

IMPACT OF LEACHABLE SULFATE ON THE QUALITY OF GROUNDWATER IN THE POCATELLO AQUIFER

C. Meehan, Department of Geology, Idaho State University, Pocatello, Idaho 83209
J. Welhan, Idaho Geological Survey, Idaho State University, Pocatello, Idaho 83209

Abstract

During the summer of 1993, groundwaters and surface waters were found to have anomalous sulfate concentrations in the Southern Pocatello municipal aquifer in an area known as the Highway Ponds. Leach tests performed on a large pile of road aggregate stockpiled near the Highway Ponds have been identified as the most likely source for the sulfate.

Correlating trends of sulfate and chloride concentrations can be found both in the main Pocatello aquifer and in Pocatello Creek groundwaters. The chloride contamination at Pocatello Creek has previously been suggested to be derived from road salt. It is hypothesized that aggregate used in roadbed construction may be responsible for elevated sulfate in the areas groundwater.

Chemical modeling has eliminated carbonate precipitation/dissolution reactions in buffering the chemistry of sulfate-impacted groundwater. Ion-exchange with clays is hypothesized to be a more significant process and is being investigated further.

Introduction

The city of Pocatello, located in Southeast Idaho, depends entirely on groundwater for its municipal water supply. The Idaho Geological Survey and Idaho State University are working with the city of Pocatello to develop a well head protection plan for the municipal well field. Part of the initial aquifer study involves creating a water balance that utilizes the chemical signatures of the aquifer and its recharge sources in an attempt to calculate recharge fluxes to the lower Portneuf River Valley aquifer southeast of the city (Figure 1). During the summer of 1993, suites of water samples were collected and analyzed for major cation and anion concentrations. It has been well documented in chemical analyses of Pocatello's municipal well waters that chloride and sulfate concentrations are linearly correlated (City of Pocatello, Water Dept., unpublished data). This relation between chloride and sulfate suggests that their introduction to the Pocatello Aquifer may be related in some way.

In the course of the study, several surface water and groundwater samples exhibited anomalous concentrations of sulfate in the vicinity of a large borrow pit located approximately one mile south of the city limits and 2 miles upgradient of the municipal well field. Further investigation identified a large pile of road aggregate as the possible source for the anomalous waters. The Idaho State Department of Transportation has identified the substance as slag they had crushed for use as road aggregate. Because this material may represent a potential source of ionic constituents that may be important in the water balance study, further investigations were initiated to evaluate its impact on the groundwater.

In the area of Pocatello Creek, a tributary valley immediately east of Pocatello (Figure 2), chloride and sulfate also are correlated with a slope similar to that recognized in the main Pocatello Aquifer. In a study of Pocatello Creek by CH²M-Hill, it was postulated that road salt used for winter de-icing was responsible for the chloride contamination in that area (CH²M-Hill, 1992; Noble, 1993), but a source for the observed sulfate enrichment was not identified. With

