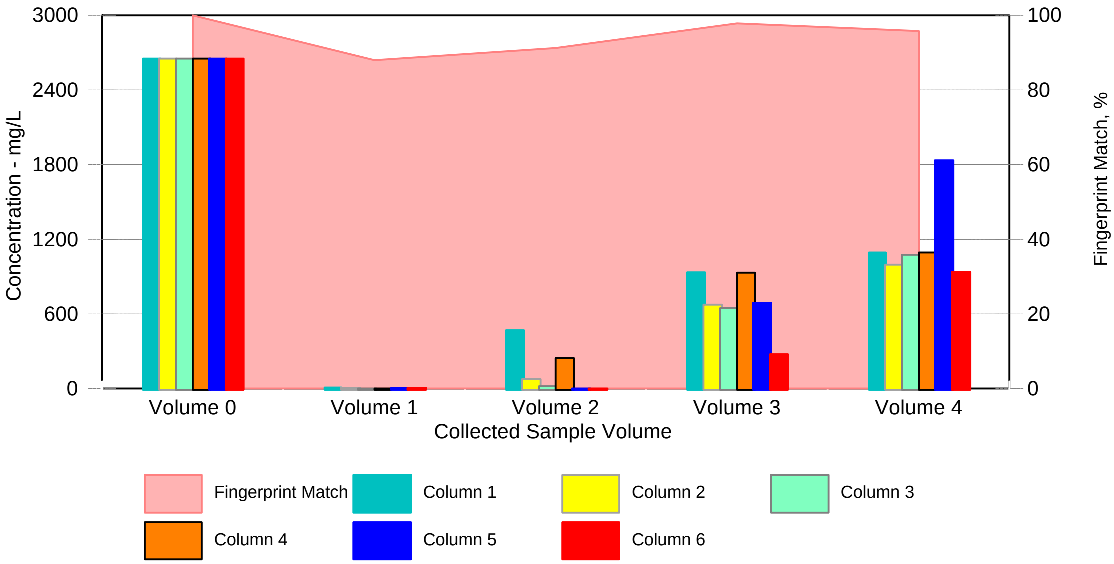


Figure 6-43. Comparative mobility of the geochemical fingerprint and trace metals in copper tailings leachate.

6.6 Arizona Copper Mines Summary

Site monitoring records from 4 copper mining operations in the State of Arizona were compiled to characterize tailings leachates. A review of this information showed that copper tailings leachates shared many of the compositional characteristic of process solutions and tailings leachates at heap leaching facilities. These specific properties included (1) the concentrations for individual constituents were highly variable, (2) the small subset of geochemical parameters were the most abundant constituents and represented more than 90 percent of the total dissolved solids, and (3) the geochemical parameters defined a multiple-ion chemical signature that uniquely fingerprinted the tailings leachate composition.

The case studies that were summarized demonstrated that the copper tailings leachate fingerprints displayed the following attributes:

1. The geochemical fingerprint at each mine was reproducible. Based on 2 to 5 years of monitoring results, the leachate at each mine had a consistent sulfate-rich, alkalinity-poor pattern. The reproducibility of the geochemical fingerprint ranged from 88 to 97 percent.
2. The tailings leachate fingerprint could be distinguished, both visually and by regression analysis, from the fingerprint of ground water upgradient of the tailings disposal area.
3. The fingerprint retained its chemical identity when leachate migrated away from the tailings disposal area. Thus, the geochemical fingerprint acts as an internal tracer to identify the leachate and areas impacted by the leachate.

4. Laboratory and field studies at the Twin Butte Mine showed that the individual geochemical parameters and the geochemical fingerprint will migrate faster than the trace metals that are present in tailings leachate.

These results suggest that the geochemical parameters, calcium, magnesium, sodium, potassium, alkalinity, chloride, nitrate, sulfate, and total dissolved solids, can be used as effective parameters to characterize copper tailings leachates at their source and monitor their migration in the environment.

Section 7

Development of a Ground-Water Monitoring Strategy for Mining Facilities

7.1 Background

The Resource Conservation and Recovery Act (RCRA) was enacted in 1976 to identify characteristics of hazardous wastes, list specific hazardous wastes subject to regulation, and to develop operational standards for owners and operators of hazardous waste treatment, storage, and disposal facilities (U.S. EPA, 1990). During the development of regulations to implement the RCRA legislation, the concept of "special wastes" was introduced. These wastes, which included mining wastes, were provisionally exempted from the RCRA Subtitle C requirements because they were generated in large volume, they were considered to pose a low risk to human health and the environment, and they were not generally amenable to management practices proposed for other types of hazardous waste. This administrative exemption was formalized with the inclusion of the Bevill Amendment as part of the 1980 reauthorization of RCRA which temporarily exempted mining and mineral processing wastes, along with several other types of wastes, from potential regulation as hazardous wastes (U.S. EPA, 1990).

The original interpretation of the Bevill Amendment to include all mining wastes as "special wastes" was challenged in court in 1985 (U.S. EPA, 1990). As a result of this action, the Environmental Protection Agency developed a more stringent interpretation of the Bevill Amendment. Based on this revised assessment, 20 specific waste streams identified in a study of the mining industry retained their Bevill Amendment exclusion while all remaining waste streams in the mineral processing industry were removed from the exclusion list on September 1, 1989.

7.2 Need for Monitoring

The decision to end the Bevill Amendment exemption for most mining wastes was based on the fact that they may pose unreasonable risk to the environment if they are not properly managed (U.S. EPA, 1987). Although there are no national requirements to monitor ground-water conditions in the vicinity of mining sites at the present time, there are four important factors that establish the need for an effective monitoring program. These factors are (1) the large number of mining sites, (2) the potential size of these sites, (3) the large volume of waste material produced, and (4) the number of constituents in mine waste leachates that could have a potential adverse impact on environmental conditions.

Number of Mining Sites

The total number of mining sites, both active and inactive, in the United States has been estimated to be as high as 82,000 (Office of Technology Assessment, 1984). By comparison, there were originally 2000 hazardous waste disposal sites in the RCRA Subtitle C Program and 15,000 municipal landfills in the RCRA Subtitle D Program. EPA Region VIII has estimated that 800 to 1500 mining sites may have to be investigated to evaluate the risks to public health and the environment (EPA, 1987). In addition, more than 50 mining sites have already been included on the Superfund National Priorities List. The 22 members of the Western Governor's Association have listed mining as a top environmental issue.

Size of Mining Sites

The size of mining operations are highly variable. Many of the smaller abandoned and inactive sites may only cover a few acres. However, the larger sites cover thousands of acres and the plume of contaminated ground water downgradient of some leaking tailings basins have been reported to extend for more than ten miles. The largest of three tailings ponds at the Twin Butte Site covered approximately 1300 acres (2 square miles). One of the largest sites on the Superfund National Priorities Site List is the Bunker Hill mining site in Northern Idaho that covers 21 square miles (U.S. EPA, 1994).

Volume of Waste Material

The total quantity of cumulative mine waste in the country has been estimated at 50 billion tons (Zilka, 1992). Currently, 1.5 billion tons of ore are processed annually by the mining industry (EPA, 1985). Only a small percentage of the processed ore is recovered as an economic product while the largest percentage of the mined ore is discarded in waste piles and tailings basins. The cyanide heap leaching process is being used to recover as little as 0.02 ounces of gold and silver per ton of ore (Miller, et. al., 1996). For these facilities, essentially all of the mined ore is eventually discarded in waste piles or tailings basins. It has been reported that 300 mining operations produced 1.3 billion tons of waste in 1985 while, in comparison, 275 million tons of waste were disposed in 3000 regulated RCRA Subtitle C facilities (EPA, 1985; Sydow, et. al., 1988). (This comparison is not meant to imply that mining waste is equivalent to hazardous waste but simply to illustrate the volume of mining waste being generated.)

Constituents of Concern

With the exception of cyanide at the heap leaching facilities, the constituents of mine waste leachates are all naturally occurring substances (alkali metals, alkaline earth metals, common anions, and trace metals). The composite monitoring results discussed in Chapter 3 indicate that as many as 25 individual mine waste leachate constituents may be present at concentrations above screening criteria levels that indicate potential harm to human or environmental health.

The extent of mining activities in the United States identifies this industry as a topic of national concern and establishes a need for uniform and effective site monitoring. However, there are several readily identifiable problems and limitations that will be encountered if existing RCRA monitoring requirements are used at mining sites. These issues include the following:

1. Performance of Detection Monitoring Parameters. The original RCRA Subtitle C Detection Monitoring parameters were pH, specific conductance, total organic carbon (TOC), and total organic halogen (TOX). An evaluation of the performance of these parameters at hazardous waste disposal sites indicated that their effectiveness was poor (Plumb and Fitzsimmons, 1984; Plumb, 1987; Plumb, 1989) and there is no indication that they would be any better at mining sites. Specific conductance could be useful as a measure of total dissolved solids but it would be limited somewhat by the fact that it is not specific to mining wastes. Also, pH could be a

potentially useful monitoring parameter. However, since the Twin Butte column study results and the Twin Butte field monitoring results demonstrate that pH is rapidly neutralized, pH would not provide for early detection of process solution and tailings leachate migration. Finally, TOC and TOX are not generally appropriate for mining sites because organic contaminants have not been identified as constituents of concern.

