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Preliminary geochemical evaluation of groundwaters from wells of the Nye County Early Warning Drilling Program

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**PRELIMINARY GEOCHEMICAL EVALUATION OF
GROUNDWATERS FROM WELLS OF THE
NYE COUNTY EARLY WARNING DRILLING PROGRAM**

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Summary

As part of the Yucca Mountain Oversight program, the Nye County Nuclear Waste Repository Project Office (NWRPO) has established a groundwater monitoring program to protect groundwater resources for the residents of Nye County in Amargosa and Pahrump Valleys. This groundwater monitoring program, referred to as the Nye County Early Warning Drilling Program (NCEWDP), involves drilling a series of wells down-gradient from Yucca Mountain for long term groundwater monitoring and also to provide much needed geologic and hydrologic information in this area. A comprehensive database of aquifer parameters in the alluvial, volcanic, and carbonate aquifers down-gradient hydrogeologically of Yucca Mountain is being assembled and the degree of communication and the inter-relationships of these aquifers is under investigation.

The Harry Reid Center for Environmental Studies (HRC) has been tasked to provide hydrochemical evaluations of the groundwater collected from the NCEWDP wells. The HRC collected a total of thirteen samples in May through July of 1999, eight samples in November, 1999, and sixteen samples in May 2000. These samples were analyzed for major ions, trace elements, and the oxidation states of arsenic (As), antimony (Sb), and selenium (Se). Sample collection and analysis were performed following the requirements of the University and Community College System of Nevada (UCCSN) Quality Assurance Program.

Piper diagrams were constructed to assist in the evaluation of the major solute data of these groundwaters. Concentrations of rare earth elements (REE) in the groundwater were plotted relative to upper continental crust (UCC) values, and multivariate statistical techniques were applied to the trace element data. The multivariate statistical techniques were required due to the large amount of data generated and the lack of more traditional approaches (e.g., Piper diagrams) for trace element interpretations. The techniques used include principal component analysis (PCA), Q-mode factor analysis, correspondence analysis (CA), and hierarchical cluster analysis (HCA).

The groundwaters from the majority of the wells (NC-EWDP-9S, -19P, -15P, -3S, -5S, -4PB, -12PB, -12PA, -1D, and SD6-ST1) are sodium potassium bicarbonate (Na-K-HCO_3) waters which is consistent with groundwaters that have chemically reacted with felsic volcanic rocks. Water from 1D is the most concentrated of all of the NCEWDP well waters which may reflect a greater age for these deep groundwaters compared to the other waters sampled in this study. On the other hand, groundwaters from 1S and the nearby well, 12PC, are classified as calcium magnesium bicarbonate (Ca-Mg-HCO_3) waters. These groundwaters are either in intimate contact with valley fill deposits composed in part of fragments of Paleozoic carbonate rocks or secondary/pedogenic carbonate minerals (e.g., caliche) that occurs within these sedimentary deposits. The chemical difference in the more shallow 12PC water, as well as the lower concentrations of major solutes, when compared to the deeper waters of 12PA and 12PB, suggest that the 12P wells record the chemical evolution of groundwaters infiltrating downward from shallower regions in the alluvial fill deposits. Groundwater from 4PA is classified as sodium potassium sulfate chloride ($\text{Na-K-SO}_4\text{-Cl}$) water. The higher concentration of sulfate (SO_4) and chloride (Cl) of 4PA water reflects reactions with either evaporite minerals, or oxidation of metal

sulfides. Groundwater from Bond Gold Well #13 (BGW) is classified as a calcium magnesium sulfate bicarbonate (Ca-Mg-SO₄-HCO₃) water indicating that the groundwater from this well is more mature and represents a mixture of Ca-Mg-HCO₃ water with sulfate bicarbonate (SO₄-HCO₃) water. We suggest that this is due to the movement of water from carbonate rocks into tuff or tuffaceous alluvium. The higher concentrations of calcium (Ca) and SO₄ in this water indicates a source of gypsum or the oxidation of metal sulfides in the alluvium.

The trends observed in total dissolved solids (TDS) for groundwater of the NCEWDP wells were also apparent in the results of the multivariate statistical analyses of the trace element data. The higher TDS groundwaters of BGW and 1D were separated from the more dilute waters using principal component 1 (PC 1). We suggest that PC 2, and dimension 1 of the CA results, describe differences in the trace element chemistry of the groundwaters that results from the different chemical compositions of the aquifer materials through which they have flowed. For instance, the NCEWDP groundwaters classified as Na-K-HCO₃ waters plot opposite to the Ca-Mg-SO₄-HCO₃ and Ca-Mg-HCO₃ waters using both PCA and CA. The trace elements associated with the sodium potassium bicarbonate (Na + K - HCO₃) waters include lithium (Li), beryllium (Be), germanium (Ge), rubidium (Rb), cesium (Cs), and barium (Ba), whereas those associated with Ca-Mg-SO₄-HCO₃ and Ca-Mg-HCO₃ waters include strontium (Sr), rhodium (Rh), titanium (Ti), nickel (Ni), and bismuth (Bi).

PC3, and to a lesser degree dimension 2 of the CA results, show a strong relationship with the percentage of As(III) suggesting that these multivariate statistical results reflect the oxidizing / reducing conditions within the groundwater. From these results, waters of wells 1S, 1D, 12PA, 12PB, and 5S are hypothesized to be more reducing, whereas waters from wells 3S and 4PB are oxidizing. The statistical techniques identify trace elements that are more concentrated in reducing waters of the region including manganese (Mn), cesium (Cs), cobalt (Co), barium (Ba), rubidium (Rb), and beryllium (Be), as well as those that are more abundant in oxidizing waters such as vanadium (V), chromium (Cr), gallium (Ga), arsenic (As), tungsten (W), and uranium (U). The statistical identification of trace elements with oxidizing and reducing environments is consistent with the geochemistry of these elements.

TABLE OF CONTENTS

	Acknowledgments.....	<i>ii</i>
	Summary.....	<i>iii</i>
1.	Introduction.....	1
2.	Hydrogeologic Setting.....	4
3.	Major Solutes.....	4
4.	Rare Earth Elements.....	5
5.	Speciation of Arsenic, Antimony, and Selenium.....	8
6.	Multivariate Statistical Analysis of Trace Elements.....	9
	6.1 Principal Components Analysis.....	10
	6.2 Q-Mode Factor Analysis.....	11
	6.3 Correspondence Analysis.....	11
	6.4 Cluster Analysis.....	12
7.	Methods.....	12
8.	Results and Discussion.....	14
	8.1 Major Solutes	14
	8.2 Rare Earth Elements	18
	8.3 Speciation of Arsenic, Antimony, and Selenium.....	21
	8.3.1 Arsenic.....	21
	8.3.2 Antimony.....	22
	8.3.3 Selenium.....	22
	8.4 Statistical Analyses of the Trace Elements	23
	8.4.1 Principal Components Analysis.....	23
	8.4.2 Q-Mode Factor Analysis.....	34
	8.4.3 Correspondence Analysis.....	37
	8.4.4 Cluster Analysis.....	39
9.	Conclusions.....	43
10.	References.....	46
	Appendix I. Data Tracking and Accession Numbers for Well Data.....	55
	Appendix II. Major Anion and Cation Concentrations.....	57
	Appendix III. Rare Earth Element Concentrations.....	59
	Appendix IV. Trace Element Concentrations.....	61

LIST OF FIGURES

Figure 1.	Map of Study Area with Approximate Subbasin Boundaries (modified from Lacznia et al., 1996).....	2
Figure 2a.	Piper Diagrams for Groundwaters of the NCEWDP.....	15
Figure 2b.	Piper Diagrams for Groundwaters of the NCEWDP.....	16
Figure 3.	Piper Diagrams for Groundwaters of the NCEWDP of NCEWDP-1S, NCEWDP-3S, and NCEWDP-9S.....	17
Figure 4.	Rare Earth Element Concentrations in Groundwater Samples Normalized to Upper Continental Crust (UCC) Values.....	20
Figure 5.	Percentage As(III) of Total As in Groundwaters of the NCEWDP..	21
Figure 6.	Scores for Principal Components 1 and 2 for Analysis Performed on all 57 Trace Elements.....	24
Figure 7.	Scores for Principal Components 1 and 2 for Analysis Performed on all 57 Trace Elements-magnified.....	25
Figure 8.	Scores for Principal Components 1 and 2 for Analysis Performed on the Subset of 25 Trace Elements.....	27
Figure 9.	Scores for Principal Components 1 and 2 for Analysis Performed on the Subset of 25 Trace Elements - Magnified.....	28
Figure 10	Scores for Principal Components 2 and 3 for Analysis Performed on the Subset of 25 Trace Elements.....	32
Figure 11	Principal Component Scores for PC 3 Versus Percentage As(III).....	33
Figure 12	Q-mode Factor Scores for Factors 1 and 2.....	35
Figure 13	Q-mode Factor Loadings for Factors 1 and 2.....	36
Figure 14	Correspondence Analysis Results for the First Two Dimensions.....	38
Figure 15	Results of Hierarchical Cluster Analysis Performed on Standardized Trace Element Concentrations.....	40
Figure 16	Results of Hierarchical Cluster Analysis Performed on Principal Component Scores.....	41
Figure 17	Results of Hierarchical Cluster Analysis Performed on Correspondence Analysis Loadings.....	42

LIST OF TABLES

Table 1.	Sampling Dates, Identifiers, Depths, and Lithologies of Screened Zones.....	3
Table 2.	Arsenic(III), Arsenic(V), Antimony(III), and Antimony(V) Concentrations	22
Table 3.	Principal Components Loadings.....	29
Table 4.	Correlation Coefficients for Major Anions, Major cations, and Trace Elements.....	30

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1. Introduction

As part of the Yucca Mountain Oversight program, the Nye County Nuclear Waste Repository Project Office (NWRPO) has established a groundwater monitoring program to protect groundwater resources for the residents of Nye County in Amargosa and Pahrump Valleys. This groundwater monitoring program, referred to as the Nye County Early Warning Drilling Program (NCEWDP), involves drilling a series of wells down-gradient from Yucca Mountain (Fig. 1) for long term groundwater monitoring and also to provide much needed geologic and hydrologic information in this area. Because the targeted region is one of the least understood hydrogeologic systems in the vicinity of Yucca Mountain, thorough investigations of hydrogeologic and hydrochemical data collected from these wells are required. A comprehensive database of aquifer parameters in the alluvial, volcanic, and carbonate aquifers down-gradient hydrogeologically of Yucca Mountain is being assembled and the degree of communication and the inter-relationships of these aquifers is under investigation. These data will be used for defining groundwater flow paths down gradient of Yucca Mountain. The objective of these investigations is to provide data that can be used to design a comprehensive groundwater monitoring system to protect the water resources of Nye County, Nevada.

The Harry Reid Center for Environmental Studies (HRC) has been tasked to provide hydrochemical evaluations of the groundwater collected from the NCEWDP wells. During 1999 - 2000, a total of 22 drill holes were completed through two phases of drilling. A number of these wells were selected by the NWRPO for groundwater sampling. This report details the progress made by the HRC in support of Phase I and II of the NCEWDP. Groundwater samples were collected from multiple zones of four Phase I wells during the months of May and November 1999. Two wells (Bond Gold Well #13 and SD6ST1), located in the general vicinity of the NCEWDP wells, were also sampled under this task and are therefore discussed in this report. The four Phase I wells, along with an additional eight Phase II wells, were again sampled in May 2000. The wells and depth of each zone sampled are listed in Table 1. Each sample was then analyzed for 57 trace elements, 6 major anions, and 4 major cations. In addition, measurements of the oxidation states of arsenic, selenium, and antimony were made. All activities were performed following implementing procedures (IPs) approved by the University and Community College System of Nevada (UCCSN) Quality Assurance Program.

Piper diagrams (Piper, 1945) were constructed to assist in the evaluation of the major solute data of these groundwaters. Concentrations of rare earth elements (REE) in the groundwater were plotted relative to upper continental crust (UCC) values (Taylor and McLennan, 1985), and multivariate statistical techniques were applied to the trace element data. The multivariate

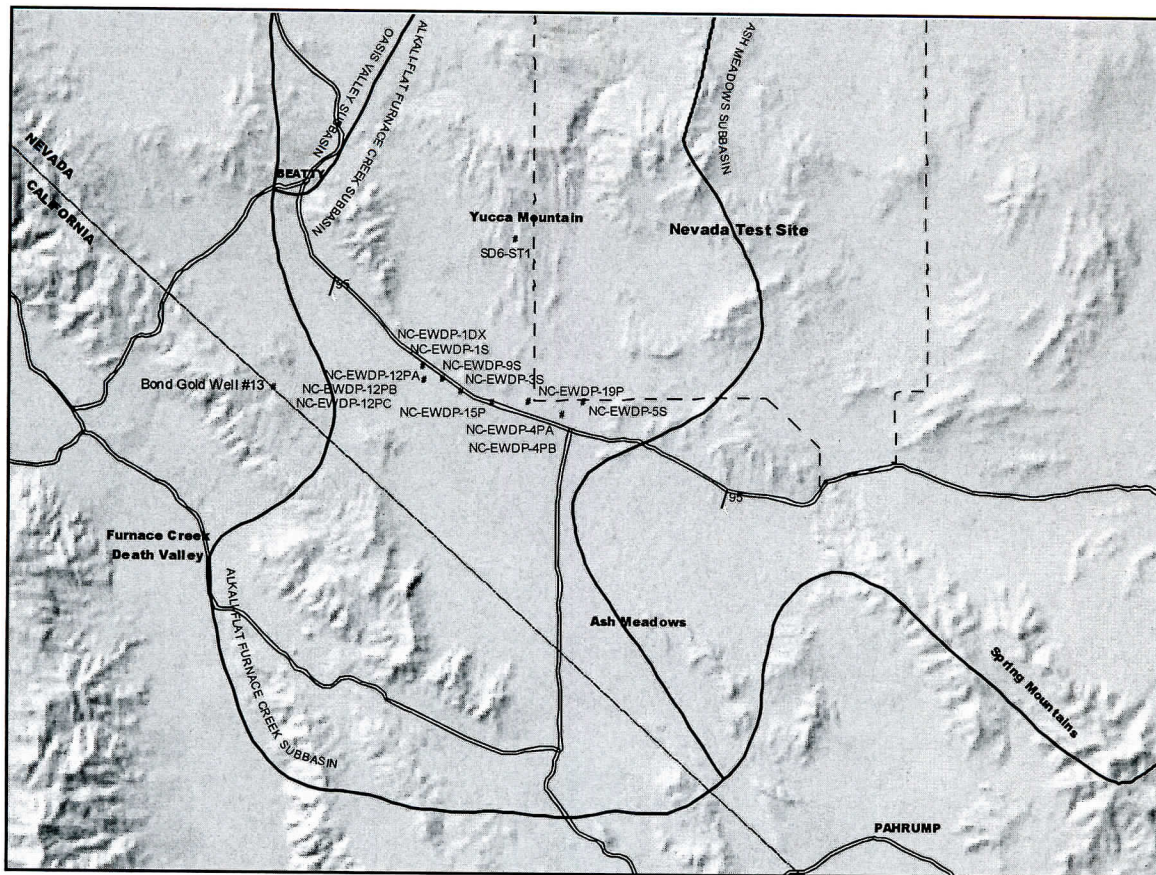


Figure 1 Map of Study Area with Approximate Subbasin Boundaries (modified from Lacznia et. al, 1996).

statistical techniques were required due to the large amount of data generated and the lack of more traditional approaches (e.g., Piper diagrams) for trace element interpretations. The techniques used include principal component analysis (PCA), Q-mode factor analysis, correspondence analysis (CA), and hierarchical cluster analysis. The emphasis of these evaluations was on the comparison of the chemistry of the waters from the different wells and also the different zones within each well. Trace elements that can be used for distinguishing between samples collected from different wells as well as the different depths within each well were subsequently identified. Groundwater trace element compositions can reflect a multitude of geochemical reactions/processes including precipitation/dissolution reactions between aquifer rocks, minerals contained within aquifer rocks, and secondary minerals formed within aquifer rocks or coating fractures, redox conditions, solution and surface complexation, and in some cases, biologically mediated reactions. Consequently, geostatistical tools were applied to the data set collected in this study as a means of searching for similarities/differences, trends and/or correlations between individual trace elements, among different well water samples, and for different depth intervals of these wells. The underlying hypothesis is that groundwaters from the same aquifer system, similar aquifer compositions (e.g., carbonate rock aquifers versus the felsic

Table 1 Sampling Dates, Identifiers, Depths, and Lithologies of Screened Zones
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Well	Sample Date	Sample Identifier	**Depth (ft)	**Lithology
NC-EWDP-1S (Zone 1)	5/18/99 11/08/99 5/19/00	1S1Zn1 1S2Zn1 1S3Zn1	160-180	Tertiary Volcanic
NC-EWDP-1S (Zone 2)	5/17/99 11/08/99 5/18/00	1S1Zn2 1S2Zn2 1S3Zn2	210-270	Tertiary Volcanic
NC-EWDP-3S (Zone 2)	5/20/99 11/15/99	3S1Zn2 3S2Zn2	340-420	Tertiary Sedimentary (top) Tertiary Volcanic
NC-EWDP-3S (Zone 3)	5/20/99* 11/15/99 5/17/00	3S1Zn3 3S2Zn3 3S3Zn3	480-525	Tertiary Volcanic
NC-EWDP-4PA	5/15/00	4PA	405-485	Valley Fill
NC-EWDP-4PB	5/26/00	4PB	740-839	Valley Fill
NC-EWDP-5S	5/17/00	5S	601-780	Valley Fill
NC-EWDP-9SX (Zone 1)	5/19/99* 11/10/99 5/20/00	9S1Zn1 9S2Zn1 9S3Zn1	90-120	Valley Fill
NC-EWDP-9SX (Zone 2)	5/19/99 11/10/99 5/20/00	9S1Zn2 9S2Zn2 9S3Zn2	140-160	Valley Fill
NC-EWDP-9SX (Zone 3)	5/19/99 11/09/99 5/19/00	9S1Zn3 9S2Zn3 9S3Zn3	250-290	Valley Fill / Tertiary Volcanic
NC-EWDP-9SX (Zone 4)	5/18/99* 11/09/99 5/19/00	9S1Zn4 9S2Zn4 9S3Zn4	330-340	Tertiary Volcanic
NC-EWDP-12PA	5/22/00	12PA	325-384	Tuffaceous Volcanoclastics
NC-EWDP-12PB	5/22/00	12PB	325-385	Volcanoclastics
NC-EWDP-12PC	5/22/00	12PC	170-230	Valley Fill
NC-EWDP-15P	5/23/00	15P	200-260	Valley Fill
NC-EWDP-19P	5/23/00	19P	359-459	Valley Fill
NC-EWDP-1DX	5/24/99* 5/25/00	1D1 1D3	2160-2240	Siltstone and Shale (perhaps Volcanoclastic)
Bond Gold Well #13	7/19/99*	BGW		
SD6ST1	6/15/99*	SD6ST1		

* Samples were collected in duplicate

**Data Tracking Numbers are listed in Appendix A.

volcanic rock aquifers), or that have experienced similar processes along flow paths, would be readily resolvable from each other by the geostatistical techniques. Perhaps more important, waters from different aquifers or waters that experienced different processes during their histories will be clearly separated by the statistical methods.

2. Hydrogeologic Setting

The study area lies within the Alkali Flat - Furnace Creek subbasin of the Ash Meadows - Death Valley flow system (Laczniak et al., 1996). This subbasin is approximately 7,250 km² and includes a large part of the western half of the Nevada Test Site (NTS) as well as Yucca Mountain (Fig. 1). The location of wells sampled along with the location of other relevant sites are shown in Figure 1. Rocks of the region consist of a thick sequence (greater than 11,000 m) of Precambrian through Paleozoic sedimentary rocks, approximately 4,000 m of Tertiary volcanic rocks, and Quaternary basin-fill deposits (Winograd and Thordarson, 1975; Plume and Carlton, 1988). Mesozoic rocks are absent from the region. The principal aquifers are the lower Paleozoic carbonate aquifer (Cambrian through Devonian), which is locally up to 4,600 m thick, and the valley-fill aquifers (Winograd and Thordarson, 1975; Dudley and Larson, 1976). In addition, Tertiary volcanic rocks on and directly west of the Nevada Test Site are locally important groundwater bearing units (especially where densely welded and fractured), and are thought to contribute groundwater to the regional Paleozoic carbonate aquifer (Winograd and Thordarson, 1975; Peterman et al., 1992; Fridrich et al., 1994). In particular, these Tertiary volcanic rocks are especially important to the NCEWDP wells owing to the fact that many of these wells are finished in these volcanic rocks, others are finished in volcanoclastics (i.e., sedimentary) rocks likely composed of weathered fragments of the Tertiary volcanic rocks. In addition, much of the valley fill is thought to consist of fragments of these felsic volcanic rocks (e.g., Claassen, 1985). Compositionally, the Tertiary volcanic rocks are chiefly rhyolites and quartz latites belonging to the southwestern Nevada volcanic field (Byers et al., 1976; Fridrich et al., 1994). These volcanic rocks crop out over a region of approximately 10,000 km², and are thought to have erupted from at least 6 separate calderas, which are known together as the Timber Mountain - Oasis Valley caldera complex (Byers et al., 1976; Fridrich et al., 1994; Frizzel and Shulters, 1990). The Tertiary volcanic rocks unconformably overlie the Paleozoic carbonates and clastics, all of which have been displaced by late Miocene extensional faulting of the basin and range extension. The basins formed by this extension were contemporaneously filled with alluvial deposits originating from the physical and chemical weathering of the Paleozoic and Tertiary rocks.

3. Major Solutes

The major solute chemistry of groundwaters is commonly evaluated using Piper diagrams. These diagrams (Piper, 1945) are constructed by plotting the proportions (in equivalents) of the major cations (Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+}) on one triangular diagram and the proportions of the major anions (HCO_3^{-} , CO_3^{2-} , Cl^{-} and SO_4^{2-}) on another. The combined information from the two

triangles is projected onto a quadrilateral. Piper diagrams are used as a method for displaying water chemistry data and classifying the water into a "type" or "hydrochemical facies" based on the relative proportions of the major ions (Drever, 1997). The concept of hydrochemical facies has been used to denote the diagnostic chemical characteristics of water solutions in hydrologic systems (Back, 1966). The facies reflect the effects of chemical processes occurring between the minerals within the lithologic framework and the groundwater. Schoff and Moore (1964) and Winograd and Thordarson (1975) have recognized four main hydrochemical facies for the groundwaters in the southern Nevada region: 1) calcium magnesium bicarbonate (Ca-Mg-HCO_3); 2) sodium potassium bicarbonate (Na-K-HCO_3); 3) calcium magnesium sodium bicarbonate (Ca-Mg-Na-HCO_3); and 4) sodium sulfate bicarbonate ($\text{Na-SO}_4\text{-HCO}_3$).

In general, the chemical composition of water in carbonate-rock aquifers is dominated by calcium (Ca), magnesium (Mg), and bicarbonate (HCO_3), whereas sodium (Na), chloride (Cl), and sulfate (SO_4) are the dominant ions in the water that comes from volcanic aquifers (e.g. Thomas et al., 1996). The hydrochemical facies are then modified, by mixing and/or chemical reactions of groundwaters with aquifer rocks/mineral phases, depending on the flow patterns of the groundwater. The movement of water from a volcanic aquifer into the regional carbonate aquifer can be deduced largely by decreased sodium concentrations or a "calcium magnesium sodium bicarbonate" facies (Schoff and Moore, 1964). Thus, the geochemical characteristics of the water can be used to trace groundwater sources and flow paths.

4. Rare Earth Elements

Because the application of rare earth elements (REE; i.e., La, atomic number 57, through Lu, atomic number 71) in the study of groundwater flow systems is a relatively recent development, and is still evolving, we provide the following review of the geochemistry of these trace elements, including some examples of their use in previous investigations of groundwater-aquifer systems. Beginning in the late 1980's, geochemists began to express increasing interest in the REE as potential tracers in groundwater-aquifer systems (e.g., Banner et al., 1989; Smedley, 1991; Fee et al., 1992; Gosselin et al., 1992). Some of the goals of these early studies included evaluating the use of the REEs to investigate groundwater-aquifer interactions and, specifically, examining the relationships between REE signatures of groundwaters and their associated aquifer materials. Because of their unique and chemically coherent behavior, the REEs have long been employed, with success, as geochemical tracers in petrogenetic studies of igneous rocks (e.g., Hanson, 1980) and to investigate trace element cycling in the oceans (Elderfield, 1988; Byrne and Sholkovitz, 1996). In addition, Sm-Nd isotopes have proven to be useful tracers of oceanic water masses on a global scale (Piepgras and Wasserburg, 1980, 1987; Stordal and Wasserburg, 1986). Consequently, sufficient precedence exists to suggest that the chemical properties which allowed investigators to use REEs as tracers in petrogenetic and oceanic studies, could also be employed in a similar fashion for groundwater studies.