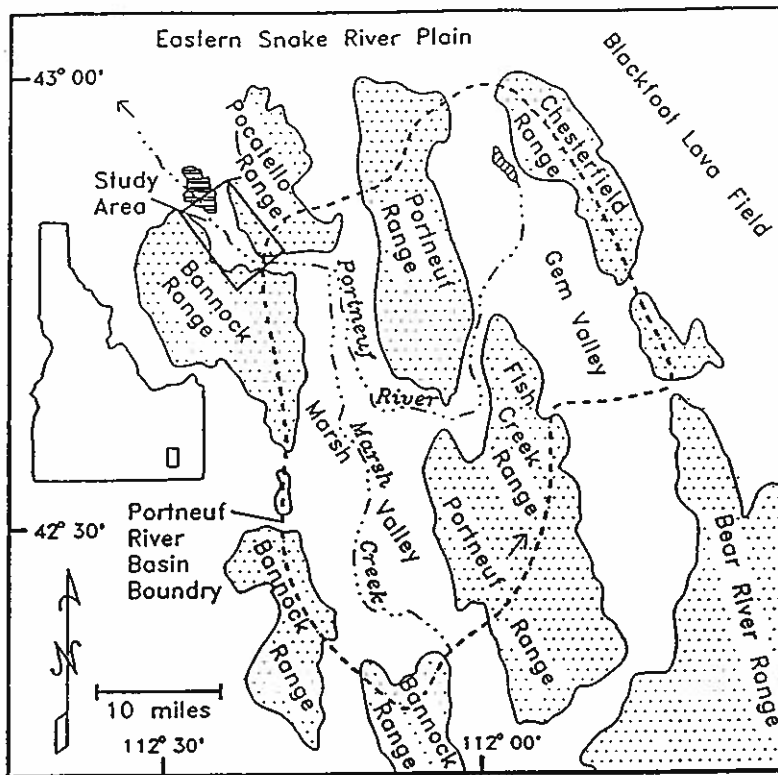


Figure 1: Location map showing Portneuf River Basin and study area for the Southern Pocatello aquifer. The Boundary for the Portneuf River Basin is denoted by the dashed line.

the discovery of the above mentioned road aggregate as a source of leachable sulfate in the borrow pit area, it was speculated that it may also be responsible for sulfate contamination at Pocatello Creek. A casual inspection of the roadbeds in Pocatello Creek revealed that similar road aggregate was used in their construction.

Further studies were conducted to see if the chloride and sulfate trends recognized at Pocatello Creek and in the main Pocatello aquifer may be related by similar processes. This paper describes the initial results of this investigation and evaluates possible chemical reaction pathways which may be influenced by aggregate-derived chemical constituents.

Geologic Setting

The city of Pocatello is situated in an alluvial valley between the Pocatello Range to the north and the Bannock Range to the south (Figure 1). These ranges consist of allocthanous upper Proterozoic and Cambrian strata of the Pocatello formation and Brigham Group that were thrust faulted during the Jurassic to Paleocene Sevier orogeny (Link et al., 1987). During the Cenozoic, south-east Idaho has extended along north trending normal faults that are characteristic of the Basin and Range Province. In the case of the Pocatello valley this process has resulted in a sediment filled half-graben structure. Pediment gravel terraces flanking the valley imply several valley sedimentary filling and downcutting episodes that are thought to be Late Tertiary to Pleistocene in age (Ore, 1982).

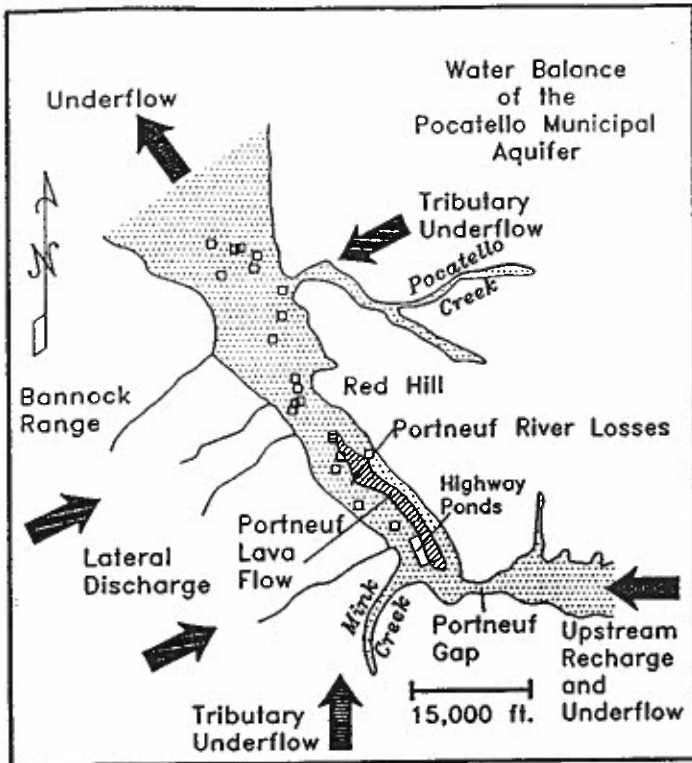


Figure 2: Pocatello Municipal Aquifer

Recharge areas to the Pocatello Municipal aquifer being used in the water balance study are designated by arrows. Also located on this map are the locations of Pocatello Creek and the Highway Ponds study area. Municipal wells are designated by open squares.