2. Volatile Organic Compound Monitoring. The final RCRA Subtitle D monitoring requirements specifies the use of VOC scans to detect the most abundant class of organic contaminants at municipal landfills (EPA, 1991). Although volatile scans perform much better than the original RCRA organic indicators (Plumb, 1987), they would not be useful at mining sites because volatile organic compounds are not predominant constituents of mine waste leachates.
3. Extensive Organic Analysis Requirements. Both the RCRA Subtitle C (EPA, 1984) and RCRA Subtitle D (EPA, 1991) programs require extensive organic analysis of ground-water samples at hazardous waste disposal sites and municipal landfills, respectively. However, extensive organic analysis would not be appropriate for mining site monitoring programs since these contaminants are essentially absent from mine waste leachates.
4. Absence of Geochemical Monitoring Requirement. The RCRA Subtitle C (EPA, 1984) and RCRA Subtitle D (EPA, 1991) programs do not specify any monitoring for the common geochemical parameters. Therefore, any attempt to use established RCRA monitoring requirements would miss the most abundant constituents in mine waste leachate.

Based on an improved understanding of the composition and behavior of mine waste leachates developed in Chapter 5 (Nevada Heap Leaching Facilities) and Chapter 6 (Arizona Copper Mines), the purpose of this Chapter is to identify a set of appropriate monitoring parameters for mining sites that will overcome the problems and limitations listed above and to integrate the selected monitoring parameters into an effective monitoring strategy for these sites.

7.3 Monitoring Parameter Criteria

The established RCRA programs at hazardous waste disposal sites (RCRA Subtitle C) and municipal landfills (RCRA Subtitle D) use a multi-phase approach to monitoring. The first phase of this strategy relies on a small number of parameters to verify that the waste containment mechanism at the site is functioning properly. This relatively low level of monitoring is continued until a leakage event is detected. At that time, the second phase of the monitoring strategy is triggered and the monitoring requirements are expanded to more fully identify and characterize contaminants that are associated with the leakage event. This tiered approach to site monitoring was chosen as the model for the monitoring strategy to be developed for mining sites.

The most critical element of the two tiered monitoring strategy is the set of monitoring parameters selected to detect leakage in the first phase of the strategy and trigger expanded analysis in the second phase of the strategy. Two sets of desirable characteristics for detection monitoring parameters were used to evaluate the potential utility and effectiveness of the geochemical fingerprint as detection monitoring parameters for mining sites. The first set of characteristics for evaluating potential ground-water indicators includes 9 functional criteria listed in Table 7-1 (Miller, 1987). This set of characteristics relates to the suitability of the parameters for a particular purpose. The second set identifies the technical factors that must be considered when selecting a tracer (indicator parameter) for potential use (Plumb and Nacht, 1984). This set of criteria generally defines how well a detection monitoring parameter will perform.

Table 7-1. Functional criteria for evaluating the performance of detection monitoring parameters.*

1. **Conceptual Accuracy.** How directly does the indicator measure changes in the conditions being monitored?
2. **Level of Environmental Data.** Is the Indicator a measure of government action, source action, or ambient changes?
3. **Availability of Data.** Does the indicator require generation of new data or utilization of existing data? Will the cost be high or low?
4. **Sampling Accuracy.** Is the indicator a representative and unbiased estimate of the condition being monitored?
5. **Measurement Accuracy.** Is the indicator measurable with existing, validated methods?
6. **Overall Consistency.** Can measurements from different location be aggregated and fairly compared?
7. **Time Period over which Changes are Reflected.** Does the indicator provide a measure of short term, medium term, or long term changes?
8. **Volume of Data Required.** How much data will be required to use the indicator in a decision-making process?
9. **Existence of Baseline.** Do baseline data already exist for comparison to new monitoring results?

* After Miller (1987).

The following provides a brief comparison of the properties of mine waste leachate fingerprints with the functional criteria for indicator parameters listed in Table 7-1.

1. Conceptual Accuracy. The individual constituents of mine waste leachates are all naturally occurring and not uniquely characteristic of the leachates. However, based on 22 case studies at heap leaching facilities and 4 case studies at copper mines, the multi-ion geochemical fingerprint is a characteristic property and a direct indicator of these leachates.

2. Level of Environmental Data. The geochemical fingerprint is a measure of ambient changes. It indicates the presence or absence of the mine waste leachate.

3. Availability of Data. As was shown in the case studies at the Nevada and Arizona facilities, this indicator can work with existing data. It may require using new techniques to evaluate and summarize the data (multi-ion graphical techniques rather than simple tabulations of chemical concentration data), but the results uniquely describe the composition and presence of mine waste leachates. The graphical summaries and regression analysis of the resulting fingerprint patterns can be performed with commercially available spreadsheet software. The cost of analysis to generate the data for fingerprinting the leachates and the cost of the software are low.

4. Sampling Accuracy. The geochemical fingerprint was a unique property of the mine waste leachates at each of the 26 case studies. The exact shape of the fingerprint pattern varied from

mine to mine but the same set of geochemical parameters was useful for characterizing the mine waste leachate and differentiating it from background conditions at each mine.

5. Measurement Accuracy. The fingerprint pattern itself is not directly measurable. However, the individual geochemical parameters that define the fingerprint are the most abundant ions in the leachates and are present at concentrations ranging from 10's to 1000's of mg/L. These concentrations are readily measurable with standard analytical techniques such as atomic absorption flame spectrophotometry, inductively coupled plasma arc, and anion chromatography.

6. Overall Consistency. The overall reproducibility of the geochemical fingerprint at each of the 26 case studies was generally greater than 90 percent. Even though the concentrations for each geochemical parameter varied by more than an order of magnitude, the reproducibility of a fingerprint pattern at a single location over time, or at several locations at an individual mine, was in the range of 90 to 99 percent. [The geochemical fingerprint varied from facility to facility but it was consistent at each individual mine.]

7. Time Periods over which Changes are Reflected. The geochemical fingerprint characterizes mine waste leachates at the source and was constant over time. Monitoring for the fingerprint provides a method to detect short term changes in the ground water in the vicinity of the mining operation when fugitive leachates migrate from the source. At approximately one-half of the heap leaching sites and all of the copper mining facilities, a geochemical fingerprint that was visually and statistically identical to the mine leachate fingerprint was identified in the ground water downgradient of the facility.

8. Volume of Data Required. Single complete sets of geochemical analyses are needed for each of the locations to be compared (i.e., upgradient of the site, site tailings basin, downgradient of the site). The conventional approach of requiring extensive replicate analyses to statistically analyze the results is not necessary with this approach.

9. Existence of Baseline. A formal baseline probably does not exist because environmental monitoring data has seldom been summarized in this manner. However, historical records can be used to construct baseline data summaries. As illustrated in the Twin Butte case study (Chapter 5.1), monitoring records from 25 years ago were used to characterize baseline conditions upgradient of the tailings disposal area and identify the time at which fugitive leachate impacted ground-water conditions downgradient of the tailings disposal area.

The potential use of the geochemical fingerprint as a detection monitoring parameter fulfills each of the functional criteria listed in Table 7-1. However, if there is a limitation on the geochemical fingerprint, it is that all of the major individual geochemical parameters must be reported in order to construct the fingerprint. This condition is more than offset by the fact that the geochemical fingerprint is an unequivocal identifier of the mine waste leachate and does not require extensive replicate analysis to evaluate or use the monitoring results. [It is possible that some of the less abundant geochemical ions, such as fluoride, nitrate, and potassium, could be deleted without significantly altering the fingerprint pattern for a leachate. While this would reduce the number of parameters needed to construct the fingerprint patterns, it would also reduce the amount of information available to perform internal checks on the quality of the data (i.e., mass balances and charge balances)].

The second set of performance criteria (Table 7-2) identified several technical factors that should be considered in selecting detection monitoring parameters (Plumb and Nacht, 1984). The following summarizes the performance of the geochemical fingerprint with respect to these criteria.

1. Should be naturally absent. Essentially all of the constituents of process solutions and mine waste leachates fail this criterion because they are naturally occurring. However, the geochemical composition of the leachates were repeatedly demonstrated in the case studies to be distinctively different from mine make up water or ground water upgradient of the site. Since the fingerprint is absent from background water and consistently present in mine waste leachates, the geochemical fingerprint functions as an internal tracer and provides a reliable mechanism to differentiate these sources at a mine site.