The unusual properties of the REEs are, in part, a function of their similar size and trivalent charge which leads to substantially different chemistry compared to their nearest neighbors in the periodic table (i.e., Ba and Hf). Moreover, because of the progressive filling of the 4f electron shell with increasing atomic number, the REEs exhibit a gradual decrease in their ionic radii from La through Lu. This phenomenon, known as the lanthanide contraction, results in subtle differences in the chemistry of the REEs that vary, predictably, with atomic number. Therefore, not only do the REEs exhibit strong fractionation as a group, but also exhibit significant within-group fractionation that facilitates investigations of complex geochemical processes.

The development and recent use of extremely sensitive analytical techniques, such as isotope dilution thermal ionization mass spectrometry (ID-TIMS; Greaves et al., 1989; Elderfield and Greaves, 1982, 1983; Schneider and Palmieri, 1994) and inductively coupled plasma mass spectrometry (ICP-MS; Smedley, 1991; Klinkhammer et al., 1994; Stetzenbach et al., 1994), to accurately measure REE concentrations in groundwater samples down to a tenth of a picomole per kilogram while using relatively small sample volumes (~ 1 liter), has allowed high quality determinations of REEs in a wide variety of groundwater samples. These studies have in turn, led to important discoveries as to the effective use of REEs as geochemical tracers in groundwater systems.

Among the first investigation of the REE signatures in groundwaters with direct applications to their use as geochemical tracers was that of Smedley (1991). The REEs were measured in mildly acidic groundwaters from a granitic and a metasedimentary (primarily slate) rock aquifer in southwestern England. The REE signatures of the groundwaters were shown to closely resemble the REE signatures of the specific rock types through which they flowed. From these observations, Smedley (1991) argued that characterizing the REE signature of groundwaters can provide a means of tracing groundwater flow based on aquifer composition. Such an approach is essentially identical to the use of strontium isotope ratios in groundwaters (e.g., Banner et al., 1989; Lyons et al., 1995). More recently, groundwater REE concentrations have been used successfully to trace groundwater flow and mixing in aquifers from Tennessee and southern Nevada, USA (McCarthy et al., 1996; Johannesson et al., 1997a, b). Johannesson et al. (1997a) demonstrated that the REE concentrations of groundwaters discharging from carbonate springs in Death Valley National Park, California, closely resembled the REE signatures of groundwaters issuing from similar carbonate springs located 50 km to the east in Ash Meadows National Wildlife Refuge, Nevada, USA. Previous investigators had argued that the Death Valley groundwaters had their origin in shallow alluvial aquifers located 30 - 35 km to the north (e.g., Winograd and Thordarson, 1975). Stable oxygen and hydrogen isotope data for waters from shallow wells in the Amargosa Desert and spring waters of the Furnace Creek region of Death Valley are similar (Claassen, 1985; Thomas et al., 1996), and thus consistent with flow between the Amargosa Desert and Death Valley. The $\delta^{18}\text{O}$ and δD values of Ash Meadows spring waters and those from Furnace Creek are identical and, consequently, are consistent with groundwater flow between Ash Meadows and Death Valley (Winograd and Friedman, 1972; Thomas et al., 1996). The REE data, however, strongly suggest that the groundwater discharging from the Furnace Creek springs in Death Valley is the same as that which issues from the springs

in Ash Meadows, up gradient from Death Valley (Johannesson et al., 1997a). Furthermore, the orientation of faults between Ash Meadows and the Furnace Creek region and hydrologic head levels in the regional carbonate aquifer support groundwater flow from Ash Meadows, beneath the alluvial deposits within the Amargosa Desert, and through the southern end of the Funeral Mountains to the Furnace Creek regions of Death Valley (Carr, 1984; Lacznia et al., 1996; Thomas et al., 1996).

Johannesson et al. (1997b) chose a relatively well understood aquifer system in southern Nevada, USA (i.e., the Ash Meadows system) to test whether careful examination of the REE concentrations in groundwaters would produce similar results, in terms of groundwater flow and mixing, as previously determined using well accepted conservative tracers. Previous investigators demonstrated, using stable hydrogen isotopes and naturally occurring radioactive uranium isotopes (i.e., ^{234}U and ^{238}U), that Ash Meadows groundwaters consist of approximately 60 - 65% groundwaters recharged in the nearby Spring Mountains and 30 - 35% of through-flow groundwater from the regional carbonate aquifer system which is assumed to be equivalent to spring discharge in Pahranaagat Valley, ~145 km to the northwest (Winograd and Friedman, 1972; Cowart, 1979; Osmond and Cowart, 1982; Farmer, 1996). Winograd and Thordarson (1975) also argued, based on the relatively conservative Na ion, that up to 5% of the total discharge from Ash Meadows springs represented groundwaters from the Na-rich felsic volcanic rocks of the Nevada Test Site.

Johannesson et al. (1997b) analyzed the REE concentrations of groundwater samples from the Spring Mountains, Pahranaagat Valley, and Ash Meadows as well as groundwaters from the volcanic aquifers on the NTS. They found, using the REE signatures of these groundwaters, that the REE signatures of the Ash Meadows groundwaters could best be replicated by a mixture of 54% groundwaters recharged in the Spring Mountains, 45% through-flow groundwaters from the Pahranaagat Valley, and approximately 1% of groundwater from the volcanic aquifers of the NTS (Farnham et al., 1999). Again, the REE signatures of the end-member groundwaters from the Spring Mountain, Pahranaagat Valley, and NTS, and, hence, the mixing ratios, are strongly controlled by the REE signature of the rocks through which these groundwaters flowed. These NTS groundwaters, for example, only reacted with felsic volcanic rocks and thus inherited REE signatures reflecting the signature of these rocks (Johannesson et al., 1996). On the other hand, the groundwaters from the Spring Mountains and Pahranaagat Valley primarily interacted with Paleozoic carbonate aquifer (Winograd and Friedman, 1972; Winograd and Thordarson, 1975), and, consequently, inherited REE signatures that chiefly resemble the REE signatures of these carbonates (Johannesson et al., 1997a, 2000). These observations further provide support that groundwater REE signatures are closely related to the REE signature of the rocks through which the groundwaters flowed.

The application of REEs as tracers of groundwater flow is hampered by the fact that these trace elements are known to be particle reactive (Koeppenastrop and DeCarlo, 1992, 1993; Sholkovitz et al., 1994; DeCarlo et al., 1998), and as such, are not expected to exhibit conservative behavior in natural waters. However, recent studies have clearly demonstrated that REEs do behave like conservative tracers in natural waters, including groundwater flow systems,

when strongly complexed with specific ligands, which can include anthropogenic organic ligands, dissolved natural organic matter, and carbonate ions (Bau and Dulski, 1996; Johannesson et al., 1997b, 1999; McCarthy et al., 1998a, b; Johannesson and Hendry, 2000; Möller et al., 2000). In any event, natural groundwater flow systems are complicated systems with numerous simultaneously occurring geochemical reactions and a variety of ongoing physical processes that can potentially lead to significant errors in interpretations of groundwater REE data. The work of Johannesson et al. (1997b) represents at best, a preliminary examination, encompassing significant simplifying assumptions, into the utility of the REEs as groundwater tracers. Simple end member compositions were assumed, based on previous investigations, for the REE mixing model, with the assumption that these end member REE compositions represented the unique REE signatures of hypothesized groundwater recharge areas. It is critical to stress that in order to test the REE mixing model of Johannesson et al. (1997b), substantially more data are required that would ideally include REE measurements on groundwater samples collected along the proposed groundwater flow paths in the region. However, the agreement between the REE mixing model and previous investigations involving more traditional, conservative tracers (e.g., $\delta^{18}\text{O}$) is quite encouraging.

5. Speciation of Arsenic, Antimony, and Selenium

The electrochemically measured redox potential (E_H) of groundwater is assumed to be related to the thermodynamically predicted concentration of the species that react reversibly at the electrode. However, an electrode measurement may not reflect the true thermodynamic redox potential. For example, Stumm and Morgan (1996) suggest that "... many and perhaps most measurements of E_H (or pE) in natural waters represent mixed potentials not amenable to quantitative interpretation....It is possible to evaluate the redox level in natural water systems by determining the relative concentrations of the members of one of the redox couples in the system and applying the electrochemical relations in reverse." The truth of the matter is that, most likely, both E_H measurements and redox couple measurements are needed in order to define the redox levels of a water system, such as water in the aquifers tapped by the wells of the NCEWDP. Together they may provide complimentary information with which to evaluate the oxidizing/reducing properties of the water in this region.

A hydride generation-atomic absorption spectrophotometric procedure is used for measuring the concentrations of the two common oxidation states (redox couples) of arsenic, antimony and selenium (Andreae, 1977; Cutter, 1985; Cutter et al., 1991), to shed light on the redox states of groundwater from wells in the NCEWDP. In this research, the following general concept is examined: if the common ionic species of, for example, arsenic were in thermodynamic equilibrium, it can be shown that:

$$\text{pE} = 14.5 - 2 \text{ pH} - \frac{1}{2} \log \left\{ \frac{[\text{H}_3\text{AsO}_3]}{[\text{H}_2\text{AsO}_4^{-2}]} \right\}$$

where pE is the negative logarithm of the effective concentration, that is, "activity" of electrons in the water, and pH is the negative logarithm of the hydrogen ion concentration (Cherry et al.,

1979). Note that the $pE = E_H \times 5046/T$ where T is the absolute temperature, or, at 25°C, $pE = E_H/0.0591$. The pE calculated in this manner is dependent upon the chemical species of the elements chosen; thus, this is one of the weaknesses of a thermodynamic approach. Similar expressions can be written for antimony, Sb(III) and Sb(V), and selenium, Se(IV) and Se(VI) and redox pairs of many other elements. A low pE suggests that the electrons are readily available in the water for reduction, and a high pE suggests that the system is oxidizing, or that few electrons are available for reduction.

Dissolved arsenic occurs in multiple oxidation states in natural waters including As(-III), As(III), and As(V). The predominate species in groundwater are arsenite [As(III)] and arsenate [As(V)]. In neutral to alkaline pH surface waters, equilibrium thermodynamics predicts that arsenate will predominate as $H_2AsO_4^- + HAsO_4^{2-}$ (Cullen and Reimer, 1989; Cutter, 1992). Under reducing conditions, arsenite as $H_3AsO_3^0 + H_2AsO_3^-$ will dominate As speciation (Cullen and Reimer, 1989; Anderson and Bruland, 1991). Interestingly, it is well established that both arsenate and arsenite can persist in reducing and oxidizing conditions, respectively, indicating that the rates of oxidation/reduction of these species are slow (Ferguson and Garvis, 1972; Cutter, 1992). Arsenic exhibits strong sorption to Fe oxides/oxyhydroxides in aquatic environments, with As(V) showing a greater tendency to adsorb to Fe oxides/oxyhydroxides at neutral to moderate pH values than As(III) (Pierce and Moore, 1982; Sadiq, 1992; Sullivan and Aller, 1996). At high pH's, however, adsorption of As(V) to Fe oxides/oxyhydroxide surfaces is weak, and arsenate species (e.g., $HAsO_4^{2-}$) are typically stable in solution (Hingston et al., 1967; Ferguson and Garvis, 1972; Andreae, 1977, 1978, 1979, 1983; Maest et al., 1992). In general, owing to its location below As in the periodic table of the elements, Sb exhibit similar speciation and geochemical behavior to As (Cutter et al., 1991; Cutter and Cutter, 1995).

Dissolved selenium exists in three oxidation states in oxidizing natural water including Se(VI) as selenate (SeO_4^{2-}), Se(IV) as selenite ($SeO_3^{2-} + HSeO_3^-$), and Se(-II) as organic selenides (Cutter and Cutter, 1995). On the other hand, particulate Se can occur in any of its oxidation states, either as adsorbed/coprecipitated selenite and selenate, organic selenides, or elemental selenium (Se(0)). Equilibrium thermodynamic predicts that dissolved selenate should only be found in oxic waters, while in anoxic waters selenite and selenate should reduce to insoluble (particulate) Se(0). Examination of Se speciation in marine and fresh waters indicates that all selenium species occur in both oxic and anoxic waters, reflecting the slow kinetics of redox reactions involving Se (Measures and Burton, 1978; Cutter, 1989; Cutter and Cutter, 1995).

6. Multivariate Statistical Analysis of Trace Elements

Several multivariate statistical techniques are used here to evaluate the trace element concentrations in the groundwater samples. For these analyses, the trace element concentrations, in units of parts-per-billion (ppb), are first assembled into a data matrix. The data matrix for the present study consists of 57 columns describing each of the trace elements and 41 rows describing the individual samples. Considerable amounts of literature exist on each of the methods used (e.g., Jöreskog, et al., 1976; Jolliffe, 1986; Davis, 1986; Greenacre, 1984); this section will provide only a summary of each technique.

6.1 Principal Components Analysis

Principal components analysis (PCA) is a multivariate statistical technique used for data reduction and for deciphering patterns within large sets of data (Wold et al., 1987). Because PCA is based solely upon eigenanalysis of the correlation or covariance matrix, no constraints such as multivariate normality are imposed on the data (Meglin, 1992). If large differences exist in the standard deviations of variables, PCA results will vary considerably depending on whether the covariance or correlation matrix is used. When the variables have widely differing variances, the first few PCs will simply explain the variables with the greatest variance. When the correlation matrix is used, each variable is normalized to unit variance and therefore contributes equally. The concentrations of the trace elements evaluated in this study vary by several orders of magnitude; some trace element concentrations are observed in ppb levels and other in ppt (i.e., parts-per-trillion) levels. PCA was therefore applied to the correlation matrix. Thus the data are first standardized by mean centering each column (i.e., the column mean is subtracted from each of the variables in the column) within the original data matrix and then dividing each of the variables within each column by the column standard deviation.

With PCA, the large data matrix is reduced to two smaller ones that consist of principal component (PC) scores and loadings. PC loadings are the eigenvectors of the correlation or covariance matrix depending on which is used for the analysis. The PC scores (s) are linear combinations of the concentration data (x) with the loadings (I) as the coefficients:

$$s_{n,c} = \sum_p x_{n,p} * I_{p,c}$$

where n identifies the sample, p identifies the particular trace element, and c identifies the principal component (Farnham et al., 2000). When the correlation matrix is used for the PCA, x refers to the standardized data. The PC scores therefore contain information on all of the trace elements combined into a single number, with the loadings indicating the relative contribution each element makes to that score.

Principal components are calculated so that they take into account the correlations present in the original data, but are uncorrelated (orthogonal) to one another. The first PC explains the most variance within the original data and each subsequent component explains progressively less. Typically, the data can be reduced to two or three dimensions (i.e., principal components) that account for the majority of the variance within the original data set. The PC scores for each groundwater sample are plotted and the plots are inspected for similarities. Groundwaters with similar trace element concentrations are observed as clusters in the PC score plots. The loadings are then evaluated to determine the elements that are responsible for these correlations. Elements with the greatest positive and negative loadings make the largest contribution. The loadings can therefore be examined to provide further insight into the processes that are responsible for the similarities in the trace element concentrations in the groundwater.

6.2 Q-Mode Factor Analysis

Although scores derived from PCA can be used to evaluate similarities between samples, PCA, an R-mode technique, is primarily used to evaluate the inter-relationships between variables (Jöreskog, et al., 1976). PCA was performed on the correlation matrix so that the trace elements with a high degree of similarity/correlation will typically load higher in the first few PCs than those that behave independently. Thus PCA results will typically reflect the *trace elements* with the greatest correlations and not necessarily the *samples* with the greatest correlation/similarity. Q-mode analysis, on the other hand, is used specifically to evaluate inter-relationships between samples (Jöreskog, et al., 1976). When evaluating groundwater geochemistry, the relative compositions of the constituents in a sample are often as important as their absolute concentrations. The original data matrix can therefore be transformed to describe an “index of proportional similarity” (Imbrie and Purdy, 1962) so that the similarity between samples is evaluated based on the proportions of their constituents. With Q-mode analysis, a similarity matrix is formed that consists of coefficients of proportional similarity, “ $\cos \theta$ ” for all possible combinations of two samples. The value of $\cos \theta$ ranges from +1 for two collinear vectors to 0 for two orthogonal vectors. With Q-mode factor analysis, each row describing each sample is normalized to unit length. This row normalization does not affect the proportionality relationship between variables but instead removes the effects of size differences between samples. This means that a concentrated sample will exhibit similarities to one that is more dilute if the relative proportion of the trace elements are the same. Like PCA, Q-mode analysis can be used for data reduction. Eigenvectors, referred again to as loadings, are extracted from the similarity matrix. The Q-mode loadings are used to describe the relative proportions of the trace elements in the samples. The majority of the variance is typically explained in the first few factors. Therefore, the PC loadings for only the first few factors can be plotted and evaluated to search for similarities between samples.

6.3 Correspondence Analysis

Correspondence analysis (CA) is a relatively new multivariate technique that was originally developed for evaluating discrete count data contained in a contingency table (Benzécri and Benzécri, 1984). Since its introduction, this technique has been widely applied to continuous data similar to that of this study (e.g., Mellinger, 1987; Razack and Dazy, 1990; Hongjin et al., 1995). The matrix transformation involves a measure of similarity between both the samples and the variables providing some of the advantages of both Q- and R-mode analysis. Normalization is performed on both the rows and columns of the data matrix allowing plotting of both the samples and variables (ie., trace elements) on the same graph. As with Q-mode analysis, the influence of the “sizes” of the samples are removed using CA (Wold *et al.*, 1987). Column normalization, similar to that described with PCA, assures that the trace elements that are present in relatively high concentrations in the groundwater samples (those measured in high ppb levels) do not dominate the analysis. Instead, proportions of the trace elements within a sample relative to the proportion in the other samples are evaluated. Trace elements that are proportionally high in a particular sample relative to all other samples will plot close to that sample on a CA plot.

6.4 Cluster Analysis

Cluster analysis is a formal multivariate technique used to detect grouping patterns in data. For the current study, hierarchical clustering links groundwater samples based on similarities in all the trace elements measured in each sample. The relative similarities in the concentration of the trace elements between samples are quantified using the Euclidean distance, defined as:

$$\text{Distance}(x, y) = [\sum_i (x_i - y_i)^2]^{1/2}$$

where x and y represent the specific groundwater sample for which the distance is calculated and i defines each of the particular trace elements. Wells with the most similar groundwater chemistry (lowest Euclidean Distances) are initially linked together, at which point the criteria used to form the clusters are relaxed progressively so that groundwaters that are chemically less similar are linked. A Hierarchical “icicle” diagram is prepared whereby well samples are formed into clusters on the x-axis and the linkage distances appear on the y-axis. The linkage distances between clusters illustrate their relative similarities. The smaller the linkage distance, the more similar the trace element chemistry of the groundwaters. Ward’s method was used to form the clusters. This method uses an analysis of variance approach to minimize the sum of squares of any two hypothetical clusters that can be formed at each step. Ward’s method forms distinct clusters that are easier to visualize than those formed by other methods (STATISTICA, 1999).

7. Methods

Sampling activities were coordinated by the Nye County Nuclear Waste Repository Project Office (NWRPO). A total of thirteen samples were collected in May 1999, eight samples were collected in November, 1999, and sixteen samples were collected in May 2000 (Table 1). Four samples were collected in duplicate during the first (May 1999) sampling. Duplicate samples were collected and analyzed identically and used to evaluate analytical reproducibility. The wells sampled, the depth of the screened intervals for each zone, and the corresponding lithology are listed in Table 1. The Data Tracking Numbers (DTNs) for these data are shown in Appendix 1.

Groundwater samples were collected following the ultra-clean sampling techniques outlined in the implementing procedure IPLV-8.3 “Groundwater Sample Collection and Control”. This procedure details pre-cleaning techniques for the sample bottles as well as the preparation, collection, preservation, transport, and storage of each sample. Prior to sample collection, each well was pumped for a number of well volumes in order to ensure that the samples were representative of the actual groundwater and not water that had been sitting in the well bore for some time. Once the pH, temperature, and conductivity of the well water (measured using an in-line probe) had stabilized, samples were collected into pre-cleaned 10 L collapsible containers. Samples were immediately filtered from the collapsible containers using a peristaltic pump equipped with precleaned (acid-washed) Teflon® tubing, and Gelman Sciences (0.45 • m) groundwater filter capsules, into precleaned, acid-washed high density linear polyethylene sample bottles. Before filling the sample bottles with a particular groundwater sample, the

bottles were rinsed three times with filtered groundwater from the well of interest in order to "condition" the sample bottles with the groundwater sample and remove any remaining HNO_3 used in sample bottle cleaning and pre-sampling storage. Sample volumes of approximately 5 L, 250 mL, and 125 mL were filtered for trace element, major cation, and major anion analysis, respectively. One liter samples were collected for the analysis of oxidation states of selenium and one liter was collected for the oxidation states of both arsenic and antimony. The samples for major cation and trace element analysis were immediately acidified to $\text{pH} < 2$ with ultra-pure nitric acid (SeaStar, Inc. sub-boiling distilled in quartz). Samples for analysis of the oxidation states of selenium were acidified with 2.5 - 3 mL of chlorine free hydrochloric acid. Samples for major anion analysis and the oxidation states of arsenic and antimony were not preserved. The sample bottles containing the groundwater samples were double bagged in clean plastic bags, placed into plastic insulated chests with ice, and transported to the laboratory where they were stored at approximately 4°C . Samples for analysis of the oxidation states of arsenic and antimony were placed in plastic bags and added to an ice slurry in a plastic insulated chest. Laboratory blanks were prepared using deionized water in the laboratory. These laboratory blanks were treated as samples, but did not leave the laboratory. In addition, field (i.e., procedural) blanks were also employed in the project. Field blanks consisted of deionized water that was carried into the field (i.e., sample collection locations) in a clean 10 L collapsible container, filtered in the same manner as the actual groundwater samples, acidified in the field with ultra-pure HNO_3 , double bagged in clean plastic bags, and returned to the laboratory for analysis.

Sample analyses were also performed following implementing procedures (IPs) approved by the UCCSN Quality Assurance Program. Major cations (Ca^{2+} , Mg^{2+} , Na^+ , and K^+), major anions (Cl^- , F^- , Br^- , SO_4^{2-} , PO_4^{3-} , and NO_3^-), and trace elements were analyzed using an atomic absorption spectrometer (IPLV-011), an ion chromatograph (IPLV-008), and an inductively coupled plasma mass spectrometer (IPLV-009) respectively. The ICP-MS was equipped with an ultrasonic nebulizer which increases the sensitivity of the instrument and decreases the potential interferences from oxide formation (Stetzenbach et al., 1994; Hodge et al., 1996). Groundwaters were also assayed for the oxidation states of arsenic As(III) and As(V), antimony Sb(III) and Sb(V), and selenium Se(IV) and Se(VI), by the selective reaction of these ions with sodium borohydride. The volatile hydrides are trapped in liquid nitrogen and subsequently, upon revolatilization, detected and quantified by the element specific atomic absorption spectrometry system (IPLV-014).

Rare earth element (REE) concentrations were determined by inductively coupled plasma mass spectrometry with ultrasonic nebulization after preconcentration by cation-exchange (Stetzenbach et al., 1994). Because oxides of Ba formed in the plasma stream can cause significant mass interferences on Eu (Jarvis et al., 1989), Ba in groundwater samples was removed from solution using a modification of the technique developed by Cerrai and Ghersini (1966) prior to ICP-MS analysis. An aliquot of each sample was passed through a cation-exchange column packed with Bio-Beads SM-2 adsorbent coated with di-(2-ethylhexyl) orthophosphoric acid. In this extraction process, Eu as well as the other REEs are adsorbed, whereas Ba is not.

The HydroChem® program, developed by RockWare Inc. (1997), was used to construct Piper diagrams. The statistical software package Statistica, Release 5.5 (STATISTICA, 1999) was used for all PCA, CA, and cluster analyses. This software package offers only the option for principal components factor analysis (PCFA), but this technique is equivalent to PCA as applied in this study. A computer program was developed in S-PLUS2000 programming language for the Q-Mode factor analysis. This computer program is not qualified under the UCCSN Quality Assurance Program. The results of Q-Mode factor analysis are therefore non-Q and are used for corroborating the results of PCA and CA.