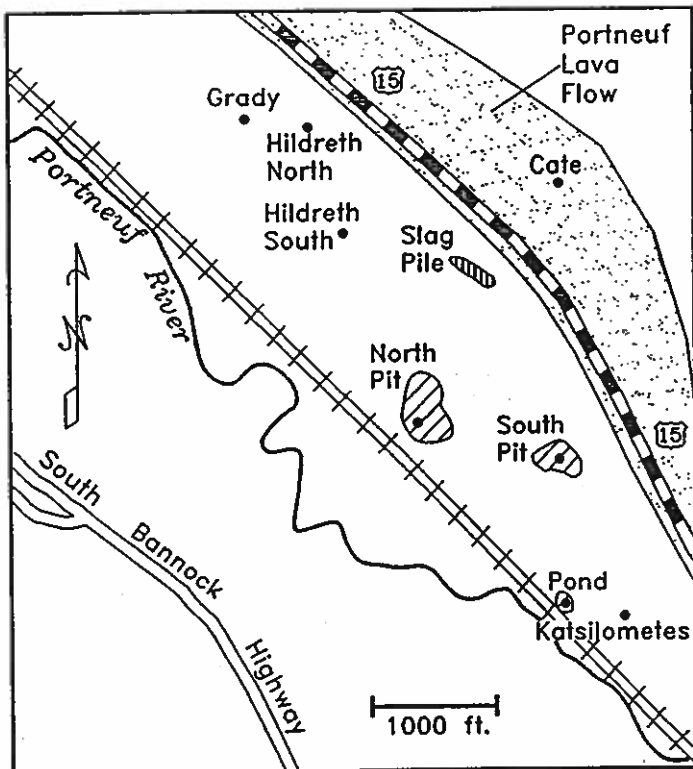


Figure 3: Location Map for Highway Ponds Study Area

Map of the Highway Ponds area where anomalous levels of high sulfate concentrations were observed in both surface waters and ground waters. Located here are the sampling points (closed circles), Portneuf River, surface waters (slanted lines), Portneuf Lava Flow (speckled), and the slag pile (vertical lines) thought to be the source of the sulfate. The Union Pacific rail line separates the Portneuf River and the Highway Ponds area.

The southern boundary of the Pocatello Valley is defined by the Portneuf Gap, sometimes called the Portneuf Narrows, where the Portneuf River cuts through the north-trending Bannock range. This narrow gap is thought to be a superposed canyon that was cut by the ancestral Bear River during the Lake Bonneville flood as it flowed into the Snake River (Link, 1982). This flood completely eroded an earlier basalt flow within the gap, but left scoured remnants within the valley near Pocatello. Drilling has shown that this flow, known as the Portneuf Lava Flow, is 50 feet thick and its base is at the same level as the valley floor (Trimble, 1976). Boulders of basalt greater than 2 meters in diameter can be found in the Bonneville flood deposits that underlie downtown Pocatello (Link, 1982).

Quaternary alluvium and flood plain silts cover most of the valley floor (Trimble, 1976). The valley strata consists of Pleistocene lacustrine and fluvial deposits related to both the ancestral American Falls Lake and the Lake Bonneville flood (See Welhan and Meehan, this volume).

Implications For Water Balance Study

The area currently being studied for water balance modeling purposes is located in a small portion of the Lower Portneuf River Basin and extends from Red Hill to the Portneuf Gap (See Figures 1 and 2). The five components of recharge to this valley aquifer that are being examined are: 1) underflow through the Portneuf Gap; 2) underflow from Mink Creek; 3) infiltration from the Portneuf River; 4) lateral underflow from the east dipping strata of the Bannock Range, west of the aquifer; 5) underflow from an adjacent alluvial aquifer east of the Portneuf lava flow.