Table 7-2. Technical factors to consider in selecting a tracer (indicator parameter) for ground-water monitoring.*

1. Should be naturally absent from the system being monitored.
   This will facilitate detection of the indicator and identification of the source.
2. Should be related to the conditions of concern.
   A. Mechanically (cause and effect)
   B. Mathematically
   The more closely the indicator parameter can be related to the source, the more effective the resultant monitoring strategy.
3. Environmental behavior of tracer should be similar to the specific contaminants or conditions being monitored.
   A. Natural cycles should be the same.
   B. Tracer should be chemically conservative.
   C. Travel velocity of the tracer should be the same as the contaminants being monitored.
4. Analytical performance characteristics should be known.
   A. Methods should be sensitive enough to detect changes in the constituent of interest.
   B. Methods should have suitable precision and accuracy.
   C. Tracer method should be less expensive than direct measurement of the condition or constituent of interest.

* After Plumb and Nacht (1984)

2. Should be related to conditions being monitored. The case studies demonstrated that the process solution and tailings leachates at each mine had a geochemical composition that was constant and reproducible over time and space. Although there is no a priori reason for this result, each of the case studies pragmatically demonstrate that the geochemical fingerprint is a characteristic property that is directly related to the composition of process solutions and tailings leachates at each mine.

3. Environmental Behavior of the tracer should be similar to the condition being monitored.

   a. Natural Cycles. The data files from the Nevada gold mines and Arizona copper mines each contained 1 to 5 years of quarterly monitoring data. The evaluation of these data sets indicated that the geochemical fingerprint for the mine waste leachates was constant over the period of record at each mine. This indicates that temporal cycles are not a major issue.

   b. Chemically conservative. The geochemical fingerprint for the process solutions and tailings leachates at each mine were constant over time. In addition, the laboratory column study at the Twin Butte Mine and assessment of field monitoring results at all sites demonstrated that the geochemical fingerprint maintained its distinctive chemical identity as the leachate migrated away from the source. Furthermore, the evaluation of monitoring results at the Phelps-Dodge facility suggests that the tailings leachate fingerprint can still be identified after a 200:1 dilution in a nearby river. Collectively, these observations indicate that the geochemical fingerprints behave in a conservative manner.

   c. Travel velocity. The Twin Butte column study demonstrated that the geochemical parameters that define a leachate fingerprint have smaller attenuation coefficients than trace metals present in the solution. As a result, the geochemical parameters migrate faster than the trace metals. In addition, the column study also demonstrated that the geochemical fingerprint for tailings leachate migrated faster than the trace metal components of the leachate. Although there was a small distortion of the fingerprint due to an acid-base reaction, and a secondary affect on alkalinity, the geochemical fingerprint of the tailings leachate was still recognizable in the initial column effluent (90 percent match). By comparison, the trace metal constituents moved more slowly through the column and their abundance was greatly distorted (25 percent match). These results were verified with field data showing the geochemical fingerprint of leachate was identifiable at several monitoring wells even though no trace metal changes were observed. These conditions were also observed at monitoring wells in the vicinity of the Nevada gold mines. Since the geochemical fingerprint travels faster than the trace metals, monitoring for the geochemical parameters should result in early detection of leachate migration.

4. Analytical performance characteristics.

   a. Sensitivity of Method. As stated during the discussion of the Functional Criterion for measurement accuracy (Table 7-1, item 5), there is no direct method for a ine leachate geochemical fingerprint. However, there are individual methods for each of the geochemical parameters that define the fingerprint. These methods (AA or ICP for alkali metals and alkaline earths, and ion chromatography for the common anions), which have been evaluated for 10 years or more (APHA, 1989), have sensitivities on the order of 0.01 to 0.1 mg/L. Since the major constituents of mine waste leachates are present at concentrations 2 to 5 orders of magnitude above these levels (Chapter 3), method sensitivity should not be an implementation issue.

   b. Method Precision and Accuracy. There are two separate elements to consider when addressing the topic of precision and accuracy for the mine waste leachate fingerprints. One topic is the precision and accuracy of the analytical method and the second topic is the precision and accuracy of the fingerprint itself.

      I. Analytical Methods. There is no specific method for mine waste leachate fingerprints. However, there are well established and evaluated methods for each of the geochemical constituents that define the fingerprints (APHA, 1989; EPA, 1979). The actual precision and accuracy that is achieved will be influenced by the method used, the concentration of the constituent, and any interferences that may be present. Based on the performance data that have been summarized in Table 7-3, the accuracy of these methods is in the range of 95 to 103 percent and the precision is in the range of 1 to 10 percent. Furthermore, based on the estimated sensitivities for each method and the high concentrations generally reported for each geochemical constituent in mine waste leachates, detection should not be a problem and sample dilution prior to analysis will be necessary. Existing methods should provide reliable measurements for each of the geochemical constituents.

II. Geochemical Fingerprint. The assessment of monitoring results from 22 gold mines and 4 copper mines demonstrated the geochemical fingerprints of mine waste leachates to have a reproducibility that was generally greater than 90 percent. The reproducibility of geochemical fingerprints for background ground water and mine make up water was also demonstrated to generally be in the range of 95 to 99 percent. These values can probably be improved slightly by a timely review of monitoring results to detect and correct data quality problems.

Table 7-3. Performance characteristics of methods for geochemical constituents in mine waste leachates.

Constituent	Concentration (mg/L)	Precision (%)	Accuracy (%)	Detection Limit (mg/L)
Calcium	36	1.6	99	0.01
Magnesium	8.2	2.4	100	0.001
Sodium	6.3	7.9	102	0.002
Potassium	52	1.5	100	0.01
Alkalinity	119	5.4		
Chloride	455	10.1	103	0.1
Fluoride	0.85	3.5	99	
Nitrate	15.1	0.2	98	0.1
Sulfate	43.7	5.7	99	0.1
Total Solids	1069	10	95	

c. Cost of Methods. Since the individual geochemical parameters are currently being reported at many mining sites such as those in Nevada and Arizona, the use of geochemical parameters as primary detection monitoring parameters will not impact these costs. However, the use of geochemical parameters as Detection Monitoring parameters could lower monitoring costs in two ways. First, by monitoring for the more mobile constituents of mine waste leachate in the detection monitoring phase rather than slower less characteristic constituents, initial monitoring for trace metals can be reduced which would reduce costs. Second, since two internal checks on data quality can be applied to the geochemical data (mass balance and charge balance), additional savings may be realized by reducing the use of conventional data quality control procedures without sacrificing the reliability or quality of the data being produced.

The characteristics and behavior of geochemical fingerprints compare favorably with the technical factors considered important for tracers and indicator parameters. The fingerprint is a characteristic property that differentiates mine waste leachates from background ground water or mine make up water. In addition, the fingerprint functions as an internal tracer that maintains it unique chemical composition as mine leachate migrates through the environment. Finally, analytical methods are available to reliably measure each of the geochemical constituents at concentrations that would be anticipated in mine waste leachates. This assessment suggests that the geochemical fingerprint can fulfill the critical need and function as an effective detection monitoring parameter at mining sites.

7.4 Proposed Monitoring Strategy

The model for this proposed monitoring strategy at mining sites is the two-tiered monitoring strategy developed by the Environmental Protection Agency for hazardous waste disposal sites and municipal landfills (EPA, 1980; EPA, 1991). The monitoring performed in each phase of this strategy has a specific objective and the monitoring parameters must be selected to achieve these objectives. In the first phase, the primary objective is not to detect water quality (environmental) problems but rather to verify that the waste containment mechanism at a site is working properly and to detect spill events or leakage events when they occur. Therefore, the most appropriate parameters for this phase are those waste constituents with the highest mobility that uniquely characterize the waste. In the second phase, the objective is to determine whether the fugitive waste detected in the first phase is causing any environmental degradation. Monitoring requirements in this phase are expanded to include all constituents of concern that may be present in the waste.

A review of monitoring records from mining operations in Nevada and Arizona identified several characteristics of mine waste leachates. These properties included the following:

1. Each constituent had a highly variable concentration.
2. A small subset of geochemical parameters always represented 90 to 95 percent of the total dissolved solids concentration of mine waste leachate.
3. When monitoring results were normalized to the total dissolved solids concentration, the process solution and tailings leachate at each mine had a consistent geochemical fingerprint with a reproducibility generally greater than 90 percent.
4. The geochemical signature remained intact as mine waste leachate migrated through the environment.
5. The trace metal components of mine waste leachate did not define a characteristic, reproducible pattern.
6. Each of the geochemical parameters that defined the mine waste leachate fingerprint had an attenuation coefficient that was approximately two orders of magnitude lower than each of the trace metals. Consequently, the geochemical parameters and the mine waste leachate fingerprint migrated faster the trace metals in the leachates.

These characteristics provide the technical basis for selecting monitoring parameters and establishing a multiple-phased monitoring strategy for mining sites that is similar to that used at RCRA hazardous waste disposal sites and municipal landfills.

Based on the evaluation of the composition and properties of mine waste leachates in Nevada and Arizona, and the corroboration of leaching studies with incinerated municipal waste ash, the following multiple-phased monitoring program can be suggested for mining sites.

1. Phase 1. Source Characterization

   The objective of this phase is to characterize the process solutions and tailings solutions at a facility. Samples collected in this phase should be analyzed for the geochemical constituents (alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, sulfate, and total dissolved solids), pH, trace metals, and other constituents of importance (i.e., cyanide at heap leaching facilities). The geochemical results are used to develop the characteristic fingerprint for the mine waste leachate at the site and the trace metal data identify constituents that should be used in the Assessment Monitoring phase of the strategy if and when it becomes necessary.