8. Results and Discussion

8.1 Major Solutes

Major solute data for the NCEWDP wells are presented in Appendix II and are also plotted on Piper diagrams (i.e., Piper, 1945) in Figs. 2 and 3. Bicarbonate and carbonate concentrations used for the Piper diagrams were provided by the U.S. Geological Survey (DTN: GS010308312322.003 and GS011108312322.006). Major solute data for all NCEWDP groundwaters are plotted in Figures 2a and 2b; the concentrations of the major solutes were averaged for those sites where multiple (i.e., replicate) measurements were made. Most of the groundwaters can be classified as Na + K - HCO₃ waters, including wells 9S, 19P, 15P, 3S, 5S, 12PB, 12PA, SD6ST1, and the 1D waters (Figs. 2a and 2b) which is consistent with groundwaters that have chemically reacted with felsic volcanic rocks such as the rhyolites and quartz latites of the Timber Mountain Caldera Complex or sedimentary rocks (i.e., volcanoclastics) and alluvial deposits composed of weathered fragments of these volcanic rocks (White, 1979; White et al., 1980). Winograd and Thordarson (1975) classified many of the groundwaters from the Yucca Mountain and Nevada Test Site regions as Na + K - HCO₃ waters, and also argued that the major solute chemistry of these waters reflect their interaction with the local, and abundant felsic volcanic rocks of the region. Indeed, all of the NCEWDP well waters that are classified as Na + K - HCO₃ waters are from tuffaceous volcanic rocks (9S zones 3 and 4; 3S), volcanoclastic deposits composed of felsic, tuffaceous volcanic materials (12PA, 12PB), or valley fill deposits (9S zones 1, 2, and most of 3; 19P; 15P; 5S). The exception, however, is well 1D which is finished in Tertiary sedimentary rocks described as siltstones and shales. Nevertheless, it is highly likely that these valley fill deposits chiefly consist of weathered and otherwise detrital fragments of the local felsic volcanic rocks. Furthermore, we suspect that the siltstones and shale reported for the deep well (i.e., 1D) could likely be felsic volcanoclastic deposits. If so, then the major solute chemistry of these deep groundwaters (viz., Na + K - HCO₃ waters) would also be consistent with chemical reactions between the groundwaters and the aquifer rocks. Interestingly, water from well 12PC differs dramatically from the other groundwaters collected from piezometer wells 12PA and 12PB (Fig. 2b). The well 12PC is the shallowest of the 12P wells (170 - 230 feet) and the screened interval of this well, samples groundwaters from the valley fill system. Claassen (1985) argued that shallow groundwaters in valley fill deposits of the Amargosa Desert are predominantly recharged by infiltration of precipitation on the alluvial deposits and, especially, via infiltration of runoff through

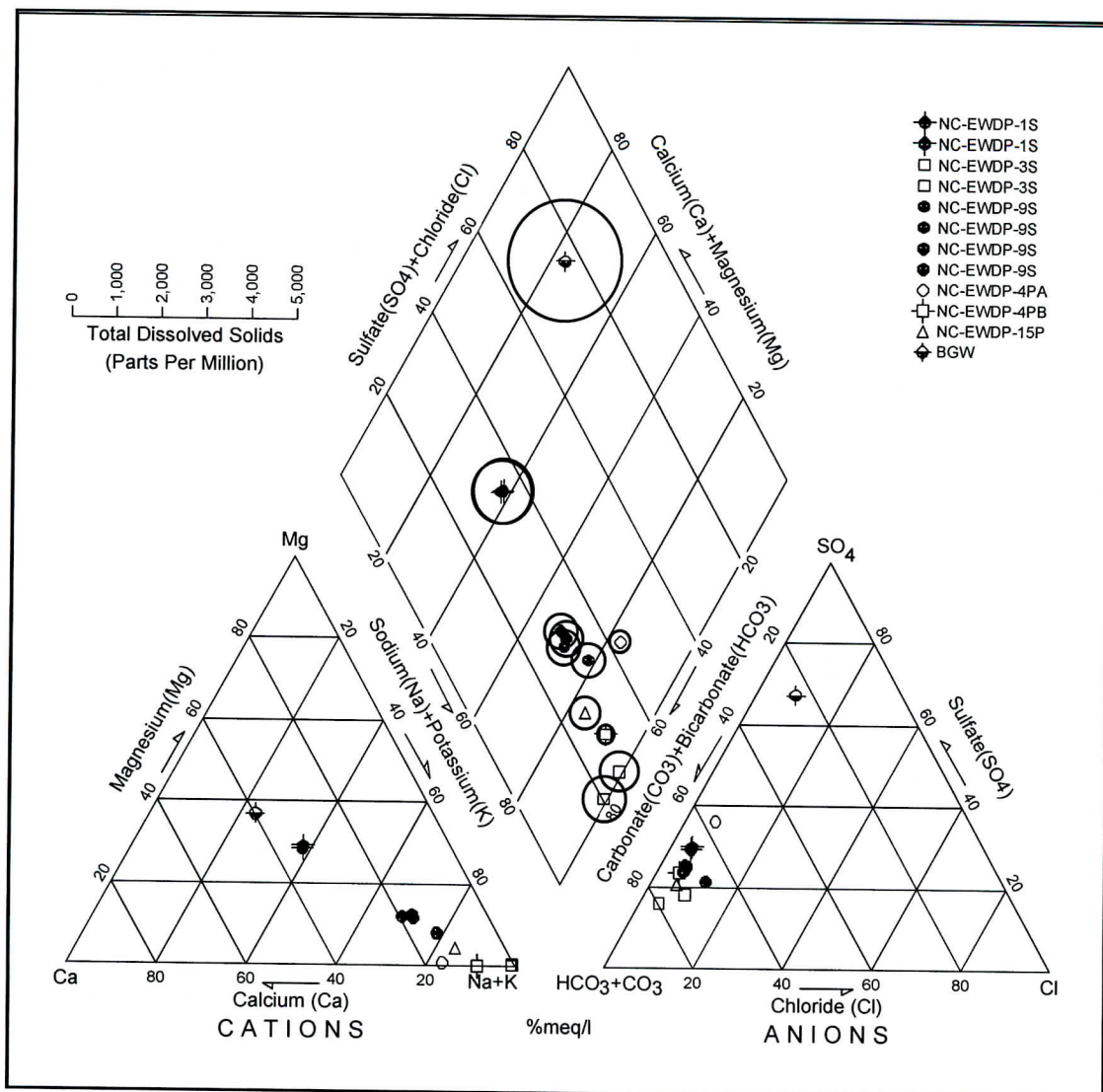


Figure 2a Piper Diagram for Groundwaters of the NCEWDP

channel (drainage) beds during storm events. It is also possible that 12PCgroundwaters, as well as the groundwater from well 1S, could be in intimate contact with valley fill deposits composed in part of carbonate rocks or by chemically reacting with pedogenic carbonate mineral contained in the alluvium. Carbonate rocks are abundant within much of southern Nevada, and caliche type deposits occur directly below ground surface in most alluvial deposits of the region (e.g., Winograd and Thordarson, 1975). The Ca + Mg + Na - HCO₃ facies was noted by Schoff and Moore (1964) as a mixing facies. Locally, alkaline earth enriched waters have been recognized from the Crater Flat-Yucca Mountain region and may reflect areas where hydrothermal alteration is important. Finally, volcanic rocks containing relatively more calcium-rich plagioclase and/or alluvium containing fragments of such volcanic rocks, may be involved in

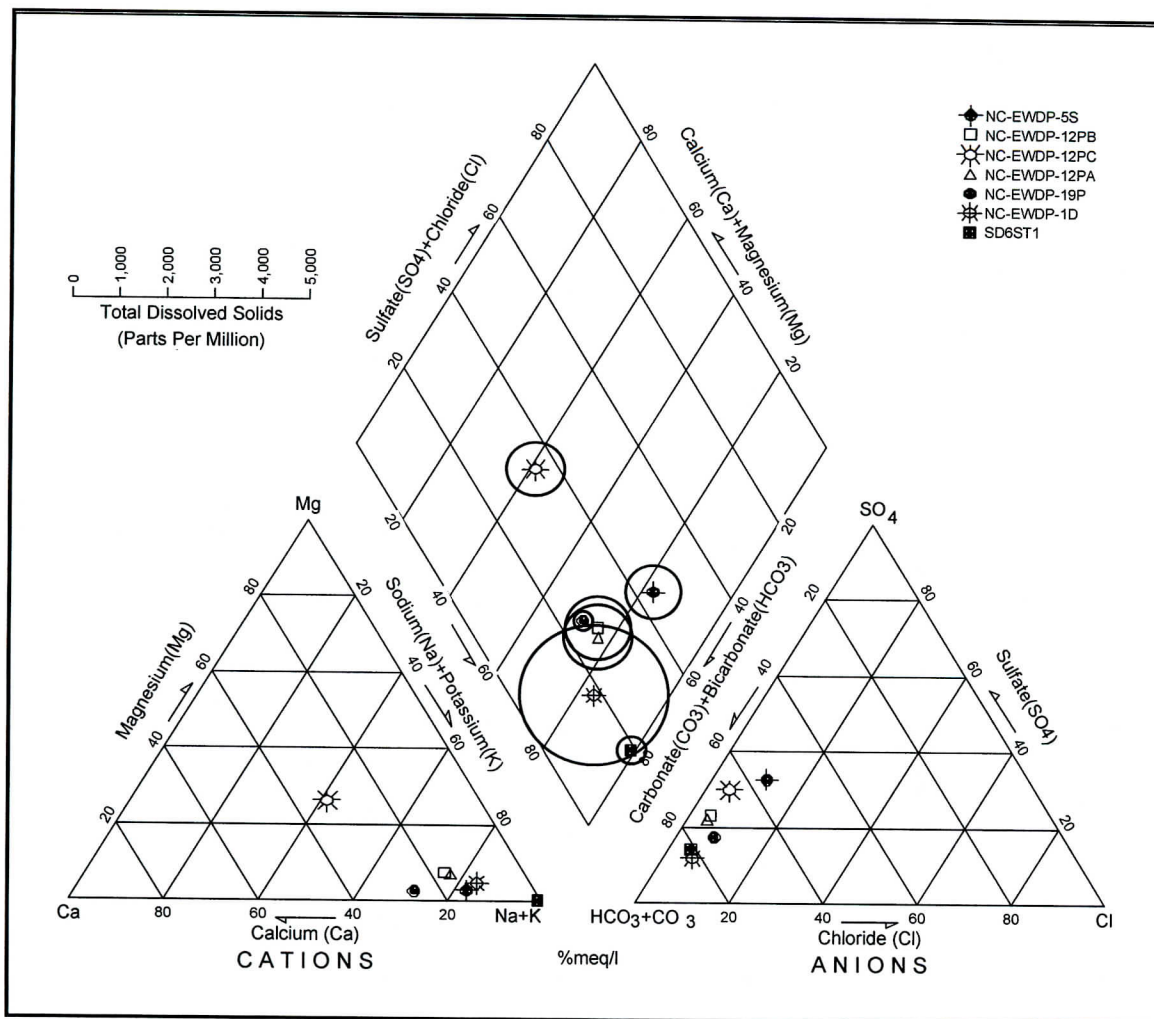


Figure 2b Piper Diagram for Groundwater of the NCEWDP.

groundwater-aquifer substrate reactions. In any event, owing to their proximity and similar water chemistry, it is highly likely that the alluvial deposits tapped by well 12PC are composed of fragments of compositionally similar volcanic rocks as those in which well 1S is completed. The groundwaters collected from the four screened intervals of well 9S show some strong chemical similarities with each other, although it is clear from Fig. 3 that the waters collected from the two deeper zones (zones 3 and 4) are more enriched in HCO_3 than the shallower groundwaters (i.e., zones 1 and 2) which exhibit roughly equal proportions of HCO_3 and $\text{SO}_4 + \text{Cl}$. The groundwaters from zones 3 and 4 plot as a tight cluster on Fig. 3 and are clearly of the $\text{Na} + \text{K} - \text{HCO}_3$ waters discussed above. The deepest screened interval (zone 4) is completely within Tertiary volcanic rocks, whereas the screened interval of zone 3 includes both valley fill deposits (76 - 87 m) and Tertiary volcanic rocks (87 - 88 m). On the other hand, the two shallower screened intervals (zones 1 and 2) only sample groundwaters from the valley fill

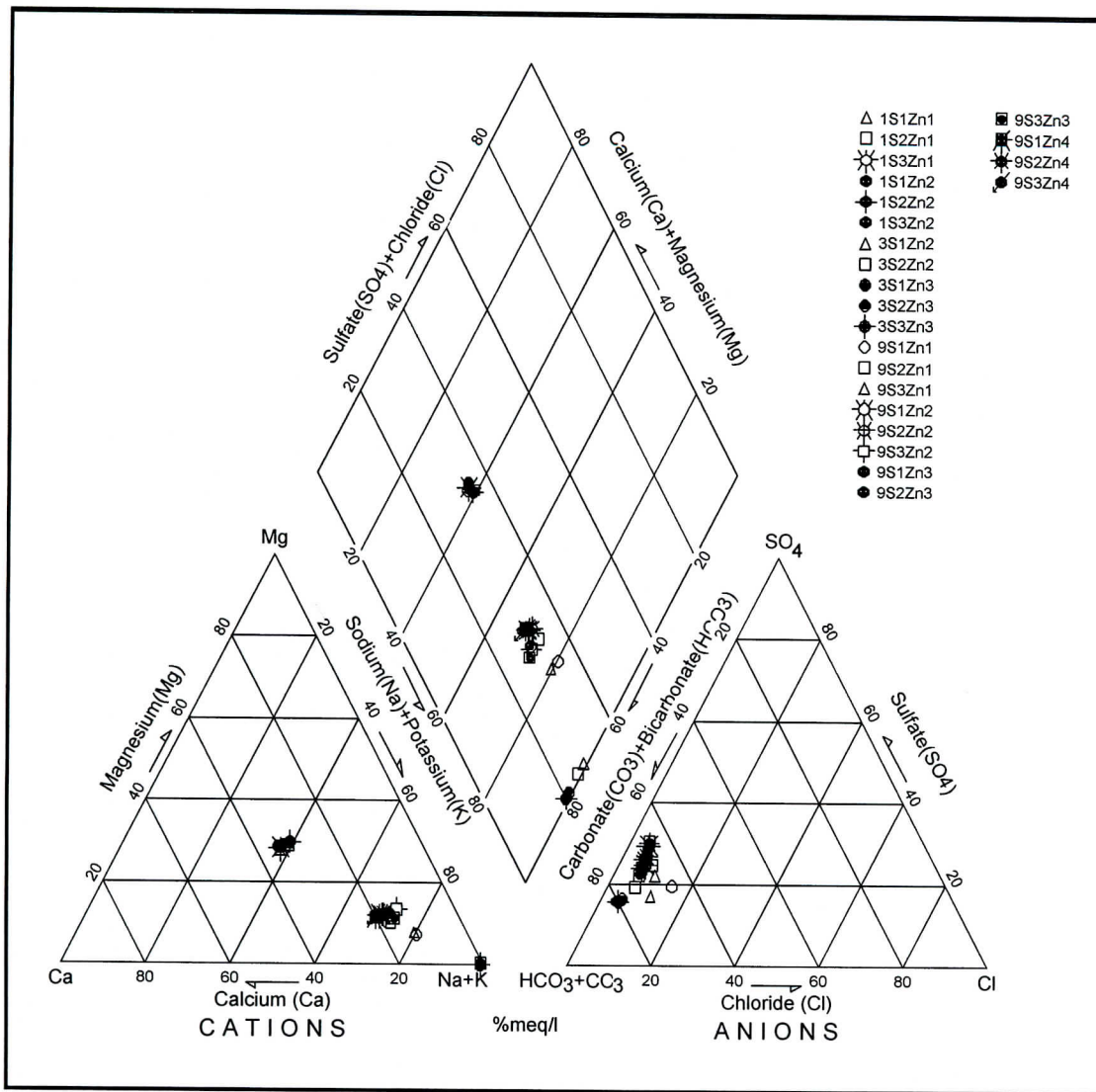


Figure 3 Piper Diagram for Groundwaters of NCEWDP-1S, NCEWDP-3S, and NCEWDP-9S

deposits. The waters from the shallowest screened interval of well 9S show the most variability, in terms of the major solute data, of well 9S groundwaters with some samples exhibiting greater enrichments in both Na + K, and more interestingly, $\text{SO}_4 + \text{Cl}$, than other 9S groundwaters, including those collected from zone 2 (Fig. 3). The major solute chemistry of the well 9S groundwaters are likely the direct result of chemical reactions between the groundwaters and the aquifer materials with which they are in intimate contact. Specifically, the groundwaters from the deeper portions of the well, and which react chemically with Tertiary volcanic rocks exhibit essentially identical major solute chemistry that is also consistent with the chemical composition of the felsic volcanic rocks with which they interact (see White et al., 1980). However, the groundwaters from the shallower screened intervals of well 9S, and especially those from zone

1, exhibit more variability and most importantly, higher $\text{SO}_4 + \text{Cl}$ concentrations. The relatively higher $\text{SO}_4 + \text{Cl}$ concentrations present in zone 1 groundwaters may reflect the presence of evaporite minerals within the alluvial deposits that are not present at depth within the volcanic rocks. On the other hand, the higher $\text{SO}_4 + \text{Cl}$ concentrations could reflect weathering reaction involving groundwater and hydrothermally altered rocks within the region.

Groundwaters from both 4PA and 1D show some interesting differences compared to the other well waters examined. First, groundwater from well 4PA is classified as a $\text{Na} + \text{K} - \text{SO}_4 + \text{Cl}$ water, and is thus different from the other waters by its proportionately lower bicarbonate concentrations. It is possible that the relatively higher concentration of $\text{SO}_4 + \text{Cl}$ of well 4PA water could reflect reactions with evaporite minerals. On the other hand, the deep groundwater from well 1D is more enriched in HCO_3 than all of the other groundwaters, and slightly more enriched in $\text{Na} + \text{K}$ (except water from well SD6ST1 and the 3S well waters, which have the highest relative proportions of $\text{Na} + \text{K}$). Furthermore, well 1D water is the most concentrated of all of the NCEWDP well waters, having the highest total dissolved solids (TDS) calculated based on our major solute data (Fig. 2). As mentioned above, these deep groundwaters are sampled from a screened interval where the aquifer rock type is identified as Tertiary siltstones and shales. We suggest that the chemical composition of groundwaters from the rocks are consistent with these Tertiary rocks being volcanoclastic sediments composed of rhyolitic/quartz latitic volcanic rocks. Moreover, the substantially higher TDS of the 1D well waters could reflect a greater age for these deep groundwaters compared to the other waters sampled in this study. However, without radiogenic isotope data it is impossible to verify or refute this hypothesis. Alternatively, the elevated $\text{SO}_4 + \text{Cl}$ relative to HCO_3 concentrations in these groundwaters may indicate the presence of hydrothermally altered rocks within the system.

Finally, the $\text{Ca-Mg-SO}_4\text{-HCO}_3$ facies was found in groundwater from BGW. The groundwater has very high concentrations of Ca, Mg, and SO_4 , and relatively lower concentrations of Na, Cl, and HCO_3 . This chemical composition indicates that the groundwater from this well is more mature and represents a mixing of Ca-Mg-HCO_3 water with $\text{SO}_4\text{-HCO}_3$ water. It was probably due to the movement of water from carbonate rocks into tuff or tuffaceous alluvium. The relatively higher concentrations of Ca and SO_4 in this water indicate a source of gypsum or other hydrothermally deposited minerals, such as those associated with the proximal Bullfrog Gold Mine south of Beatty, Nevada.

8.2 Rare Earth Elements

The REE data for the NCEWDP well waters are presented in Appendix III. Moreover, the REE data for these groundwaters are plotted in Fig. 4 normalized to upper continental crust (UCC) values (Taylor and McLennan, 1985). Normalization to UCC values allows us to examine the relative distributions of the REEs in NCEWDP groundwaters as compared to their distributions in upper continental crustal rocks. Consequently, we can evaluate the potential geochemical processes occurring in the groundwaters which act to fractionate the REEs from the upper

continental crustal abundances.

Almost all of the NCEWDP groundwaters exhibit heavy REE (HREE) enrichments over the light REEs (LREE) when normalized to UCC (Fig. 4). Exceptions include samples 4PA, 4PB, and 19B, which exhibit flatter patterns (i.e., less fractionation compared to crustal abundances). The HREE enrichments reported for most of these groundwaters are consistent with solution complexation with carbonate ions, which act to enhance the stability of HREEs in solution owing to the formation of strong HREE complexes with carbonate ions, and adsorption, which preferentially affects LREEs owing to the greater affinity for surface sites in the presence of strong, dissolved complexing ligands (Cantrell and Byrne, 1987; Lee and Byrne, 1993; Benedict et al., 1997; Johannesson et al., 1996, 1999). Many of the groundwaters exhibit significant negative UCC-normalized Eu anomalies, which probably, in part, reflects a rock/aquifer material inherited signature (Johannesson and Lyons, 1994). Upper continental crustal rocks are commonly depleted in Eu compared to Sm and Gd, owing to the inclusion of Eu^{2+} in sites within calcic plagioclase, and because calcic plagioclase is removed earlier from melts during fractional crystallization (e.g., Hanson, 1980). We should point out, however, that owing to the typical poor recoveries of Eu during the laboratory extraction process, as well as interference from Ba oxides in the plasma stream of the ICP-MS, caution is warranted when considering the Eu value reported here.

The groundwaters from NCEWDP well 1S have among the largest HREE enrichments of the NCEWDP groundwater examined in this study (Fig. 4). The 1S well waters are followed by the 1D sample, and 3S well waters (Fig. 4). Interestingly, although enriched in the HREEs compared to the LREEs, NCEWDP well 9S waters have flatter UCC-normalized REE patterns than the 1S, 1D, and 3S well waters. However, the REE patterns of 9S waters are not as flat as those observed from wells 4PA, 4PB, and 19B (Fig. 4). Groundwaters from the deeper screened intervals of well 9S (zones 3 and 4) have larger, negative Eu anomalies than groundwaters collected from the shallower screened intervals (zones 1 and 2). The large, negative Eu anomalies could reflect chemical reactions between these deeper groundwaters and the Tertiary felsic volcanic rocks which are characterized by similar Eu anomalies (Johannesson et al., 1997a). However, it is again important to stress the need for caution when interpreting the Eu values of the groundwater samples owing to the difficult nature of quantifying Eu in such samples.

Although the UCC-normalized REE patterns of 9S waters are somewhat flatter than some of the other groundwaters studied, well waters from wells 4 and 19P have the flattest patterns and are not typically enriched in the HREEs. Indeed, the shallow groundwaters (samples 4PA and 19P) are enriched in the middle REEs (MREE) compared to both the LREEs and HREEs. MREE enriched patterns have commonly been ascribed to the dissolution of secondary precipitate minerals such as Fe oxides/oxyhydroxides, which are themselves typically enriched in MREEs.

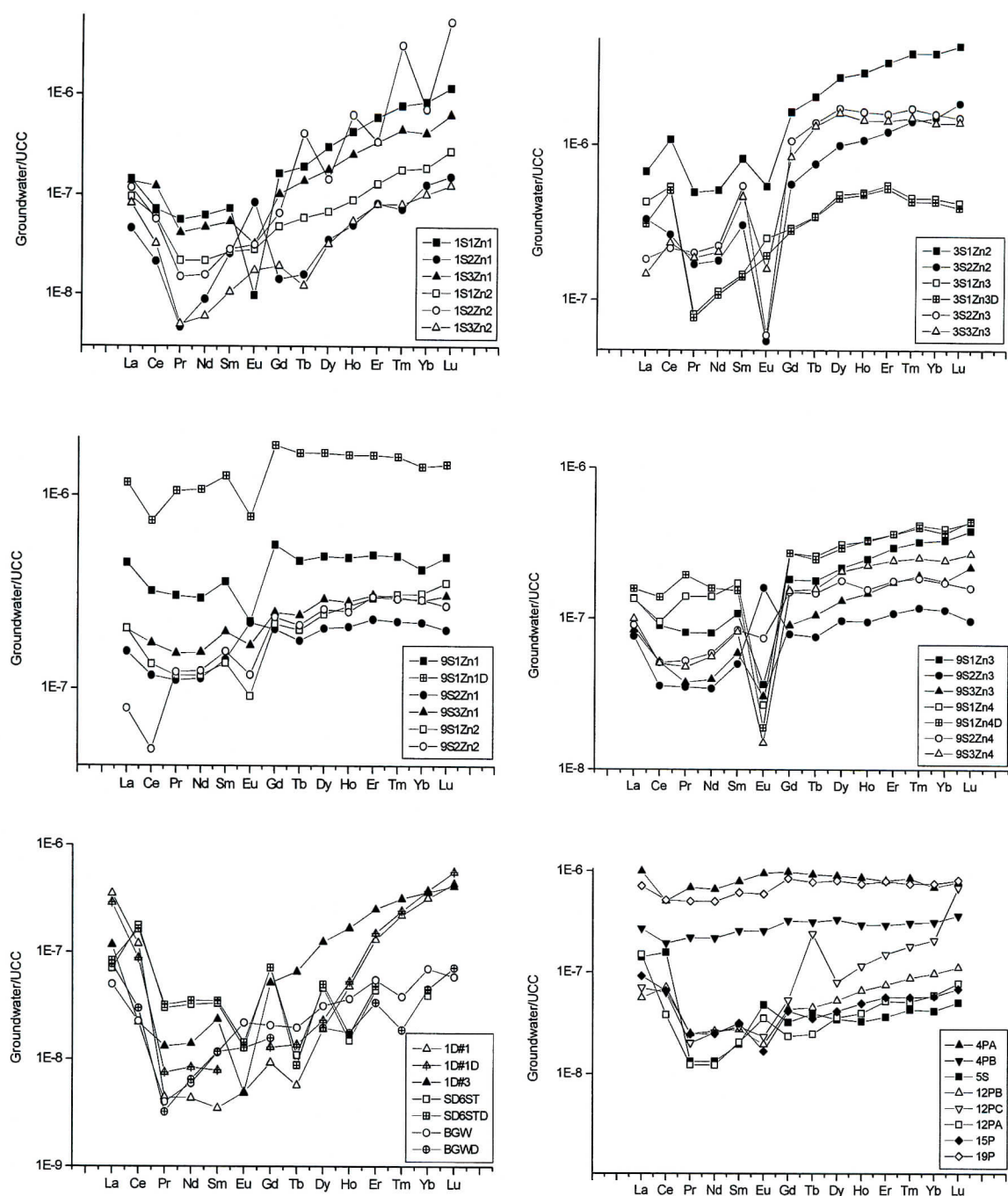


Figure 4. Rare Earth Element Concentrations in Groundwater Samples Normalized to Upper Continental Crust (UCC) Values. (This graph is for corroborative use only. The data in this graph are not to be used for quality-affecting work.)