As previously mentioned, chemical characterization of the main aquifer's groundwater and recharge sources has been undertaken. The amount of water supplied to the aquifer by each source may be calculated using the concentrations of certain constituents (i.e. sulfate, nitrate, chloride) in the various recharge sources contributing to the main aquifer. The concentrations of these constituents in the main aquifer should reflect only their amounts as delivered by the previously defined recharge sources. It is therefore important to understand the chemical impact that road aggregate may have on aquifer chemistry, if the chemical mass balance method is to properly quantify recharge fluxes.

Sampling and Analytical Methods

The results of the chemical analyses for the borrow pit area are shown in Table 1. Sampling locations are shown in Figure 3. The samples labeled North Pit, South Pit, and Pond refer to small bodies of water, known as the Highway Ponds, that lie within a large gravel pit excavated for road aggregate during the construction of Interstate Highway 15. The chemical signature of these ponds, as well as their water level elevations, indicate that they represent the surface expression of local groundwater. This is further supported by the emergence of these ponds only during periods of above-normal precipitation and high groundwater levels.

Regionally, groundwater flow in the area is along the axis of the valley, approximately from southeast to northwest. The sample designated Katsilometes refers to an irrigation well upgradient from the borrow pits and represents background aquifer water quality. The Portneuf River adjacent to the irrigation well was also sampled. Hildreth North, Hildreth South, and Grady are residential wells located downgradient of the aggregate pile. The sample designated Cate is a water well owned by a heavy equipment company. It is located in what is considered to be a separate aquifer, east of the Portneuf lava flow, which is known to be locally contaminated.

All samples were collected in one liter polyethylene containers and analyzed in the field for pH and specific conductance. Samples from residential wells were taken from household water taps in which the water was allowed to run for several minutes to ensure the sample was representative of the well water. Total alkalinity for each sample was analyzed on the day of collection by titration with standardized acid.

After filtering samples through a 0.45 micron filter, major ion analyses were performed within one week of collection. Of these, sulfate, chloride, nitrate, silica, and magnesium were analyzed with a HACH DR/2000 spectrophotometer, using standardized procedures and multiple runs to ensure the accuracy and precision were well defined. In some cases, dilution with deionized water was necessary to place a sample within the detection limits of a particular test. When this became necessary, several analyses were made at varying dilution ratios and the deionized water itself was tested to insure its integrity. Total hardness was analyzed by EDTA titration. Calcium was calculated by subtracting the magnesium concentrations determined from the spectrophotometric analyses from total hardness. Sodium and potassium were analyzed by flame atomic absorption spectroscopy. Multiple runs of analyses using the spectrophotometer have shown the relative standard deviation at the 1 sigma level is less than 4 mg/l for all elements except magnesium, which was 7 mg/l. The standard deviation at the 1 sigma level for calcium is 10 mg/l.

TABLE 1: CHEMICAL ANALYSIS FOR WATER WELLS IN THE POCATELLO AQUIFER
 Concentrations of ions are all given as mg/kg of solution. Alkalinity is represented as HCO_3^- in mg/kg of solution. Specific conductance (S.C.) is in umho/cm. (Note: this table represents selected analyses only, and is not a complete listing of all background water compositions and other wells in the southern Pocatello aquifer for which data are available)

