

Interpretation of Chemistry Data from Seepage, Observation Well, and Reservoir Water Samples collected at Horsetooth Dam during July 2004

TSC Technical Memorandum No. 8290-04-02

by

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Introduction

This technical memorandum summarizes chemistry data from reservoir, seepage, and observation well water samples collected at Horsetooth Dam on July 13-14, 2004. Samples were received by the Denver Environmental Chemistry Laboratory on July 16, 2004, and the final data were reported to me on September 28, 2004. These samples are the first set of seepage water samples to be collected after completion of modifications to Horsetooth Dam and re-filling of the reservoir.

Seepage, well, and reservoir water were analyzed for the chemical constituents pH, conductivity (EC), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), bicarbonate, (HCO_3^-), carbonate (CO_3^{2-}), hydroxide (OH^-), sulfate (SO_4^{2-}), chloride (Cl⁻), and trace elements aluminum (Al), iron (Fe), manganese (Mn), and silicon (Si). Seepage, well, and reservoir water have been sampled and analyzed at intervals since 1951 in response to concerns about seepage at Horsetooth Dam, Ft. Collins, Colorado. Previous geochemical evaluation of seepage data and evaluation of risks resulting from the potential failure modes lead to modification of the four dams that contain Horsetooth Reservoir.

Chemical data from seepage and well water at Horsetooth Dam has consistently suggested that mineral dissolution of calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and silica (SiO_2) has been occurring in the foundation and abutments since first filling. The tilted geology of the foundation is composed of brecciated sedimentary claystone deposits with layered beds of limestone (notably the Forelle Limestone) and gypsum (the Blaine gypsum) associated with the Lykins formation. Samples were initially collected from the downstream seep at SM-3 shortly after reservoir filling in 1951, and indications of soluble mineral dissolution have been noted in technical memos for water samples collected since 1987.

Samples and Locations

Samples were collected from several wells and seepage locations. Information about these samples, obtained from Chuck Sullivan (in his travel report dated September 9, 2004), are summarized in Table 1. Samples are organized by abutment and distance from dam axis. Refer to the map in figure 1 for sampling locations.

Methodology

Samples were analyzed by the Denver Environmental Chemistry Laboratory following established consensus methods (USEPA 1983, 1986, American Public Health Association, 1998). The EPA methods are summarized in the lab report included in the Appendix. In this report, concentrations for major ions are reported in units of milligrams per liter (mg/L) and milliequivalents per liter (meq/L), and trace elements are reported in

millimoles per liter (mMol/L) and micromoles per liter ($\mu\text{Mol/L}$). For each analyzed constituent, same date reservoir meq/L was subtracted from seepage meq/L to calculate net difference meq/L.

Saturation indices (SI) are reported for carbonate-containing minerals (calcite, dolomite, magnesite), gypsum (and amorphous silica (MINTEQA2 compound 2077004 $\text{SiO}_2(\text{A,PT})$) were calculated using the MINTEQA2 model (Allison, et al., 1991) and have been included with the Horsetooth summary data spreadsheet file (transmitted by email on 11-5-04). The SI's were calculated assuming temperature = 10°C and that samples were in equilibrium with atmospheric O_2 and CO_2 at partial pressures for elevation 5,640 ft. Trace elements (Al, Fe, Mn, Si) reported below detection limits were re-coded as one-tenth the reported limit of detection for input into the MINTEQA2 model. Negative SI values suggest under saturation and that the water will dissolve the mineral. Positive SI values suggest over saturation and that the mineral will tend to precipitate. SI values near 0 suggest that the mineral is in equilibrium with the seepage water.

Results and Discussion

Major ions results are summarized in Table 2, and trace elements in Table 3. Differences in meq/L between reservoir and downstream samples are summarized in table 4, and MINTEQA2-calculated mineral saturation indices are presented in table 5. Figures 2 (wells and piezometers) and 3 (surface seeps) show radar diagrams for major ions in meq/L with the reservoir sample reproduced on each graph (light blue polygon). Trace element data are graphed similarly in figures 4 (wells and piezometers) and 5 (surface seeps). Once again, the reservoir sample polygon is included on each graph. Note that the radar diagrams plot data on a log scale, so any dark polygon visible beyond the reservoir polygons suggest a significant increase in concentration. Figures 6 (wells and piezometers) and 7 (surface seeps) plot difference data in meq/L on bar charts for each sample.

Increased sulfate (SO_4) along with Ca relative to the reservoir suggests gypsum dissolution along flow paths, and all seepage and well samples showed elevated Ca and at least some elevated SO_4 . DH91-5 (91.2 mg/L), DH98-5 (165 mg/L) and 5C (176 mg/L), and DH99-11 (82.5 mg/L) showed significantly elevated SO_4 . These samples show the SO_4 spike clearly in the figure 6 bar charts.

Trace element data in Table 3 (and figures 5 and 6) show that no samples contained Fe or Al higher than the reservoir sample (Fe = $148 \mu\text{g/L}$, Al = $325 \mu\text{g/L}$). Elevated Mn relative to the reservoir ($< 4.00 \mu\text{g/L}$) was observed in several wells: DH91-4 = $17.9 \mu\text{g/L}$, DH-91-5 = $59.1 \mu\text{g/L}$, DH-92-7 = $169 \mu\text{g/L}$, suggesting some bacterial activity in these wells and either stagnant conditions or very slow seepage flow through these intersection points. All well and surface seepage samples (except for SM-9) show elevated Si, suggesting some weathering of clays or dissolution of amorphous silica along seepage flow paths.