8.3 Speciation of Arsenic, Antimony, and Selenium

Many difficulties were faced during the first year of the oxyanion speciation project. The main difficulty arose from the inadequate instrumentation that was available. Initially, two separate AA instruments were utilized. The first instrument was found to be inoperable and the second eventually became inoperable as well. The progress over this period was therefore primarily toward method development and the development of the implementing procedure. The data generated during this time are not reported here. New instrumentation was utilized and techniques for the analysis were better identified after this period. Therefore, only the results for the samples collected in May 2000 are discussed herein.

8.3.1 Arsenic

The results for the determination of arsenic species, along with the As(III)/As(V) values, in waters from the NCEWDP wells are listed in Table 2. A plot showing the percentage of As(III) relative to the total arsenic concentrations is shown in Fig. 5. The As(III)/As(V) values range from 0.002, where less than 1% of the arsenic is in the lower oxidation state, to 1.96 in water from well 1D, where roughly 70% of the arsenic is in the lower or “reduced” state (Fig. 5). Significant amounts of As(III) are observed in many of the waters from these wells. This is especially true in waters of 1D, 1S2 (1S3Zn2), and 5S but is also the case for waters from 1S1 (1S3Zn1), 12PB, 15P suggesting a relatively reducing environment in these groundwaters when compared to the others. The opposite is true for those waters of 3S3 (3S3Zn3), 4PB, 4PA, and 9S4 (9S3Zn4).

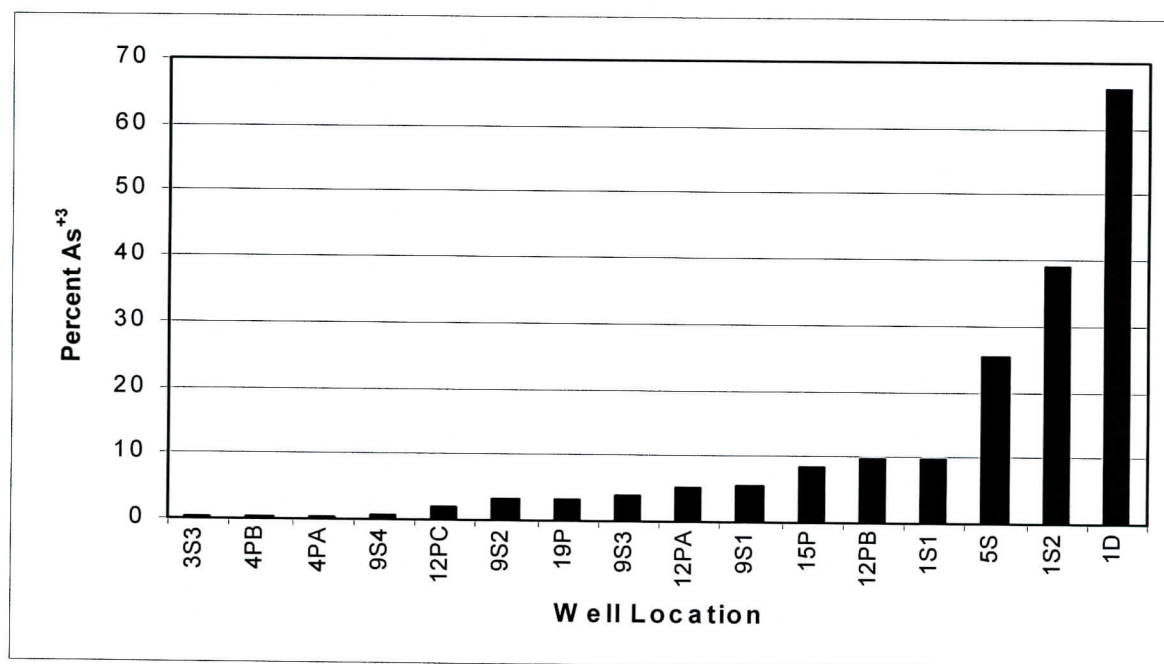


Figure 5 Percentage As(III) of Total As in Groundwaters of the NCEWDP.

Table 2 Arsenic (III), Arsenic (V), Antimony (III), and Antimony (V) Concentrations (MO0205UCC008JB.001)

Well	Sample Identifier [As]	Sample Identifier [Se]	As(III) ppb	As(V) ppb	As(III)/As(V)	Sb(III) ppb	Sb(V) ppb
1S Zn 1	556044	556045	0.46	4.24	0.11	<DL	0.11
1S Zn 2	556054	556055	0.25	0.39	0.64	<DL	0.08
3S Zn 3	556282	556283	0.07	39.2	0.002	<DL	0.07
9S Zn 1	556287	556288	0.48	8.18	0.059	<DL	0.35
9S Zn 2	556299	556040	0.51	15.1	0.034	<DL	0.23
9S Zn 3	556032	556033	0.36	9.11	0.040	<DL	0.15
9S Zn 4	556277	556278	0.07	11.5	0.006	<DL	0.31
5S	556272	556273	0.22	0.65	0.34	<DL	0.04
1D	556302	555999	5.30	2.71	1.96	<DL	0.03
4PA	556028	556029	0.04	12.3	0.003	<DL	0.09
4PB	556267	556268	0.08	40.5	0.002	<DL	0.25
12PA	556049	556050	0.13	2.31	0.056	<DL	0.07
12PB	555953	555954	0.13	1.21	0.11	<DL	0.08
12PC	556003	556004	0.24	13.1	0.018	<DL	0.09
19P	556297	556298	0.35	10.2	0.034	<DL	0.06
15P	556201	556200	1.33	14.3	0.093	<DL	0.23

8.3.2 Antimony

The results of the antimony oxidation state analysis are shown in Table 2. The concentration of antimony in these waters is considerably less than arsenic (Table 2). Unfortunately, all concentrations of Sb(III) are below the instrument's detection limit. Therefore, little information on the relative oxidizing/reducing properties of the groundwater can be obtained from these analyses. ICP/MS offers improved detection limits over those of the AA system and will therefore be used for future analyses of Sb(III) and Sb(V).

8.3.3 Selenium

Selenium oxidation state data are not reported for the samples collected from the NCEWDP wells. Selenium analyses were found to be quite sensitive to most lots of hydrochloric acid used for sample preservation. Also, several of the groundwater samples contained an unknown substance that precluded the analysis of selenium. Reliable selenium oxidation state data were therefore not obtained. It is expected that the use of ion chromatography with ICP/MS instrumentation will improve these analyses in the future.

8.4 Statistical Analyses of the Trace Elements

The trace element concentration data, with the exception of the rare earth elements, are listed in Appendix IV

8.4.1 Principal Components Analysis

Principal Components Analysis (PCA) was performed on the data matrix containing the concentrations of 57 trace element for a total of 41 samples. Plots of the first two principal components, explaining a total of 47% of the variance within the original data set, are shown in Figs. 6 and 7; Fig. 7 shows a magnification of the portion identified in Fig. 6. The majority of the samples fall within four clusters with the remaining samples, 3S1Zn2, 9S1Zn1D, and 1D#3, plotting outside of the main cluster. Samples from 1D and Bond Gold Well, with their respective duplicates, form two clusters; another cluster consists primarily of samples from the 3S well but also includes waters from 19P, 4PA, and 4PB; the fourth cluster contains samples from 1S and 9S which are somewhat separated by PC1. A significant degree of noise is observed in these PC score plots (Figs. 6 and 7). Other than samples clustering with their respective duplicates, tight clustering of the samples collected from the same site is not observed. Overlap in clustering is observed between samples collected from 9S and 1S and also between those collected from 9S and 3S. These phenomena are expected when PCA is performed on the correlation matrix, because all of the trace elements are given equal weight, and thus elements exhibiting low concentrations that vary as much between samples collected from the same location as between samples collected from different wells are given equal weight to those elements that are measured more precisely and that may be better descriptors for the system being evaluated. With the exception of 9S1Zn1, all samples plot relatively close to their duplicates suggesting that the variability observed with some of the trace elements is probably not due to the ICP-MS measurement, but instead may be due to sampling.

The main goal of these evaluations is to address the degree of communication between the different zones as well as the different aquifers sampled. Evidence to this end can be provided by determining the relative similarity in the trace element chemistry between samples collected from the different zones within the same well and also between samples collected from different wells. The trace elements that are most suitable for this purpose are those that are measured the most consistently in samples collected from the same site and depth, and that vary substantially depending on the aquifer sampled. Many of the NCEWDP wells and specific depths within these wells were sampled multiple times. A subset of the trace element data was therefore selected based on the reproducibility between the multiple measurements made on each site relative to the variability observed between all sites. In a recent paper, Farnham et al. (2002) used simulation experiments to determine a reasonable cut-off for eliminating variables (trace elements) from a data set based on the ratio of the variance between duplicates to the variance across all samples for that trace element. In other words, the trace elements are removed from a data set if: 1) large differences were observed in their measured concentrations between

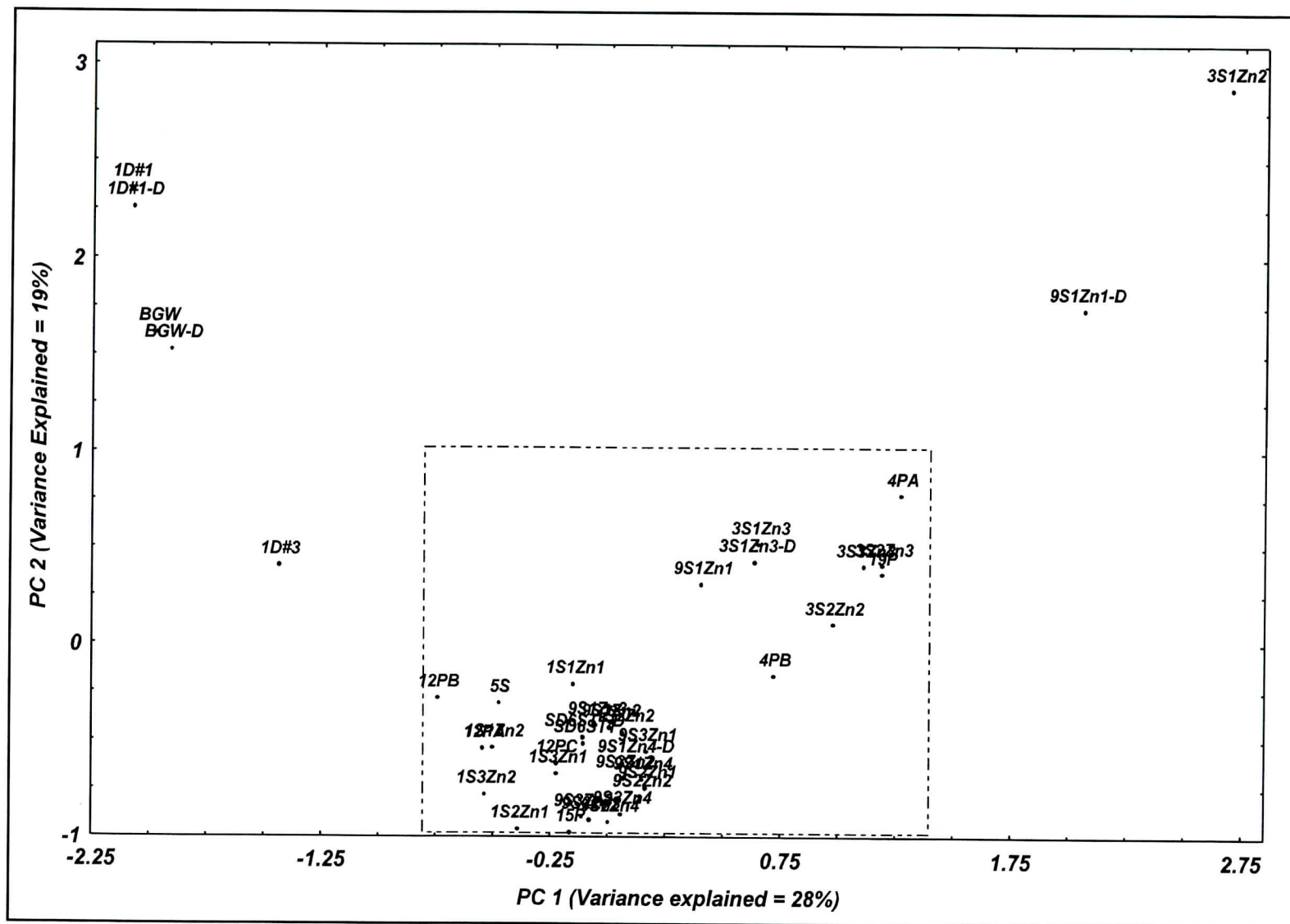


Figure 6 Scores for Principal Components 1 and 2 for Analysis Performed on All 57 Trace Elements

Figure 7 Scores for Principal Components 1 and 2 For Analysis Performed on All 57 Trace Elements - Magnified

duplicate samples and 2) if the concentration of that trace element is relatively similar in all samples within the data set. An overall optimum value for this cut-off was found to be 30% (the variance between duplicates is equal to or less than 30% of the variance for that element within the entire data set). This criterion was extrapolated to address variance between all samples collected from the same well and depth instead of only the duplicate samples; the trace elements were removed if the variance in their measurements between the samples from the same well and depth was equal to or greater than 30% of the variance for that trace element within all of the samples in the data set. The subset selected and used for further PCA analysis contains the following trace elements: Li, Be, Al, Ti, V, Cr, Mn, Co, Ni, Ga, Ge, As, Rb, Sr, Mo, Ru, Rh, Te, Cs, Ba, W, Ir, Au, Bi, U.

PCA was then applied to this subset of elements and the score plot for the first two PCs, now explaining 58% of the total variance in the data, are shown in Fig. 8. The results of the PCA for these trace elements again show BGW and 1D have significantly different trace element concentrations than the other well waters. These samples plot separately from the majority of the other well water samples on plots of PC 1 vs. PC 2 (Fig. 8). BGW and 1D, especially 1D#3, plot similarly on PC1 but are distinct in their PC2 values. These wells were excluded in the magnified portion of this plot shown in Fig. 9. Three clusters containing the majority of the samples are identified in Fig. 9. Samples from well 1S are contained in cluster 1 (Fig. 9). Cluster 2 contains samples from all zones of well 9S along with wells 15P, 4PA, and SD6ST1 (Fig. 9). 3S samples are contained in another cluster, cluster 3, that is clearly distinct from all other samples (Fig. 9). 12PC plots between clusters 1 and 2, and 19P lies between clusters 2 and 3. The three clusters are well separated by PC 2, but some overlap is observed between clusters 2 and 3 when only PC 1 is considered (Fig. 9). Samples from wells 12PA, 12PB, and 5S are similar to the well waters of 3S and 19P when only PC 2 is considered, but are distinct in their PC 1 values (Fig. 9). The sample from 4PB plots closest to 3S but is still distinct from all samples included in this data set (Fig. 9). Interestingly, the two zones sampled from 3S are separated by PC 1 and the two zones of 1S can be distinguished when both PC 1 and PC 2 are employed. No clear separation of the four zones in well 9S are observed from the PCA results of these data (Fig. 9).

Evaluation of the PC loadings, listed in Table 3, reveal some strong trends within these data. For instance, the concentration of the trace elements with negative PC 1 loadings, in general, are higher in those samples that have negative PC 1 scores (ie., 1D, BGW, 5S, 12PB, and 12PA) when compared to those with positive PC 1 scores (Figs. 8 and 9). The majority of the trace elements have negative loadings demonstrating the overall greater concentration of the trace elements in the deeper, and probably more mature waters of BGW and 1D. A similar trend is observed when evaluating those trace elements with positive PC 1 loadings (W, V, As, Ga, Al, U, and Mo); the concentrations of these elements are typically lower in the samples from 1D, BGW, 5S, 12PB, and 12PA. These trends are more clearly observed when considering PC 2. The trace elements with both negative PC 1 and PC 2 loadings (Ba, Cs, Rb, Li, Be, and Ge) exist in greater concentrations in the waters of well 1D while those with negative PC 1 and positive PC 2 loadings (Sr, Rh, Bi, Ti, and Ni) are greater in concentration in the BGW samples. With

Figure 8 Scores for Principal Components 1 and 2 Performed on the Subset of 25 Trace Elements

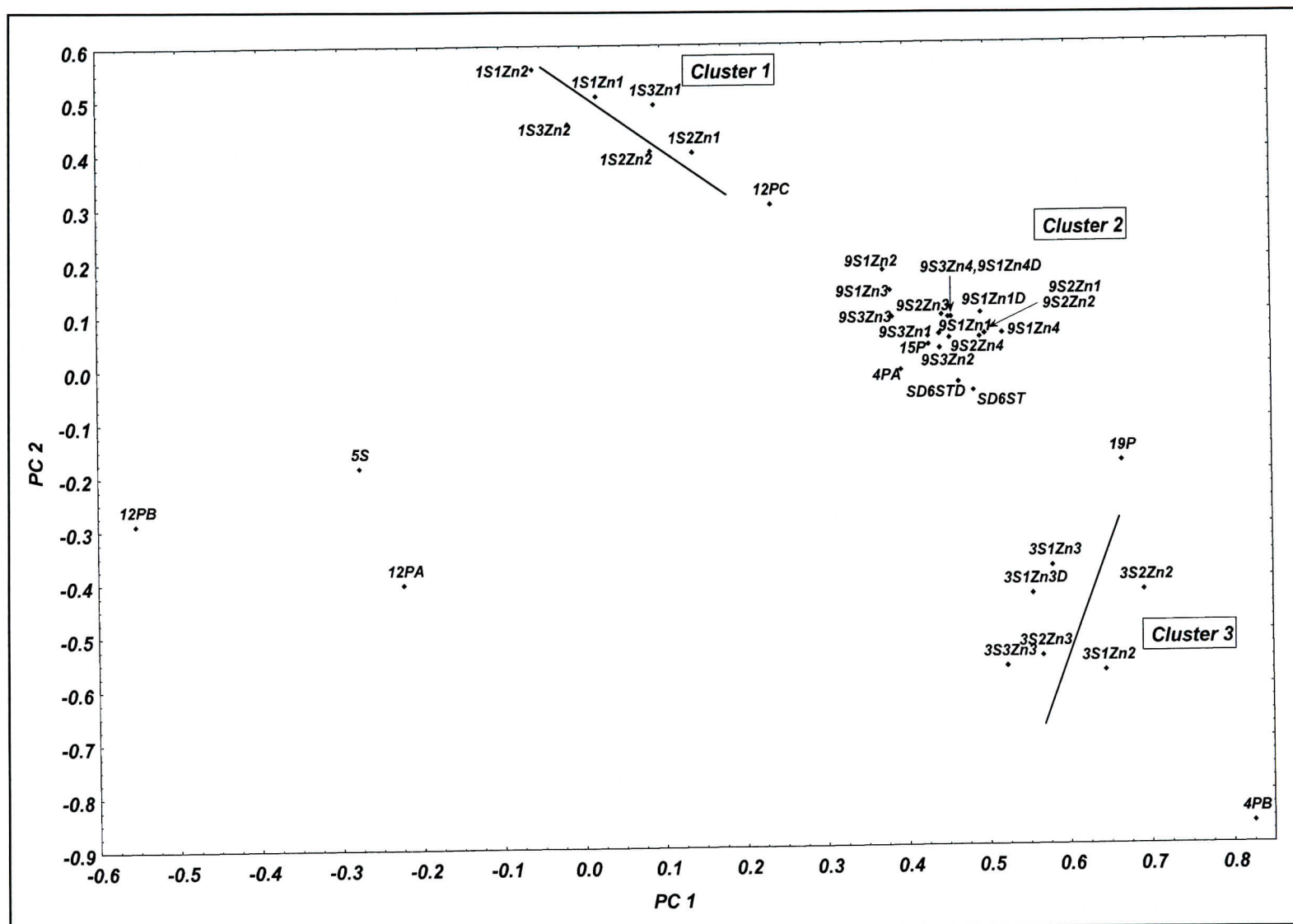


Figure 9 Scores for Principal Components 1 and 2 for Analysis Performed on Subsets of 25 Trace Elements - Magnified

Table 3. Principal Component Loadings

	PC 1	PC 2	PC 3
Li	-0.71	-0.65	-0.08
Be	-0.66	-0.58	0.14
Al	0.27	-0.18	-0.59
Ti	-0.58	0.75	-0.17
V	0.43	-0.13	-0.51
Cr	-0.41	-0.29	-0.56
Mn	-0.61	-0.33	0.16
Co	-0.57	0.10	0.10
Ni	-0.57	0.74	-0.24
Ga	0.30	-0.24	-0.73
Ge	-0.50	-0.60	-0.31
As	0.42	-0.30	-0.69
Rb	-0.80	-0.58	0.10
Sr	-0.82	0.52	-0.04
Mo	0.17	-0.21	-0.07
Ru	-0.81	0.18	-0.38
Rh	-0.81	0.53	-0.08
Te	-0.90	-0.07	-0.29
Cs	-0.78	-0.58	0.02
Ba	-0.82	-0.47	0.14
W	0.56	-0.25	-0.66
Ir	-0.87	0.25	-0.33
Au	-0.37	-0.39	0.21
Bi	-0.63	0.65	-0.33
U	0.16	0.46	-0.17

the exception of Bi, these trace elements (Sr, Rh, Ti, and Ni) are also relatively greater in concentration in the samples with positive PC 1 and PC 2 scores (wells 1S and 12PC). The elements with the greatest positive PC 1 and negative PC 2 loadings (As, W, Ga, Mo, Al, U, and V) are also greater in concentration for the samples with corresponding positive PC 1 and negative PC 2 scores (3S and 4PB).

Table 3 lists the correlation coefficients between the trace elements and the major anions (Br^- , Cl^- , SO_4^{2-}) and cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+). An interesting relationship between the PC 2 loadings and the correlations between the trace elements and major solutes is revealed in Table 4. The trace elements with the greatest correlations with Na ($r = 0.84$) and K ($r = 0.70$) also have the greatest negative PC 2 loadings (Li, Be, Ge, Rb, Cs, and Ba). This trend is also observed, to a lesser degree, with F. On the other hand, the trace elements with the greatest correlations with Ca^{2+} ($r = 0.83$), Mg^{2+} ($r = 0.84$), and SO_4^{2-} ($r = 0.91$) are the same trace elements that have the greatest positive PC 2 loadings (Ti, Ni, Sr, Rh, and Bi). This trend is also consistent with Cl^- (Table 4). These observations suggest that PC 2 describes differences in the trace element

Table 4 Correlation Coefficients for Major Anions, Major Cations, and Trace Elements

	Br⁻	Cl⁻	F⁻	SO₄²⁻	Ca²⁺	Mg²⁺	K⁺	Na⁺
Br⁻	1.00							
Cl⁻	0.14	1.00						
F⁻	-0.16	0.17	1.00					
SO₄²⁻	0.02	0.77	-0.30	1.00				
Ca²⁺	-0.04	0.72	-0.36	0.93	1.00			
Mg²⁺	-0.09	0.64	-0.45	0.93	0.98	1.00		
K⁺	-0.02	0.57	0.69	0.09	0.21	0.04	1.00	
Na⁺	0.07	0.54	0.85	0.04	0.03	-0.10	0.90	1.00
Li	0.00	0.47	0.85	-0.02	-0.00	-0.14	0.91	0.99
Be	-0.05	0.45	0.69	0.02	0.09	-0.03	0.84	0.85
Al	-0.07	-0.24	-0.07	-0.20	-0.25	-0.23	-0.18	-0.16
Ti	0.03	0.78	-0.30	0.98	0.89	0.90	0.05	0.01
V	-0.14	-0.32	-0.12	-0.29	-0.33	-0.30	-0.31	-0.30
Cr	-0.12	0.29	0.32	0.02	0.03	-0.06	0.45	0.37
Mn	0.57	0.45	0.37	0.09	0.13	-0.03	0.68	0.62
Co	0.07	0.42	0.10	0.39	0.45	0.36	0.48	0.31
Ni	-0.05	0.73	-0.20	0.96	0.83	0.84	0.05	0.02
Ga	-0.05	-0.31	0.30	-0.26	-0.43	-0.37	-0.24	0.06
Ge	-0.12	0.25	0.84	-0.14	-0.16	-0.25	0.70	0.84
As	-0.14	-0.36	0.27	-0.35	-0.53	-0.45	-0.29	0.06
Rb	-0.04	0.53	0.73	0.03	0.15	-0.01	0.99	0.91
Sr	-0.03	0.88	-0.09	0.94	0.94	0.90	0.40	0.29
Mo	0.54	-0.02	0.07	-0.20	-0.33	-0.36	-0.04	0.08
Ru	-0.10	0.85	0.36	0.60	0.53	0.47	0.54	0.53
Rh	-0.03	0.86	-0.09	0.91	0.93	0.88	0.38	0.28
Te	0.10	0.83	0.51	0.53	0.47	0.38	0.73	0.79
Cs	-0.03	0.55	0.74	0.03	0.12	-0.03	0.95	0.91
Ba	0.01	0.58	0.57	0.13	0.29	0.14	0.95	0.85
W	-0.17	-0.39	0.17	-0.44	-0.63	-0.52	-0.42	-0.12
Ir	-0.09	0.84	0.27	0.71	0.66	0.59	0.55	0.49
Au	-0.02	0.28	0.42	0.07	0.09	0.03	0.49	0.55
Bi	-0.05	0.81	-0.11	0.93	0.79	0.80	0.13	0.14
U	-0.19	-0.09	-0.33	0.29	0.30	0.40	-0.39	-0.29

chemistry of the groundwater resulting from the aquifer materials through which it has flowed. Most of the NCEWDP groundwaters (9S, 19P, 15P, 3S, 5S, 12PB, 12PA, SD-6, and 1D) were classified as Na + K - HCO₃ waters, consistent with groundwaters that have chemically reacted with felsic volcanic rocks such as the rhyolites and quartz latites (e.g., White et al., 1980). The scores for the majority of these waters plot negatively on PC 2 (Figs. 8 and 9). The Na + K - HCO₃ geochemical facies, defined by the elevated concentrations of Na and K, is consistent with those trace elements that are highly loaded negatively on PC 2 (Li, Be, Ge, Rb, Cs, and Ba). Indeed, the trace elements Ba, Rb, Li, and Ge typically exhibit greater concentrations in granites and shales when compared to limestones (Drever, 1997). The greater concentrations of these trace elements are also consistent with those reported for a group of rocks analyzed from within the study area (Schuraytz and Vogel, 1989; Broxton et al., 1989). Groundwaters from BGW, which have the greatest positive PC 2 scores, are classified as belonging to the Ca + Mg - SO₄²⁻ - HCO₃ hydrochemical facies. This facies is thought to result from mixing of Ca + Mg - HCO₃ water with SO₄²⁻ - HCO₃ water; probably due to the movement of water from carbonate rocks into tuff or tuffaceous alluvium (e.g., Stetzenbach et al., 2001). Groundwaters from 1S and 12PC, also have positive PC 2 scores. These waters are of the Ca + Mg - HCO₃ facies which is representative of valley fill deposits composed in part of carbonate rocks (Winograd and Thordarson, 1975). The concentrations of the trace elements, Sr and Ni, are typically greater in limestone when compared to granites (Drever, 1997). This is not consistent for Ti which is reported as “major” in granites but not in carbonates (Drever, 1997). Titanium, however, is thought to be relatively insoluble in most groundwaters (Middelburg et al., 1988). Only a limited amount of data are available for the other elements with positive PC 2 loadings (Rh and Bi).