DATE	SAMPLE	Ca	Mg	Na	K	SO4	Cl	NO3	Si	Alk	pH	S.C.
Highway Pond Area and Downgradient Wells:												
06/15/93	Hildreth S	77.0	38.4	53.7	22.2	127	54.2	14.9	24.9	356	7.6	NA
12/06/93	Hildreth S	70.7	25.8	46.2	14.8	60	45	8.8	27.6	301	7.6	NA
06/04/03	Pond	78	38.4	NA	NA	90	50	1.3	17	376	7.5	NA
06/21/93	Pond	68	38.4	43.4	10.3	100	45.2	3.08	35.6	373	8.2	725
06/04/93	North Pit	74	32.4	NA	NA	42	32	7.48	22.1	333	7.2	600
06/21/93	North Pit	73	27	36.1	6.76	44	34.5	7.04	23.8	328	7.7	475
12/06/93	North Pit	93	31.1	43.5	5.8	39	41.5	7.48	24.7	341	7.64	NA
06/04/93	South Pit	66	28.8	NA	NA	42	33.5	7.04	13.8	301	8.2	575
06/21/93	South Pit	50.7	26.4	30	5.26	44	42.2	3.52	11.7	290	8.2	475
12/06/93	South Pit	85.7	28.7	44	5.73	38	33.5	7.04	22.3	296	8.14	NA
06/15/93	Hildreth N	71	30.6	45.6	6.7	53	36.5	10.5	25.7	339	7.6	NA
12/06/93	Hildreth N	77.9	23.8	38.1	6.3	43	36	8.4	25.1	305	7.5	NA
06/15/93	Grady	76	28	35.8	6.6	47	44.7	8.4	27	339	7.5	NA
12/06/93	Grady	75	22	37	5.9	37	33	8.4	25	306	7.5	NA
Background Water Quality:												
06/21/93	Portneuf	61.3	20.8	24	5.03	27	27.7	2.6	21.1	253	8.3	375
12/06/93	Portneuf	96.2	38.7	48.4	8.26	45	36	7.04	25.9	364	8.4	NA
06/15/93	Katsilomet	66.4	27.8	45.1	7.36	44	43.5	6.16	25.2	336	7.5	406
East of Portneuf Lava Flow:												
06/21/93	Cate	128	58.8	69	6.62	110	252	38.3	22.2	298	7.4	1100
12/06/93	Cate	153	53.3	80	8.38	105	207	38.2	21.4	296	7.6	NA
Aggregate Leach Test:												
3 Days	Aggregate	196	4.8	8.6	17.7	500	2.25	1.76	38.4	0.00	8.2	750

A leach test was performed on a sample of the crushed aggregate that is stockpiled near the Highway Ponds. Deionized water was placed in contact with the aggregate for three days and the resulting solution was analyzed with the above mentioned methods. The results of this test are shown in Table 1 (sample designated as aggregate). This test showed that sulfate, calcium, and potassium are major soluble components and can be leached from the aggregate pile. The analyses of the Hildreth South well, which is directly down gradient from the aggregate pile, show significant increases in sulfate and potassium levels above normal background concentrations. Calcium however, does not show a statistically significant increase, suggesting that its concentration as a soluble component in the groundwater is being buffered by some process (e.g. precipitation, ion-exchange).

Table 2 shows trace element data for aggregate samples and Hildreth South well water which were obtained by induced neutron activation analysis (INAA) and gamma spectral analysis. Due to the lack of standards that were available at the time of these analyses and the lack of quality assurance tests, the results here are considered to be preliminary; only the largest elemental enrichments above detection are summarized in Table 2.

Table 2: INAA ANALYSES: All values are in mg/kg of solids. Solution concentrations for samples Aggregate/DI Water and Hildreth Sth. in mg/kg solution are approximately 0.00077 times the values shown, as explained in the text.

Date	Sample	Cr	As	Rb	Sr	Ba	U	Cs	Ce	Nd
	Primary Aggregate	861	435	26.3	720	650	97.2	3.15	77.6	116
	Leached Aggregate	1526	680	36	585	710	96	3.8	80	106
	Aggregate/DI Water	0.89	2	40	755	10	0.32	0.88	0.4	0.4
06/15/93	Hildreth Sth.	15	6	25	835	228	2.6	0.11	0.86	8.2

Samples labeled primary aggregate and leached aggregate represent the solid aggregate prior to, and after leaching in deionized water for three weeks. The sample designated Aggregate/DI Water represents the water which was in contact with the aggregate for three weeks. The two water samples (Aggregate DI and Hildreth S.) were filtered and evaporated to dryness so that their solid residues could be activated for INAA and gamma spectral analysis. Since the values in Table 2 for these two water samples represent mg/kg of the solid, they must be multiplied by 7.7×10^{-4} to convert them to mg/kg of solution. This conversion was obtained from the calculated total dissolved solids content (TDS) of the original waters based on their major ion analyses (TDS about 770 mg/L for each sample).