2. Phase 2. Detection Monitoring

   The objective of this phase is to provide an early warning of fugitive mine waste leachate that may be migrating away from the source. Samples from monitoring locations around the site should be analyzed for the most mobile constituents characteristic of the waste. Based on results presented throughout this report, these samples should be analyzed for alkalinity, calcium, chloride, fluoride, magnesium, nitrate, potassium, sodium, sulfate, and total dissolved solids. The use of geochemical parameters in this phase will directly target constituents that represent approximately 95 percent of the total dissolved solids in mine waste leachates, target the most mobile class of mine waste leachate constituents, and provide the necessary information to develop a geochemical fingerprint to uniquely identify and detect the leachate. The same set of parameters can also be used to fingerprint ground water in the vicinity of the mine.

   a. If the ground-water fingerprint downgradient of the mining site matches the background fingerprint, process solution or tailings leachate are not migrating from the source and the site remains in the Detection Monitoring phase.

   b. If the ground-water fingerprint downgradient of the mining site no longer resembles the background fingerprint and begins to resemble the characteristic geochemical fingerprint of the mine waste leachate, the results indicate that fugitive process solution or tailings leachate from the facility has been detected. Since the more abundant and mobile components of the leachate have been detected, the third phase of the strategy is triggered to identify and evaluate other leachate constituents that may be present.

3. Phase 3. Assessment Monitoring

   The objective of this phase of the program is to determine whether the less abundant and less mobile constituents associate with the detected mine waste leachate are adversely impacting environmental quality. Samples from this phase of the program should be analyzed for trace metals and other constituents of concern.

   a. If trace metal analyses are included in the Source Characterization phase of the program, the expanded analyses could be limited to only those parameters that represent a potential water quality problem.

   b. If trace metal analyses are not conducted in the Source Characterization phase, complete trace metal scans should be performed on the collected samples.

4. Phase 4. Corrective Action.

   The objective of this phase is to establish a course of action that will address the problems detected in phase 2 and more fully characterized in phase 3.

7.5. Implementation of Proposed Monitoring Strategy

The previous Section outlined a philosophical approach for mining sites based on the characteristic geochemical fingerprint pattern identified in mine waste leachates. The purpose of this Section is to provide more detailed guidance and suggestions for implementing the proposed monitoring strategy. The topics that will be addressed for each phase of the proposed strategy are summarized in Table 7-4.

Table 7-4. Conceptual outline of a multiple-phase monitoring strategy for mining sites.

Phase I.	**Source Characterization**
	A. Sample process solution and tailings leachates quarterly during the first year of operation.
	B. Analyze samples for geochemical parameters, total dissolved solids, trace metals, and other constituents of concern.
	C. Perform quality assurance review of data.
	D. Prepare source geochemical fingerprint.
	E. Identify Assessment Monitoring parameters.
	F. Reduce sampling frequency in second and subsequent years.
Phase II.	**Detection Monitoring**
	A. Install monitoring wells.
	B. Collect quarterly ground-water samples.
	C. Analyze samples for geochemical parameters. During the first year, other parameters should be included to establish background conditions.
	D. Perform quality assurance review of data.
	E. Prepare geochemical fingerprint and compare to background fingerprint and source fingerprint. 1. If the ground-water fingerprint matches the upgradient fingerprint, continue Detection Monitoring. 2. If the ground-water fingerprint matches the source fingerprint, initiate Assessment Monitoring.
Phase III.	**Assessment Monitoring**
	A. Resample monitoring wells.
	B. Analyze samples for geochemical parameters plus parameters of concern (I.E.).
	C. Perform quality assurance review of data.
	D. Identify extent of area impacted and contaminants of concern.
Phase IV.	**Corrective Action**
	Develop plan to correct and remediate problem.

7.5.1 Phase I. Source Characterization

The monitoring performed in this phase of the strategy has two objectives. The first objective is to develop the characteristic fingerprint pattern for the facility being monitored. This is accomplished by analyzing the collected samples for the geochemical parameters needed to define the fingerprints. The second objective is to identify mine waste leachate constituents that should be included in the Assessment Monitoring phase because they may cause environmental degradation. This is accomplished by analyzing source characterization samples for trace metals and other constituents of concern in process solutions and tailings leachates.

7.5.1.A Source Characterization Sampling

Collect samples from the process solutions and tailings leachates quarterly for the first year of operation. The techniques for collecting environmental samples that are to be analyzed for inorganic constituents and cyanide are well-established and presented elsewhere (APHA, 1989, EPA, 1986, EPA, 1979). Quarterly monitoring results should provide a baseline to assess possible temporal trends at a facility although this was not observed to be an issue in the case studies.

7.5.1.B Source Sample Analysis

The samples collected in this phase should be subjected to rather complete analysis as is being done in Nevada and Arizona. The samples should be analyzed for geochemical constituents, trace metals, total dissolved solids, pH, and other constituents of concern such as cyanide at heap leaching facilities. The geochemical analysis to be performed include calcium, magnesium, sodium, potassium, alkalinity, chloride, fluoride, nitrate, and sulfate. [It may be possible to delete some of the less abundant geochemical constituents such as fluoride, nitrate, and potassium as experience is gained with the approach.] Also, it is important that an independent estimate of the total dissolved solids concentration (either a direct measurement of total dissolved solids or a measurement of conductivity) be obtained in this phase. The list of trace metal analyses may be influenced somewhat by the technology that is available. If Inductively Coupled Plasma Arc instruments are available, a complete spectrum of 20 to 25 metals can be obtained from a single sample. If individual atomic absorption analyses are to be performed, a shorter list may be more practical. Other analyses that should be performed on these samples include pH and cyanide (heap leaching facilities).

7.5.1.C Conduct Initial Review of Data

It is important that the data be reviewed for acceptability as soon as they are received from the laboratory. Since the geochemical ions represent 90 to 95 percent of the total dissolved solids concentration of mine waste leachates, there are two simple, rapid, and effective checks that can be performed on the quality of the data without incurring extra expense.

7.5.1.C.i Mass Balance

Calculate the sum of the individual geochemical ion concentrations and compare the result to the total dissolved solids concentration. The calculated sum of the individual ions should be within limits specified in the Quality Assurance Project Plan for the monitoring program [an acceptable range of 80 to 120 percent was used in this study].

[CAUTION: Most laboratories report alkalinity in units of mg $CaCO_3$/L. Prior to performing the mass balance, alkalinity should be converted to units of mg HCO_3^-/L (i.e., multiply reported alkalinity by a conversion factor of 0.61)].

7.5.1.C.ii Charge Balance

A second quality assurance check that can be applied because the geochemical ions represent the major portion of the total dissolved solids concentration of mine waste leachate is a charge balance. For this check, the sum of the cations, expressed in meq/L, should equal the sum of the anions, also expressed in meq/L. For this calculation, the reported analytical results for each of the geochemical ions must be divided by the equivalent weight (formula weight divided by valence) of that ion. The sum of the positively charged geochemical cations should equal the sum of the negatively charged geochemical anions (within limits specified in the Quality Assurance Project Plan for the monitoring program) because all solutions must be electrically neutral. [Trace metals and other constituents such as cyanide can usually be excluded from these calculations because they represent such a small portion of the total dissolved solids concentration and they are generally present in a particulate or complexed state that does not contribute to the total dissolved solids concentration of the sample.]

7.5.1.C.iii Data Assessment

If the source characterization data satisfy the two quality assessment checks (a mass balance of 80 to 120 percent and a charge balance of -20 to +20 percent were used in this project), the data can be used as intended. However, if either of the checks in 7.5.1.C.i or 7.5.1.C.ii are not satisfied, there are problems with the data set. When this happens, the data set should be reviewed to identify possible transcription or clerical errors. If this process does not identify any errors, the samples can be reanalyzed since the holding time for all geochemical parameters, except alkalinity, is on the order of several months. If necessary, another set of samples can be collected for analysis.

7.5.1.D Prepare Geochemical Fingerprint

The geochemical data collected in this phase are used to construct or define the fingerprint for the mine waste leachate. The concentration for each geochemical parameter is normalized to the total dissolved solids concentration of the leachate (i.e., individual concentrations are divided by the total dissolved solids concentration). Plot the results as a bar chart or histogram to identify the geochemical fingerprint. It is important that the ions be plotted in the same order so that fingerprint patterns from different sampling times or different sampling locations can be compared. The results from separate surveys can be compared using regression analysis (available in most commercially available spreadsheet software programs) to develop a quantitative estimate of the reproducibility of the fingerprint.

7.5.1.E Identification of Contaminants of Concern

The monitoring results obtained in Step 7.5.1.B can be compared to the screening criteria summarized in Table 3.2 or other appropriate and relevant environmental criteria to identify contaminants of concern. Mine waste leachate constituents that are present at concentrations above the criteria represent a potential environmental problem and should be included in the Assessment Monitoring phase of the program.