A plot of the PC 2 and PC 3 scores is shown in Fig. 10. An additional 13% of the variance is explained in PC 3 suggesting that this component may also capture important information within these data. Each of the samples collected from the same well, with the exception of 1D#1 and 1D#3, cluster together somewhat in PC 3. No distinct clusters within PC3 are observed. The trace elements with the greatest positive PC 3 loadings include Be, Mn, Co, and Ba (Table 3). Those with the greatest negative PC 3 loadings include V, Cr, Ga, As, and W (Table 3). Interestingly, four of the trace elements with negative PC 3 loadings V, Cr, As, and W typically exist as the more soluble oxyanions in oxidizing waters, whereas three of the trace elements with positive PC 3 loadings, Mn, Ba, and Co, may be more soluble in oxygen depleted waters (Hem, 1989). This suggests that PC 3 reflects the oxidizing / reducing conditions within the groundwater. In fact, a strong relationship between PC 3 and the percentage of As(III) is observed (Fig. 11). By examining the trace element data obtained for waters of the NCEWDP, it is apparent that the well containing the highest concentration of reduced arsenic, 1D#3 (Fig. 5), has remarkably high concentrations of Mn, Ba, Be and Co and the lowest concentrations of U, V, W, and Cr. The solubility of Mn, as Mn²⁺, is very high in low pE (reducing) waters and much less so in oxidizing waters. Generally, under oxidizing conditions, manganese will precipitate as Mn(IV) oxide with significant amounts of Co, Pb, Zn, Cu, Ni, and Ba often coprecipitating as well (Hem, 1989). This suggests that the trace elements with the greatest positive PC 3 loadings (Table 3) are those that are most abundant in reducing waters. The trace elements with the greatest negative PC 3 loadings include V, Cr, Ga, As, and W. Because of the tendency

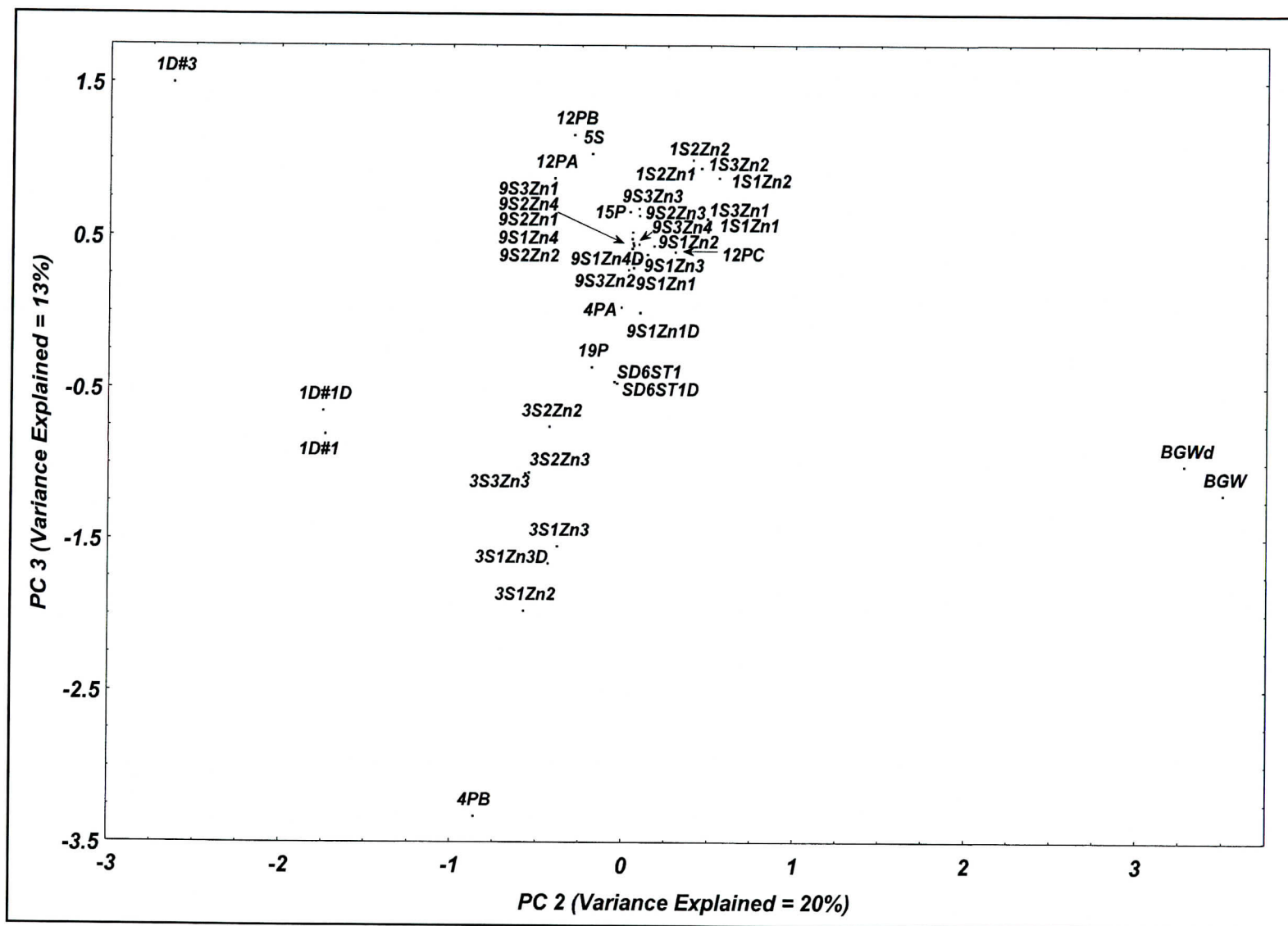


Figure 10 Scores for Principal Components 2 and 3 For Analysis Performed on Subset of 25 Trace Elements

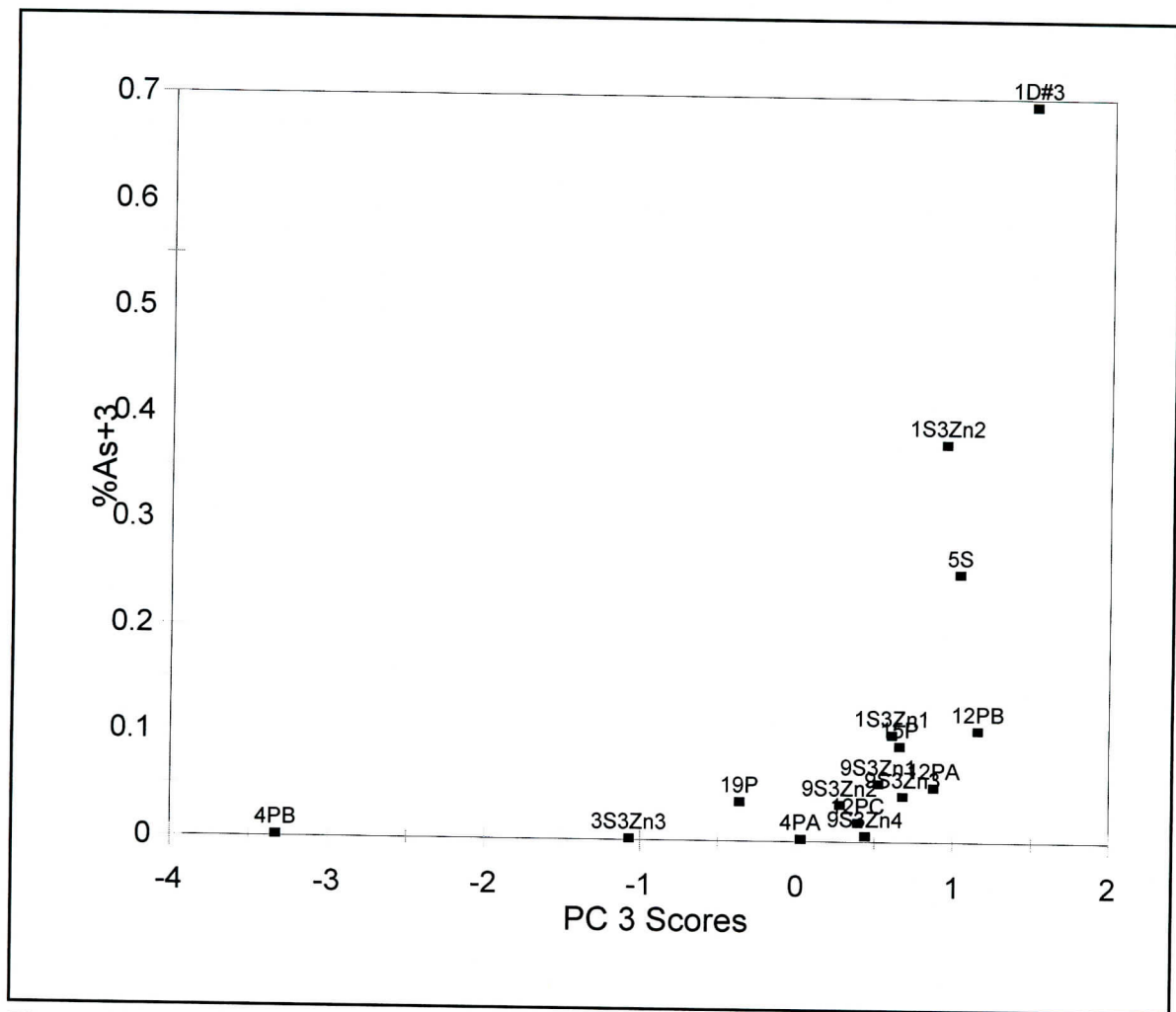


Figure 11 Principal Component Scores for PC 3 Versus Percentage As(III)

to form oxyanions, a fairly high solubility for V, Cr, As, and W is possible in oxidizing alkaline environments (Hem, 1989). In oxidizing, moderate to high pH waters, V is expected to occur in solution as the oxyanion HVO_4^{2-} (Collier, 1984; Jeandel et al., 1987; Shiller and Boyle, 1987; Domagalski et al., 1990). However, under reducing conditions vanadium could occur as the oxycation $\text{V}(\text{OH})_2^+$ (Hem, 1989; Shiller and Boyle, 1987; Domagalski et al., 1990) which would exhibit strong adsorption to the aquifer materials. Also, the less highly oxidized forms of vanadium have relatively low solubilities unless the pH is below about 4.0 (Hem, 1989). Chromium concentrations are generally quite low in anaerobic groundwaters that contain ferrous iron which may reflect reduction of soluble chromate (CrO_4^{2-}) to insoluble chromic ion, Cr^{3+} , by Fe^{2+} (Langmuir, 1997). The redox sensitive element, As, is quite soluble in oxidized groundwaters as an oxyanion such as HAsO_4^{2-} and H_2AsO_4^- , but in reduced waters is incorporated into insoluble minerals (Langmuir, 1997). The predominant form of the trace element W in seawater is WO_4^{2-} which again is also a soluble oxyanion (Hem, 1989).

8.4.2 Q-Mode Factor Analysis

Q-mode factor analysis was performed on the entire data set as well as the data set containing the subset of 25 trace elements used for PCA. No significant differences were observed in the Q-mode results, therefore only the results of the analysis of the subset are described herein. A total of 76% of the variance is explained in factor 1 and 19% is explained in factor 2. The amount of variance explained by the first two Q-mode factors is much greater than that observed using PCA. This is due, in part, to the reduction in the total variance of the similarity matrix that occurs from the row normalization procedure, the variance due to differences in the total concentration of each sample, is removed using this technique. Also, because the similarity matrix consists of row normalized data and is not column normalized, the elements that are present at greater levels will tend to dominate the analysis. The first few factors will therefore typically describe the variance of the trace elements with the greatest concentrations. This is illustrated in the plot of the scores for the first two Q-mode factors shown in Fig. 12, which shows, for example, the greater dominance of Sr and Li in the Q-mode results. These elements are typically much greater in concentration when compared to all others measured (Appendix III). The results of Q-Mode factor analysis are used for corroborating the results of PCA and CA and are not to be used for quality affecting work.

The factor loadings for the first two factors are shown in Fig. 13. As discussed earlier, the Q-mode factor loadings describe the relative proportions of the trace elements in the groundwater samples. Although the concentration of the trace elements in the samples collected from 1D are in general greater than those for most of the samples included in this data set, Q-mode analysis demonstrates that the relative proportions of these elements are similar to those found in the samples from 9S (Fig. 13). Similarly, the samples collected from BGW now plot close to those collected from 1S and 12PC. Three clusters are identified in Figure 13. Cluster 1 contains groundwater samples collected from SD6ST1 and 3S, suggesting that these waters have similar trace element compositions. Samples from 12PA, 4PA, 19P plot within cluster 2 which also contains waters from 9S and 1D. Cluster 3 contains groundwater samples from 1S and BGW. Samples from 4PB, 5S, 12PB, and 15P plot distinct from these three clusters (Fig. 13). No clear separation of the zones within 1S, 3S, or 9S is observed in Fig. 13.

Furthermore, Figure 13 suggests that Factor 1 describes the combined relative proportions of Sr and Li concentrations, whereas Factor 2 separates the groundwaters based on greater proportions of Li (samples with positive factor 2 loadings) and Sr (samples with negative Factor 2 loadings). For instance, the waters contained in cluster 1 (Fig. 13) 1S, BGW, and 12PC plot negatively on Factor 2 and have concentrations of Sr that are 6 to 30 times greater than Li. The waters 3S and SD6ST1 plot positively on Factor 2 and have concentrations of Li that are a factor of 40 to 200 greater than that of Sr. The Li/Sr ratios in waters that plot closest to cluster 2 (4PB and 15P) are roughly 2, whereas those waters with factor 2 loadings around zero have Li/Sr ratios from 0.5 to 1.0. Again, from Table 2, it is clear that Li concentrations are correlated to Na^+ ($r = 0.99$) and K^+ ($r = 0.91$), and Sr concentrations are correlated to Ca^{2+} ($r = 0.94$), Mg^{2+} ($r = 0.90$), and SO_4^{2-} ($r = 0.94$).

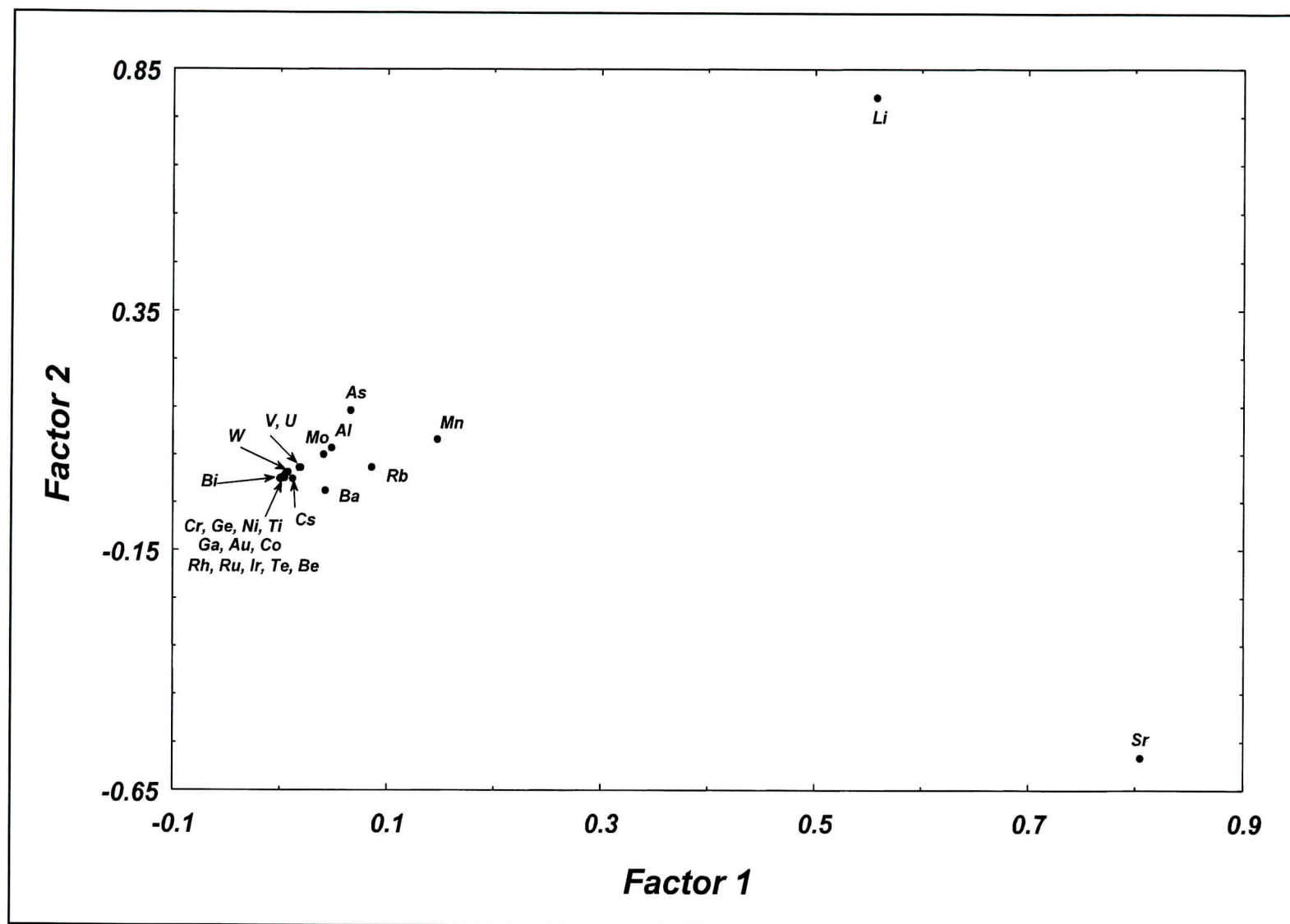


Figure 12 Q-Mode Factor Scores for Factors 1 and 2.

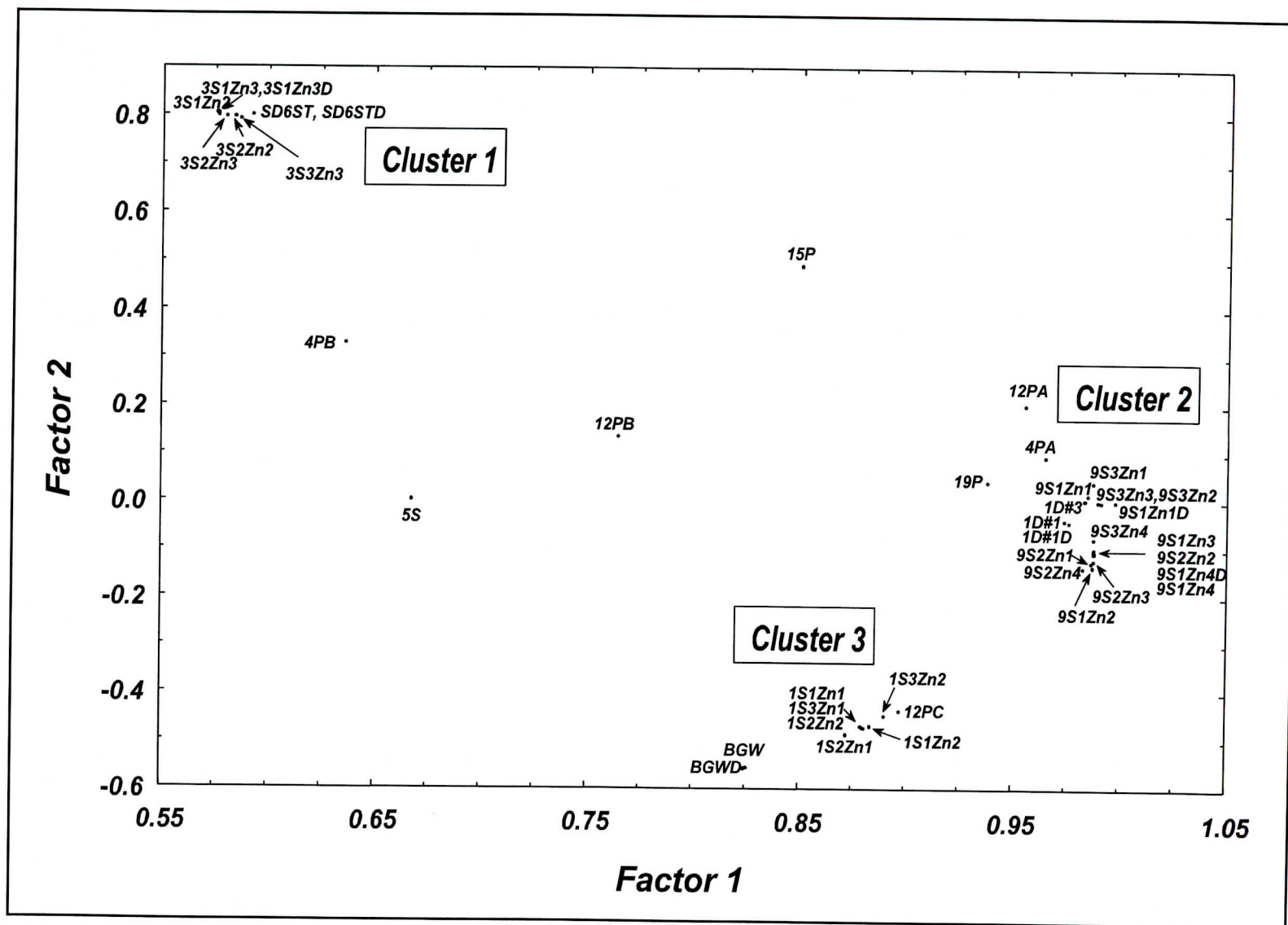


Figure 13 Q-mode Factor Loadings for Factors 1 and 2

8.4.3 Correspondence analysis

Correspondence analysis (CA) may be a superior method for assessing relative similarities in the trace element compositions of groundwater samples. With CA the original data matrix is both row and column normalized. Similar to PCA of the correlation matrix, the effect of order of magnitude differences in the concentrations of the various trace elements are removed. Similarly, the effect of total concentration is removed from the analysis. As with Q-mode analysis, CA will view samples as similar even though significant differences in the total concentration of the trace elements may exist. Instead, CA identifies the trace elements that are dominant within a sample relative to the other samples. Because row and column standardization is performed, both the samples and variables (ie., trace elements) can be plotted on the same graph (Fig. 14). In Fig. 14, samples collected from 1S, 12PC, and BGW, along with the trace elements Ni, Sr, Rh, Ti, and Bi, are contained in one cluster. Interestingly, dimension 2 separates Zones 1 and 2 of the 1S samples. Samples collected from 9S are contained in a relatively tight cluster (Fig. 14). No consistent separation of the four zones is observed for 9S samples. The trace elements that cluster with the 9S samples include Ru, Te, and Ir. The samples collected from the 3S well plot in a relatively tight cluster that is in close proximity to the samples collected from SD6ST1 and 4PB. As with the 1S samples, dimension two separates the two zones, zones 2 and 3, within the 3S well (Fig. 14). The trace elements that plot in the vicinity of these samples (3S, SD6ST1, and 4PB) consist of As, W, Al, V, Cr, Ge, and Mo. The sample collected from 19P lies between the 9S samples and the samples collected from 3S, SD6ST1, and 4PB. Samples collected from 12PB and 5S plot together along with Mn. Samples from 1D and 12PA plot relatively close together. The trace elements that plot in close proximity to these samples (1D and 12PA) include Cs, Co, Ba, Be, and Rb.