From the data in Table 2 it appears that some Sr and Rb may be leached from the aggregate. Concentrations of other analyzed elements are less than one mg/kg of solution. Since no trace element analyses were performed on upgradient well waters, it is not possible to determine if Hildreth South water shows any significant increase in other elements. More analyses are being performed to address this. The aggregate does contain significant amounts of uranium (97 ppm), which is considered a soluble, highly mobile aqueous species in this type of groundwater.

~~performed to address this. The aggregate does contain significant amounts of uranium (97 ppm), which is considered a soluble, highly mobile aqueous species in this type of groundwater.~~ However, the concentration of uranium in solution for the prolonged leach test was less than 0.3 ppb. It appears that it is not readily mobilized and does not pose a threat to groundwater.

The pile of aggregate in question appears to be heterogeneous in its bulk composition. Contrary to what was expected, the leached aggregate had higher concentrations for most of the analyzed elements than the sample of unleached slag. Two other leaching tests performed by other parties on slag have shown different amounts of leachable sulfate. A leach test performed by CH²M-Hill yielded twice as much sulfate as our test (R. Noble, personal comm., 1993), while another test performed by FMC on uncrushed slag had a sulfate concentration of less than 1 ppm (P. French, pers. comm. 1994). These results suggest that grain size may be an important factor in controlling the amount of leachable sulfate.

Interpretations of Highway Ponds Area Data

Figure 4 is a Piper diagram that depicts the relative concentrations of the major cations (calcium, magnesium, sodium and potassium) and anions (chloride, sulfate, carbonate and bicarbonate) in waters from the Highway Pond area, the Portneuf River, and wells east of the Portneuf Basalt and main municipal aquifer. The lower right hand portion of this figure depicts two trends of increasing chloride and sulfate proportions which deviate from the tight clustering of main aquifer background water. One trend observed in wells east of the Portneuf Basalt (plotted as "-" symbols), suggests that those waters are affected by chloride and sulfate addition in a proportion that differs from the main aquifer. The second trend shown in Figure 4 (as "@" symbols), reflects the addition of only sulfate in the Highway Ponds area.

Neither trend in anion compositions in Figure 4 is associated with a cation trend. Sulfate and chloride are expected to behave conservatively in these groundwaters; their concentrations change only due to additions and source dilution. In contrast the cationic constituents (including heavy metals) would not be expected to behave conservatively, since their concentrations are affected by common mineral dissolution reactions, precipitation reactions, and ion exchange on clays.

It has been brought to our attention that the Highway Department may add sulfate-containing salts to road aggregate to augment winter de-icing capabilities. However road salt used by the Highway Department contains more than 95 percent sodium chloride (P. French, pers. comm., 1994), and there has been no significant sodium or chloride observed in the leach tests on the aggregate that have been run to date. The Idaho State Department of Transportation and Bannock Paving (who provided the Department of Transportation with the crushed aggregate at the Highway Ponds) both confirmed that no additives were introduced to the stockpile in question (K. Magleby, pers. comm., 1994; L. Robson, pers. comm., 1994).

As previously mentioned, sulfate was found to be readily leachable from the aggregate source, and could explain the enrichment of sulfate observed in groundwater near the Highway Ponds. It is possible that the Highway Ponds area is connected hydrologically under the Portneuf lava flow with the eastern aquifer, which is known to be locally contaminated with chloride, sulfate, and nitrate (see Cate Well analysis, Table 1). However, our aggregate leach test produced high-sulfate, low-chloride water, which is more characteristic of the type of waters observed at the Highway Ponds. If the area east of the basalt were the source of sulfate for the Highway Ponds, then increased concentrations of chloride and nitrate would also be expected.

