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Factor analytical approaches for evaluating groundwater trace element chemistry data

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Abstract

The multivariate statistical techniques principal component analysis (PCA), Q-mode factor analysis (QFA), and correspondence analysis (CA) were applied to a dataset containing trace element concentrations in groundwater samples collected from a number of wells located downgradient from the potential nuclear waste repository at Yucca Mountain, Nevada. PCA results reflect the similarities in the concentrations of trace elements in the water samples resulting from different geochemical processes. QFA results reflect similarities in the trace element compositions, whereas CA reflects similarities in the trace elements that are dominant in the waters relative to all other groundwater samples included in the dataset. These differences are mainly due to the ways in which data are preprocessed by each of the three methods.

The highly concentrated, and thus possibly more mature (i.e. older), groundwaters are separated from the more dilute waters using principal component 1 (PC 1). PC 2, as well as dimension 1 of the CA results, describe differences in the trace element chemistry of the groundwaters resulting from the different aquifer materials through which they have flowed. Groundwaters thought to be representative of those flowing through an aquifer composed dominantly of volcanic rocks are characterized by elevated concentrations of Li, Be, Ge, Rb, Cs, and Ba, whereas those associated with an aquifer dominated by carbonate rocks exhibit greater concentrations of Ti, Ni, Sr, Rh, and Bi. PC 3, and to a lesser extent dimension 2 of the CA results, show a strong monotonic relationship with the percentage of As(III) in the groundwater suggesting that these multivariate statistical results reflect, in a qualitative sense, the oxidizing/reducing conditions within the groundwater. Groundwaters that are relatively more reducing exhibit greater concentrations of Mn, Cs, Co, Ba, Rb, and Be, and those that are more oxidizing are characterized by greater concentrations of V, Cr, Ga, As, W, and U.
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1. Introduction

A groundwater monitoring program, referred to as the Nye County Early Warning Drilling Program (NCEWDP), was recently established to protect groundwater resources downgradient from the potential nuclear waste repository at Yucca Mountain, Nevada [1]. A series of wells were drilled for long-term groundwater monitoring and to provide geologic and hydrologic information for this area. The study area, shown in Fig. 1, lies within the Alkali Flat-Furnace Creek subbasin of the Ash

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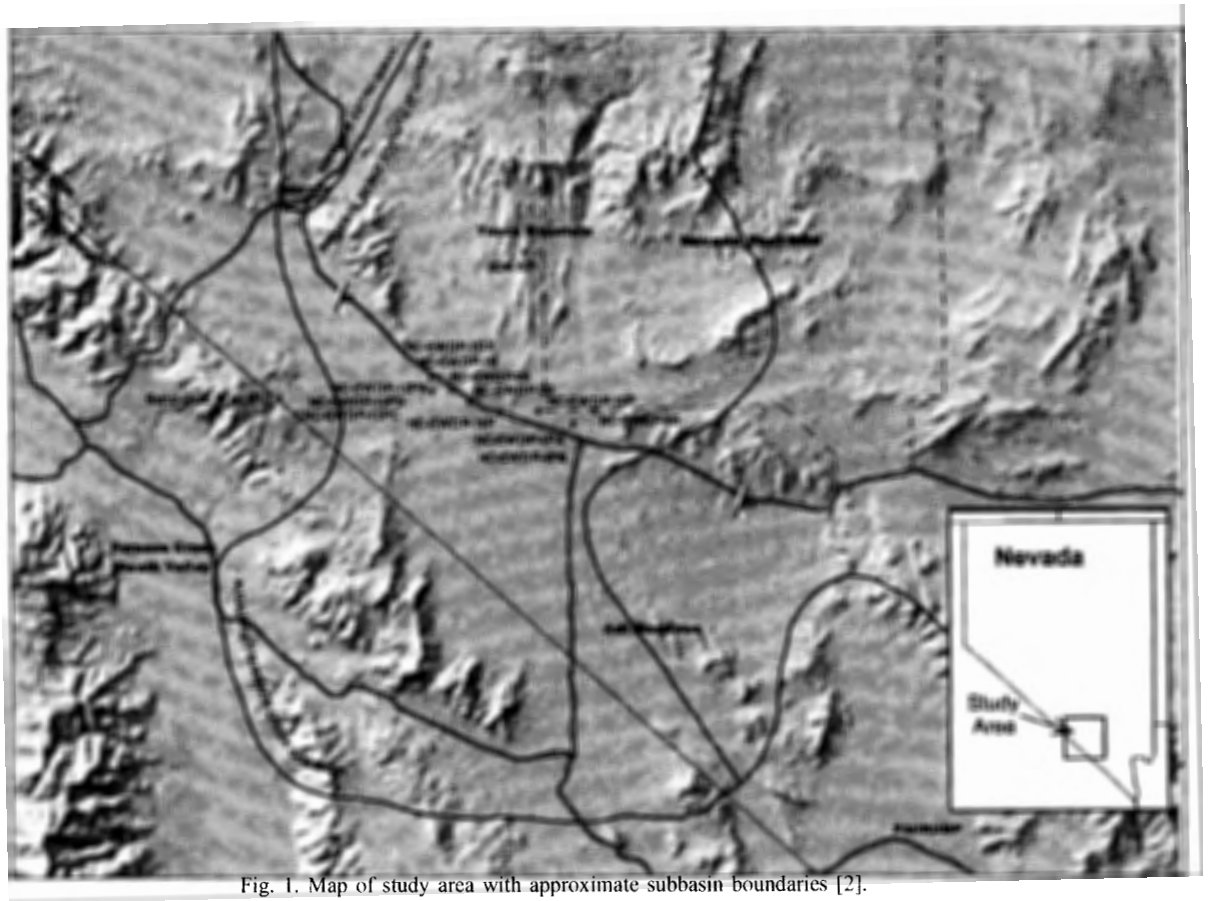

Fig. 1. Map of study area with approximate subbasin boundaries [2].

Meadows-Death Valley flow system which occupies approximately 7250 km^2 [2]. The principal aquifers of this flow system include a lower Paleozoic carbonate aquifer, valley-fill aquifers, and also localized aquifers consisting of tertiary volcanic rocks [3,4].

Groundwater samples were collected from 14 wells of the NCEWDP (Fig. 1) and analyzed for a total of 57 trace elements. Multiple zones were sampled from three of these wells and several of the wells were sampled multiple times. Three multivariate statistical techniques were applied to the extensive dataset collected in this study. The goals of these analyses are to: (1) provide insight into the geochemical processes occurring in the groundwater; (2) determine the extent of communication between groundwaters from different depths; and (3) to help ascertain groundwater flow directions. The underlying hypothesis is that groundwaters from the same aquifer system, from aquifers with similar compositions (e.g. carbonate rock aquifers or the tertiary volcanic aquifers), or that have experienced similar processes along flow paths, would be readily resolvable by these techniques. Perhaps more important, waters from different aquifers or that experienced different processes during their histories ought to be clearly separated by these methods.

1.1. Review of multivariate statistical techniques

Three multivariate statistical techniques are used in this study to evaluate the trace element concentrations in the groundwater samples. For these analyses, the trace element concentrations, in 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 [5–11]; this section will provide only a summary of each technique.

1.2. 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 [8]. Because PCA is based solely upon eigenanalysis of the correlation or covariance matrix, no constraints such as multivariate normality are imposed on the data [12]. 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 elements concentrations are observed in ppb levels and other in ppt levels. PCA was therefore applied to the correlation matrix for this study. Thus, the data are first standardized by mean centering each column (i.e. the column mean is subtracted from each of the values in the column) within the original data matrix and then dividing each of the values 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 (l) as the coefficients:

$$s_{n,c} = \sum x_{n,p} \times l_{p,c}$$

where n identifies the sample, p identifies the particular trace element, and c identifies the principal component [8,13]. 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 dataset. 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.