7.5.1.F Reduction of Source Characterization Monitoring

If a reproducible geochemical fingerprint is obtained in step 7.5.1.D and there are no major changes in operation, consideration can be given to reducing the Source Characterization sampling frequency after the first year. One suggestion would be to reduce geochemical monitoring to a semiannual frequency and to reduce trace metal monitoring to an annual frequency.

7.5.2 Detection Monitoring

The primary objective of this phase of the monitoring program is to provide a reliable early warning that mine waste leachates are migrating away from the source and into the adjacent environment. The most appropriate monitoring parameters for this phase are those that target the most mobile constituents of mine waste leachate. Since the geochemical parameters are more mobile than the trace metals (they have attenuation coefficients that are two order of magnitude lower than the trace metals) and they function as an internal trace to identify mine waste leachates, they were selected as the Detection Monitoring parameters.

7.5.2.A Install Monitoring Wells

No definitive guidance can be offered on the number of wells required. However, depending on the complexity of the geologic setting and the size of the facility, one or more upgradient wells and multiple downgradient wells should be considered. Based on the primary constituents of mine waste leachates, well construction material should not be a critical factor.

7.5.2.B First Year Monitoring

During the first year of monitoring, ground-water samples should be collected quarterly and analyzed for the same set of parameters used in the Source Characterization phase (7.5.1.B). The geochemical data parameters provide a means to characterize ground-water conditions in the vicinity of the mine and detect mine waste leachate if it should migrate away from the source. The trace metal and other constituent data will define background conditions in the event that Assessment Monitoring is necessary.

7.5.2.B.i Perform Quality Assurance Mass Balance

Use the geochemical monitoring results to perform a mass balance on the ground-water data (7.5.1.C.i). The same ions that define the mine waste leachate are also the most abundant ions in ground water and the sum of the individual ions should equal the total dissolved solids concentration (within required limits specified in the Quality Assurance Project Plan for the monitoring program).

7.5.2.B.ii Perform Quality Assurance Charge Balance

Ground water must be electrically neutral, therefore, the sum of the cation concentrations, expressed in meq/L, should equal the sum of the anion concentration, expressed in meq/L (within required limits specified in the Quality Assurance Project Plan for the monitoring program).

7.5.2.B.iii Data Quality Assessment

If the monitoring data satisfy the checks in step 7.5.2.B.i and 7.5.2.B.ii, the data are acceptable for use in 7.5.2.C. However, if the data fail either of the checks, the data should be reviewed for transcription, clerical, or analytical errors. If necessary, the samples should be reanalyzed or fresh samples should be collected.

7.5.2.B.iv Quality of Other Data

Conventional quality assurance principles can be applied to the other data to assess their quality. This will require collecting and analyzing a portion of these samples in replicate.

7.5.2.C Evaluation of Monitoring Results

The geochemical monitoring results from each monitoring location are normalized to the total dissolved solids concentration at that location (i.e., actual concentrations are divided by the total dissolved solids concentration). Prior to performing this step, alkalinity results must be converted from units of mg $CaCO_3$/L to units of mg HCO_3^-/L or the ionic sum will exceed the total dissolved solids concentration. These results are used to prepare the geochemical fingerprint for each location.

7.5.2.C.i Upgradient Fingerprint Preparation

The normalized values for each parameter should be less than 1.0 and the sum of the individual ions should be less than or equal to 1.0 (if the data quality assurance checks were satisfied). The graphical fingerprint should be prepared with the geochemical parameters presented in the same order used in the Source Characterization fingerprints (7.5.1.D). As was demonstrated in each of the case studies, the upgradient geochemical fingerprint should be distinctly different from the mine waste leachate fingerprint.

7.5.2.C.ii Downgradient Fingerprint Assessment

Prepare the geochemical fingerprint for each downgradient monitoring location following the same conventions used in 7.5.1.D and 7.5.2.C.i. Compare the resultant fingerprint graphically and with regression analysis to the upgradient fingerprint.

a. If the two fingerprints are similar, the facility is not leaking because the more mobile characteristic constituents of mine waste leachate have not been detected. The site remains in the Detection Monitoring phase and repeats step 7.5.2.B for the next regularly scheduled sampling.

b. If the two fingerprints are dissimilar (i.e., the downgradient ground-water fingerprint resembles the source fingerprint rather than the upgradient ground-water fingerprint), the detection of the more mobile, characteristic components of mine waste leachate indicates that the site is leaking. Assessment Monitoring should be initiated.

7.5.2.D Monitoring in the Second and Subsequent Years

In the second and subsequent years, consideration should be given to reducing the monitoring requirements as long as mine waste leachate has not been detected. During this period, quarterly monitoring should be continued for the geochemical parameters. However, monitoring for the other constituents could be reduced to an annual frequency or possibly dropped from the program.

7.5.3 Assessment Monitoring

This phase is triggered when the more mobile, characteristic geochemical ions in mine waste leachate have been detected at one or more location downgradient of the site. At that time, the site monitoring program is expanded to include the less mobile and less abundant constituents of the leachate. These constituents are the trace metals and other constituents of concern (7.5.1.B). These monitoring results are reviewed and compared to background conditions to determine whether the fugitive mine waste leachate may be causing any other environmental degradation other than that caused by the Detection Monitoring parameters.

7.5.3.A Resampling Activities

The monitoring well(s) in which the mine waste leachate fingerprint was detected in step 7.5.2.C.ii.B should be resampled.

7.5.3.B Assessment Monitoring Sample Analysis

These samples should be analyzed for the less abundant and less mobile constituents of mine waste leachate. The geochemical parameters and total dissolved solids analyses should be supplemented with trace metals and other constituents of concern that were identified in 7.5.1.E (Contaminants of Concern).

7.5.3.C Review of Assessment Monitoring Data

7.5.3.C.i Extent of Contamination

The geochemical fingerprint data will identify the location(s) impacted by fugitive mine waste leachate. A contouring of these locations will define the extent of the area that has been impacted.

7.5.3.C.ii Identification of Environmental Problems

A review of the geochemical data will identify the existence of secondary water quality problems due to the presence of mine waste leachate (i.e., high total dissolved solids concentration). A review of the monitoring results for the contaminants of concern and a comparison of these results to the background concentrations established during the first year of the Detection Monitoring phase (7.5.2.B) will identify water quality problems and potential environmental problems that can be attributed to the fugitive mine waste leachate.

7.5.4 Corrective Action

The Assessment Monitoring results will define the extent of contamination and the specific contaminants associated with fugitive mine waste leachate that may degrade environmental conditions adjacent to the mine. With this information, it should be possible to correct the cause of the spill or leakage event, utilize hydraulic control to limit the spread of the fugitive leachate, and/or initiate appropriate remediation activities.

7.6 Discussion

The size and number of mining sites, particularly in the western United States, establish the need for a uniform approach to monitoring these types of facilities. The conventional approach to monitoring these sites would be to identify constituents that could degrade water quality or the environment (i.e., constituents present at concentrations above some established criteria or screening level) and monitor for these parameters. Although this approach is logical, mine waste leachates present several unique challenges that will limit its effectiveness.

A major problem with a conventional monitoring approach is the tendency to focus on trace metals (i.e., copper, chromium, lead, cadmium, etc.) because they may be present in relatively high concentrations in mine waste leachates, they are known to cause water quality problems, and there are established criteria for these substances. The difficulty with this approach is that constituents of mine waste leachate such as trace metals are all naturally occurring substances. Therefore, simple detection of a naturally occurring substance is not a reliable indication that an adjacent mining site is the source. A second problem is that the trace metals collectively represent a very small percentage of the constituents in mine waste leachate (0.8 percent of Meteoric Water Mobility Test leachates, 1.4 percent of heap leaching process solutions, and 1.4 percent of copper tailings leachates). Thus, monitoring for these substances targets the smallest changes that are likely to be caused by fugitive mine waste leachate. A third related issue is the highly variable concentrations of naturally occurring substances in mine waste leachates. The non-normal distributions of mine waste leachate constituents will increase monitoring costs by requiring additional sampling and replicate analysis in order to determine whether a measured concentration represents an actual change from background conditions. Finally, as illustrated with the Twin Butte column study, the trace metals are the least mobile and more reactive constituents in these leachates. As a result, monitoring for these constituents will not provide an early detection of mine waste leachate migration and will miss any environmental degradation cause by the more mobile geochemical parameters.

A review of regulatory monitoring records for gold and copper mining facilities has identified a viable solution to the monitoring challenges created by mining wastes. The solution is to utilize the common geochemical parameters as primary monitoring parameters at mining sites. This approach offers the following advantages:

1. Although each of the inorganic parameters used to define the mine waste leachate fingerprint are naturally occurring, they collectively define a unique chemical signature or fingerprint that can be used to characterize the leachate at its source. The concentrations for each of the geochemical ions were variable but the process solutions and tailings leachates at each mine had a reproducible geochemical fingerprint (> 90 percent).

2. The same set of geochemical ions can also be used to fingerprint ground water and surface water in the vicinity of a mine. Since the mine waste leachate has a different ionic composition, the same geochemical parameters used to characterize the leachate can also be used to detect and monitor its migration through the environment.