Limestone (calcite) also appears to be dissolving along all flow paths sampled in this event. HCO_3^- is elevated for all downstream samples; however, some of this increase may be caused by microbial metabolism of organic carbon during seepage transit. Along the well interception flow paths, the largest increases in Ca were observed for DH98-5 (516 mg/L) and 5C (512 mg/L). With surface seeps, highest Ca was observed for SM-9 (51.4 mg/L) and SM-11B (44.1 mg/L). The other SM samples showed very similar results with respect to elevated HCO_3^- and Ca. Dolomite ($\text{CaMg}(\text{CO}_3)_2$) dissolution is also suggested by the Table 4 increases in Mg for all samples. Another possibility for increased Mg may be that the local limestone contains a proportion of Mg in the calcite.

Mineral saturation indices in Table 5 show that all seepage and well samples remain undersaturated with respect to soluble minerals, and that SI values are generally less negative compared to the reservoir water. Except for amorphous silica (SiO_2), reservoir water is an aggressive solvent for all soluble minerals. Water in DH-98-5 appears to be near equilibrium with respect to gypsum (SI = -0.58, $\Delta_{\text{SO}_4} = +3.5$ meq/L) suggesting that SO_4 concentration in this well may be regulated by gypsum dissolution. The DH98-5 SI's may also suggest stagnant conditions where near equilibrium conditions are present.

Suspended Sediments in Well Samples: Notably high levels of suspended solids were observed in 3 well samples: DH91-4 (243 mg/L), DH92-7 (1,230 mg/L), DH98-5 (222 mg/L), and DH98-5C (272 mg/L). Residue from samples DH-92-7 and DH98-5 were likely caused by stirring of drill hole sediments during hand baling of the wells. The DH-91-4 sample was pumped, but field notes suggest that this well recharges slowly, so pumping may have also stirred and mobilized sediments. The slow recharge of these wells suggest is that sampling turbulence is the likely cause of suspended sediments in these samples.

DH-92-7, whose screen intersects the Harriman Shale, contained suspended residue that was mostly clay particles (see memorandum No. 8340-04-18, from Doug Hurcomb, dated October 22, 2004). Initial samples purged from this well also exhibited an "organic odor" suggestive of stagnant conditions in the hole. The presence of elevated Mn (169 $\mu\text{g/L}$) also suggests anaerobic reducing conditions in this well.

In DH98-5 and 5C, duplicate well samples with a screen in the Blaine Gypsum, the suspended residues were classified as chiefly calcite by petrographic examination. DH98-5 also showed unbalanced ions concentrations, suggesting that low HCO_3^- alkalinity and/or elevated Ca and Mg may have been caused by subsampling heterogeneity. For example, a sub sample containing particulate calcite may have been analyzed for Ca (high bias for Ca), but the alkalinity sample did not have suspended materials (potential low bias for HCO_3^-). Suspended particulates from DH-91-4, with a screen in the Glendo Shale, also contained mostly calcite.

Surface Seepage Sample Notes: SM-1 analysis results showed a poor ion balance (-77 percent), and the culprit for this sample appears to be elevated HCO_3^- , which appears to be an order of magnitude higher than expected. The unexpectedly low pH (5.77) for this sample also suggests that water emerging at SM-1 is fairly acidic, perhaps from very slow flow conducive to bacterial activity.

Surface seeps also show several samples suggesting gypsum dissolution: SM-3, SM-7, and SM-9. Along these flow paths, it appears that seepage is contacting gypsum deposits and some of the subsurface gypsum is continuing to dissolve. Gypsum dissolution on the left abutment below Satanka at SM-9 warrants close scrutiny during future sampling events as gypsum dissolution was not previously noted in surface seeps on this side of the dam.

Conclusions and Recommendations:

It appears that limestone and gypsum are continuing to be dissolved by underground seepage at Horsetooth Dam. This is not a surprising result given the foundation and abutment geology. However, it is probably too early to determine if these dissolution rates are greater than those observed before repairs. Perhaps some of the increases observed in the July 2004 samples including flushing of increased concentration "stagnant" or remnant seepage water that remained in the abutments and foundation formations during construction. These remnant waters may also be reflected in the well samples. The complete flushing of prior bank storage may take several seasons of reservoir filling.

One sampling, however, does not prove the bank storage theory, and I recommend additional sampling events during low and high-water points along with continued surveillance of seepage volume for several more years. If concentrations reach a constant level and seepage flows do not increase with similar hydrostatic heads, then monitoring frequency may be significantly reduced. The suggestion of gypsum dissolution emerging at the left side SM-9 surface seep should be carefully monitored.

The next sampling event should also specify analyses on samples filtered through 0.45 μm filter media. This should eliminate spurious ion balance problems from acid titration of calcite particles during alkalinity tests, and any spectral artifacts or interferences from analyzing samples with finely-sized suspended mineral solids.

Now that the chemistry lab at the TSC is closed, future samples will also need to be contracted. Please contact me well before the next sampling so I can help arrange for a suitable contract lab and analytical request.

TABLES

Interpretation of Chemistry Data from Seepage, Observation Well, and Reservoir Water Samples collected at Horsetooth Dam during July 2004

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Table 1 Seepage and well samples collected in July 2004 from Horsetooth Dam.