1.3. 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 [5]. 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 factor analysis (QFA), on the other hand, is used specifically to evaluate interrelationships between samples [5]. 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" [14] so that the similarity between samples is evaluated based on the proportions of their constituents. With Q-mode factor 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. Column

Table 1
Trace element concentrations in groundwaters of the wells of the Nye County Early Warning Drilling Program

Well	Depth (ft)	Sample date	Code	Concentration (ppb)																
				Li	Al	Ti	V	Cr	Mn	Ni	Ge	As	Rb	Sr	Mo	Cs	Ba	W	U
NC-EWDP-1S	160–180	18 May 1999	1S1Zn1	78.4	4.24	1.35	2.50	0.38	29.4	1.85	0.57	7.08	28.1	622	4.93	1.39	42.3	0.38	8.80
NC-EWDP-1S	160–180	8 November 1999	1S2Zn1	69.4	3.13	1.16	1.11	0.07	25.5	0.63	0.48	1.57	28.0	620	3.90	1.21	36.1	0.43	7.30
NC-EWDP-1S	160–180	19 May 2000	1S3Zn1	73.5	2.97	2.18	2.35	0.32	10.6	0.68	0.55	5.91	24.7	553	3.54	1.27	39.9	0.38	8.31
NC-EWDP-1S	210–270	17 May 1999	1S1Zn2	78.5	4.63	1.51	1.44	0.13	60.4	1.88	0.55	1.90	28.7	625	4.94	1.29	36.3	0.35	8.32
NC-EWDP-1S	210–270	8 November 1999	1S2Zn2	74.6	2.97	1.13	0.57	0.09	45.7	0.43	0.48	0.60	28.6	607	4.02	1.15	29.6	0.35	6.69
NC-EWDP-1S	210–270	18 May 2000	1S3Zn2	75.2	2.99	2.08	0.52	0.01	99.9	0.69	0.40	0.29	25.5	550	2.97	0.98	29.7	0.31	5.57
NC-EWDP-3S	340–420	20 May 1999	3S1Zn2	191	7.58	0.78	11.0	1.23	0.99	0.13	1.27	37.6	10.1	2.19	23.2	0.31	0.17	4.36	2.92
NC-EWDP-3S	340–420	15 November 1999	3S2Zn2	171	6.80	0.49	5.34	0.45	1.74	0.05	1.43	33.9	8.69	3.34	12.6	0.26	0.29	2.96	2.30
NC-EWDP-3S	480–525	20 May 1999	3S1Zn3	259	7.79	0.49	2.05	0.07	6.94	0.05	3.54	46.0	7.35	2.22	9.08	0.29	0.21	2.28	14.0
NC-EWDP-3SDup	480–525	20 May 1999	3S1Zn3D	276	8.18	0.39	2.07	0.07	6.99	0.04	3.72	48.5	7.45	2.24	9.36	0.29	0.19	2.37	13.7
NC-EWDP-3S	480–525	15 November 1999	3S2Zn3	268	6.19	0.47	1.03	0.05	1.05	0.03	3.16	36.4	7.58	4.38	10.4	0.26	0.31	2.57	5.93
NC-EWDP-3S	480–525	17 May 2000	3S2Zn3	258	9.54	0.70	0.65	0.01	1.88	0.11	3.52	29.9	7.34	6.03	9.81	0.34	0.34	2.94	4.72
NC-EWDP-9S	90–120	19 May 1999	9S1Zn1	65.8	8.72	0.88	0.89	0.18	1.47	0.50	0.34	4.09	8.79	89.8	14.6	0.76	2.05	2.03	0.51
NC-EWDP-9SDup	90–120	19 May 1999	9S1Zn1D	78.2	13.1	1.62	2.86	0.25	17.7	0.61	0.25	9.59	12.8	113	10.1	1.26	6.19	1.97	3.26
NC-EWDP-9S	90–120	10 November 1999	9S2Zn1	83.8	4.85	0.41	2.38	0.25	8.01	0.20	0.44	8.45	13.6	155	5.97	1.27	7.23	1.46	4.19
NC-EWDP-9S	90–120	20 May 2000	9S3Zn1	100	4.57	0.61	1.82	0.30	1.50	0.18	0.33	7.75	16.1	128	7.21	1.07	2.88	1.22	2.18
NC-EWDP-9S	140–160	19 May 1999	9S1Zn2	84.7	4.91	0.68	2.03	0.34	11.0	0.55	0.73	9.53	11.1	162	4.91	1.58	7.83	1.15	4.44
NC-EWDP-9S	140–160	10 November 1999	9S2Zn2	91.0	5.84	0.46	2.15	0.34	6.09	0.17	0.80	11.2	10.7	163	5.10	1.34	7.53	1.31	4.88
NC-EWDP-9S	140–160	20 May 2000	9S3Zn2	103	6.07	0.64	2.51	0.46	4.40	0.18	0.90	13.2	11.1	145	5.18	1.36	6.91	1.32	4.69
NC-EWDP-9S	250–290	19 May 1999	9S1Zn3	79.8	4.01	0.63	1.93	0.26	5.91	0.32	0.86	9.54	11.5	142	5.60	1.66	4.51	1.33	4.52
NC-EWDP-9S	250–290	9 November 1999	9S2Zn3	78.0	2.36	0.37	1.48	0.23	7.56	0.19	0.65	7.83	11.1	146	5.14	1.34	3.78	1.15	3.66
NC-EWDP-9S	250–290	19 May 2000	9S3Zn3	95.3	1.69	0.45	1.19	0.18	3.80	0.17	0.57	6.40	10.0	134	5.28	0.96	3.10	1.09	2.35
NC-EWDP-9S	330–340	18 May 1999	9S1Zn4	88.0	6.50	0.55	2.39	0.36	5.21	0.42	0.90	12.1	12.3	156	4.79	1.60	4.20	1.21	4.60
NC-EWDP-9SDup	330–340	18 May 1999	9S1Zn4D	90.7	7.08	0.78	2.38	0.35	4.95	0.47	0.90	12.4	12.4	159	4.81	1.68	4.37	1.24	4.41
NC-EWDP-9S	330–340	9 November 1999	9S2Zn4	83.4	3.33	0.43	2.16	0.33	3.70	0.22	0.85	11.0	11.2	160	4.72	1.49	4.95	1.20	3.99
NC-EWDP-9S	330–340	19 May 2000	9S3Zn4	98.0	2.05	0.60	2.38	0.31	3.17	0.27	0.93	11.7	11.3	162	4.82	1.53	5.45	1.26	4.61
NC-EWDP-1D	2160–2240	24 May 1999	1D #1	742	1.62	1.68	0.20	3.11	411	4.23	5.84	3.36	286	1174	4.99	84.1	165	0.31	0.01
NC-EWDP-1DDup	2160–2240	24 May 1999	1D #1D	707	1.92	1.74	0.18	2.69	409	4.01	6.01	3.11	270	1111	4.22	92.6	158	0.25	0.01
NC-EWDP-1D	2160–2240	25 May 2000	1D #3	727	2.49	0.88	0.07	0.09	147	0.24	2.72	8.37	258	1002	2.69	90.4	154	0.13	0.01
SD6-ST1	2810	15 June 1999	SD6ST	72.9	6.39	0.20	2.86	0.36	18.0	2.22	1.01	13.0	5.73	0.36	4.41	0.26	0.37	1.80	4.28
SD6-ST1Dup	2810	15 June 1999	SD6STD	72.9	6.06	0.22	2.75	0.36	18.1	2.15	1.02	12.8	5.69	0.37	4.39	0.26	0.37	1.82	4.26
Bond Gold Well #13	1005	19 July 1999	BGW	81.0	1.03	10.2	0.30	0.65	37.0	41.0	0.16	0.19	5.35	2491	2.94	0.43	15.8	0.01	8.82
Bond Gold Well #13Dup	1005	19 July 1999	BGWD	78.2	0.68	10.5	0.27	0.65	35.7	36.7	0.17	0.25	5.02	2553	2.97	0.43	14.6	0.01	7.89
NC-EWDP-12PB	325–385	22 May 2000	12PB	269	1.79	0.95	0.21	0.14	444	7.46	1.86	1.15	74.6	292	21.3	0.91	22.0	0.11	0.85
NC-EWDP-12PC	170–230	22 May 2000	12PC	76.0	1.53	1.37	3.10	0.26	21.6	1.07	0.68	11.6	31.4	465	4.95	1.35	28.1	1.12	7.89
NC-EWDP-12PA	325–384	22 May 2000	12PA	324	3.36	1.00	0.46	0.07	150	2.21	2.51	1.76	83.5	301	19.7	1.82	10.1	0.12	1.00
NC-EWDP-15P	200–260	23 May 2000	15P	109	2.61	0.32	1.92	0.12	43.3	0.80	0.61	9.28	11.0	49.6	8.91	0.90	1.37	0.63	2.90
NC-EWDP-19P	359–459	23 May 2000	19P	36.9	16.3	0.62	12.1	1.11	26.3	0.45	0.19	7.61	10.1	56.4	14.0	0.60	1.89	0.71	0.57
NC-EWDP-4PB	740–839	26 May 2000	4PB	58.1	77.9	0.39	10.5	3.48	41.9	1.30	0.46	30.8	5.91	35.8	7.40	0.86	2.12	3.21	0.61
NC-EWDP-4PA	405–485	15 May 2000	4PA	47.8	10.3	1.42	3.76	1.73	31.2	0.44	0.47	9.93	8.02	59.5	2.63	0.86	5.57	0.75	0.78
NC-EWDP-5S	601–780	17 May 2000	5S	180	1.78	2.09	0.03	0.01	553	1.21	0.33	1.26	23.7	321	28.0	4.21	26.6	0.18	0.73
Method detection limits (MDL)				0.01	0.14	0.01	0.01	0.01	0.01	0.02	0.01	0.03	0.004	0.02	0.005	0.005	0.01	0.96	0.004