3. The geochemical ions (calcium, magnesium, potassium, sodium, alkalinity, chloride, fluoride, nitrate, and sulfate) represent approximately 95 percent of the total dissolved solids concentrations of mine waste leachate. Therefore, monitoring for these constituents directly targets the most abundant constituents in the leachate and the largest environmental concentration changes likely to be caused by mine waste leachate.

4. The Twin Butte column study demonstrated that each of the geochemical parameters have significantly lower attenuation coefficients than the trace metals present in mine waste leachates. Therefore, in addition to characterizing mine waste leachate, the fingerprint acts as an internal tracer and provides early detection of leachate migration.

5. The geochemical fingerprint fulfills essentially all of the requirements for an effective tracer or monitoring parameter. This includes chemical conservativeness over time and space, relatively high mobility, and the ability to reliable measure with routinely available techniques.

6. The relatively high abundance of the geochemical parameters provides two internal checks on the quality of the monitoring data being produced.

Based on the useful and characteristic properties of the geochemical fingerprint, a multiple phased monitoring program for mining sites was outlined that is philosophically similar to the monitoring strategy developed by the U.S. Environmental Protection Agency for hazardous waste disposal sites and municipal landfills (EPA, 1980, EPA, 1991). The critical component of this strategy is the designation of the common geochemical constituents as primary monitoring parameters for the characterization and monitoring of mine waste leachates. These parameters provide the data necessary to characterize the process solution and tailings leachates, to differentiate mine waste leachate from regional ground water and surface water, and provide detection for the most mobile and most abundant constituents in the leachate. After the leachate has been detected, more extensive monitoring is initiated to determine whether the less abundant and less mobile constituents in the leachate may also be present. This approach should provide a reliable mechanism to identify and detect fugitive mine waste leachates in a cost-effective manner.

The technique recommended for presenting and evaluating monitoring results from a mining site is a modified STIFF Diagram. When the data for the individual geochemical parameters are normalized to the total dissolved solids concentration of the mine waste leachate and presented in a consistent manner, the results produce a reproducible graphical fingerprint that characterizes the ionic composition of the leachate. As illustrated in each of the case studies, the simultaneous use of data for all the geochemical parameters offers two distinct benefits. First, when the data are normalized to the total dissolved solids concentration, it is a relatively simple matter to assess the quality of the data (data sets with an ionic sum significantly different from a value of 1.0 should be considered suspect and reviewed for problems). Second, the graphical fingerprint provides a rapid method to compare monitoring results at the same location over time or at different locations on a site. Regression analysis can be used to provide a statistical estimate of the reproducibility or comparability of different fingerprint patterns.

The convention of normalizing geochemical data to total dissolved solids concentrations was used throughout this report for the reasons given above. However, during the course of this study, other data summation conventions were also explored. These options included expressing results in units of concentration (mg/L), moles (M/L), and milliequivalents (meq/L). Examples of these different conventions are presented and compared in Figure 7-1.

Eight sets of quarterly monitoring results from the Hycroft gold mine pregnant pond are presented in Figure 7-1a. These results show that chloride is the most abundant ion in the pregnant pond at 2000 mg/L, sulfate is the second most abundant ion at slightly less than 2000 mg/L, and sodium is the third most abundant ion at slight less than 1000 mg/L. Even with the one suspect value for sodium, the reproducibility of the ionic composition pattern for this solution was estimated by regression analysis to be 93 percent ($r^2 = 0.933$).

The same set of monitoring results from the Hycroft pregnant pond were converted to units of mm/L by dividing the individual concentrations by the appropriate molecular weight. As shown in Figure 7-1b, chloride is still the most abundant ion in the pattern at approximately 60 mm/L. However, sodium is now the second most abundant ion and sulfate is the third most abundant ion. The reproducibility of this fingerprint pattern is 91 percent ($r^2 = 0.908$). The small difference in pattern reproducibility between Figure 7-1a and 7-1b is the enhanced distortion of the single suspect value for sodium.

The pregnant pond monitoring data were converted to units of meq/L by dividing the individual concentrations by the equivalent weight of each geochemical parameter (Figure 7-1c). When the data are presented in these units, chloride is still the most abundant ion but sodium and sulfate are now equally abundant. The reproducibility of this pattern was estimated to be 90 percent ($r^2 = 0.903$).

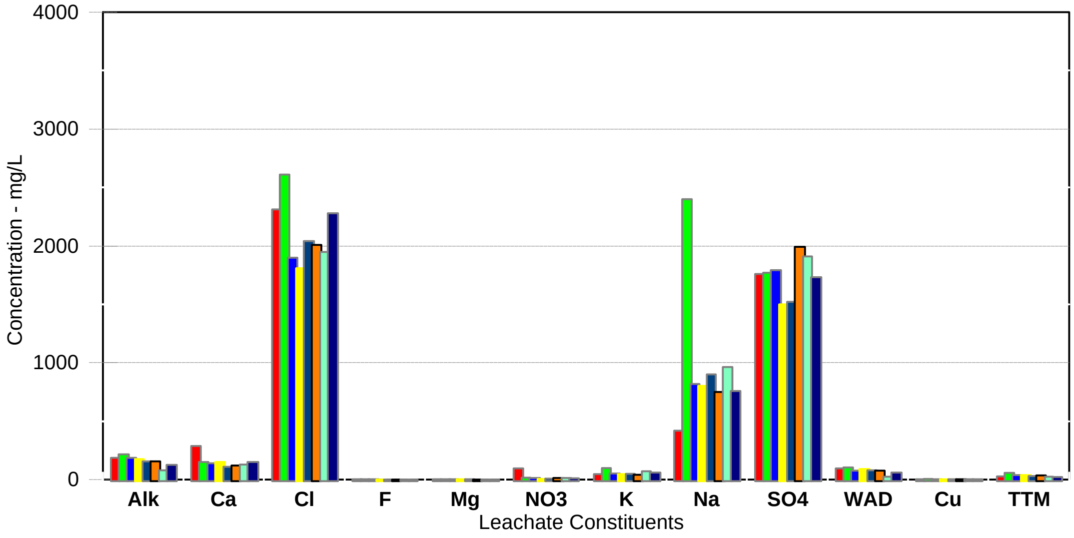


Figure 7-1a. Hycroft pregnant pond geochemical data in mg/L. Average regression coefficient r^2 value = 0.933.

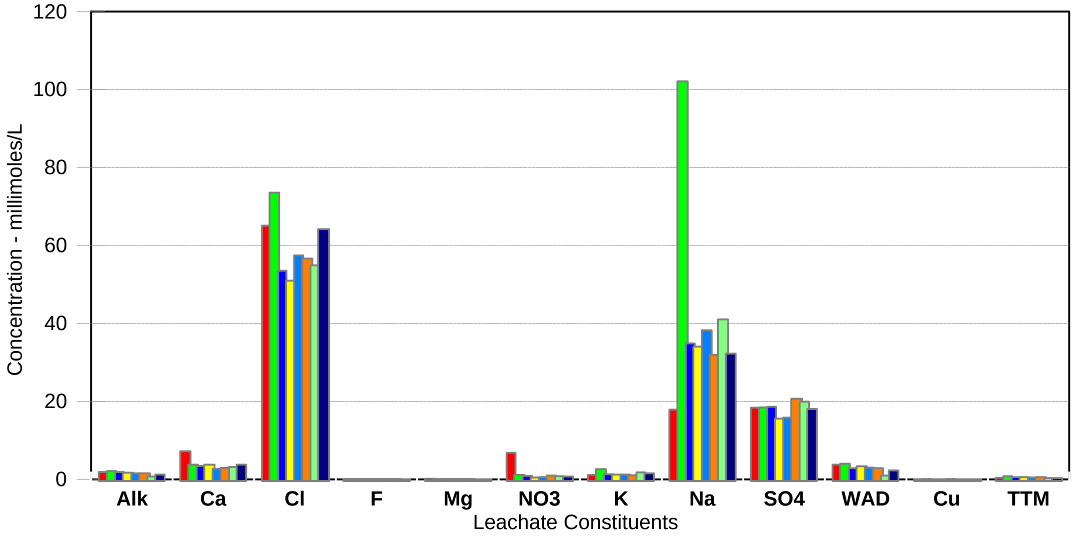


Figure 7-1b. Hycroft pregnant pond geochemical data in mm/L. Average regression coefficient r^2 value = 0.908.

Finally, the pregnant pond data are presented in units of percent total dissolved solids in Figure 7-1d. In this case, chloride is the most abundant ion, sulfate is the second most abundant ion, and sodium is the third most abundant ion in the fingerprint. The estimated reproducibility of these geochemical fingerprints was 93 percent ($r^2 = 0.933$) which is identical to that calculated for the concentration data (Figure 7-1a).