Station ID	Abutment L or R	Lateral Distance from Dam Axis (ft - m)		Pump Depth, ft	Screen Depth, ft	Notes
IW-3R	L	525	160.0	0	surf	@ 9+08, Right toe drain - inspection well on left side of outlet
SM-9	L	965	294.1	0	na	@ 17+10, Satanka Dike seepage
SM-4	L	1,245	379.5	0	na	@ 10+75, Seepage Pond, collects all left side seepage
DH91-4	L	32	9.75	140	145-126	@ 14+00, sediment, static level 128.3', Glendo Shale
DH99-11	L	32	9.75	150	392-310	@ 11+89, static level 135.1', Lower Lykins (Forelle - Blaine)
DH91-5	L	485	147.8	34.5	234-184	@ 11+97, static level 28.2', Forelle Limestone
DH92-7	L	570	173.7	54.6	61-51	@ 14+32, sediment, static level 54.6', hand-baled sample, Harriman Shale
DH98-5**	L	615	187.5	50	375-341	@ 10+56, sediment, static level 7.1', hand-baled sample,, Blaine Gypsum
DH98-5C**	L	615	187.5	50	375-341	duplicate of DH98-5
DH97-3	L	620	189.0	100	120-101	@ 13+00, static level 24.8', Forelle Formation
SM-1	R	470	143.3	0	na	@ 8+50 right side of outlet
SM-11	R	490	149.4	0	na	@ 8+20 right side of outlet
SM-11B	R	940	286.5	0	na	@ 6+40 new right side seepage measurement site
SM-2	R	1,272	387.7	0	na	@ 8+95, right (east) of Hansen Canal
SM-3	R	2,920	890.0	0	na	@ 13+10, deeper seepage - Forelle
SM-7	R	3,750	1,143	0	na	@ 5+50, all seepage collection point

** Samples DH98-5 and DH98-5C are from the same drill hole.

Table 2 Major ions concentrations for reservoir, well and surface seepage samples collected at Horsetooth Dam July, 13-14, 2004.

Sample ID	Lab EC μS/cm	TDS mg/L	TSS mg/L	Lab pH	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	HCO ₃ mg/L	CO ₃ mg/L	SO ₄ mg/L	Cl mg/L
RESN	72	46	<4.0	6.56	9.26	1.57	2.68	<1.00	39.0	<1.0	3.10	1.41
DH91-4	307	194	243	7.26	43.7	11.3	3.66	<1.00	192	<1.0	8.05	1.15
DH91-5	386	248	<4.0	7.82	58.0	7.32	3.39	<1.00	125	<1.0	91.2	1.12
DH92-7	471	282	1230	7.39	56.1	20.5	6.46	1.55	298	<1.0	1.72	2.50
DH97-3	214	128	<4.0	7.70	29.3	6.83	3.18	<1.00	132	<1.0	5.81	1.24
DH98-5	2340	1470	222	7.71	516	36.6	5.75	<1.00	105	<1.0	165	1.00
DH98-5C	2340	1460	272	7.75	512	35.4	5.79	1.29	113	<1.0	176	1.02
DH99-11	346	218	8.2	8.21	44.3	13.0	4.86	1.70	128	<1.0	82.5	1.09
IW-3R	252	170	<4.0	7.89	35.4	7.16	4.43	<1.00	145	<1.0	8.10	1.25
SM-1	294	186	4.60	5.77	38.8	10.1	5.35	<1.00	1360	<1.0	9.84	1.97
SM-2	270	168	<4.0	8.32	37.0	10.2	5.28	<1.00	169	<1.0	8.62	1.65
SM-3	211	132	<4.0	7.64	30.6	4.97	3.13	<1.00	109	<1.0	20.1	1.23
SM-4	243	148	<4.0	7.76	28.7	8.99	8.51	<1.00	150	<1.0	7.52	2.32
SM-7	237	144	<4.0	7.88	34.4	6.54	3.92	<1.00	127	<1.0	22.6	1.34
SM-9	289	248	<4.0	8.12	51.4	14.0	7.70	<1.00	190	<1.0	52.1	2.53
SM-11	273	166	<4.0	8.24	36.4	10.3	5.26	<1.00	158	<1.0	9.76	1.95
SM-11B	306	192	<4.0	8.12	44.1	10.7	5.15	<1.00	207	<1.0	4.51	1.01
DH98-5D	4	<10.0	<4.0	5.61	0.11	<0.03	<0.03	<1.00	2.4	<1.0	0.20	<0.04
DH91-1B	3	<10.0	<4.0	5.74	0.15	<0.03	0.05	<1.00	2.7	<1.0	<0.15	<0.04
Detection limit:	2	10.0	4	10	0.03	0.03	0.03	1.00	1.0	1.0	0.15	0.04

Table 3 Trace element concentrations for reservoir, well and surface seepage samples collected at Horsetooth Dam July 13-14, 2004.

Sample ID	SiO ₂ mg/L	Fe µg/L	Al µg/L	Mn µg/L
RESN	4.32	148	325	<4.00
DH91-4	14.0	76.8	203	17.9
DH91-5	8.92	8.32	<30.0	59.1
DH92-7	19.7	46.2	<30.0	169
DH97-3	9.24	5.60	<30.0	<4.00
DH98-5	19.5	<4.00	<30.0	22.0
DH98-5C	18.2	<4.00	<30.0	23.3
DH99-11	9.10	8.39	39.6	9.51
IW-3R	8.67	<4.00	<30.0	<4.00
SM-1	9.22	6.40	<30.0	<4.00
SM-2	8.69	7.20	<30.0	<4.00
SM-3	7.47	35.2	69.7	<4.00
SM-4	7.28	<4.00	<30.0	<4.00
SM-7	7.38	27.6	41.3	<4.00
SM-9	2.18	15.2	<30.0	12.0
SM-11	8.97	<4.00	<30.0	<4.00
SM-11B	8.47	11.6	<30.0	6.12
DH98-5D	<0.04	<4.00	<30.0	<4.00
DH91-1B	<0.04	<4.00	<30.0	<4.00
Detection limit:	0.04	4.00	30.0	4.00

Table 4 Differences (Δ_{ion}) between seepage and reservoir samples expressed in milliequivalents per liter (meq/L).