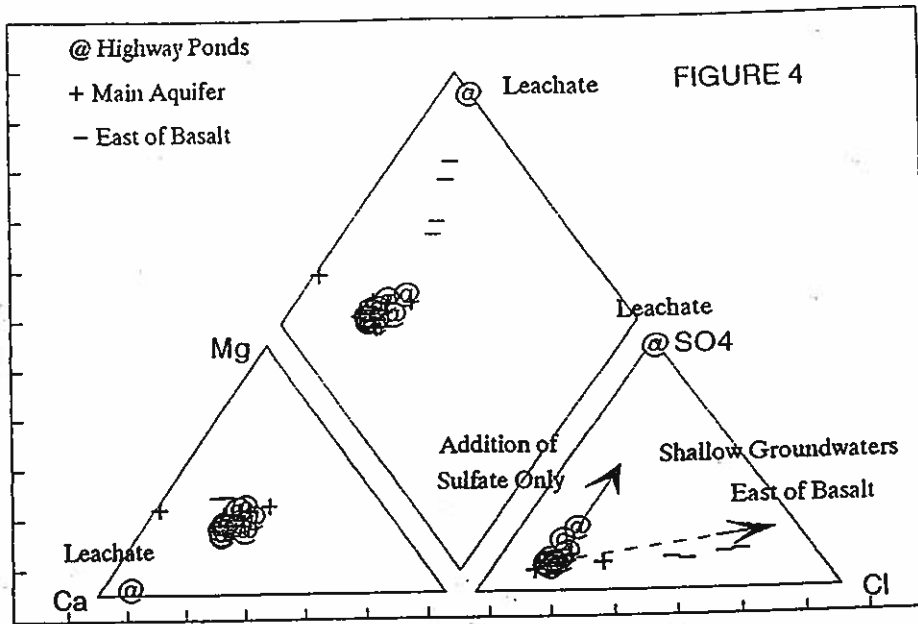


Figure 4: Piper diagram of groundwaters from the Southern Pocatello Aquifer, Highway Ponds, and area east of the Portneuf Lava Flow. This figure depicts two regional trends of increasing Cl and SO₄ proportions which deviate from the main aquifer background water. Wells east of the Portneuf Basalt suggest Cl and SO₄ addition in proportions that differ from the addition of only sulfate at the Highway Ponds. Leachate refers to the solution derived from the leachate.