Well	Depth (ft)	Sample date	Code	Concentration (ppt)								
				Be	Co	Ga	Ru	Rh	Ir	Au	Bi	Te
NC-EWDP-1S	160–180	18 May 1999	1S1Zn1	11.0	204	4.01	1.52	12.8	4.41	13.9	0.68	6.11
NC-EWDP-1S	160–180	8 November 1999	1S2Zn1	9.48	128	1.80	1.11	5.13	2.44	13.7	0.70	8.8
NC-EWDP-1S	160–180	19 May 2000	1S3Zn1	7.15	76.0	2.46	1.46	6.98	3.08	9.19	1.81	11.2
NC-EWDP-1S	210–270	17 May 1999	1S1Zn2	9.7*	519	3.85	1.74	11.1	3.44	31.9	0.69	3.97
NC-EWDP-1S	210–270	8 November 1999	1S2Zn2	9.14	219	2.60	1.55	5.07	2.99	45.2	1.26	7.18
NC-EWDP-1S	210–270	18 May 2000	1S3Zn2	3.33	115	4.08	1.84	6.70	3.65	9.97	0.72	15.5
NC-EWDP-3S	340–420	20 May 1999	3S1Zn2	2.78	15.2	63.1	7.21	0.43	4.75	53.6	4.09	15.8
NC-EWDP-3S	340–420	15 November 1999	3S2Zn2	5.67	8.10	49.7	1.16	1.04	0.99	9.09	1.62	11.8
NC-EWDP-3S	480–525	20 May 1999	3S1Zn3	3.24	5.88	239	3.20	0*	1.73	8.80	2.72	17.6
NC-EWDP-3SDup	480–525	20 May 1999	3S1Zn3D	8.49	5.61	241	3.37	0*	2.94	15.5	3.13	18.3
NC-EWDP-3S	480–525	15 November 1999	3S2Zn3	9.03	5.82	215	0.97	0.38	2.26	12.2	1.87	15.5
NC-EWDP-3S	480–525	17 May 2000	3S2Zn3	3.21	5.25	213	0.86	0.95	3.66	12.7	1.08	16.7
NC-EWDP-9S	90–120	19 May 1999	9S1Zn1	4.93	22.4	21.8	6.31	1.07	1.72	16.1	3.00	5.15
NC-EWDP-9SDup	90–120	19 May 1999	9S1Zn1D	9.44	27.1	39.7	4.35	1.61	1.84	13.4	2.05	4.73
NC-EWDP-9S	90–120	10 November 1999	9S2Zn1	18.5	18.1	16.7	0.81	1.44	2.52	9.55	0.49	7.2*
NC-EWDP-9S	90–120	20 May 2000	9S3Zn1	11.6	9.70	10.2	1.57	1.28	4.78	13.7	0.53	7.24
NC-EWDP-9S	140–160	19 May 1999	9S1Zn2	2.04	30.0	6.53	2.89	4.40	5.19	28.9	0.74	1.98
NC-EWDP-9S	140–160	10 November 1999	9S2Zn2	13.6	14.7	6.67	0.70	1.19	2.06	9.62	0.90	6.3*
NC-EWDP-9S	140–160	20 May 2000	9S3Zn2	15.9	11.0	6.71	1.28	1.65	4.0*	23.9	0.65	6.92
NC-EWDP-9S	250–290	19 May 1999	9S1Zn3	7.98	17.5	5.11	3.96	2.61	4.02	7.63	0.71	6.63
NC-EWDP-9S	250–290	9 November 1999	9S2Zn3	7.77	15.2	4.47	0.90	1.24	2.82	14.3	0.78	8.4*
NC-EWDP-9S	250–290	19 May 2000	9S3Zn3	10.6	8.81	3.01	1.72	1.36	8.15	47.0	0.40	8.15
NC-EWDP-9S	330–340	18 May 1999	9S1Zn4	11.8	21.5	4.82	1.22	2.68	0*	9.85	0.34	2.54
NC-EWDP-9SDup	330–340	18 May 1999	9S1Zn4D	10.9	24.4	6.04	2.33	2.71	2.42	15.9	0.41	3.42
NC-EWDP-9S	330–340	9 November 1999	9S2Zn4	21.1	15.0	4.77	0.80	1.60	2.14	9.74	0.72	8.6*
NC-EWDP-9S	330–340	19 May 2000	9S3Zn4	4.23	12.0	4.88	1.16	1.61	5.33	21.1	0.44	2.42
NC-EWDP-1D	2160–2240	24 May 1999	1D #1	505	511	14.8	17.1	14.4	28.9	45.7	9.12	49.6
NC-EWDP-1DDup	2160–2240	24 May 1999	1D #1D	576	441	12.9	15.7	17.6	25.2	24.2	7.78	55.0
NC-EWDP-1D	2160–2240	25 May 2000	1D #3	127	44.0	8.04	2.65	8.20	5.71	133	1.65	26.7
SD6S11	2810	15 June 1999	SD6S1	11.1	64.4	189	5.01	0.63	6.55	37.8	0.66	7.04
SD6S11Dup	2810	15 June 1999	SD6S1D	5.97	63.3	187	5.49	0.75	7.08	31.1	0.70	7.10
Bond Gold13	1005	19 July 1999	BGW	6.27	407	4.98	14.8	32.0	27.6	85.3	36.8	38.8
Bond Gold13Dup	1005	19 July 1999	BGWD	3.15	385	4.41	14.7	29.3	27.9	61.8	29.1	34.9
NC-EWDP-12PB	325–385	22 May 2000	12PB	55.2	116	10.1	1.74	2.76	5.27	50.7	0.72	10.2
NC-EWDP-12PC	170–230	22 May 2000	12PC	19.0	101	3.36	1.46	5.22	4.69	21.5	0.85	7.14
NC-EWDP-12PA	325–384	22 May 2000	12PA	96.1	361	6.74	1.71	2.96	3.64	15.7	0.47	15.8
NC-EWDP-15P	200–260	23 May 2000	15P	11.4	72.2	27.5	1.13	0.88	2.95	23.5	1.93	5.73
NC-EWDP-19P	359–459	23 May 2000	19P	11.7	42.3	36.8	1.17	0.68	4.61	9*	0.79	4.83
NC-EWDP-4PB	740–839	26 May 2000	4PB	20.7	181	279	1.32	0.52	7.39	49.1	0.65	5.17
NC-EWDP-4PA	405–485	15 May 2000	4PA	0*	39.7	45.7	0.74	0.84	3.53	16.3	2.19	5.43
NC-EWDP-5S	601–780	17 May 2000	5S	6.0*	255	26.5	1.97	4.74	3.34	20.6	2.02	22.2
Method detection limits (MDL)				14	3.5	4.8	4.1	3.7	4.2	57	4.3	8.7