The results of the CA are consistent with those obtained using PCA, especially PC 2 and PC 3. With the exception of the 1D waters, the samples are distributed similarly along dimension 1 of the CA results as PC 2. The distribution of samples along dimension 1 of the CA results is also similar to that observed in the Piper diagram (Fig. 2). Waters with greater Ca + Mg (BGW, 1S, and 12PC) plot to the left of the origin in Fig. 14, whereas those with greater Na + K plot to the right. Interestingly, dimension 2 of the CA results is somewhat similar to the scores of PC 3. Waters that plot positively on Dimension 2, 1S3Zn2, 1D, 12PA, 12PB, and 5S also plot positively on PC 3. These waters are thought to be relatively reducing when compared to the others. These results are consistent with those trace elements that plot along with these waters in dimension 2 of the CA results (Mn, Cs, Co, Ba, Rb, and Be); with the exception of Cs and Rb, these trace elements also loaded high positively in PC 3. Similarly, based on the PCA results, the waters of 3S and 4PB were thought to be more oxidizing. This again is consistent with the trace elements that are plotting close to these waters in Fig. 14. Interestingly, U also plots quite negatively on dimension 2 (Fig. 14). In oxidizing environments, highly soluble U(VI) dominates, occurring in solution as the uranyl ion (UO_2^{2+}) and uranyl - carbonate complexes such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. In reducing environments U(VI) is reduced to U(IV) and precipitated (Langmuir, 1997).

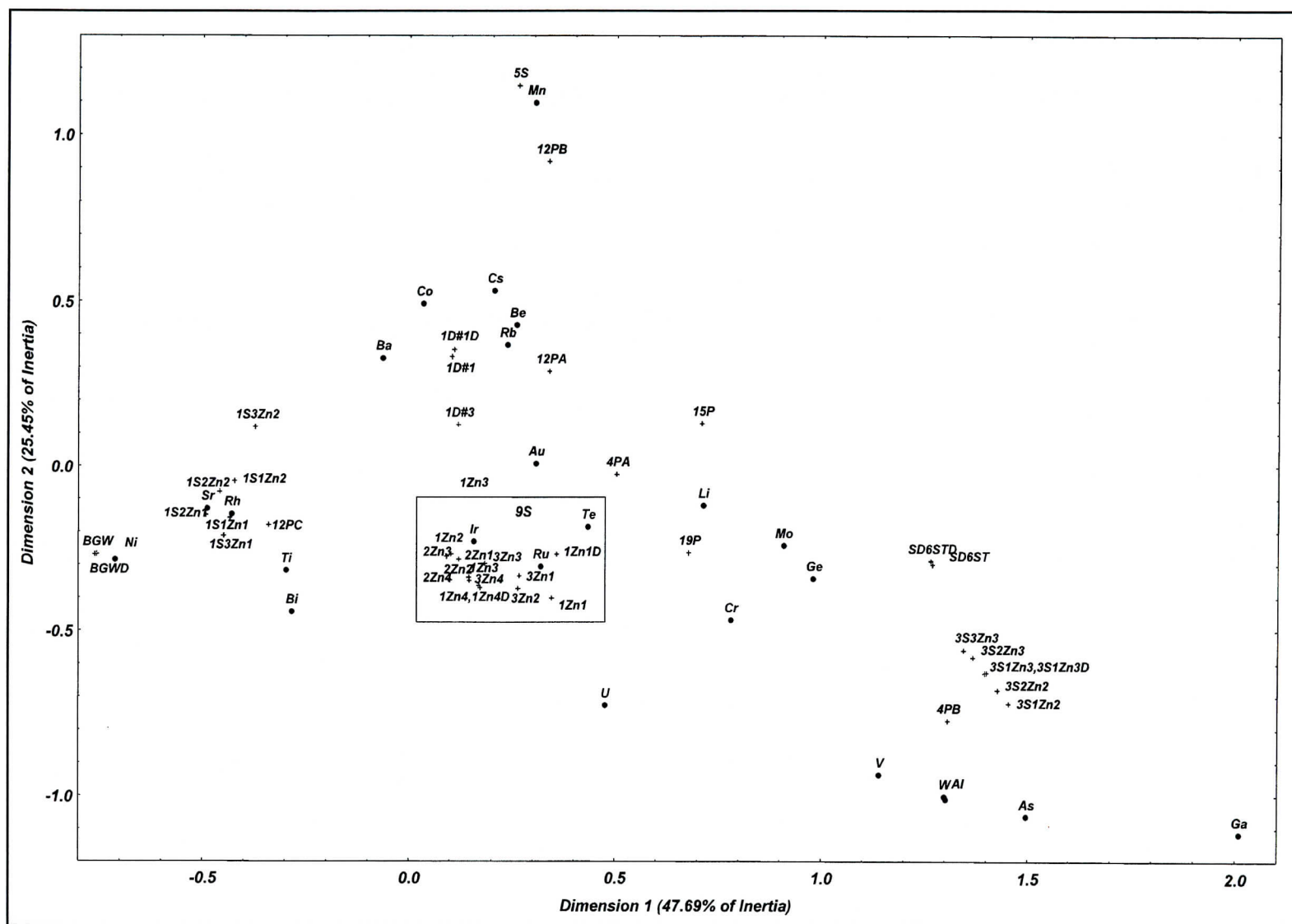


Figure 14 Correspondence Analysis Results for the First Two Dimensions

8.4.4 Cluster Analysis

Hierarchical Cluster Analysis (HCA) was performed on three data sets: 1) the standardized trace element concentrations; 2) the principal component scores; and 3) the results of correspondence analysis. The trace element data were first standardized so that equal contribution of each trace element is maintained and so that the trace elements with significantly greater concentrations (ie., Li and Sr) do not dominate the cluster analysis. HCA was then performed on the standardized data set consisting of the 25 trace elements used also for PCA. Selection of the subset was again performed to eliminate those trace elements that were reported to have lower relative precision between the multiple measurements made on samples collected from the same depth and well when compared to the variability over all samples within the data set. Four clusters are identified in the dendrogram resulting from HCA of the standardized trace element data shown in Fig. 15. Cluster 1 consists of BGW and 1D. The linkage distance between these two wells and the rest of those sampled is large suggesting significant differences in the concentrations of the trace elements in these waters. Also, the linkage distance between 1D and BGW is relatively large indicating substantial differences in trace element concentrations between these samples. Cluster 2 consists of waters collected from 12PA, 12PB, 5S, 3S, 4PB and 19P with sub-clustering of zones 2 and 3 of 3S. Cluster 3 contains waters from SD6ST1, 9S, 15P, and 4PA with no consistent sub-clustering of the four zones within 9S. Cluster 4 consists of 1S and 12PC.

HCA was then performed on the scores for the first three PCs and again four clusters were identified (Fig. 16). Relatively similar clustering was observed for the HCA performed on PC scores as that performed on the standardized data (compare Figs. 15 and 16). For instance, BGW and 1D are included in Cluster 1, 3S and 4PB are included in Cluster 2, SD6ST1, 9S, 15P, and 4PA are included in Cluster 3, and 1S is included in Cluster 4. One difference between these analyses is that 12PB, 12PA, and 5S are included in cluster 2 when the standardized data are used and cluster 4 when clustering was based on the PC scores. Also, groundwater from 19P is included in cluster 2 when the standardized data are used and Cluster 3 when clustering was based on the PC scores.

The results obtained from HCA performed on the results of CA are substantially different than those obtained from the standardized data and PC scores (Fig. 17). Although four clusters were again identified, the samples included in these clusters differ from those discussed above. For example, samples from SD6ST1 cluster with the waters of 3S and 4PB (Cluster 1), samples from 1D cluster with 12PB, 5S, and 15P (Cluster 2) samples from 9S cluster with 19P and 4A (Cluster 3), and BGW clusters with 1S and 12PC (Cluster 4). Sub-clustering of the two zone of 1S and 3S is also observed in Fig. 17.

The variability in the clustering results between the three data sets reflects the different types of approaches used for each analysis. Clustering based on the standardized concentrations compares the concentrations of each of the trace elements in each of the samples, giving each trace element equal weight, and groups those samples with the most similar overall trace

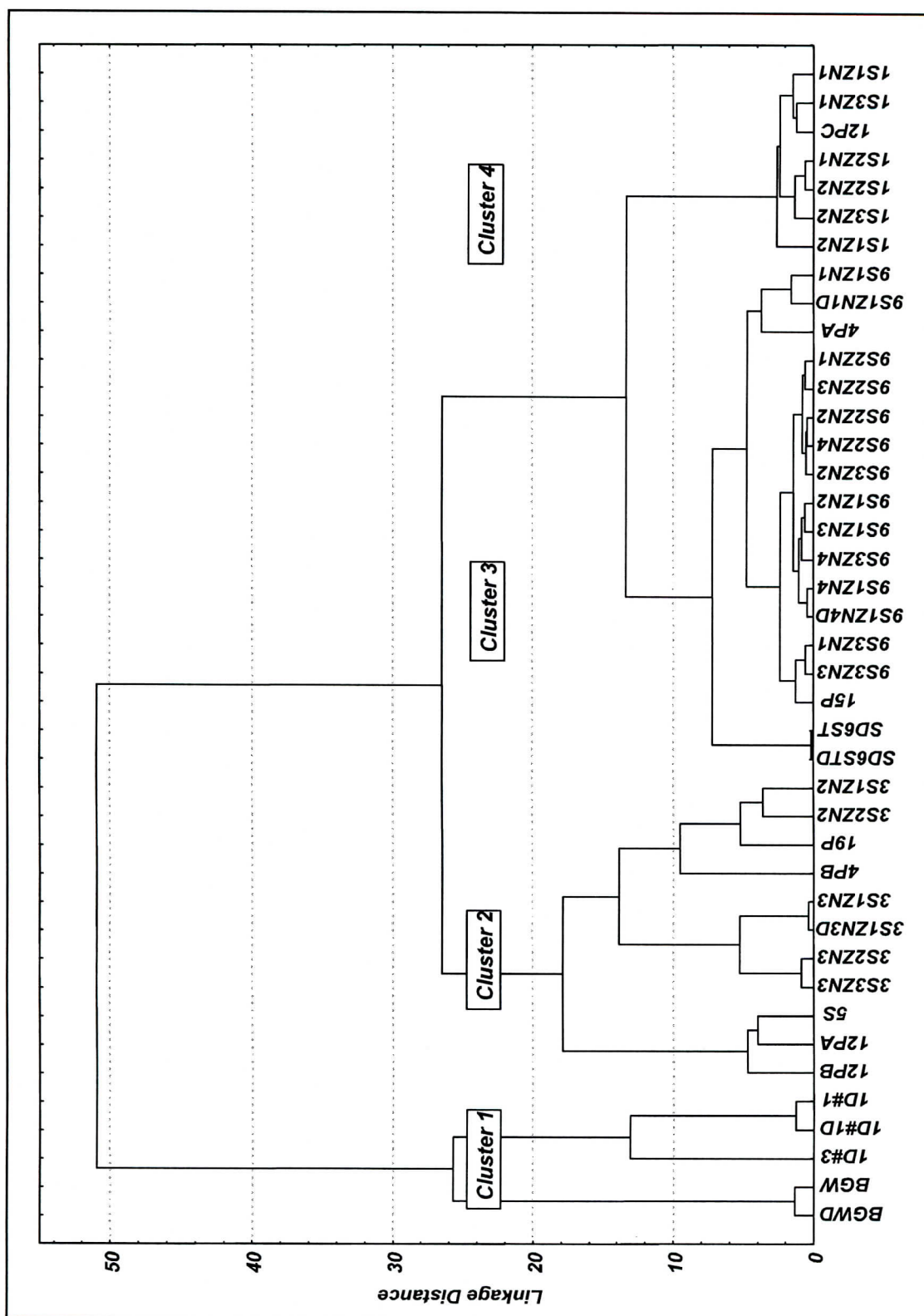


Figure 15 Results of Hierarchical Cluster Analysis Performed on Standardized Trace Element Concentrations

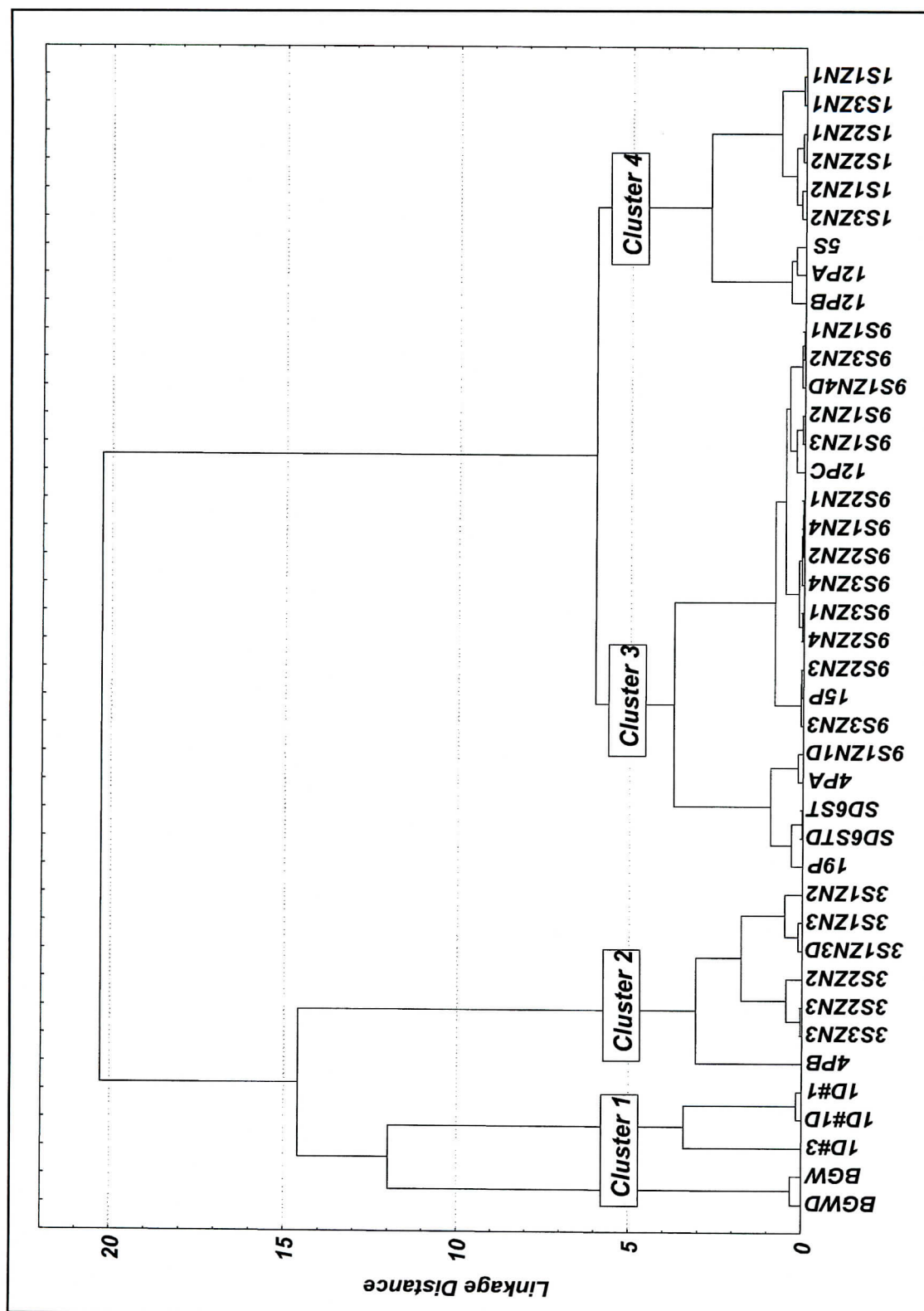


Figure 16 Results of Hierarchical Cluster Analysis Performed on Principal Component Scores

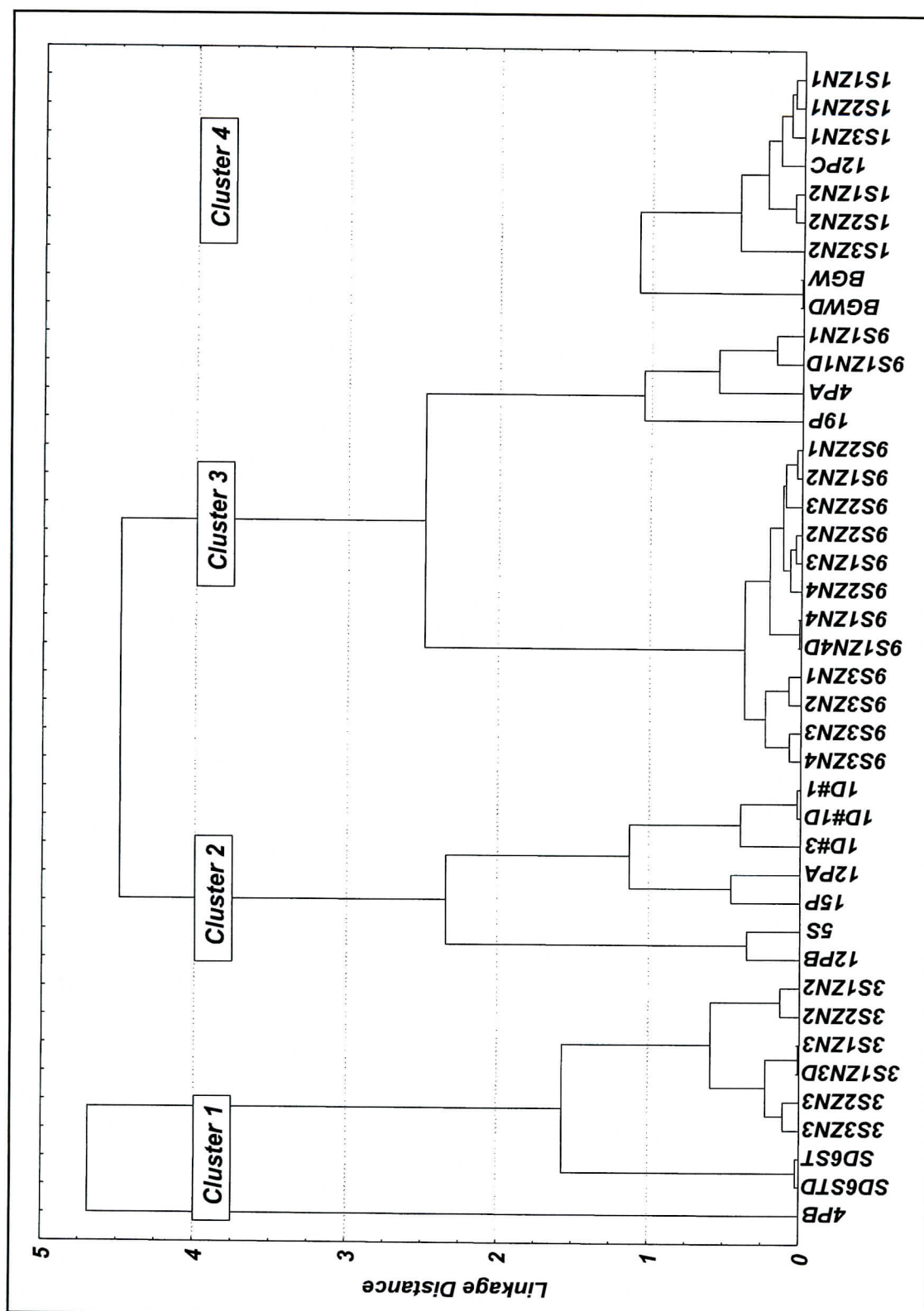


Figure 17 Results of Hierarchical Cluster Analysis Performed on Correspondence Analysis Loadings.

element chemistry. Clustering based on the PCA results instead focuses on the similarities in the trace element chemistry in the samples based on the different geochemical processes described in the first three principal components. For instance, PC 1 explains the overall differences in the total concentration of the trace elements within the samples. For example, the deeper, more mature groundwaters (BGW and 1D), with greater overall trace element concentrations, are separated from those that are more dilute. PC 2 reflects the composition of the trace elements resulting from the different aquifer materials through which it has flowed, and PC 3 reflects the oxidizing / reducing conditions within the groundwater/aquifer system. Cluster analysis performed on the PC scores therefore groups the groundwater samples based on similarities in the trace element chemistry resulting from these processes. Correspondence analysis, on the other hand, removes the differences due to the total concentration of the trace elements within the samples. Instead, cluster analysis performed on these data results in clustering of groundwater samples based on similarities in the trace elements that are dominant in the waters. Because the trace elements within the groundwaters are thought to evolve along a flow path, dissolving trace elements present within the aquifer materials, it is also important to evaluate the proportions of the trace elements within these waters and not only the absolute concentrations; groundwater along a flow path may be similar in composition but considerably different in the overall concentration of the trace elements (ie., more concentrated).

9. Conclusions

Most of the groundwaters (9S, 19P, 15P, 3S, 5S, 4PB, 12PB, 12PA, SD6ST1, and 1D) are Na + K - HCO₃ waters (Fig. 2) which is consistent with groundwaters that have chemically reacted with felsic volcanic rocks such as the rhyolites and quartz latites of the Timber Mountain Caldera Complex (White, 1979; White et al., 1980).

Groundwaters from 1S and the nearby well, 12PC, are classified as Ca + Mg - HCO₃ waters (Fig. 2). The chemical difference in the more shallow 12PC water, as well as the slightly lower overall concentrations of major solutes when compared to the deeper waters of 12PA and 12PB (Fig 2b), suggest that the 12P wells could be recording the chemical evolution of groundwaters infiltrating downward from shallower regions in the alluvial fill deposits. In this case, shallow and relatively more dilute Ca + Mg - HCO₃ waters could evolve towards Na + K - HCO₃ waters via chemical reactions with aquifer rocks including cation exchange processes, with the waters becoming more concentrated as the residence time in the system is increased.

The groundwaters collected from the four screened intervals of 9S are chemically quite similar (Fig. 3). The groundwaters from the deeper portions of the well, and which react chemically with Tertiary volcanic rocks, exhibit essentially identical major solute chemistry that is also consistent with the chemical composition of the felsic volcanic rocks with which they interact (see White et al., 1980). Relatively higher SO₄ + Cl is observed in the shallower screened interval of well 9S (zone 1) suggesting the presence of evaporite minerals within the alluvial deposits that are not present at depth within the volcanic rocks.

Groundwater from 4PA is classified as Na + K - SO₄ + Cl water (Fig. 2a). It is possible that the relatively higher concentration of SO₄ + Cl of 4PA water could reflect reactions with evaporite minerals.

Groundwater from BGW is classified as a Ca + Mg - SO₄ + HCO₃ water (Fig. 2a) suggesting that the groundwater from this well is more mature and represents a mixing of Ca + Mg - HCO₃ water with SO₄ + HCO₃ water. This is probably due to the movement of water from carbonate rocks into tuff or tuffaceous alluvium. The relatively higher concentrations of Ca and SO₄ in this water indicates a source of gypsum or other hydrothermally deposited minerals.

1D water is the most concentrated of all of the NCEWDP well waters (Fig. 2b) which could reflect a greater age for these deep groundwaters compared to the other waters sampled in this study.

The trends observed in the major solute concentrations in the groundwater of the NCEWDP were also apparent in the results of the multivariate statistical analyses of the trace element data. For instance, the higher concentration, and possibly more mature, groundwaters of BGW and 1D were separated from the more dilute waters using PC 1 (Fig. 8). PC 2, on the other hand, appears to describe differences in the trace element chemistry of the groundwaters resulting from the aquifer materials through which it has flowed. The majority of the NCEWDP groundwaters that were classified as Na + K - HCO₃ waters (9S, 19P, 15P, 3S, 5S, 12PB, 12PA, SD-6, and 1D), plot negatively on PC 2 (Figs. 8 and 9). The Na + K - HCO₃ geochemical facies, defined by the elevated concentrations of Na and K, is consistent with those trace elements that are highly loaded negatively on PC 2 (Li, Be, Ge, Rb, Cs, and Ba). In fact, these trace elements show a relatively high correlation to Na and K (Table 4). The concentrations of the trace elements Ba, Rb, Li, and Ge are typically greater in granites and shales when compared to limestones (Drever, 1997) and thus would be expected to dominate in waters that have reacted with felsic volcanic rocks. Groundwaters plotting positive on PC 2 (Figs. 8 and 9) appear to be associated with carbonate rocks or valley fill deposits composed in part of carbonate rocks. Groundwaters from BGW, which have the greatest positive PC 2 scores, are classified as belonging to the Ca + Mg - SO₄ - HCO₃ hydrochemical facies. Groundwaters from 1S and 12PC, also have positive PC 2 scores and are classified as Ca + Mg - HCO₃ waters. The trace elements that are highly loaded positively on PC 2 (Ti, Ni, Sr, Rh, and Bi) also have the greatest correlations with Ca, Mg, and SO₄. The concentrations of the trace elements Sr and Ni are typically greater in limestone when compared to granites (Drever, 1997).