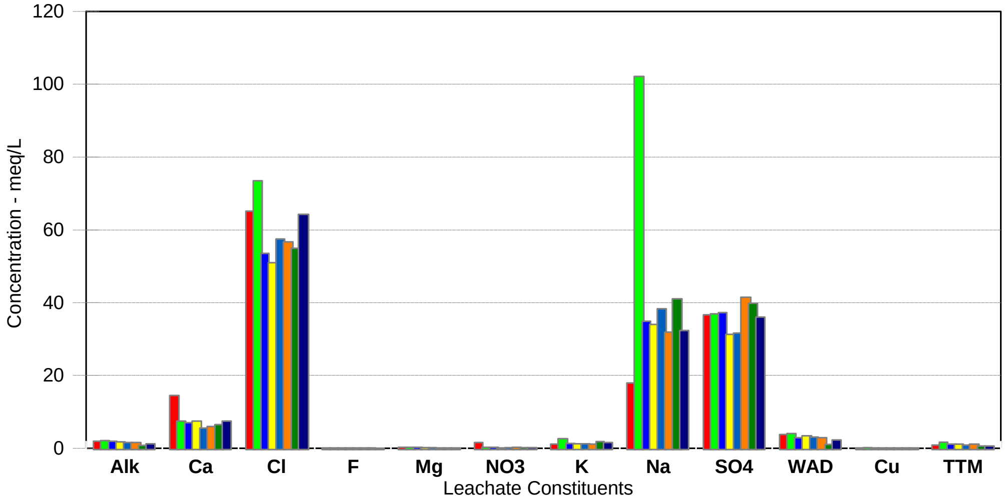


Figure 7-1c. Hycroft pregnant pond geochemical data in meq/L. Average regression coefficient r^2 value = 0.903.

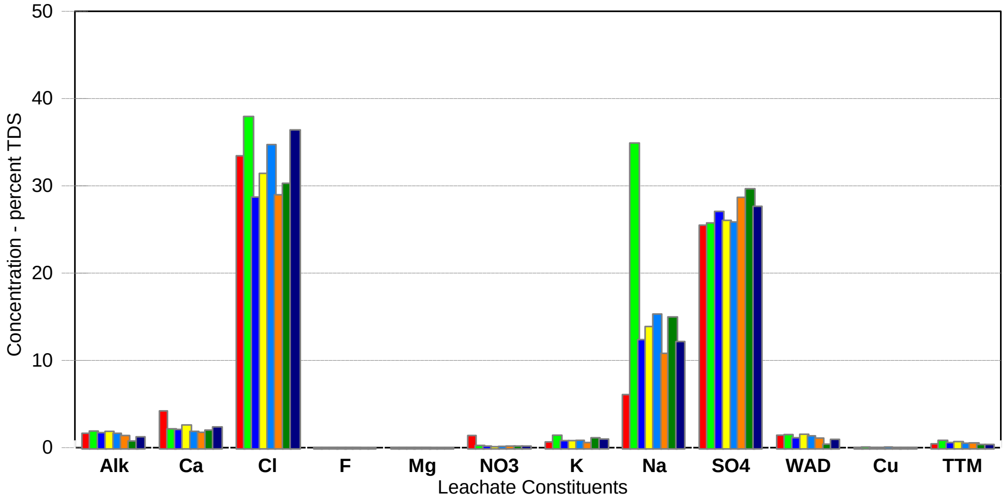


Figure 7-1d. Hycroft pregnant pond data in percent TDS. Average regression coefficient r^2 value = 0.933.

The demonstration in Figure 7-1 serves two purposes. First, it shows that the absolute shape of the fingerprint pattern is dependent on the units used to express the data. Second, regardless of the units selected, the monitoring results define a characteristic reproducible pattern for the pregnant pond (90 to 93 percent in this example). Thus, it is essential that a single convention be selected and used consistently to evaluate and assess the monitoring results. As stated above, the convention that appears to be most useful is that of expressing the data in units of percent total dissolved solids. This convention provides a rapid quality assurance check (the Hycroft data set with the one suspect sodium value is the only set with an ionic sum greater than 1.0) and the uniform y-axis is convenient for comparing monitoring results from different locations.

Another feature of the proposed monitoring strategy is that trace metal monitoring (after the first year) is not implemented until the Assessment Monitoring phase. Although trace metals are frequently considered to be the contaminants of concern at mining sites, this decision can be justified based on the environmental behavior of mine leachate constituents. The technical issues that support this approach are as follows:

1. Each of the trace metals are naturally occurring substances. Also, it was not possible to identify a multi-ion trace metal signature in the process solutions and tailing leachates in any of the case studies. The significance of this point is that trace metals detected in the Detection Monitoring phase would not be a reliable indication of the presence of mine waste leachate.

2. The concentration of individual trace metals in mine waste leachates are highly variable. The non-normal distribution of these constituents means that considerable effort must be directed at characterizing their distribution and verifying the significance of observed concentration changes. These efforts will increase the costs and time required to determine whether mine waste leachates from a site are impacting the nearby environment.

3. The trace metals migrate more slowly than the geochemical constituents. As demonstrated in the Twin Butte column study, trace metal migration was clearly retarded in a soil column that was only two feet long. Since the trace metals have a slower rate of migration, there is no need to monitor for these constituents until there is a reason to do so.

By structuring the proposed monitoring strategy as indicated in Table 7-4, the larger concentration changes caused by the faster migrating geochemical parameters and the presence of the characteristic mine waste leachate fingerprint provide a reliable basis for trace metal monitoring in the second phase of the strategy.

One parameter that did not receive much attention during the review of the compiled monitoring data was pH. This is another parameter that is generally considered to be a constituent of concern at mining sites (copper tailings leachates had a pH of 2 or less and the pregnant and barren pond solutions at gold mining sites had a pH greater than 10). However, acid-base reactions are extremely fast and the pH of mine waste leachates can be rapidly neutralized during the initial migration of mine waste leachates. As examples, copper tailings leachate was neutralized in a two foot laboratory soil column, a low pH was not detected in any of the wells shown to be impacted by Twin Butte tailings leachate, and high pH was not detected at any of the heap leaching facilities where process solution was detected in the ground water. In each case, the geochemical fingerprint of the mine waste leachate was detected but the extreme pH associated with the source had been neutralized. Consequently, pH may be used as a general site characterization parameter but it is not likely to provide early detection of mine waste leachate migration.

One final consideration is the impact of the proposed monitoring strategy on monitoring costs. While no formal cost-benefit study has been conducted, it is anticipated that the proposed approach will reduce these costs. These lower costs can be achieved in several ways. First, since trace metals do not provide an early or effective method of detecting mine waste leachates, deletion of trace metal analyses (after the first year) from the Detection Monitoring phase will reduce sample collection and analysis costs. Second, since the geochemical fingerprint serves as an internal tracer, the need for repetitive sampling to characterize the concentration variability for individual leachate constituents may be reduced. Third, since the collective use of the geochemical parameters to fingerprint mining wastes also includes two independent checks on data quality, the need for independent quality assurance activities is reduced. Each of these factors suggests that the proposed strategy can be implemented at lower costs than more extensive sampling and analysis programs such as those currently being used in the states of Nevada and Arizona.

7.7 Summary

The primary objective of this project was to identify and select monitoring parameters for mining sites. A review of monitoring records from more than two dozen mines in Nevada and Arizona demonstrated that mine waste leachates had a distinctive geochemical fingerprint that differentiated it from regional ground water. Furthermore, the parameters that defined the fingerprint were the most mobile and abundant constituents in the leachate and the fingerprint maintained its characteristic identity as mine waste leachate migrated through the subsurface. Therefore, the geochemical parameters, calcium, magnesium, sodium, potassium, alkalinity, chloride, fluoride, nitrate, and sulfate, were selected as suitable monitoring parameters.

The selected monitoring parameters were incorporated into a multiple phase monitoring strategy that is functionally similar to that developed for hazardous waste disposal sites and municipal landfills. The initial phase of this strategy is Source Characterization in which the mine waste leachates are analyzed for the designated geochemical parameters to develop the characteristic fingerprint that acts as an internal tracer. The second phase of the strategy is Detection Monitoring in which monitoring is conducted for the geochemical ions that define the leachate fingerprint. As long as the abundant and mobile geochemical ions are not detected, the site can remain in the Detection Monitoring mode. However, when several simultaneous changes characteristic of mine waste leachate are detected at one or more site monitoring locations, the Assessment Monitoring phase of the strategy is initiated. When this occurs, site monitoring requirements are expanded to determine whether the less abundant and slower moving constituents of mine waste leachate such as trace metals are also present and impacting environmental conditions.

Section 8

Summary

There are an estimated 20,000 active mining sites and approximately 60,000 inactive or abandoned sites in the United States. These facilities are currently generating 1.5 billion tons of mining wastes per year. The large number of mining sites and the high volume of mining waste generated by this industry identifies an area of environmental concern. However, despite this concern, a uniform national program for effective monitoring of mining sites must still be developed. This situation is due, in part, to a poor understanding of the chemical composition and environmental behavior of mine waste leachates. Therefore, this project was undertaken to develop a better understanding of the composition of these waste streams and to identify a set of parameters that would be useful for the effective monitoring of these facilities.