normalization is typically performed for R-mode analysis (e.g. PCA), whereas each row is normalized to unit length with Q-mode factor analysis. This row normalization does not affect the proportionality relationship between variables but 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 factor analysis can be used for data reduction. Eigenvectors, referred again to as loadings, are extracted from the similarity matrix. The loadings describe the proportion of each individual sample necessary to project the variables onto the factor axis as opposed to describing the proportion of each variable used to project each sample onto the factor axis as in R-mode analysis [7]. Therefore, the Q-mode factor loadings, rather than the scores, are plotted to explore relationships between samples. With QFA, the loadings are used to describe the relative proportions of the trace elements in the samples.

1.4. 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 [15]. Since its introduction, this technique has been widely applied to continuous data similar to that of this study [16–19]. 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. With CA, normalization is performed on both the rows and columns of the data matrix allowing plotting of both the samples and variables (i.e. trace elements) on the same graph. As with Q-mode factor analysis, the influence of the "sizes" of the samples are removed using CA [8]. Column normalization, similar to that described with PCA, assures that the trace elements that are present in relatively high concentrations in the groundwater samples 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.

2. Methods

The wells sampled are identified in Table 1, along with the sample collection date, and the depth of the sampled zones. Samples collected and analyzed in duplicate are identified in Table 1 as "dup". Samples were collected into pre-cleaned, 10 L collapsible containers after pumping the well for three well volumes and once the pH, temperature, and conductivity of the well water had stabilized. Samples were then filtered from the collapsible containers using a peristaltic pump equipped with precleaned (acid-washed) Teflon® tubing, and Gelman Sciences (0.45 μm) groundwater filter capsules, into 1 L 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. The samples were immediately acidified to pH <2 with ultra-pure nitric acid (SeaStar Inc., sub-boiling distilled in quartz), double bagged in clean plastic bags, placed into plastic chests with ice, and transported to the laboratory where they were stored at approximately 4 °C. Laboratory blanks, consisting of deionized water, remained in the laboratory and were treated as samples. In addition, field (i.e. procedural) blanks were also prepared and analyzed. Analyses for trace elements were performed using a Perkin-Elmer Elan 5000 inductively coupled plasma mass spectrometer (ICP-MS), equipped with an ultrasonic nebulizer [20,21]. In addition, samples were collected for analysis of major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) and major anions (Cl^{-}, F^{-}, Br^{-}, SO_4^{-2}, PO_4^{3-}, and NO_3^{-}) in a manner similar to the trace element samples with the exception that 125 ml volumes were collected and the anion samples were not acidified. Analyses were performed using an atomic absorption spectrometer and an ion chromatograph for cation and anion analyses, respectively.

The statistical software package STATISTICA [22] was used for all PCA, and CA. For PCA, STATISTICA normalizes the loadings to the eigenvalue (λ) resulting in loadings given by $l^* = l \times \lambda$.

A computer program was developed in S-PLUS2000 [23] programming language for the Q-mode factor analysis.

3. Results

3.1. Principal components analysis

A significant degree of noise was observed in the score plots when all 57 trace elements were included in the PCA. Other than samples clustering with their respective duplicates, tight clustering of the samples collected from the same site was not observed. These results are not surprising because PCA was performed on the correlation matrix; trace elements exhibiting low concentrations that vary as much between samples collected from the same well as between samples collected from different wells are given equal weight to those elements that are measured more precisely and that vary substantially depending on the aquifer sampled. A subset of trace elements 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 [24], simulation experiments were used to determine a reasonable cut-off for eliminating variables (trace elements) from a dataset 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 dataset if: (1) large differences are observed in their measured concentrations between duplicate samples; and (2) if the concentration of that trace element is relatively similar in all samples within the dataset. 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 dataset [24]). This criterion was extrapolated to address variance between all samples collected from the same well and depth instead of only the duplicate samples. The subset selected and used for further PCA includes the following trace elements (Table 1): Li, Be, Al, Ti, V,

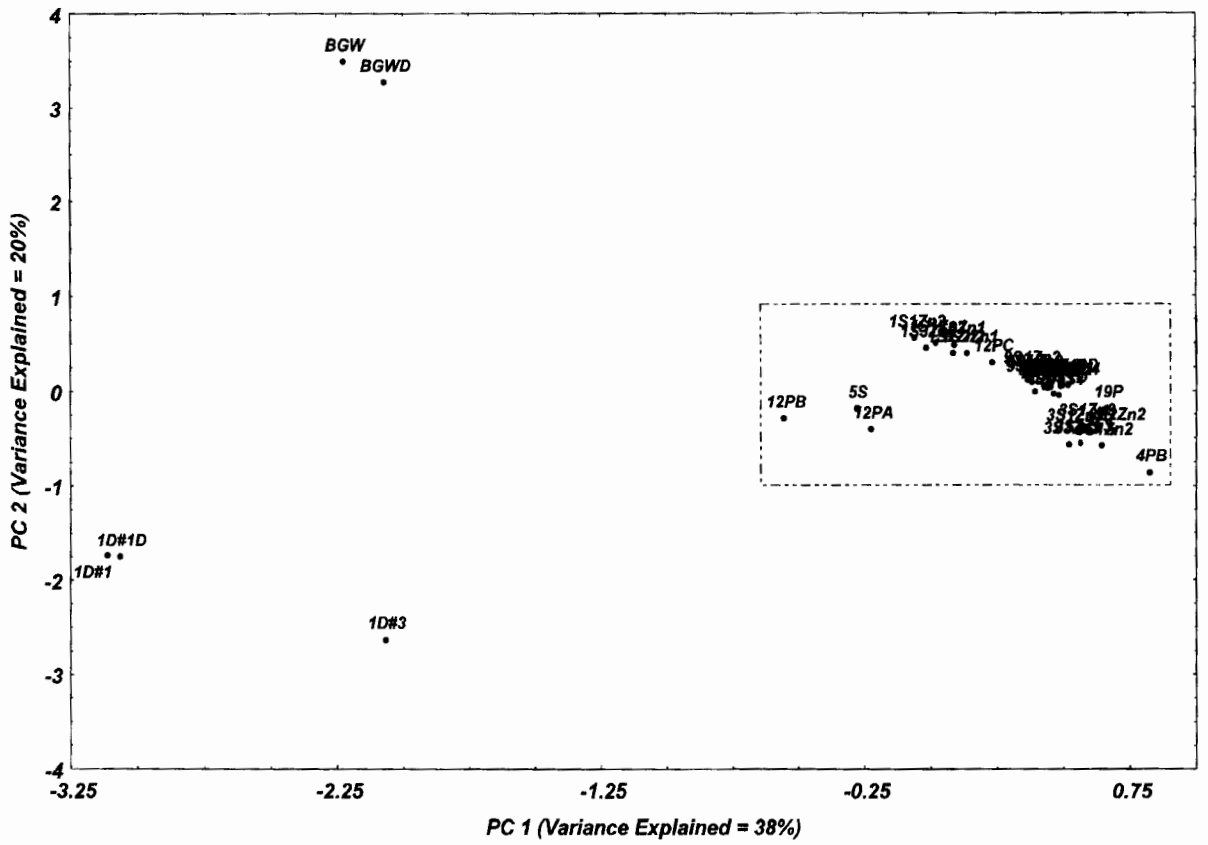

Fig. 2. Scores for principal components 1 and 2.