Sample ID	pH	Ca	Mg	K	Na	HCO₃	CO₃	SO₄	Cl	$\Sigma ions$
DH91-4	0.70	1.72	0.80	0.00	0.04	2.51	0.00	0.10	-0.01	5.17
DH91-5	1.26	2.43	0.47	0.00	0.03	1.41	0.00	1.83	-0.01	6.17
DH92-7	0.83	2.34	1.56	0.04	0.16	4.24	0.00	-0.03	0.03	8.34
DH97-3	1.14	1.00	0.43	0.00	0.02	1.52	0.00	0.06	0.00	3.03
DH98-5	1.15	25.29	2.88	0.00	0.13	1.08	0.00	3.37	-0.01	32.74
DH98-5C	1.19	25.09	2.78	0.03	0.14	1.21	0.00	3.60	-0.01	32.84
DH99-11	1.65	1.75	0.94	0.04	0.09	1.46	0.00	1.65	-0.01	5.93
IW-3R	1.33	1.30	0.46	0.00	0.08	1.74	0.00	0.10	0.00	3.68
SM-1	-0.79	1.47	0.70	0.00	0.12	21.65	0.00	0.14	0.02	24.10
SM-2	1.76	1.38	0.71	0.00	0.11	2.13	0.00	0.11	0.01	4.46
SM-3	1.08	1.06	0.28	0.00	0.02	1.15	0.00	0.35	-0.01	2.86
SM-4	1.20	0.97	0.61	0.00	0.25	1.82	0.00	0.09	0.03	3.77
SM-7	1.32	1.25	0.41	0.00	0.05	1.44	0.00	0.41	0.00	3.56
SM-9	1.56	2.10	1.02	0.00	0.22	2.47	0.00	1.02	0.03	6.87
SM-11	1.68	1.35	0.72	0.00	0.11	1.95	0.00	0.14	0.02	4.29
SM-11B	1.56	1.74	0.75	0.00	0.11	2.75	0.00	0.03	-0.01	5.37

Table 5 Mineral saturation indices for reservoir, well, and seepage water samples from Horsetooth Dam. Positive values suggest oversaturation, negative values suggest undersaturation.

	Calcite	Dolomite	Gypsum	Magnesite	Amorphous Silica
RESN	-4.91	-10.5	-3.39	-6.08	-1.17
DH91-4	-2.89	-6.28	-2.47	-3.88	-0.771
DH91-5	-1.7	-4.21	-1.36	-2.99	-0.967
DH92-7	-2.54	-5.43	-3.08	-3.37	-0.622
DH97-3	-2.16	-4.88	-2.73	-3.20	-0.952
DH98-5	-3.33	-7.72	-0.597	-4.87	-0.623
DH98-5C	-1.03	-3.14	-0.571	-2.59	-0.654
DH99-11	-1.03	-2.51	-1.51	-1.96	-0.961
IW-3R	-1.71	-4.03	-2.52	-2.8	-0.981
SM-1	NC	NC	NC	NC	NC
SM-2	-0.838	-2.15	-2.49	-1.80	-0.980
SM-3	-2.28	-5.26	-2.18	-3.46	-1.04
SM-4	-2.06	-4.54	-2.64	-2.69	-1.06
SM-7	-1.75	-4.14	-2.09	-2.87	-1.05
SM-9	-1.13	-2.75	-1.64	-2.1	-1.58
SM-11	-1.00	-2.47	-2.44	-1.95	-0.968
SM-11B	-4.20	-8.94	-2.71	-5.22	-0.988

FIGURES

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Figure 2 - Log-scale radar diagrams showing the Reservoir water (blue polygon) with drill hole samples (dark polygons) collected from Horsetooth Dam in July 2004. The data represent meq/L except for pH.