Significant amounts of As(III), relative to As(V), suggest a reducing environment in the groundwaters of 1D, 1S2 (1S3Zn2), and 5S and to a lesser degree in the waters of 1S1 (1S3Zn1), 12PB, 15P (Fig. 5). The opposite is true for 3S3 (3S3Zn3), 4PB, 4PA, and 9S4 (9S3Zn4). As(III) and As(V) data are reported for only the May 2000 samples (Table 2). Interestingly, a strong relationship between PC3 and the percentage of As(III) was observed suggesting that PC 3 reflects the oxidizing / reducing conditions within the groundwater (Fig. 11). Four of the trace elements with negative PC 3 loadings V, Cr, As, and W typically exist as the more soluble oxyanions in oxidizing waters, whereas three of the trace elements with

positive PC 3 loadings, Mn, Ba, and Co, may be more soluble in oxygen depleted waters (Hem, 1989). The well containing the highest concentration of reduced arsenic, 1D#3 (Fig. 5), has remarkably high concentrations of Mn, Ba, Be and Co and the lowest concentrations of U, V, W, and Cr. The solubility of Mn, as Mn^{2+} , is very high in low pE (reducing) waters and much less so in oxidizing waters.

With the exception of the 1D waters, the samples are distributed similar to PC 3 along dimension 1 of the CA results. Waters with greater Ca + Mg (BGW, 1S, and 12PC) plot to the left of the origin in Fig. 14, whereas those with greater Na + K plot to the right. Waters that plot positively on Dimension 2, 1S3Zn2, 1D, 12PA, 12PB, and 5S also plot positively on PC 3. These waters are thought to be relatively reducing when compared to the others. These results are consistent with those trace elements that plot along with these waters in dimension 2 of the CA results (Mn, Cs, Co, Ba, Rb, and Be); with the exception of Cs and Rb, these trace elements also loaded high positively in PC 3. Similarly, based on the PCA results, the waters of 3S and 4PB were thought to be more oxidizing. This again is consistent with the trace elements that are plotting close to these waters in Fig. 14. Interestingly, U also plots quite negatively on dimension 2 (Fig. 14). In oxidizing environments, highly soluble U(VI) dominates, occurring in solution as the uranyl ion (UO_2^{2+}) and uranyl-carbonate complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. In reducing environments U(VI) is reduced to U(IV) and precipitated.

From the results of the cluster analyses, it is clear that the concentrations of the trace elements within the samples from BGW and 1D are quite different from the other waters of the NCEWDP and also from each other (Figs 15 and 16). These samples have much greater concentrations of many of the trace elements. Compositionally, the waters of BGW appear to be similar to those of 1S and 12PC (Fig. 17). The composition of the trace elements in groundwater samples from 1D appear to be similar to those of 12PB, 5S, 15P, and 12PA (Fig. 17). Interestingly, these waters also have a greater percentage of As(III) than most of the others (Fig. 5). It appears that this cluster consists of more reducing waters in a volcanic aquifer. Although a greater percentage of As(III) was also measured in 1S, the composition of trace elements in these waters differs from those of 1D, 12PB, 5S, 15P, and 12PA.

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APPENDIX I

Data Tracking and Accession
Numbers for Well Data

Well	Depth(ft) YMP DTN	Lithology YMP DTN
NC-EWDP-1S	MO0110NYE03832.082	MO0007NYE01275.009
NC-EWDP-3S (Zone 3)	MO0110NYE03842.084	MO0007NYE01320.011
NC-EWDP-4PA	MO0009NYE01521.034	MO0007NYE01520.016
NC-EWDP-4PB	MO0009NYE01551.035	MO0007NYE01550.019
NC-EWDP-5S	MO0110NYE03844.085	MO0007NYE01237.006
NC-EWDP-9SX	MO0110NYE03846.086	MO0007NYE01331.013
NC-EWDP-12PA	MO0009NYE02661.038	MO0007NYE02679.027
NC-EWDP-12PB	MO0009NYE02662.039	MO0007NYE02703.029
NC-EWDP-12PC	MO0009NYE02663.040	MO0007NYE02566.025
NC-EWDP-15P	MO0009NYE02710.042	MO0007NYE01826.022
NC-EWDP-19P	MO0009NYE02709.041	MO0007NYE02224.023
NC-EWDP-1DX	MO0110NYE03828.081	MO0007NYE01310.015
SD6ST1	SNF40060298001.001	SNF40060298001.001

Well	Depth(ft) YMP Accession Number	Lithology YMP Accession Number
Bond Gold Well #13	MOL.19961209.0058	
SD6ST1	MOL.19991202.0307	MOL.19991202.0307

APPENDIX II

Major Anion and Cation Concentrations

Well	Zone	*DTN DID	Sample Date	SPC Code (Anions)	SPC Code (Cations)	Br ⁻ (ppm)	Cl ⁻ (ppm)	F ⁻ (ppm)	NO ₃ ⁻ (ppm)	SO ₄ ⁻² (ppm)	PO ₄ ⁻³ (ppm)	Ca ⁺² (ppm)	Mg ⁺² (ppm)	K ⁺ (ppm)	Na ⁺ (ppm)
NC-EWDP-1S	1	1	5/18/99	00556343	00553679	<0.05	16.1	0.63	3.44	129	<0.2	62.3	30.5	8.81	72.6
NC-EWDP-1S	1	2	11/08/99	00556184	00556183	<0.06	14.5	0.59	3.19	133	<0.1	55.9	31.0	8.47	74.3
NC-EWDP-1S	1	3	5/19/00	00556048	00556047	<0.05	15.3	0.65	3.61	126	<0.3	59.4	30.11	8.26	70.9
NC-EWDP-1S	2	1	5/17/99	00556341	00553523	<0.05	15.9	0.62	2.85	127	<0.2	61.8	31.2	8.70	71.0
NC-EWDP-1S	2	2	11/08/99	00556177	00556176	<0.06	14.7	0.59	2.63	128	<0.1	53.7	31.2	8.62	72.5
NC-EWDP-1S	2	3	5/18/00	00556058	00556057	<0.05	15.6	0.65	2.59	120	<0.3	56.4	30.0	8.16	69.0
NC-EWDP-3S	2	1	5/20/99	00556352	00553662	<0.05	23.6	2.73	1.47	47.5	<0.2	0.62	<0.25	3.57	128
NC-EWDP-3S	2	2	11/15/99	00556144	00556143	<0.06	12.6	2.72	1.77	49.2	<0.1	0.55	0.08	2.99	121
NC-EWDP-3S	3	1	5/20/99	00556353	00553603	<0.05	8.70	3.47	0.04	48.3	<0.2	0.85	<0.25	3.02	137
NC-EWDP-3SD	3	1	5/20/99	00556354	00553521	<0.05	8.66	3.45	0.04	48.4	<0.2	0.95	<0.25	3.05	137
NC-EWDP-3S	3	2	11/15/99	00556138	00556137	<0.06	11.4	3.25	<0.1	48.5	<0.1	0.69	0.09	2.77	146
NC-EWDP-3S	3	3	5/17/00	00556286	00556285	<0.05	9.74	3.45	<0.1	47.1	<0.3	0.83	0.09	2.78	142
NC-EWDP-9S	1	1	5/19/99	00556347	00553670	<0.05	28.5	1.97	0.53	36.8	<0.2	6.90	3.21	4.18	76.0
NC-EWDP-9SD	1	1	5/19/99	00556348	00553668	<0.05	23.9	2.05	3.47	53.2	<0.2	15.0	4.37	5.11	84.1
NC-EWDP-9S	1	2	11/10/99	00556171	00556170	<0.06	14.0	1.97	3.52	58.3	<0.1	16.7	6.00	6.08	78.4
NC-EWDP-9S	1	3	5/20/00	00556291	00556290	<0.05	16.1	1.79	1.84	49.4	<0.3	11.3	4.31	5.62	79.4
NC-EWDP-9S	2	1	5/19/99	00556349	00553663	<0.05	11.1	2.02	2.89	58.8	<0.2	19.3	7.57	4.49	79.6
NC-EWDP-9S	2	2	11/10/99	00556164	00556163	<0.06	9.85	2.04	3.56	61.7	<0.1	17.6	7.38	3.98	78.1
NC-EWDP-9S	2	3	5/20/00	00556043	00556042	<0.05	10.0	1.97	3.57	55.9	<0.3	13.1	7.63	3.84	75.9
NC-EWDP-9S	3	1	5/19/99	00556350	00553677	<0.05	9.90	2.05	3.26	59.0	<0.2	19.8	7.28	3.94	79.2
NC-EWDP-9S	3	2	11/09/99	00556157	00556156	<0.06	9.63	2.10	2.41	55.9	<0.1	15.5	7.11	3.71	77.8
NC-EWDP-9S	3	3	5/19/00	00556035	00556034	<0.05	10.1	1.96	1.82	49.3	<0.3	14.0	6.12	3.60	73.2
NC-EWDP-9S	4	1	5/18/99	00556344	00553664	<0.05	9.68	2.01	3.28	59.2	<0.2	20.9	7.24	3.70	77.9
NC-EWDP-9SD	4	1	5/18/99	00556345	00556358	<0.05	9.67	2.01	3.29	61.5	<0.2	19.5	7.18	3.69	76.3
NC-EWDP-9S	4	2	11/09/99	00556150	00556149	<0.06	9.55	2.11	3.43	62.3	<0.1	17.9	7.31	3.5	77.0
NC-EWDP-9S	4	3	5/19/00	00556281	00556280	<0.05	9.92	1.97	3.57	57.3	<0.3	19.1	7.17	3.46	74.6
NC-EWDP-1D	1	1	5/24/99	00556356	00553678	<0.05	47.4	6.13	0.04	115	<0.2	44.5	11.2	66.6	318
NC-EWDP-1DD	1	1	5/24/99	00556357	00553669	<0.05	48.4	6.11	0.04	115	<0.2	45.0	11.4	66.2	318
NC-EWDP-1D	3	3	5/25/00	00555961	00556338	<0.05	37.9	6.06	<0.1	111	<0.3	38.1	10.2	57.6	330
SD6ST1	1	1	6/15/99	00553659	00553676	<0.05	6.45	3.75	5.77	25.7	<0.2	0.42	<0.006	1.51	92.0
SD6ST1D	1	1	6/15/99	00553657	00553675	<0.05	6.41	3.79	5.83	25.7	<0.2	0.38	<0.006	1.47	91.7
Bond Gold13	1	1	7/19/99	00553613	00553612	0.18	59.9	0.57	0.49	614	<0.2	146	82.4	6.63	93.6
Bond Gold13D	1	1	7/19/99	00553614	00553610	0.17	60.2	0.56	0.50	618	<0.2	146	82.5	6.79	95.1
NC-EWDP-12PA	3	3	5/22/00	00556053	00556052	<0.05	14.3	3.21	2.10	99.3	<0.3	28.1	7.65	25.8	141
NC-EWDP-12PB	3	3	5/22/00	00555957	00555956	<0.05	14.3	3.15	1.97	101	<0.3	29.2	7.80	25.6	135
NC-EWDP-12PC	3	3	5/22/00	00556007	00556006	<0.05	14.8	0.98	3.48	118	<0.3	52.2	25.6	9.87	70.4
NC-EWDP-15P	3	3	5/23/00	00556203	00556202	<0.05	8.87	2.21	5.05	42.2	<0.3	10.1	2.33	3.28	83.9
NC-EWDP-19P	3	3	5/23/00	00556002	00556001	<0.05	7.87	1.62	5.14	23.0	<0.3	14.1	0.88	3.94	42.6
NC-EWDP-4PA	3	3	5/15/00	00556031	00556030	<0.05	7.33	1.20	6.42	52.8	<0.3	9.60	0.27	2.81	55.8
NC-EWDP-4 PB	3	3	5/26/00	00556271	00556270	<0.05	5.39	1.59	3.72	34.0	<0.3	5.68	0.04	1.67	69.7
NC-EWDP-5S	3	3	5/17/00	00556276	00556275	0.21	32.5	0.94	1.68	124	<0.3	22.4	2.68	8.83	142

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

APPENDIX III

Rare Earth Element Concentrations

Well	Zone	*DTN	Sample Date	SPC Code	La (ppt)	Ce (ppt)	Pr (ppt)	Nd (ppt)	Sm (ppt)	Eu (ppt)	Gd (ppt)	Tb (ppt)	Dy (ppt)	Ho (ppt)	Er (ppt)	Tm (ppt)	Yb (ppt)	Lu (ppt)
NC-EWDP-1S	1	1	5/18/99	00553556	4.3	4.6	0.40	1.6	0.33	0.01**	0.62	0.12	1.1	0.34	1.4	0.26	1.9	0.37
NC-EWDP-1S	1	2	11/08/99	00556182	1.4**	1.4**	0.03**	0.23	0.12	0.07	0.05	0.01**	0.12	0.04	0.19	0.02**	0.28	0.05
NC-EWDP-1S	1	3	5/19/00	00556046	4.1	7.8	0.30	1.2	0.24	0.03**	0.39	0.09	0.63	0.21	0.78	0.15	0.92	0.20
NC-EWDP-1S	2	1	5/17/99	00553555	2.9**	3.8	0.15	0.57	0.12	0.02**	0.18	0.04**	0.24	0.07	0.30	0.06	0.41	0.09
NC-EWDP-1S	2	2	11/08/99	00555916	3.5	3.6	0.11	0.41	0.13	0.03**	0.25	0.27	0.50	0.51	0.79	1.0	1.6	1.7
NC-EWDP-1S	2	3	5/18/00	00556056	2.5**	2.1**	0.04**	0.16	0.05	0.02**	0.07	0.01**	0.11	0.04	0.19	0.03**	0.22	0.04
NC-EWDP-3S	2	1	5/20/99	00553551	20	70	3.5	13	3.7	0.48	6.2	1.3	9.5	2.3	7.8	1.3	8.6	1.4
NC-EWDP-3S	2	2	11/15/99	00556142	10	17	1.2	4.7	1.4	0.05	2.1	0.49	3.5	0.87	2.8	0.47	3.3	0.60
NC-EWDP-3S	3	1	5/20/99	00553554	13	34	0.57	3.0	0.66	0.22	1.1	0.22	1.7	0.40	1.3	0.15	1.0	0.14
NC-EWDP-3SD	3	1	5/20/99	00553552	9.3	33	0.54	2.8	0.64	0.17	1.1	0.22	1.6	0.39	1.2	0.14	0.95	0.13
NC-EWDP-3S	3	2	11/15/99	00556136	5.5	14	1.4	5.9	2.5	0.05	4.1	0.89	6.0	1.3	3.7	0.57	3.5	0.48
NC-EWDP-3S	3	3	5/17/00	00556284	4.4	15	1.3	5.3	2.1	0.14	3.2	0.85	5.6	1.2	3.3	0.50	3.1	0.45
NC-EWDP-9S	1	1	5/19/99	00553550	13	21	2.1	7.6	1.6	0.20	2.1	0.29	1.7	0.38	1.1	0.16	0.91	0.15
NC-EWDP-9SD	1	1	5/19/99	00553542	35	47	7.5	28	5.7	0.69	7.0	1.1	5.9	1.3	3.7	0.53	3.1	0.47
NC-EWDP-9S	1	2	11/10/99	00556169	4.7	7.5	0.79	2.9	0.64	0.19	0.77	0.11	0.72	0.17	0.53	0.07	0.49	0.06
NC-EWDP-9S	1	3	5/20/00	00556289	6.1	11	1.1	4.0	0.89	0.15	0.95	0.15	1.02	0.23	0.71	0.10	0.63	0.10
NC-EWDP-9S	2	1	5/19/99	00553541	6.2	8.6	0.83	3.0	0.61	0.08	0.82	0.13	0.85	0.22	0.68	0.10	0.69	0.11
NC-EWDP-9S	2	2	11/10/99	00556162	2.4**	3.1	0.87	3.2	0.70	0.10	0.90	0.14	0.91	0.20	0.69	0.10	0.64	0.09
NC-EWDP-9S	2	3	5/20/00	00556041	5.3	6.7	0.76	2.9	0.65	0.09	0.72	0.13	0.85	0.22	0.70	0.11	0.69	0.12
NC-EWDP-9S	3	1	5/19/99	00553549	4.1	5.8	0.58	2.1	0.49	0.03**	0.69	0.11	0.76	0.20	0.68	0.11	0.73	0.12
NC-EWDP-9S	3	2	11/09/99	00556155	2.3**	2.3**	0.25	0.9	0.23	0.14	0.30	0.05	0.34	0.08	0.25	0.04	0.25	0.03
NC-EWDP-9S	3	3	5/19/00	00555935	2.6**	3.6	0.27	1.0	0.27	0.03**	0.35	0.07	0.46	0.12	0.40	0.06	0.39	0.07
NC-EWDP-9S	4	1	5/18/99	00553544	4.0	6.1	0.99	3.6	0.77	0.02**	1.0	0.17	1.1	0.26	0.84	0.14	0.87	0.14
NC-EWDP-9SD	4	1	5/18/99	00553545	4.7	8.9	1.4	4.1	0.69	0.02**	1.0	0.16	1.0	0.27	0.84	0.13	0.82	0.14
NC-EWDP-9S	4	2	11/09/99	00556148	2.7**	3.3	0.37	1.5	0.38	0.07	0.57	0.09	0.63	0.13	0.41	0.06	0.38	0.05
NC-EWDP-9S	4	1	5/19/00	00556279	3.0**	3.2	0.34	1.5	0.37	0.01**	0.58	0.10	0.72	0.18	0.56	0.08	0.54	0.09
NC-EWDP-1D	1	1	5/24/99	00553547	11	7.7	0.03**	0.11	0.02**	0.004**	0.04	0.004**	0.07	0.04**	0.30	0.07	0.71	0.14
NC-EWDP-1DD	1	1	5/24/99	00553548	8.7	5.6	0.05	0.22	0.04	0**	0.05	0.01**	0.08	0.04	0.35	0.08	0.83	0.18
NC-EWDP-1D	1	1	5/25/00	00556337	3.5	1.4**	0.09	0.36	0.11	0.004**	0.20	0.04	0.44	0.14	0.59	0.11	0.81	0.13
SD6ST1	1	1	6/15/99	00553535	2.1**	11	0.21	0.84	0.15	0.01**	0.27	0.01**	0.16	0.01**	0.10	0**	0.09	0**
SD6ST1D	1	1	6/15/99	00553536	2.5**	11	0.23	0.91	0.16	0.01**	0.27	0.01**	0.18	0.01**	0.11	0**	0.10	0**
Bond Gold13	1	1	7/19/99	00553688	1.5**	1.4**	0.03**	0.15	0.05	0.02**	0.08	0.01**	0.11	0.03**	0.13	0.01**	0.16	0.02**
Bond Gold13D	1	1	7/19/99	00553690	2.3**	1.9**	0.02**	0.17	0.05	0.01**	0.06	0**	0.07	0.01**	0.08	0.01**	0.10	0.02**
NC-EWDP-12PB	3	1	5/22/00	00555955	1.7**	4.5	0.18	0.69	0.12	0.02**	0.17	0.03**	0.19	0.05	0.17	0.03**	0.22	0.04
NC-EWDP-12PC	3	1	5/22/00	00556005	2.1**	4.1	0.14	0.66	0.13	0.02**	0.20	0.16	0.28	0.09	0.35	0.06	0.46	0.22
NC-EWDP-12PA	3	1	5/22/00	00556051	4.5	2.4**	0.09	0.32	0.09	0.03**	0.09	0.02**	0.13	0.03**	0.12	0.02**	0.13	0.03**
NC-EWDP-15P	3	1	5/23/00	00556204	2.8**	4.2	0.18	0.64	0.14	0.01**	0.16	0.02**	0.15	0.04**	0.13	0.02**	0.13	0.02**
NC-EWDP-19P	3	1	5/23/00	00556000	21	33	3.6	13	2.8	0.53	3.2	0.50	2.8	0.61	1.8	0.25	1.67	0.26
NC-EWDP-4 PB	3	1	5/26/00	00556269	8.1	12	1.6	5.7	1.2	0.23	1.2	0.20	1.2	0.24	0.68	0.10	0.69	0.12
NC-EWDP-4PA	3	1	5/15/00	00555937	30	33	4.9	17	3.6	0.84	3.8	0.60	3.2	0.70	1.9	0.28	1.54	0.25
NC-EWDP-5S	3	1	5/17/00	00556274	4.3	10	0.09	0.35	0.09	0.04	0.12	0.03**	0.12	0.03**	0.08	0.01**	0.09	0.02**
Method Detection Limits (MDL)					3.5	2.7	0.04	0.04	0.03	0.04	0.03	0.04	0.04	0.04	0.03	0.03	0.04	0.03

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

**Value is below the MDL

APPENDIX IV

Trace Element Concentrations

Well	Zone	*DTN	Sample Date	SPC Code	Concentration (ppb)										
					Li	Al	Ti	V	Cr	Mn	Ni	Cu	Zn	Ge	As
NC-EWDP-1S	1	1	5/18/99	00553556	78.4	4.24	1.35	2.50	0.38	29.4	1.85	1.35	32.6	0.57	7.08
NC-EWDP-1S	1	2	11/08/99	00556182	69.4	3.13	1.16	1.11	0.07	25.5	0.63	0.25	53.8	0.48	1.57
NC-EWDP-1S	1	3	5/19/00	00556046	73.5	2.97	2.18	2.35	0.32	10.6	0.68	0.36	17.1	0.55	5.91
NC-EWDP-1S	2	1	5/17/99	00553555	78.5	4.63	1.51	1.44	0.13	60.4	1.88	1.43	15.0	0.55	1.90
NC-EWDP-1S	2	2	11/08/99	00555916	74.6	2.97	1.13	0.57	0.09	45.7	0.43	0.24	30.7	0.48	0.60
NC-EWDP-1S	2	3	5/18/00	00556056	75.2	2.99	2.08	0.52	0.01	99.9	0.69	0.34	17.5	0.40	0.29
NC-EWDP-3S	2	1	5/20/99	00553551	191	7.58	0.78	11.0	1.23	0.99	0.13	2.85	5.69	1.27	37.6
NC-EWDP-3S	2	2	11/15/99	00556142	171	6.80	0.49	5.34	0.45	1.74	0.05	0.19	2.93	1.43	33.9
NC-EWDP-3S	3	1	5/20/99	00553554	259	7.79	0.49	2.05	0.07	6.94	0.05	2.49	3.26	3.54	46.0
NC-EWDP-3SD	3	1	5/20/99	00553552	276	8.18	0.39	2.07	0.07	6.99	0.04	2.48	3.60	3.72	48.5
NC-EWDP-3S	3	2	11/15/99	00556136	268	6.19	0.47	1.03	0.05	1.05	0.03	0.08	1.77	3.16	36.4
NC-EWDP-3S	3	3	5/17/00	00556284	258	9.54	0.70	0.65	0.01	1.88	0.11	0.15	0.14**	3.52	29.9
NC-EWDP-9S	1	1	5/19/99	00553550	65.8	8.72	0.88	0.89	0.18	1.47	0.50	1.65	8.31	0.34	4.09
NC-EWDP-9SD	1	1	5/19/99	00553542	78.2	13.1	1.62	2.86	0.25	17.7	0.61	1.60	4.69	0.25	9.59
NC-EWDP-9S	1	2	11/10/99	00556169	83.8	4.85	0.41	2.38	0.25	8.01	0.20	0.14	3.59	0.44	8.45
NC-EWDP-9S	1	3	5/20/00	00556289	100	4.57	0.61	1.82	0.30	1.50	0.18	0.24	2.60	0.33	7.75
NC-EWDP-9S	2	1	5/19/99	00553541	84.7	4.91	0.68	2.03	0.34	11.0	0.55	1.86	34.8	0.73	9.53
NC-EWDP-9S	2	2	11/10/99	00556162	91.0	5.84	0.46	2.15	0.34	6.09	0.17	0.10	8.61	0.80	11.2
NC-EWDP-9S	2	3	5/20/00	00556041	103	6.07	0.64	2.51	0.46	4.40	0.18	0.17	4.27	0.90	13.2
NC-EWDP-9S	3	1	5/19/99	00553549	79.8	4.01	0.63	1.93	0.26	5.91	0.32	1.51	16.3	0.86	9.54
NC-EWDP-9S	3	2	11/09/99	00556155	78.0	2.36	0.37	1.48	0.23	7.56	0.19	0.12	8.31	0.65	7.83
NC-EWDP-9S	3	3	5/19/00	00555935	95.3	1.69	0.45	1.19	0.18	3.80	0.17	0.15	3.93	0.57	6.40
NC-EWDP-9S	4	1	5/18/99	00553544	88.0	6.50	0.55	2.39	0.36	5.21	0.42	1.49	98.6	0.90	12.1
NC-EWDP-9SD	4	1	5/18/99	00553545	90.7	7.08	0.78	2.38	0.35	4.95	0.47	1.42	120	0.90	12.4
NC-EWDP-9S	4	2	11/09/99	00556148	83.4	3.33	0.43	2.16	0.33	3.70	0.22	0.11	10.8	0.85	11.0
NC-EWDP-9S	4	1	5/19/00	00556279	98.0	2.05	0.60	2.38	0.31	3.17	0.27	0.19	3.24	0.93	11.7
NC-EWDP-1D		1	5/24/99	00553547	742	1.62	1.68	0.20	3.11	411	4.23	6.86	26.3	5.84	3.36
NC-EWDP-1DD		1	5/24/99	00553548	707	1.92	1.74	0.18	2.69	409	4.01	8.41	12.8	6.01	3.11
NC-EWDP-1D		1	5/25/00	00556337	727	2.49	0.88	0.07	0.09	147	0.24	0.22	1.04	2.72	8.37
SD6ST1		1	6/15/99	00553535	72.9	6.39	0.20	2.86	0.36	18.0	2.22	2.00	20.7	1.01	13.0
SD6ST1D		1	6/15/99	00553536	72.9	6.06	0.22	2.75	0.36	18.1	2.15	1.86	20.8	1.02	12.8
Bond Gold13		1	7/19/99	00553688	81.0	1.03	10.2	0.30	0.65	37.0	41.0	1.91	15.8	0.16	0.19
Bond Gold13D		1	7/19/99	00553690	78.2	0.68	10.5	0.27	0.65	35.7	36.7	1.78	14.6	0.17	0.25
NC-EWDP-12PB		3	5/22/00	00555955	269	1.79	0.95	0.21	0.14	444	7.46	0.18	23.9	1.86	1.15
NC-EWDP-12PC		3	5/22/00	00556005	76.0	1.53	1.37	3.10	0.26	21.6	1.07	0.29	1.93	0.68	11.6
NC-EWDP-12PA		3	5/22/00	00556051	324	3.36	1.00	0.46	0.07	150	2.21	0.19	9.17	2.51	1.76
NC-EWDP-15P		3	5/23/00	00556204	109	2.61	0.32	1.92	0.12	43.3	0.80	0.11	0.21	0.61	9.28
NC-EWDP-19P		3	5/23/00	00556000	36.9	16.3	0.62	12.1	1.11	26.3	0.45	0.17	2.61	0.19	7.61
NC-EWDP-4 PB		3	5/26/00	00556269	58.1	77.9	0.39	10.5	3.48	41.9	1.30	0.30	0.90	0.46	30.8
NC-EWDP-4PA		3	5/15/00	00555937	47.8	10.3	1.42	3.76	1.73	31.2	0.44	0.20	1.14	0.47	9.93
NC-EWDP-5S		3	5/17/00	00556274	180	1.78	2.09	0.03	0.01	553	1.21	0.21	1.21	0.33	1.26
Method Detection Limits (MDL)					0.01	0.14	0.01	0.01	0.01	0.01	0.02	0.01	0.15	0.01	0.03