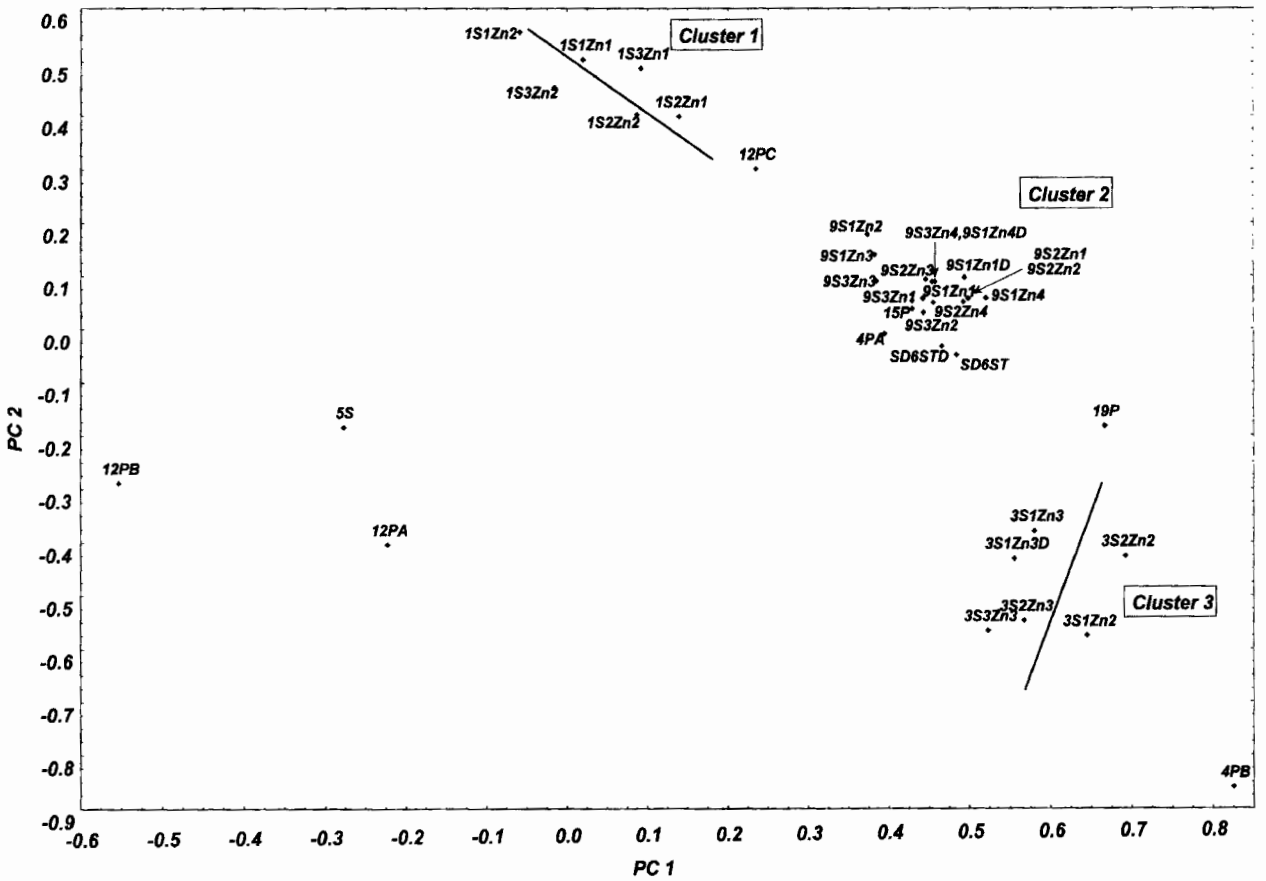

Fig. 3. Scores for principal components 1 and 2—magnified.

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. The score plot for the first two PCs, explaining 58% of the total variance in the data, is shown in Fig. 2. The results of the PCA for these trace elements show that 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 the PC 1 versus PC 2 diagram(Fig. 2). BGW and 1D (especially 1D #3) plot similarly on PC 1 but are distinct in their PC 2 values. These wells were excluded in the magnified portion of this plot shown in Fig. 3. Three clusters containing the majority of the samples are identified in Fig. 3 as follows: (1) samples from well 1S are contained in cluster 1; (2) cluster 2 contains samples from all zones of well 9S, along with wells 15P, 4PA, and SD6ST; and (3) samples from well 3S are contained in a separate cluster, cluster 3, that is clearly distinct from all others. Well water from 12PC plots close to cluster 1, and that from19P 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. 3). 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. 3). The sample from well 4PB plots closest to 3S but is still distinct from all samples included in this dataset (Fig. 3). 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 trace element data (Fig. 3). This suggests that the zones

Table 2
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

sampled for 1S and 3S may not be directly communicating.

Evaluation of the PC loadings, listed in Table 2, reveal some strong trends within these trace element data. The majority of the trace elements have negative PC 1 loadings demonstrating an overall greater concentration for most trace elements in the deeper, and probably more mature waters (i.e. older and/or having longer residence time in the aquifer) of BGW and 1D.

An interesting relationship between the PC 2 loadings and the correlations between the trace elements and major solutes (Br, Cl, SO_4, Ca, Mg, Na, K) is revealed in Table 3. Those trace elements most strongly correlated with Na ($r \geq 0.84$) and K ($r \geq 0.7$) 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, trace elements that are strongly correlated with Ca ($r \geq 0.83$), Mg ($r \geq 0.84$), and SO_4 ($r \geq 0.91$), are the same trace elements that have the greatest positive PC 2 loadings (i.e. Ti, Ni, Sr, Rh, and Bi). This trend is also consistent with Cl^- (Table 3). One interpretation of these observations is that PC 2 describes differences in the trace element concentration of groundwaters that reflect differences in trace element compositions of the aquifer materials through which the water flowed (i.e. distinguishes groundwaters in aquifers dominated by volcanic versus carbonate rocks). Most of the NCEWDP groundwaters (9S, 19P, 15P, 3S, 5S, 12PB, 12PA, SD6, and 1D) are classified as Na + K–HCO_3 waters [25], consistent with groundwaters that have chemically reacted with felsic volcanic rocks such as the rhyolites and quartz latites of the surrounding region [3,26]. The scores for the majority of these waters plot negatively on PC 2 (Figs. 2 and 3). Na + K–HCO_3 hydrochemical 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 (carbonates) [27]. The greater concentrations of these trace elements are also consistent with those reported for a group of rocks analyzed from within the study area [28,29]. Groundwater from BGW, which has the greatest positive PC 2 scores, is classified as belonging to the Ca + Mg–SO_4–HCO_3 hydrochemical facies [25]. This facies is thought to result from mixing of Ca + Mg–HCO_3 water with SO_4–HCO_3 water, which may reflect the movement of water from carbonate rocks into tuff or tuffaceous alluvium (predominantly volcanic rock) [30]. Groundwaters from 1S and 12PC also have positive PC 2 scores. These waters are of the Ca + Mg–HCO_3 facies, which is representative of water that has flowed through the valley fill deposits composed, in part, of carbonate rocks [3]. The concentrations of Sr and Ni are typically higher in limestone when compared to granites [27]. This is not consistent for Ti which is commonly reported as "major" in granites, but not in carbonates [27]. Titanium, however, is thought to be relatively insoluble in most groundwaters [31]. Only a limited amount of data are available for the other trace elements with positive PC 2 loadings (Rh and Bi).