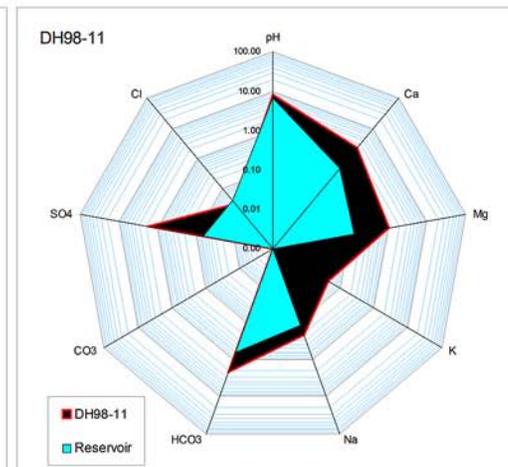
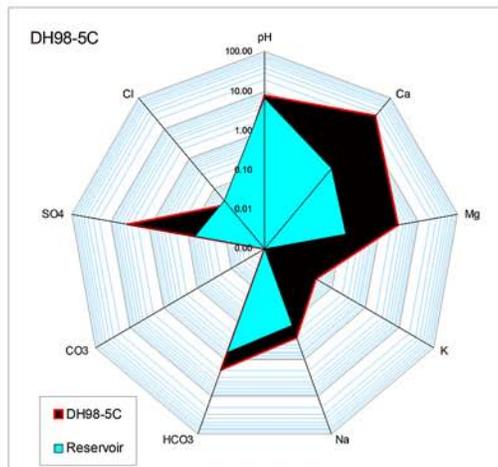
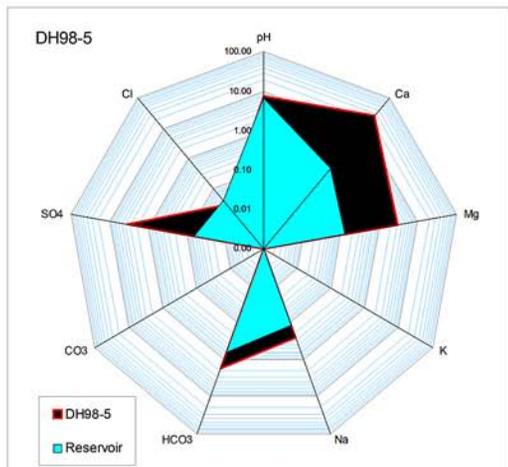
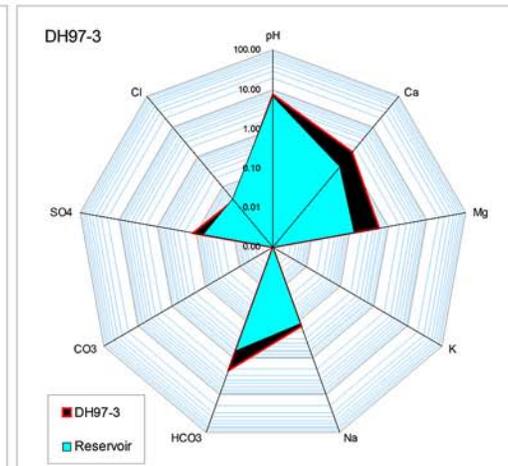
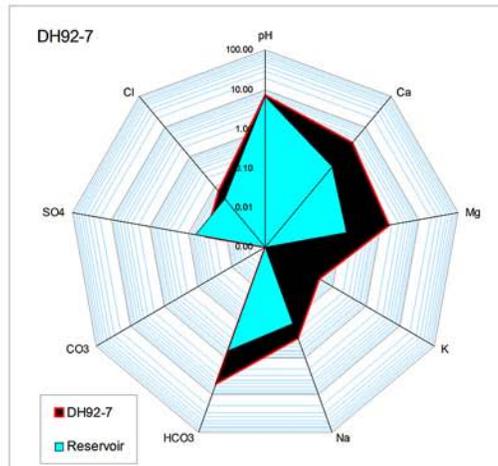
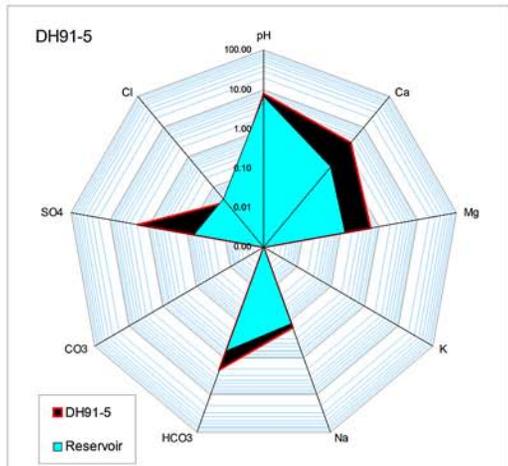
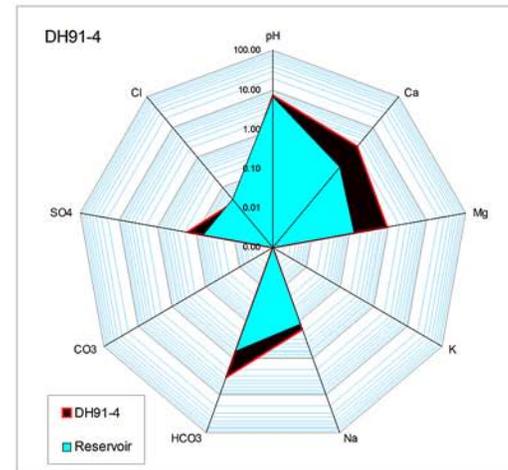


Figure 3 Radar diagrams showing major ions data for reservoir (inner blue polygons) and seepage (outer black polygons).