The approach that was used throughout this study consisted of compiling, reviewing, and evaluating routine site monitoring data that had been submitted to regulatory agencies in the States of Nevada and Arizona. This technique was used because both states have established extensive monitoring requirements for mining operations in advance of any federal requirements, both the Nevada Department of Environmental Protection and the Arizona Department of Environmental Quality agreed to cooperate during the study, and gold and copper mining, which represent 80 percent of the operating mines in the United States, are major activities in these states.

There are several advantages that justify the use of existing monitoring records. First, project results were acquired in a relatively short period of time. In a matter of seven working days, site files for 40 gold mines and 7 copper mines were reviewed. The monitoring records from two dozen gold mines and 5 copper mines were selected for use during the project. Second, the technique provides information on a larger number of facilities than would be possible if actual site characterization and sampling had to be conducted within project budget constraints. This made it possible to assess the occurrence of identified trends at a larger number of sites and extrapolate project results to mine sites in general. Third, the use of existing data produced monitoring records up to 17 years in length. This made it possible to assess temporal trends that exceeded the length of this study.

The monitoring results varied somewhat for each site, depending on the type of mine and conditions specified in the operating permits, but included data on the composition of gold mining process solutions (pregnant ponds and barren ponds), tailings solutions at gold and copper mines, tailings reclaim water, plant make up water, and ground water in the vicinity of each mine. These samples were generally collected on a quarterly basis and subjected to complete inorganic analysis for major geochemical ions (calcium, magnesium, sodium, potassium, chloride, alkalinity, and sulfate), 20 - 28 trace metals, pH, conductivity, and total dissolved solids. In addition, the samples from the gold mining facilities were analyzed for cyanide.

The first step in the data evaluation process was simply to enter the monitoring results in a spreadsheet format to facilitate a review of the data. This initial review identified four characteristic properties of mine waste leachates.

1. A large number of mine waste leachate constituents may be present at concentrations that could impair water use or degrade environmental conditions. A total of 30 different constituents (8 geochemical parameters, 19 trace metals, pH, phosphorus, total dissolved solids and cyanide) exceeded screening criteria at one or more of the mine sites included in the study.
2. A short list of geochemical parameters that included alkalinity, calcium, chloride, magnesium, sodium, and sulfate were repeatedly present as the most abundant constituents in mine waste leachates.
3. Trace metals, which are frequently cited as contaminants of concern, collectively represented less than five percent of the total dissolved solids concentration in mine waste leachate.
4. The observed concentrations for each mine waste leachate constituent were highly variable and generally displayed a non-normal distribution. Mass balance calculations and charge balance calculations demonstrated that the variable concentrations were typical of mine waste leachate and not an artifact due to poor quality data.

Each characteristic property of mine waste leachate was repeatedly observed in monitoring records for each site included in the study.

The second step in the data evaluation process was to determine some unique property of mine waste leachate that could be used to unequivocally identify it. Since each of the leachate constituents except cyanide are naturally occurring and their concentrations are highly variable, this effort focused on the use of multiple ion fingerprint patterns and constituent ratios for this purpose. The initial effort in this area utilized Stiff Diagrams that have previously been used to characterize oil field brines, ground water, and incinerated municipal waste ash leachates. Although a qualitative recurring pattern was observed, the results were limited because of the highly variable scale between different data sets (mine waste leachate constituent concentrations from the same mine varied by a factor of 2 or more and mine waste leachate - ground water comparisons from the same mine varied by an order of magnitude or more).

The problem of highly variable concentrations was resolved by simply dividing the individual mine waste leachate concentrations by the total dissolved solids concentration of the leachate. The resultant normalized concentrations were summarized in modified Stiff Diagrams in which the monitoring results were plotted as histograms rather than geometric shapes. There were several inherent advantages to summarizing the data in this manner:

1. The modified Stiff Diagrams were easily prepared with readily available spreadsheet software.
2. The individual geochemical data sets could be rapidly reviewed for data quality acceptability. Since the sum of the ions must be less than or equal to the total dissolved solids concentration, each of the normalized concentrations must be less than 1.0 and the sum of the ions should approximate 1.0 (a project-specific data quality objective of 0.8 to 1.2 was used). Data sets that failed these criteria were reviewed for possible data entry errors and/or flagged as suspect.

3. The use of normalized concentrations provided a common y-axis that permitted a direct visual comparison of the geochemical fingerprint patterns from different times at the same location or from different sampling locations.

4. The individual data sets are amenable to regression analysis which provides a statistical estimate of the similarity between two geochemical fingerprint patterns.

An important observation is the fact that the common geochemical parameters in mine process solution and tailings leachates defined a consistent multi-ion signature or chemical fingerprint. Even though the concentrations of these ions, alkalinity, calcium, chloride, fluoride, magnesium, potassium, sodium, and sulfate, varied by a factor of two or more, the relative ionic composition of the leachates remained constant. The estimated reproducibility of the geochemical fingerprints was generally in the range of 90 to 98 percent. Attempts to define a corresponding trace metal fingerprint for mine waste leachates were unsuccessful because of the greater variability associated with the individual trace metals.

The properties of the mine waste leachate fingerprint patterns were evaluated by using routine monitoring results from 22 Nevada heap leaching facilities and 4 Arizona copper mines as a series of case studies. Each of these examples demonstrated that the process solutions and tailings leachates at each mine had a distinctive, characteristic geochemical composition. A comparison of the geochemical fingerprints from different locations in the recirculating process solutions (barren ponds and pregnant ponds) and different locations in tailings disposal areas repeatedly demonstrated that the chemical signature was spatially consistent. Also, an assessment of monitoring results from different surveys demonstrated that the fingerprint pattern was consistent over time. The chemical fingerprint varied from mine to mine and was undoubtedly influenced by site-specific factors such as the ore supply being mined, the quality of the mine make-up water, and the process used to recover the mineral (i.e., ore pretreatment, cyanide concentration, leaching time, and pH). However, the same set of geochemical parameters was useful for preparing a reproducible chemical fingerprint that uniquely defined the composition of the process solution and tailings leachate at each mine.

The case studies demonstrated that the same set of geochemical parameters could be used to fingerprint make-up water and other water supplies in the vicinity of a mine. In all 26 examples, the make-up water and upgradient ground-water fingerprint patterns were graphically and statistically distinct from the process solution and tailings leachate fingerprints. Therefore, even though the geochemical fingerprints are defined by common, naturally occurring substances, they provide a reliable mechanism to characterize mine waste leachate at its source and distinguish it from ground water and surface water near the mine.

The information compiled and reviewed during this study also provided insight into the environmental behavior of mine waste leachate. First, the Twin Butte laboratory demonstrated that the geochemical fingerprint would retain its unique chemical identity as tailings leachate migrated through a soil column under controlled conditions. An evaluation of the field monitoring data for the case studies reinforced this observation because the process solution fingerprint was identified in the ground water at approximately one-half of the Nevada heap leaching facilities and the tailings leachate fingerprint was identified downgradient of all the Arizona copper mining facilities. Second, the Twin Butte column study, and complimentary field monitoring data from the same facility, demonstrated that the geochemical fingerprint for tailings leachate migrated through a soil column faster than the trace metals of environmental concern that may be present in the leachate.

The results obtained through an assessment of monitoring data from gold and copper mines in Nevada and Arizona suggest that the geochemical fingerprint shares many of the characteristics of an ideal tracer. First, the results from 26 independent mining operations demonstrated that the geochemical fingerprint can characterize the process solution and tailings leachate at the source. Second, the geochemical fingerprint can differentiate mine waste leachate from other water sources in the proximity of the mine. Third, the unique chemical fingerprint can be used to identify fugitive mine waste leachate as it migrates away from the source. Finally, the geochemical fingerprint will migrate faster than the less characteristic components of mine waste leachate. Therefore, it has been suggested that the suite of geochemical parameters can collectively function as effective detection monitoring parameters at mining sites.

Based on an improved understanding of the composition and behavior of process solutions and tailings leachates, a multiple phased monitoring strategy has been proposed for mining sites. The first phase of this strategy consists of source characterization in which the abundant geochemical parameters are used to develop a unique chemical signature or fingerprint for the mine waste leachate. Extensive analysis for trace metals and other less abundant constituents in the leachate would be optional. In the second phase of the strategy, ground-water samples from the perimeter of the site (i.e., upgradient and downgradient) would be analyzed for the same suite of geochemical parameters used in the first phase. This information would be used to develop a characteristic fingerprint for the regional ground water upgradient of the facility and to detect early migration of fugitive process solution or tailings leachate. If and when the mine waste fingerprint is identified in the ground-water samples, the third phase of the strategy would be initiated. At that time, the analytical requirements of the site monitoring program would be expanded to include the less abundant and less mobile constituents that may be present in the leachate (i.e., trace metals). This proposed strategy, which should provide a technically reliable and cost effective approach to monitoring at mining sites, is functionally similar to the multi-phased programs developed by the U.S. Environmental Protection Agency for RCRA hazardous waste disposal sites and RCRA municipal landfills.