A plot of the PC 2 and PC 3 scores is shown in Fig. 4. An additional 13% of the variance is explained in PC 3 suggesting that this component may also explain important information within these data. Each of the samples collected from the same well, with

Table 3
Correlation coefficients for major anions, major cations, and trace elements

	Br^-	Cl^-	F^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+
Br^-	1.00							
Cl^-	0.14	1.00						
F^-	−0.16	0.17	1.00					
SO_4^{2-}	0.02	0.77	−0.30	1.00				
Ca^{2+}	−0.04	0.72	−0.36	0.93	1.00			
Mg^{2+}	−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

the exception of 1D #1 and #3, cluster weakly in PC 3. However, no distinct clusters within PC 3 are observed. Trace elements with the greatest positive PC 3 loadings include Be, Mn, Co, and Ba (Table 2). Those with the greatest negative PC 3 loadings include V, Cr, Ga, As, and W (Table 2). Interestingly, four of the trace elements with negative PC 3 loadings (V, Cr, As, and W) typically occur as soluble oxyanions in oxidizing waters, whereas three of the trace elements with positive PC 3 loadings (Mn, Ba, and Co) are commonly more soluble in oxygen depleted waters [32]. This suggests that PC 3 reflects, in part, the oxidizing / reducing conditions within the groundwater. Further evidence to this end is provided by As(III) and As(V) concentrations, listed in Table 4, measured for a group of samples collected during the May 2000 sampling of the NCEWDP wells [25]. The oxidation states of As were measured by hydride generation atomic absorption spectrometry [33,34]. A strong monotonic relationship between PC 3 and the percentage of As(III) is observed. The rank correlation coefficient [35] for this relationship is 0.90. Close inspection of the trace element data obtained for NCEWDP waters reveals that the well containing the highest concentration of reduced arsenic (i.e. 1D #3; 5.3 ppb) also has high concentrations of Mn, Ba, Be and Co; as well as the lowest concentrations of U, V, W, and Cr. The solubility of Mn, as Mn^{2+}, is very high in low pH (reducing)

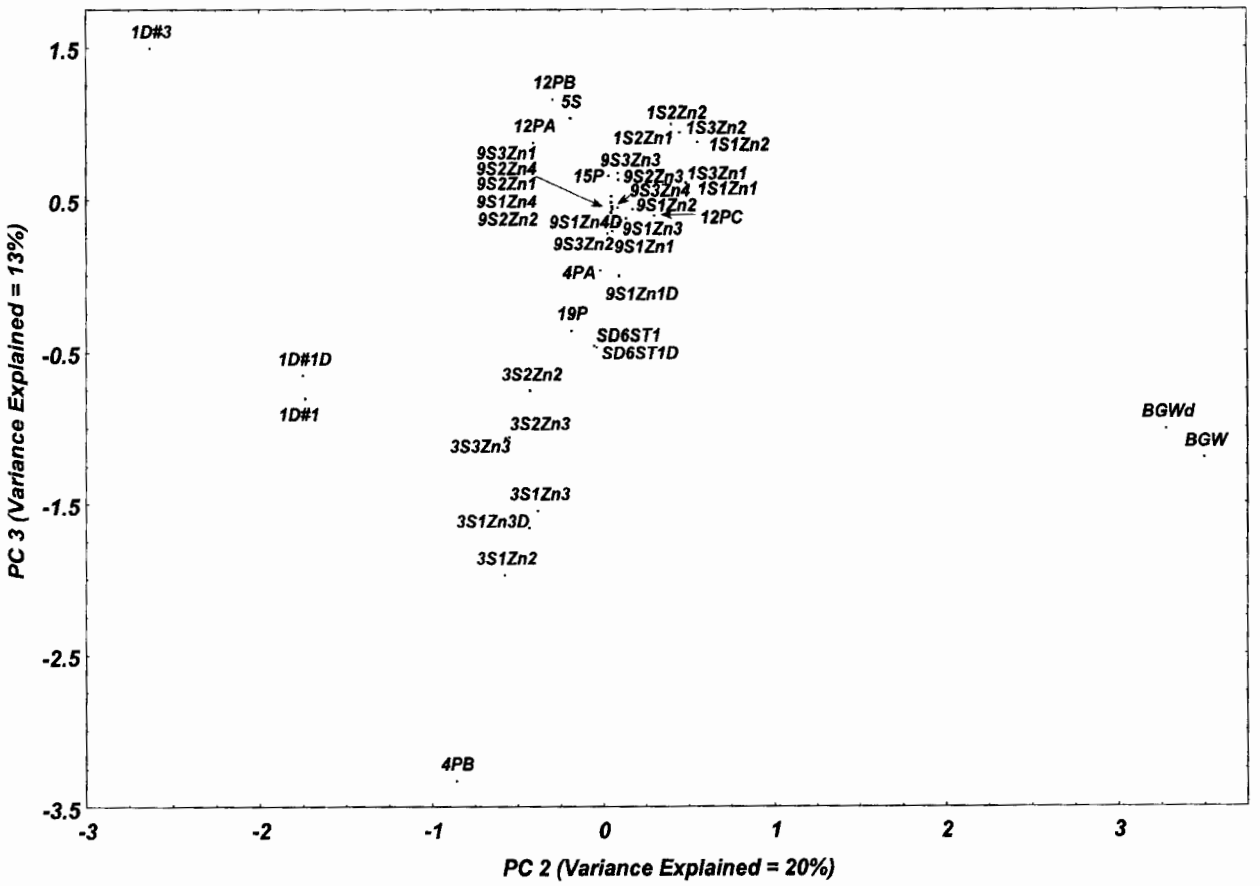

Fig. 4. Scores for principal components 2 and 3.

waters, and much less so in oxidizing waters [32]. Under oxidizing conditions, manganese will precipitate as Mn(IV)-oxide scavenging other trace elements such as Co, Pb, Zn, Cu, Ni, and Ba from solution in the process [32]. Consequently, it appears that the trace elements with the greatest positive PC 3 loadings (Table 2) are also those that might be expected to exhibit relatively high abundances in reducing waters. Trace elements with the greatest negative PC 3 loadings include V, Cr, Ga, As, and W. Because of their tendency to form oxyanions, these elements are typically relatively soluble in oxidizing alkaline, environments [32]. In oxidizing, moderate to high pH waters, vanadium is expected to occur in solution as the oxyanion HVO_4^{2-} [36–39]. However, under reducing conditions vanadium could occur as the oxycation $V(OH)_2^+$ [38,39] 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 [32]. Chromium concentrations are generally low in anaerobic groundwaters that contain ferrous iron, which may reflect reduction of soluble chromate (CrO_4^{2-}) to the insoluble chromic ion, Cr^{3+}, by Fe^{2+} [40]. The redox sensitive element, As, is commonly relatively soluble in oxidized groundwaters occurring as the oxyanion AsO_4^{2-} or $H_2AsO_4^-$. However, in reducing waters, arsenic tends to be incorporated in insoluble minerals [40–42]. The predominant forms of the trace element W in seawater is WO_4^{2-}, which again is also a soluble oxyanion [32]. From these results, waters of wells 1S, 1D, 12PA, 12PB, and 5S are thought to be relatively reducing compared to the more oxidizing waters from wells 3S and 4PB.

Table 4
Concentrations of As(III) and As(V)

Well	As(III) (ppb)	As(V) (ppb)
NC-EWDP-1S Zn 1	0.46	4.24
NC-EWDP-1S Zn 2	0.25	0.39
NC-EWDP-3S Zn 3	0.07	39.2
NC-EWDP-9S Zn 1	0.48	8.18
NC-EWDP-9S Zn 2	0.51	15.1
NC-EWDP-9S Zn 3	0.36	9.11
NC-EWDP-9S Zn 4	0.07	11.51
NC-EWDP-5S	0.22	0.65
NC-EWDP-1D	5.30	2.71
NC-EWDP-4PA	0.04	12.3
NC-EWDP-4PB	0.08	40.5
NC-EWDP-12PA	0.13	2.31
NC-EWDP-12PB	0.13	1.21
NC-EWDP-12PC	0.24	13.1
NC-EWDP-19P	0.35	10.2
NC-EWDP-15P	1.33	14.3

3.2. Q-mode factor analysis

Q-mode factor analysis was performed on the entire dataset as well as the dataset containing the subset of 25 trace elements used for PCA. No significant differences were observed in the Q-mode factor results, therefore only the results of the analysis of the subset are described herein. A total of 76% of the variance in the dataset 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 (e.g. 38 and 20% for PC 1 and PC 2, respectively). Because the similarity matrix consists of row-normalized data and is not column-normalized, the first few factors typically describe the variance of those 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. 5. This figure, for example, shows the dominance of Sr and Li in the Q-mode factor results. Both of these elements exhibit higher concentrations in NCEWDP groundwaters when compared to all others measured (Table 1).