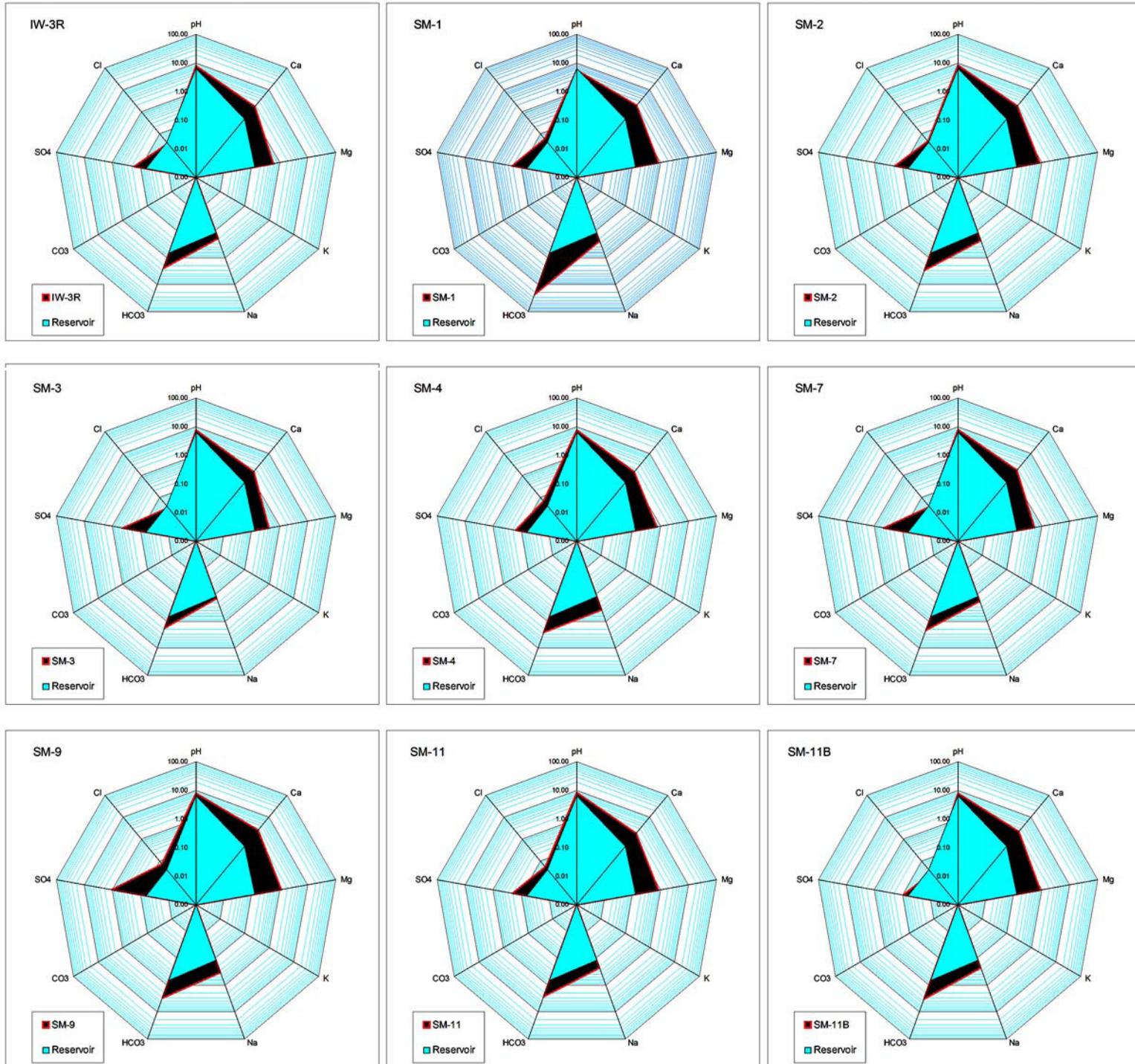


Figure 4 - Log-scale radar diagrams showing trace elements with pH and sum of ions data. Note varying concentration units where Al, Fe, and Mn are in $\mu\text{Mol/L}$, Si is in mMol/L , and sum of ions are in $\mu\text{eq/L}$. Reservoir water (blue polygon) with drill hole samples (dark polygons) collected from Horsetooth Dam in July 2004.

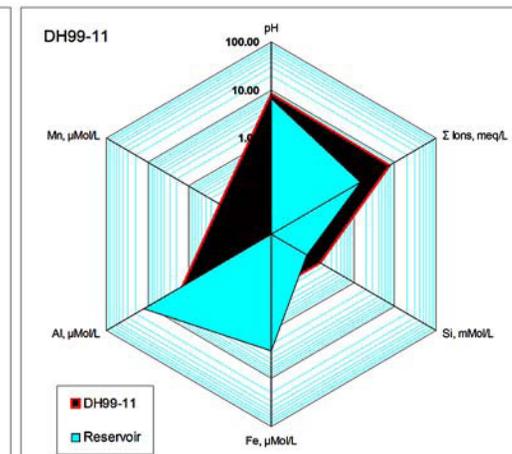
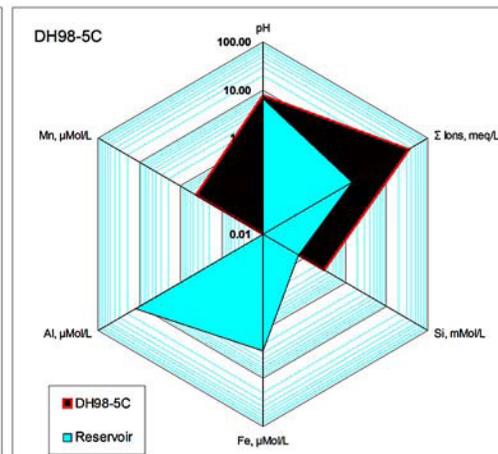
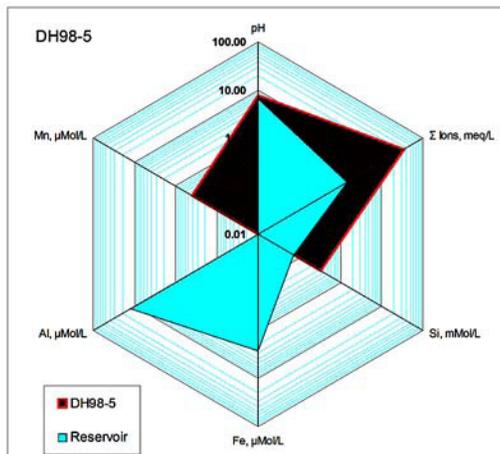
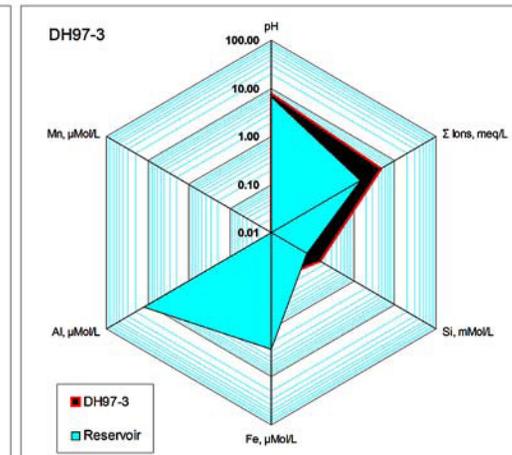
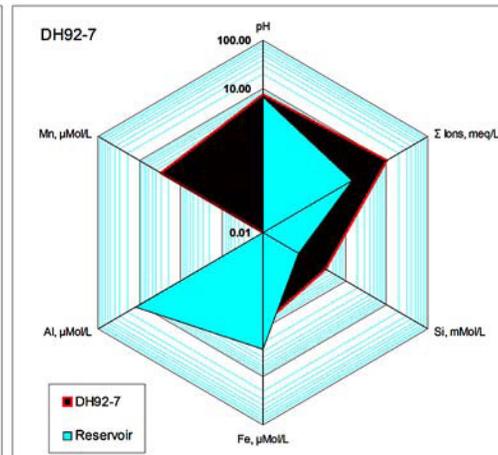
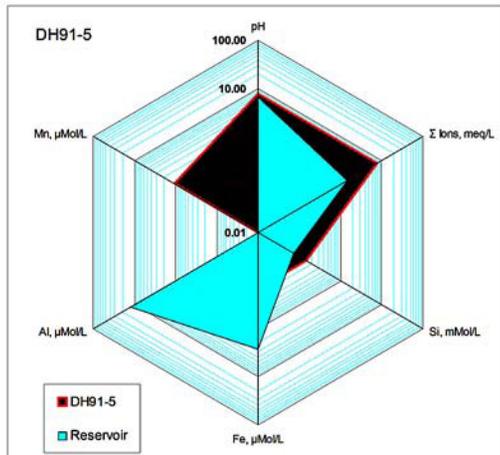
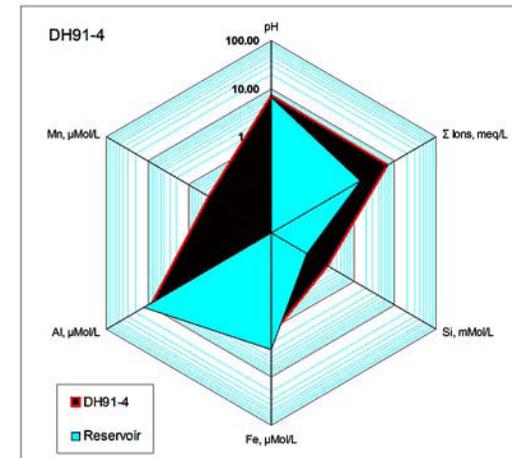