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

**Value is below the MDL

Well	Zone	*DTN	Sample Date	SPC Code	Concentration (ppb)									
					Se	Rb	Sr	Mo	Sb	Cs	Ba	W	Pb	U
NC-EWDP-1S	1	1	5/18/99	00553556	1.04	28.1	622	4.93	0.41	1.39	42.3	0.38	0.05**	8.80
NC-EWDP-1S	1	2	11/08/99	00556182	0.40	28.0	620	3.90	0.24	1.21	36.1	0.43	0.01**	7.30
NC-EWDP-1S	1	3	5/19/00	00556046	0.58	24.7	553	3.54	0.24	1.27	39.9	0.38	0.01**	8.31
NC-EWDP-1S	2	1	5/17/99	00553555	0.86	28.7	625	4.94	0.25	1.29	36.3	0.35	0.02**	8.32
NC-EWDP-1S	2	2	11/08/99	00555916	0.50	28.6	607	4.02	0.19	1.15	29.6	0.35	0.01**	6.69
NC-EWDP-1S	2	3	5/18/00	00556056	0.46	25.5	550	2.97	0.15	0.98	29.7	0.31	0.01**	5.57
NC-EWDP-3S	2	1	5/20/99	00553551	1.43	10.1	2.19	23.2	0.49	0.31	0.17	4.36	0.22	2.92
NC-EWDP-3S	2	2	11/15/99	00556142	0.79	8.69	3.34	12.6	0.36	0.26	0.29	2.96	0.08**	2.30
NC-EWDP-3S	3	1	5/20/99	00553554	0.64	7.35	2.22	9.08	0.82	0.29	0.21	2.28	0.08**	14.0
NC-EWDP-3SD	3	1	5/20/99	00553552	0.61	7.45	2.24	9.36	0.82	0.29	0.19	2.37	0.09**	13.7
NC-EWDP-3S	3	2	11/15/99	00556136	0.09	7.58	4.38	10.4	0.19	0.26	0.31	2.57	0.04**	5.93
NC-EWDP-3S	3	3	5/17/00	00556284	0.10**	7.34	6.03	9.81	0.10	0.34	0.34	2.94	0.03**	4.72
NC-EWDP-9S	1	1	5/19/99	00553550	0.35	8.79	89.8	14.6	0.29	0.76	2.05	2.03	0.06**	0.51
NC-EWDP-9SD	1	1	5/19/99	00553542	0.68	12.8	113	10.1	0.49	1.26	6.19	1.97	0.04**	3.26
NC-EWDP-9S	1	2	11/10/99	00556169	0.50	13.6	155	5.97	0.40	1.27	7.23	1.46	0.09**	4.19
NC-EWDP-9S	1	3	5/20/00	00556289	0.45	16.1	128	7.21	0.40	1.07	2.88	1.22	0.05**	2.18
NC-EWDP-9S	2	1	5/19/99	00553541	0.77	11.1	162	4.91	0.41	1.58	7.83	1.15	0.06**	4.44
NC-EWDP-9S	2	2	11/10/99	00556162	0.50	10.7	163	5.10	0.38	1.34	7.53	1.31	0.06**	4.88
NC-EWDP-9S	2	3	5/20/00	00556041	0.72	11.1	145	5.18	0.38	1.36	6.91	1.32	0.02**	4.69
NC-EWDP-9S	3	1	5/19/99	00553549	0.78	11.5	142	5.60	0.41	1.66	4.51	1.33	0.07**	4.52
NC-EWDP-9S	3	2	11/09/99	00556155	0.37	11.1	146	5.14	0.32	1.34	3.78	1.15	0.13**	3.66
NC-EWDP-9S	3	3	5/19/00	00555935	0.46	10.0	134	5.28	0.27	0.96	3.10	1.09	0.02**	2.35
NC-EWDP-9S	4	1	5/18/99	00553544	0.86	12.3	156	4.79	0.42	1.60	4.20	1.21	0.03**	4.60
NC-EWDP-9SD	4	1	5/18/99	00553545	0.90	12.4	159	4.81	0.41	1.68	4.37	1.24	0.04**	4.41
NC-EWDP-9S	4	2	11/09/99	00556148	0.59	11.2	160	4.72	0.33	1.49	4.95	1.20	0.03**	3.99
NC-EWDP-9S	4	1	5/19/00	00556279	0.65	11.3	162	4.82	0.36	1.53	5.45	1.26	0.01**	4.61
NC-EWDP-1D	1	1	5/24/99	00553547	0.45	286	1174	4.99	0.10	84.1	165	0.31	0.02**	0.01
NC-EWDP-1DD	1	1	5/24/99	00553548	0.21**	270	1111	4.22	0.10	92.6	158	0.25	0.01**	0.01
NC-EWDP-1D	1	1	5/25/00	00556337	0.00**	258	1002	2.69	0.01	90.4	154	0.13	0.004**	0.01
SD6ST1	1	1	6/15/99	00553535	0.92	5.73	0.36	4.41	0.31	0.26	0.37	1.80	0.35	4.28
SD6ST1D	1	1	6/15/99	00553536	0.95	5.69	0.37	4.39	0.32	0.26	0.37	1.82	0.38	4.26
Bond Gold13	1	1	7/19/99	00553688	1.09	5.35	2491	2.94	0.02	0.43	15.8	0.01	0.02**	8.82
Bond Gold13D	1	1	7/19/99	00553690	1.45	5.02	2553	2.97	0.01	0.43	14.6	0.01	0.02**	7.89
NC-EWDP-12PB	3	3	5/22/00	00555955	0.54	74.6	292	21.3	0.12	0.91	22.0	0.11	0.01**	0.85
NC-EWDP-12PC	3	3	5/22/00	00556005	0.82	31.4	465	4.95	0.18	1.35	28.1	1.12	0.01**	7.89
NC-EWDP-12PA	3	3	5/22/00	00556051	0.52	83.5	301	19.7	0.10	1.82	10.1	0.12	0.5**	1.00
NC-EWDP-15P	3	3	5/23/00	00556204	0.67	11.0	49.6	8.91	0.29	0.90	1.37	0.63	0.01**	2.90
NC-EWDP-19P	3	3	5/23/00	00556000	0.44	10.1	56.4	14.0	0.19	0.60	1.89	0.71	0.03**	0.57
NC-EWDP-4 PB	3	3	5/26/00	00556269	0.64	5.91	35.8	7.40	0.34	0.86	2.12	3.21	0.03**	0.61
NC-EWDP-4PA	3	3	5/15/00	00555937	0.86	8.02	59.5	2.63	0.17	0.86	5.57	0.75	0.12**	0.78
NC-EWDP-5S	3	3	5/17/00	00556274	0.85	23.7	321	28.0	0.30	4.21	26.6	0.18	0.01**	0.73
Method Detection Limits (MDL)					0.32	0.004	0.02	0.005	0.005	0.005 ^a 0.004 ^b	0.01	0.006	0.14	0.004

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

**Value is below the MDL

^a Detection Limit for May 1999 and 2000 analyses, ^b Detection Limit for Nov 1999 analyses

Well	Zone	*DTN	Sample Date	SPC Code	Concentration (ppt)										
					Be	Co	Ga	Y	Zr	Nb	Ru	Rh	Pd	Ag	Cd
NC-EWDP-1S	1	1	5/18/99	00553556	11.0**	204	4.01**	27.5	11.4**	8.68	1.52**	12.8	5.05**	0.86**	36.9
NC-EWDP-1S	1	2	11/08/99	00556182	9.48**	128	1.80**	8.2	8.7**	3.98	1.11**	5.13	3.56**	1.24**	5.52**
NC-EWDP-1S	1	3	5/19/00	00556046	7.15**	76.0	2.46**	25.6	15.4**	11.2	1.46**	6.98	6.4**	2266	6.28
NC-EWDP-1S	2	1	5/17/99	00553555	9.7**	519	3.85**	12.0	8.36**	5.72	1.74**	11.1	6.54**	2.52**	28.1
NC-EWDP-1S	2	2	11/08/99	00555916	9.14**	219	2.60**	7.2	24.2**	5.14	1.55**	5.07	6.87**	2.52**	5.38**
NC-EWDP-1S	2	3	5/18/00	00556056	3.33**	115	4.08**	11.2	12.8**	9.55	1.84**	6.70	5.84**	6.78**	4.54
NC-EWDP-3S	2	1	5/20/99	00553551	2.78**	15.2	63.1	97.9	43.6	7.20	7.21	0.43**	12.6**	7.02**	39.6
NC-EWDP-3S	2	2	11/15/99	00556142	5.67**	8.10	49.7	25.1	18.5**	2.51**	1.16**	1.04**	3.77**	3.19**	9.59
NC-EWDP-3S	3	1	5/20/99	00553554	3.24**	5.88	239	112	118	5.39	3.20**	0**	7.26**	2.86**	12.5
NC-EWDP-3SD	3	1	5/20/99	00553552	8.49**	5.61	241	112	131	5.37	3.37**	0**	7.22**	2.34**	9.12
NC-EWDP-3S	3	2	11/15/99	00556136	9.03**	5.82	215	44.8	69.5	5.03	0.97**	0.38**	5.86**	1.61**	8.58
NC-EWDP-3S	3	3	5/17/00	00556284	3.21**	5.25	213	32.9	218	14.5	0.86**	0.95**	9.1**	8.09**	6.04
NC-EWDP-9S	1	1	5/19/99	00553550	4.93**	22.4	21.8	19.5	36.6	4.21	6.31	1.07**	10**	3.92**	34.2
NC-EWDP-9SD	1	1	5/19/99	00553542	9.44**	27.1	39.7	54.2	85.5	4.92	4.35	1.61**	8.31**	1.97**	22.4
NC-EWDP-9S	1	2	11/10/99	00556169	18.5	18.1	16.7	9.2	20.5**	2.19**	0.81**	1.44**	7.70**	1.08**	6.75**
NC-EWDP-9S	1	3	5/20/00	00556289	11.6**	9.70	10.2	15.4	49.3	13.2	1.57**	1.28**	7.6**	1.28**	5.79
NC-EWDP-9S	2	1	5/19/99	00553541	2.04**	30.0	6.53	15.2	18.5**	6.93	2.89**	4.40	13**	5.07**	14.7
NC-EWDP-9S	2	2	11/10/99	00556162	13.6**	14.7	6.67	5.1	26.2	2.70**	0.70**	1.19**	4.38**	3.41**	4.31**
NC-EWDP-9S	2	3	5/20/00	00556041	15.9	11.0	6.71	14.2	28.5	16.6	1.28**	1.65**	8.88**	7.62**	3.85
NC-EWDP-9S	3	1	5/19/99	00553549	7.98**	17.5	5.11	13.2	19.8**	1.76	3.96**	2.61**	6.89**	3.58**	9.80
NC-EWDP-9S	3	2	11/09/99	00556155	7.77**	15.2	4.47**	5.6	14.2**	3.02**	0.90**	1.24**	4.24**	2.12**	4.23**
NC-EWDP-9S	3	3	5/19/00	00555935	10.6**	8.81	3.01**	9.93	46.3	14.1	1.72**	1.36**	9.31**	6.88**	3.25**
NC-EWDP-9S	4	1	5/18/99	00553544	11.8**	21.5	4.82	14.3	11.7**	3.82	1.22**	2.68**	5.32**	0.97**	18.3
NC-EWDP-9SD	4	1	5/18/99	00553545	10.9**	24.4	6.04	16.0	7.90**	5.01	2.33**	2.71**	9.94**	4.64**	19.5
NC-EWDP-9S	4	2	11/09/99	00556148	21.1	15.0	4.77**	6.5	15.8**	3.51**	0.80**	1.60**	3.75**	0.43**	5.03**
NC-EWDP-9S	4	1	5/19/00	00556279	4.23**	12.0	4.88	16.4	53.8	20.7	1.16**	1.61**	9.39**	58.6	4.49
NC-EWDP-1D	1	1	5/24/99	00553547	505	511	14.8	20.1	40.4	11.8	17.1	14.4	46.9	2.30**	33.8
NC-EWDP-1DD	1	1	5/24/99	00553548	576	441	12.9	22.3	25.8	11.2	15.7	17.6	60.5	2.33**	28.8
NC-EWDP-1D	1	1	5/25/00	00556337	1277	44.0	8.04	18.2	75.2	26.4	2.65**	8.20	103	11.2**	3.85
SD6ST1	1	1	6/15/99	00553535	11.1**	64.4	189	2.35**	41.8	5.47	5.01	0.63**	34.8	5.79**	8.65
SD6ST1D	1	1	6/15/99	00553536	5.97**	63.3	187	2.84	31.7	4.69	5.49	0.74**	42.4	3.78**	10.5
Bond Gold13	1	1	7/19/99	00553688	6.27**	407	4.98	34.1	8.81**	8.77	14.8	32.0	40.8	3.07**	47.9
Bond Gold13D	1	1	7/19/99	00553690	3.15**	385	4.41**	29.4	4.55**	8.36	14.7	29.3	22.2**	2.83**	49.3
NC-EWDP-12PB	3	1	5/22/00	00555955	55.2	1160	10.1	7.86	166	19.0	1.74**	2.76**	21.9**	16.6**	17.3
NC-EWDP-12PC	3	1	5/22/00	00556005	19.0	101	3.36**	14.2	81.6	8.53	1.46**	5.22	7.9**	21.8**	6.12
NC-EWDP-12PA	3	1	5/22/00	00556051	96.1	361	6.74	5.39	50.9	10.9	1.71**	2.96**	9.79**	6.29**	14.2
NC-EWDP-15P	3	1	5/23/00	00556204	11.4**	72.2	27.5	3.10	12.7**	6.51	1.13**	0.88**	93.00	11.8**	5.47
NC-EWDP-19P	3	1	5/23/00	00556000	11.7**	42.3	36.8	28.8	137	10.4	1.17**	0.68**	7.34**	15.7**	8.93
NC-EWDP-4 PB	3	1	5/26/00	00556269	20.7	181	279	9.18	61.4	11.0	1.32**	0.52**	6.31**	6.36**	5.62
NC-EWDP-4PA	3	1	5/15/00	00555937	0**	39.7	45.7	32.3	95.0	13.1	0.74**	0.84**	7.95**	14.9**	41.8
NC-EWDP-5S	3	1	5/17/00	00556274	6.0**	255	26.5	36.3	41.4	12.6	1.97**	4.74	11.5**	12.8**	19.3
Method Detection Limits (MDL)					14	3.5	4.8	2.8	26	3.7	4.1	3.7	24	49	8.1

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

**Value is below the MDL

Well	Zone	*DTN	Sample Date	SPC Code	Concentration (ppt)										
					In	Sn	Te	Hf	Ta	Re	Ir	Pt	Au	Tl	Bi
NC-EWDP-1S	1	1	5/18/99	00553556	0.04**	15.1	6.11**	4.68**	3.82**	17.0	4.41	3.57**	13.9**	112	0.68**
NC-EWDP-1S	1	2	11/08/99	00556182	0.06**	12.7	8.81	6.8**	4.8**	11.0	2.44**	5.64**	13.7**	90.9	0.70**
NC-EWDP-1S	1	3	5/19/00	00556046	0.04**	22.2	11.2	4.77**	6.19**	11.4	3.08**	6.91**	9.19**	72.0	1.81**
NC-EWDP-1S	2	1	5/17/99	00553555	0.13**	12.4	3.97**	8.27**	7.95**	17.9	3.44**	3.90**	31.9**	99.3	0.69**
NC-EWDP-1S	2	2	11/08/99	00555916	0.01**	14.1	7.18**	10.2**	7.5**	11.2	2.99**	9.08**	45.2**	73.7	1.26**
NC-EWDP-1S	2	3	5/18/00	00556056	0.27**	22.7	15.5	3.22**	13.1**	11.5	3.65**	6.26**	9.97**	56.1	0.72**
NC-EWDP-3S	2	1	5/20/99	00553551	0.40**	49.9	15.8	3.8**	3.87**	20.3	4.75	4.73**	53.6**	154	4.09**
NC-EWDP-3S	2	2	11/15/99	00556142	0.23**	0**	11.8	2.9**	3.4**	8.63	0.99**	3.68**	9.09**	76.6	1.62**
NC-EWDP-3S	3	1	5/20/99	00553554	0.42**	43.8	17.6	5.58**	5.75**	25.7	1.73**	20.1	8.80**	152	2.72**
NC-EWDP-3SD	3	1	5/20/99	00553552	0.17**	51.4	18.3	6.26**	8.25**	29.3	2.94**	5.93**	15.5**	139	3.13**
NC-EWDP-3S	3	2	11/15/99	00556136	0.17**	0**	15.5	11.0**	14.6**	8.30	2.26**	5.93**	12.2**	61.6	1.87**
NC-EWDP-3S	3	3	5/17/00	00556284	0.08**	28.5	16.7	31.8	12.1**	6.31**	3.66**	9.82**	12.7**	44.6	1.08**
NC-EWDP-9S	1	1	5/19/99	00553550	0.13**	86.5	5.15**	3.67**	4.50**	18.2	1.72**	54.9	16.1**	170	3.00**
NC-EWDP-9SD	1	1	5/19/99	00553542	0.43**	29.7	4.73**	5.45**	4.32**	17.7	1.84**	7.31**	13.4**	142	2.05**
NC-EWDP-9S	1	2	11/10/99	00556169	0.02**	28.7	7.2**	5.1**	5.8**	7.22	2.52**	10.5**	9.55**	88.1	0.49**
NC-EWDP-9S	1	3	5/20/00	00556289	0.21**	33.4	7.24**	12.8**	9.55**	7.60	4.78	11.0**	13.7**	58.2	0.53**
NC-EWDP-9S	2	1	5/19/99	00553541	0.14**	32.5	1.98**	6.72**	9.34**	12.4	5.19	17.6	28.9**	129	0.74**
NC-EWDP-9S	2	2	11/10/99	00556162	0.08**	20.2	6.3**	8.46**	4.9**	6.42	2.06**	2.85**	9.62**	84.1	0.90**
NC-EWDP-9S	2	3	5/20/00	00556041	0.17**	23.0	6.92**	19.8**	13.8**	7.17	4.0**	456	23.9**	59.3	0.65**
NC-EWDP-9S	3	1	5/19/99	00553549	0.50**	10.7	6.63**	2.19**	3.78**	16.5	4.02**	2.72**	7.63**	144	0.71**
NC-EWDP-9S	3	2	11/09/99	00556155	0.31**	15.9	8.4**	14.7**	7.9**	6.33	2.82**	3.85**	14.3**	66.5	0.78**
NC-EWDP-9S	3	3	5/19/00	00555935	0.08**	21.1	8.15**	37.2	12.9**	6.78**	8.15	5.35**	47.0**	53.1	0.40**
NC-EWDP-9S	4	1	5/18/99	00553544	0.03**	8.55	2.54**	5.13**	6.01**	9.62	0**	2.74**	9.85**	80	0.34**
NC-EWDP-9SD	4	1	5/18/99	00553545	0.10**	8.49	3.42**	4.32**	6.58**	9.85	2.42**	7.19**	15.9**	78	0.41**
NC-EWDP-9S	4	2	11/09/99	00556148	0.08**	10.8	8.6**	12.2**	6.3**	6.49	2.14**	3.91**	9.74**	64.7	0.72**
NC-EWDP-9S	4	1	5/19/00	00556279	0.01**	28.5	2.42**	64.5	6.35**	6.92**	5.33	4.38**	21.1**	4.17**	0.44**
NC-EWDP-1D		1	5/24/99	00553547	0.68**	50.6	49.6	20.6	7.98**	64.5	28.9	46.8	45.7**	210	9.12
NC-EWDP-1DD		1	5/24/99	00553548	0.60**	52.7	55.0	9.59**	8.12**	65.1	25.2	38.9	24.2**	169	7.78
NC-EWDP-1D		1	5/25/00	00556337	0.37**	20.3	26.7	11.8**	48.9	3.07**	5.71	28.9	1335	73.3	1.65**
SD6ST1		1	6/15/99	00553535	0.31**	20.0	7.04**	5.77**	18.5	14.7	6.55	4.03**	37.8**	149	0.66**
SD6ST1D		1	6/15/99	00553536	0.26**	23.1	7.10**	4.86**	17.6	16.6	7.08	4.38**	31.1**	158	0.70**
Bond Gold13		1	7/19/99	00553688	0.77**	31.2	38.8	2.39**	8.60**	61.0	27.6	4.25**	85.3	253	36.8
Bond Gold13D		1	7/19/99	00553690	0.86**	26.8	34.9	2.42**	7.19**	64.8	27.9	4.39**	61.8	232	29.1
NC-EWDP-12PB	3		5/22/00	00555955	0.22**	17.4	10.20	17.1**	22.50	11.5	5.27	18.9	50.7**	116	0.72**
NC-EWDP-12PC	3		5/22/00	00556005	0.33**	14.6	7.14**	5.17**	9.34**	12.5	4.69	5.14**	21.5**	73.0	0.85**
NC-EWDP-12PA	3		5/22/00	00556051	0.21**	12.4	15.80	8.16**	13.5**	11.0	3.64**	17.9	15.7**	60.0	0.47**
NC-EWDP-15P	3		5/23/00	00556204	0.14**	20.2	5.73**	4.71**	7.74**	6.5**	2.95**	60.4	23.5**	61.6	1.93**
NC-EWDP-19P	3		5/23/00	00556000	0.28**	15.9	4.83**	26.80	4.62**	6.64**	4.61	7.49**	9**	52.5	0.79**
NC-EWDP-4 PB	3		5/26/00	00556269	0.16**	12.2	5.17**	12.9**	8.49**	6.93**	7.39	22.1	49.1**	40.5	0.65**
NC-EWDP-4PA	3		5/15/00	00555937	0.16**	27.1	5.43**	53.80	7.25**	5.43**	3.53**	4.43**	16.3**	43.6	2.19**
NC-EWDP-5S	3		5/17/00	00556274	0.33**	32.5	22.2	14.2**	6.56**	5.7**	3.34**	38.2	20.6**	61.7	2.02**
Method Detection Limits (MDL)					6.3	6.3	8.7	21	18	7.0	4.2	13	57	16	4.3

*Data Tracking Numbers (DTN): 1) UN0010SPA008KS.001 Data Identification Numbers: 2) 008IW.001, 3) 008IW.002

**Value is below the MDL