The factor loadings for the first two factors are shown in Fig. 6. As mentioned earlier, the Q-mode factor loadings describe the relative proportions of the

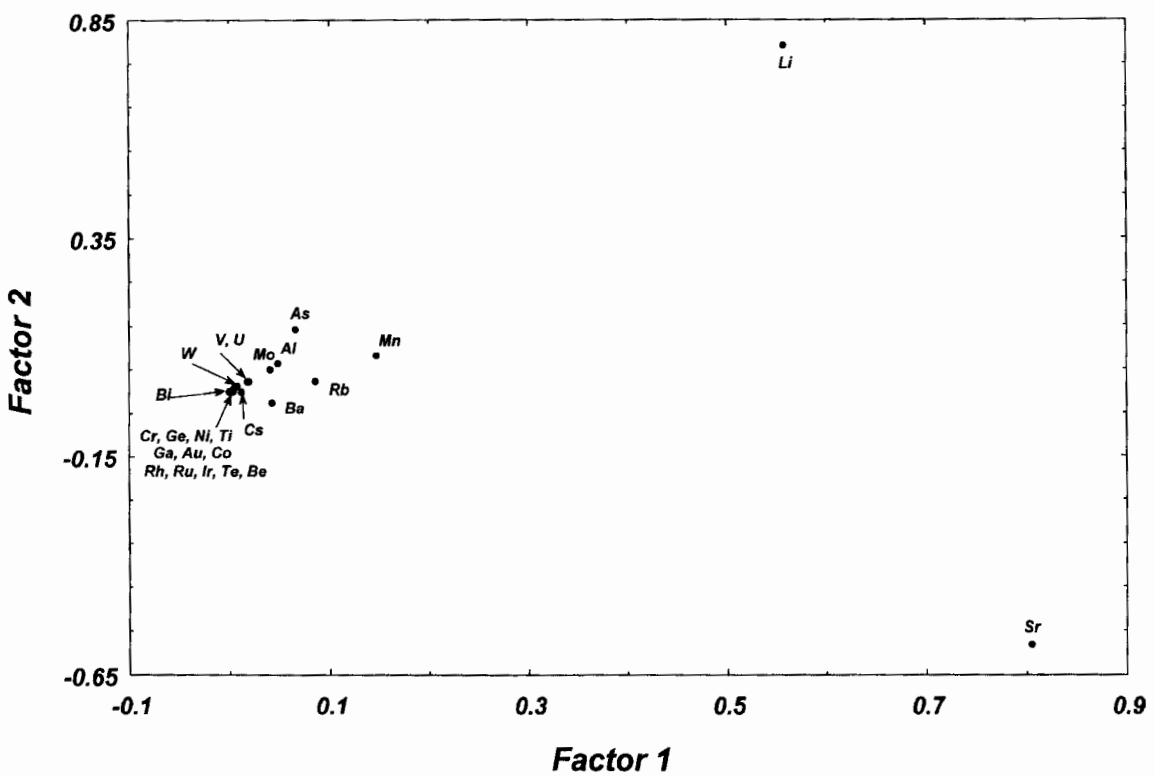

Fig. 5. Q-mode factor scores for factors 1 and 2.

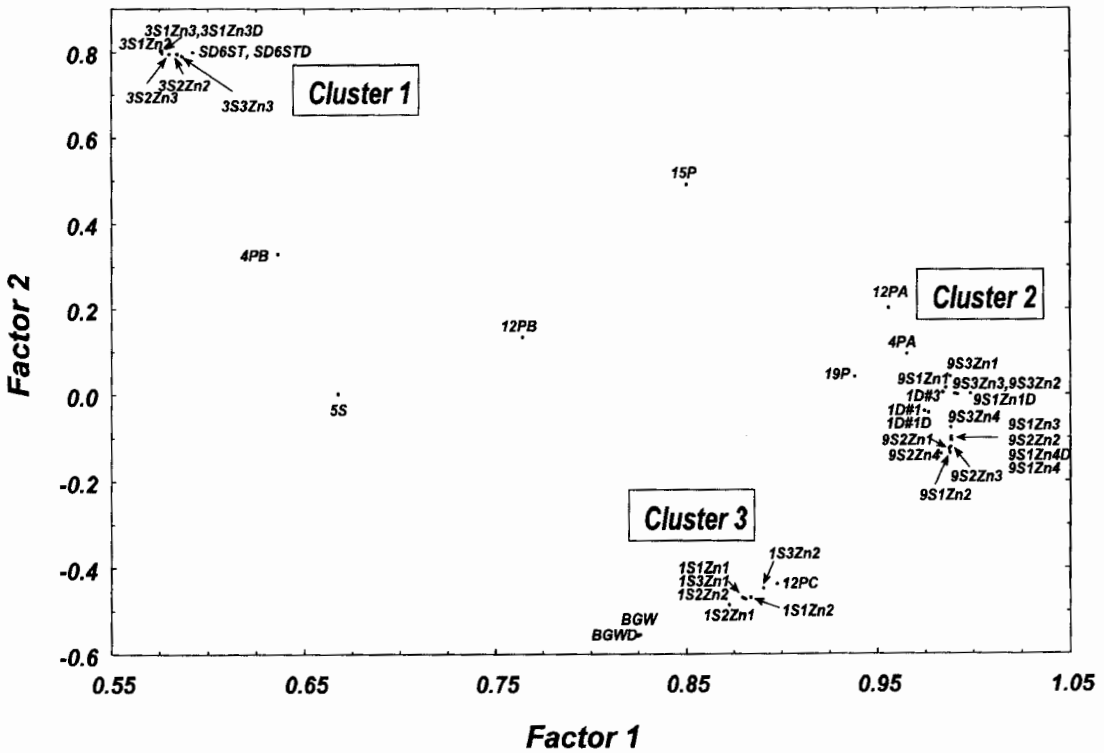

Fig. 6. Q-mode factor loadings for factors 1 and 2.

trace elements in the groundwater samples. Although the concentration of most of the trace elements in the samples collected from well 1D are greater than those for the majority of the groundwater samples included in the dataset, QFA demonstrates that the relative proportions of these elements are similar to those found in the samples from well 9S (Fig. 6). Similarly, the samples collected from well BGW plot close to those collected from wells 1S and 12PC. Three clusters are identified in Fig. 6. Cluster 1 contains groundwater samples collected from wells SD6ST1and 3S, suggesting that these waters have similar trace element compositions. Samples from wells 12PA, 4PA, 19P plot within cluster 2 which also contains waters from wells 9S and 1D. Cluster 3 contains groundwater samples from wells 1S, 12PC and BGW. Samples from wells 4PB, 5S, 12PB, and 15P plot distinct from these three clusters (Fig. 6). No clear separation of the zones within wells 1S, 3S, or 9S is observed in Fig. 6. This suggests that the separation of 1S and 3S zones observed in the PC score plot (Fig. 3) is a result of overall concentration differences and not differences in the relative proportions of the trace elements. Furthermore, Fig. 6 suggests that QFA Factor 1 (QF 1) describes the combined relative proportions of Sr and Li concentrations, whereas QF 2 separates the groundwaters based on greater proportions of Li (samples with positive QF 2 loadings) and Sr (samples with negative factor loadings). For instance, the waters contained in cluster 3 (i.e. wells 1S, BGW, and 12PC; Fig. 6) plot negatively on factor 2 and have concentrations of Sr that are 6–30 times greater than Li (Table 1). The waters from wells 3S and SD6ST plot positively on QF 2 and have concentrations of Li that are a factor of 40–200 greater than that of Sr (Table 1). The Li/Sr ratios in waters that plot closest to cluster 2 (i.e. 4PB and 15P) are roughly 2, whereas those waters with factor 2 loadings around zero have Li/Sr ratios ranging from 0.5 to 1.0. On the other hand, the samples with negative factor 2 loadings (wells 1S, 12PC, and BGW), exhibit Sr/Li ratios between 6 and 32. Again, from Table 3, it is clear that Li concentrations are correlated to Na ($r = 0.99$) and K ($r = 0.91$), and Sr concentrations are correlated