Figure 5 - Log-scale radar diagrams showing trace elements, pH and sum of ions for seepage samples.

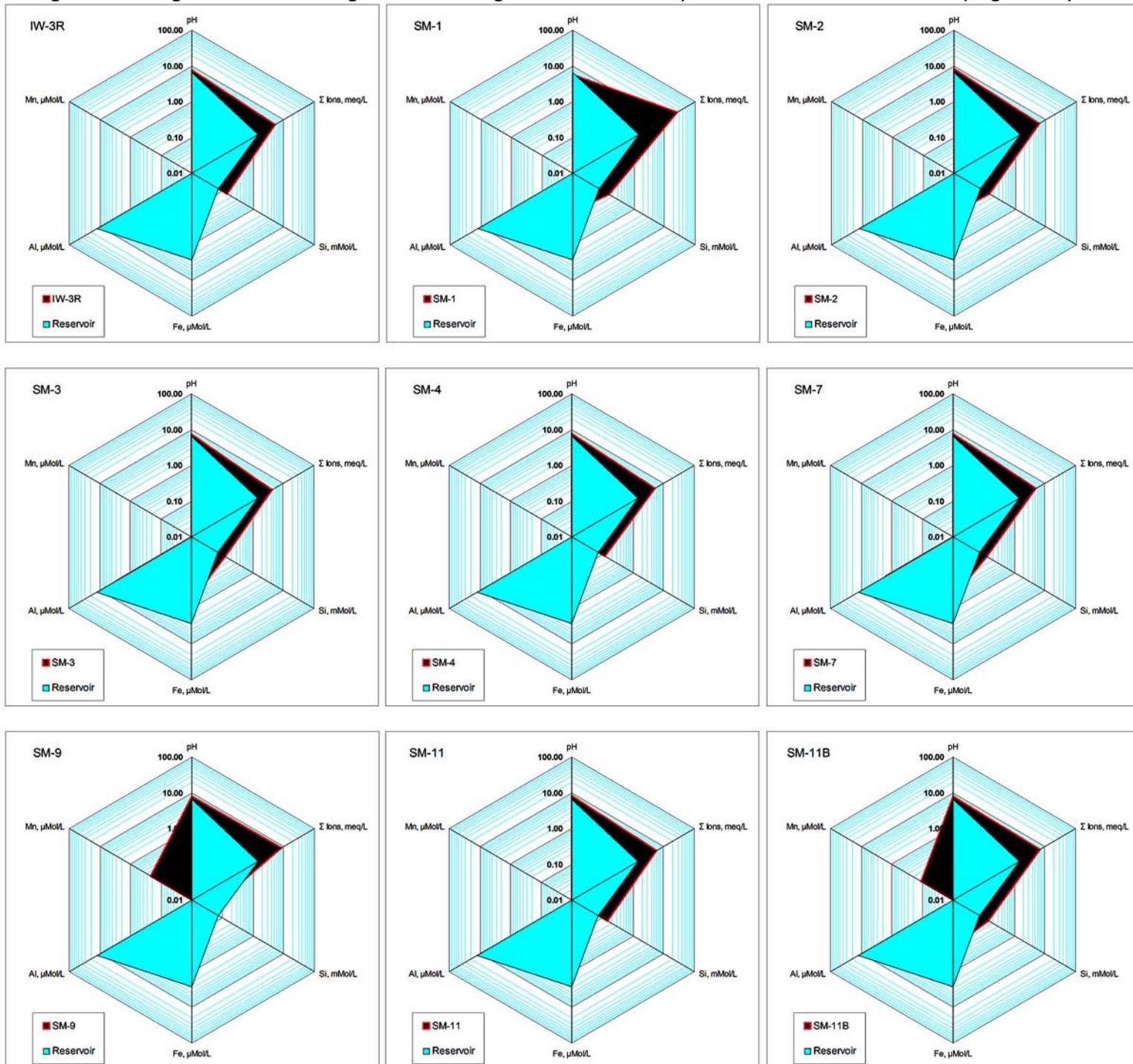


Figure 6 - Bar charts for DH samples from Horsetoorth Dam showing increases and decreases in major ions concentrations in meq/L between the reservoir and well water. Increases in groundwater concentrations along the seepage flow paths may be caused by dissolution of minerals or biotic processes. Scales vary for each well sample.

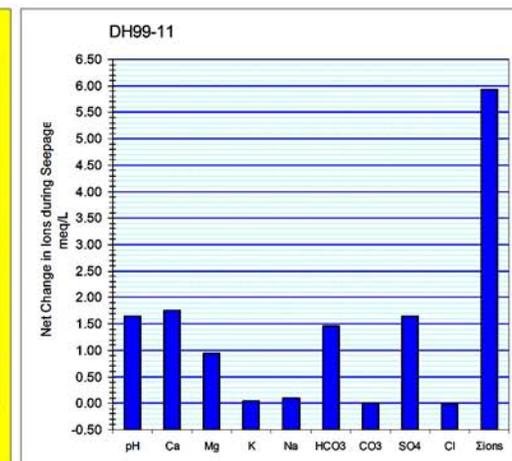
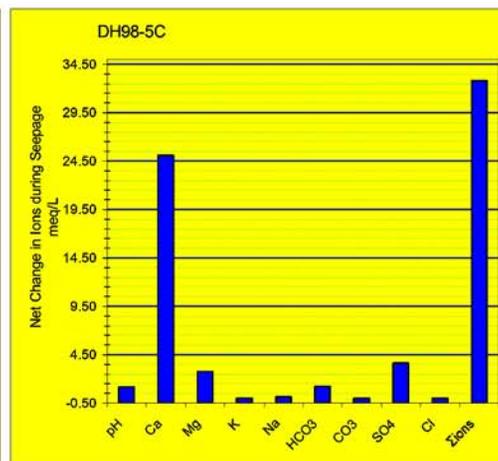
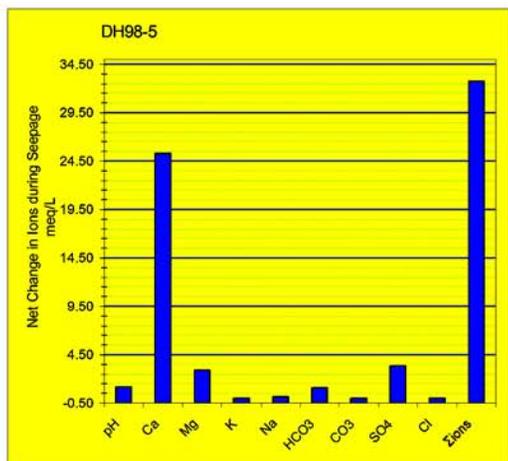
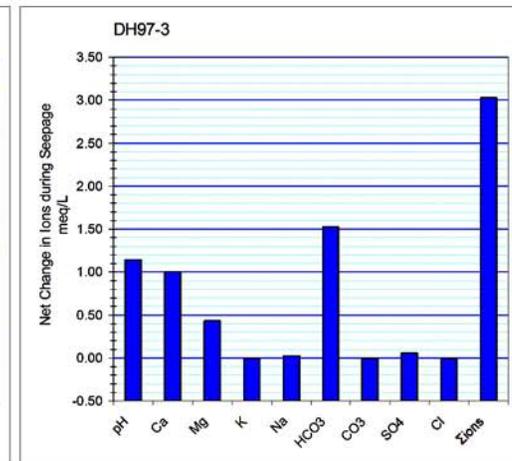
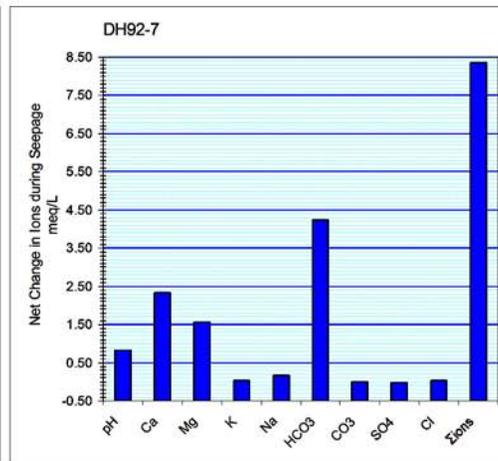
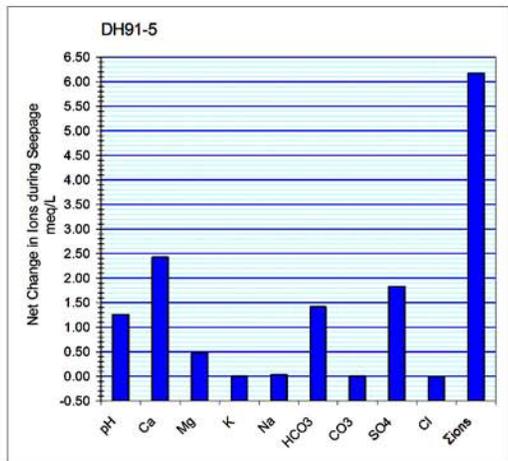
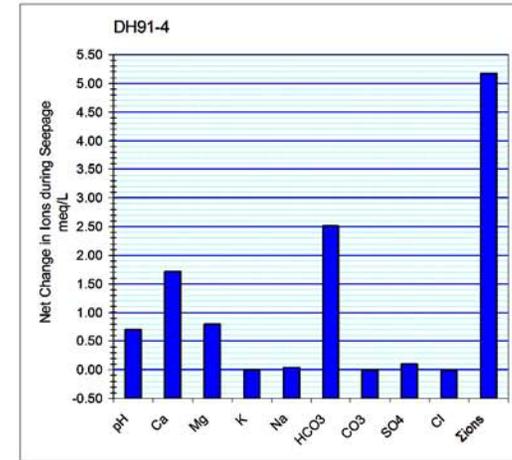


Figure 7 - Differences between seepage and reservoir concentrations in meq/L.