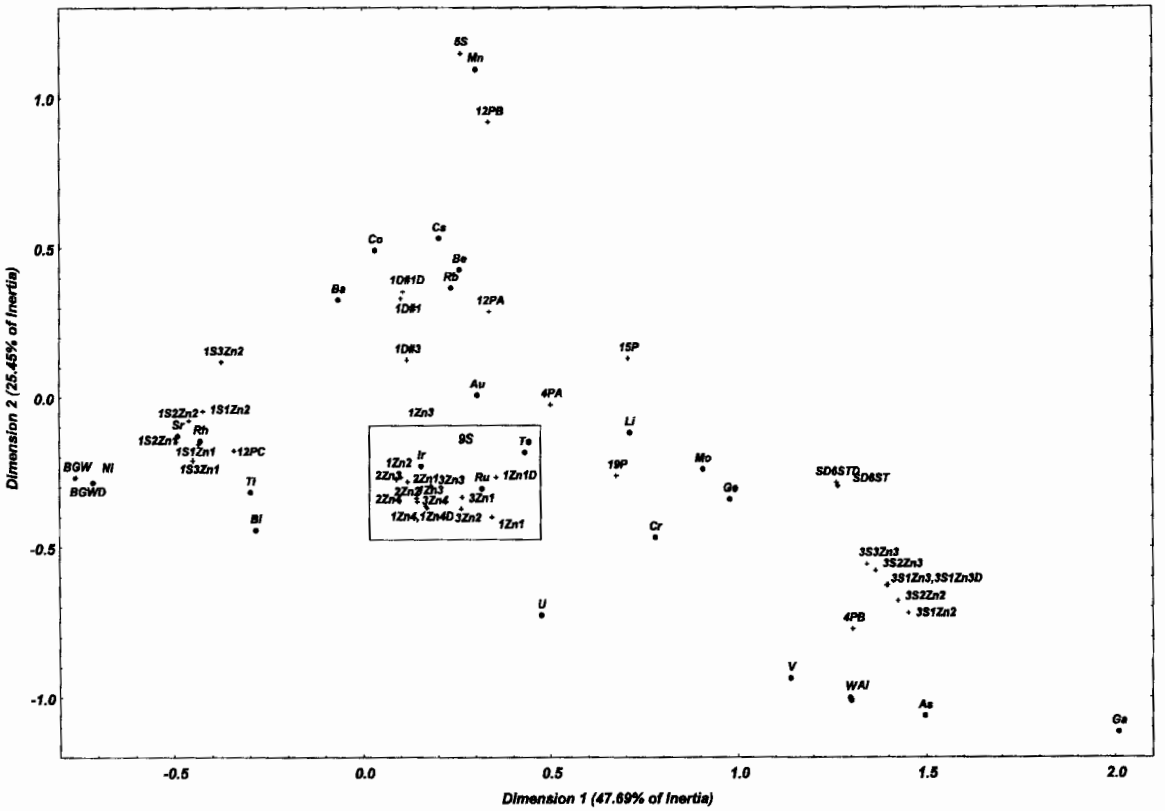

Fig. 7. Correspondence analysis results for the first two dimensions.

to Ca ($r = 0.94$), Mg ($r = 0.90$), and SO_4 ($r = 0.94$).

3.3. Correspondence analysis

The R- and Q-mode factor loadings for the first two dimensions of the CA results are shown in Fig. 7. Samples collected from wells 1S, 12PC, and BGW, along with the trace elements Ni, Sr, Rh, Ti, and Bi, are contained in one cluster (Fig. 7). Correspondence analysis dimension 2 (CA-D2) separates the zones of the 1S samples. Samples collected from well 9S are contained in a relatively tight cluster with no consistent separation of the four zones (Fig. 7). The trace elements that cluster with the groundwater samples from well 9S include Ru, Te, and Ir. The samples collected from the 3S well plot in a relatively tight cluster near samples collected from wells SD6ST1 and 4PB. As with the 1S samples, dimension 2 separates the two zones, zones 2 and 3, within the 3S well (Fig. 7). The trace elements that plot in the vicinity of these samples (i.e. wells 3S, SD6ST1, and 4PB) consist of As, W, Al, V, Cr, Ge, and Mo. The sample collected from well 19P lies between the 9S samples and the samples collected from wells 3S, SD6ST1, and 4PB. Samples collected from wells 12PB and 5S plot together along with the element Mn. Samples from wells 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 in the case of PC 2 and PC 3. With the exception of the 1D well waters, the samples are distributed similarly along CA-D1 of the CA results as with PC 2. Waters with greater Ca + Mg concentrations (i.e. BGW, 1S, and 12PC) plot to the left of the origin in Fig. 7, whereas those with greater Na + K concentrations plot to the right. Dimension 2 of the CA results is somewhat similar to the PC 3 scores; the rank correlation coefficient [35] between CA-D2 and the percentage of As(III) is 0.70. Groundwaters that plot positively on CA-D2 (wells 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 from the region (Table 4). These results are again consistent with those trace elements that plot along with these waters in CA-D2 (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 (V, As, and W) that are plotting close to these waters in Fig. 7. Interestingly, U also plots quite negatively on dimension 2 (Fig. 7). In oxidizing environments, highly soluble U(VI) will dominate over U(IV), occurring in solution as the uranyl ion (UO_2^{2+}) and uranyl-carbonate complexes such as $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ [43]. In reducing environments U(VI) is reduced to U(IV) and precipitated as a solid phase.

4. Conclusions

The differences in the specific aspect of the trace element chemistry that each of the multivariate statistical technique evaluates, made each one valuable for the exploratory data analysis performed in this study. Different normalizations of data used by these techniques bring out varying aspects of groundwater geochemistry. Each technique contributed new and important information that was useful in evaluating the chemical similarities and differences in these groundwaters. The results of multivariate statistical analysis of the trace element chemistry in the groundwaters of the NCEWDP demonstrated the diversity in the chemical composition of the groundwaters of the area. With the exception of waters from wells 1S, BGW, and 12PC, the groundwaters of the NCEWDP were characterized by rock-water interaction with aquifers dominated by volcanic rocks. The trace element chemistry of the waters from 1S, BGW, and 12PC instead reflect rock-water interaction within an aquifer dominated by carbonate rocks. Perhaps of most interest, the combined use of these statistical and chemical techniques strongly suggest that groundwaters of 1D, 12PA, 12PB, 5S and 15P are somewhat reducing, whereas the rest of the waters, especially those of 3S and 4PB are more oxidizing.

Knowledge of the redox conditions of the groundwaters is important when evaluating the mobility of radionuclides associated with the high-level nuclear waste planned to be contained in a repository, potentially at Yucca Mountain, Nevada. In the rare event of a breach of the repository, the spent fuel consisting primarily of UO2 may leach into the groundwater.

Leaching of the spent fuel by groundwater could release U to the environment along with the associated radionuclides, ^{90}Sr, ^{99}Tc, ^{125}I, ^{137}Cs, and long-lived radioisotopes of Am, Np, and Pu [40]. Geochemical modeling experiments described by [40] indicate that some of the radionuclides (Am, Pu, and Th) are highly insoluble in an environment of near neutral pH whether oxidizing or reducing, while other radionuclides are insoluble in low-Eh environments but may be highly soluble at high Eh values (Np, Tc, U).

The current dataset does not provide conclusive information regarding groundwater flow paths in this area. Drilling of additional wells, upgradient of those reported in this study, is currently in progress. Multivariate statistical evaluations of the trace element concentrations in these additional groundwaters may then provide a better understanding of flow directions down gradient from the potential repository.

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