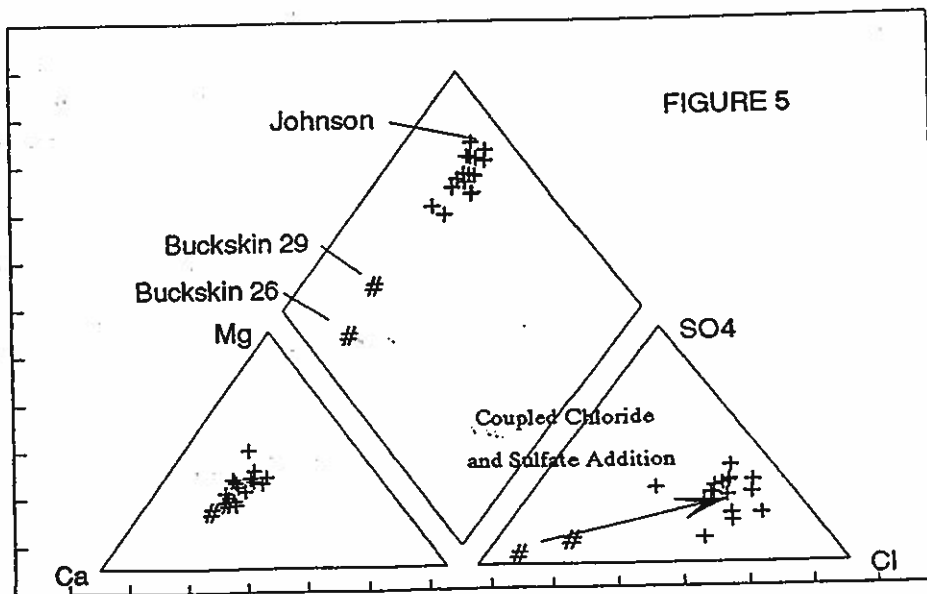


Figure 5: Piper Diagram of groundwaters from Pocatello Creek. This diagram displays the trend of sulfate and chloride enrichment in Pocatello Creek groundwaters. This trend is hypothesized to be from Cl derived from roadsalt and SO₄ leached from road aggregate. Buckskin 26 and 29 are upgradient in relation to the rest of the waters in this diagram.

could explain the high sulfate levels in the pond that is directly adjacent to the Union Pacific Railroad. Further evidence of sulfate leaching by surface waters is provided by the dramatic decrease in sulfate and potassium concentrations in the Hildreth South well between June 1993 and December 1993. Such a variation would be consistent with a surface source of sulfate that was mobilized during spring runoff. Percolation of this sulfate-rich surface water to the water table would raise local groundwater sulfate levels in spring, but by December, as the pulse of vadose zone recharge diminished, the local sulfate input to the water table would also be expected to decrease, with an ensuing decrease in groundwater sulfate levels due to normal groundwater dilution processes.

Implications of Sulfate Leaching at Pocatello Creek

Figure 5 is a Piper diagram displaying the relative concentrations of ions in groundwaters in residential wells at Pocatello Creek, analyzed by the Division of Environmental Quality and the District Health Department. This figure also displays a trend of chloride and sulfate enrichment (compare to Figure 4).

It has been hypothesized that road salt used for de-icing may be responsible for the chloride contamination in Pocatello Creek ground waters (CH²M-Hill, 1992; Noble, 1993). Groundwater at Pocatello Creek shows a direct correlation between sodium and chloride, which is also observed in the Southern Pocatello main aquifer. This may suggest a similar scenario for the introduction of chloride into the Pocatello Aquifer.

It is widely accepted that material similar to the aggregate stockpiled in the Highway Pond borrow pits has been widely used in road and rail bed construction throughout Bannock County (G. Brown, pers. comm., 1993). We suggest that features constructed with this aggregate may provide a source of leachable sulfate to groundwaters. After finding similar aggregate in a casual inspection of the Pocatello Creek roadbeds, it was hypothesized that aggregate may be responsible for the high sulfate levels observed in groundwaters in that area.

Figures 6(a) and 6(b) illustrate the linear correlation between chloride and sulfate in the Southern Pocatello Aquifer and Pocatello Creek. Figure 6(a) shows the two trends displayed in the Piper diagram in Figure 4 (sulfate addition and groundwater east of the Portneuf Basalt). A third trend in Figure 6(a) shows coupled chloride-sulfate addition that is characteristic of the main Southern Pocatello aquifer. The chloride-sulfate trend in Pocatello Creek ground waters (Figure 6(b)) is almost identical to the third trend observed in the main aquifer in Figure 6(a).

On the basis of these data, it is hypothesized that chloride and sulfate enrichments observed in local groundwaters may be due to a combination of road salting and road bed leaching. Infiltration of runoff along roadbeds in the spring may introduce salt derived from winter de-icing applications; this chloride-enriched water may subsequently acquire sulfate from the dissolution of road bed material. Such a coupled mechanism for the introduction of road salt-derived chloride and road bed-derived sulfate would explain the observed correlation of elevated chloride and sulfate in area groundwaters, and would imply that road runoff may be a potentially significant point of introduction for surface-derived contaminants to the aquifer. The hypothesis for a coupled chloride-sulfate enrichment from roadbed runoff and leaching was further examined by modeling the possible chemical processes and reaction paths which may be involved in such a scenario.

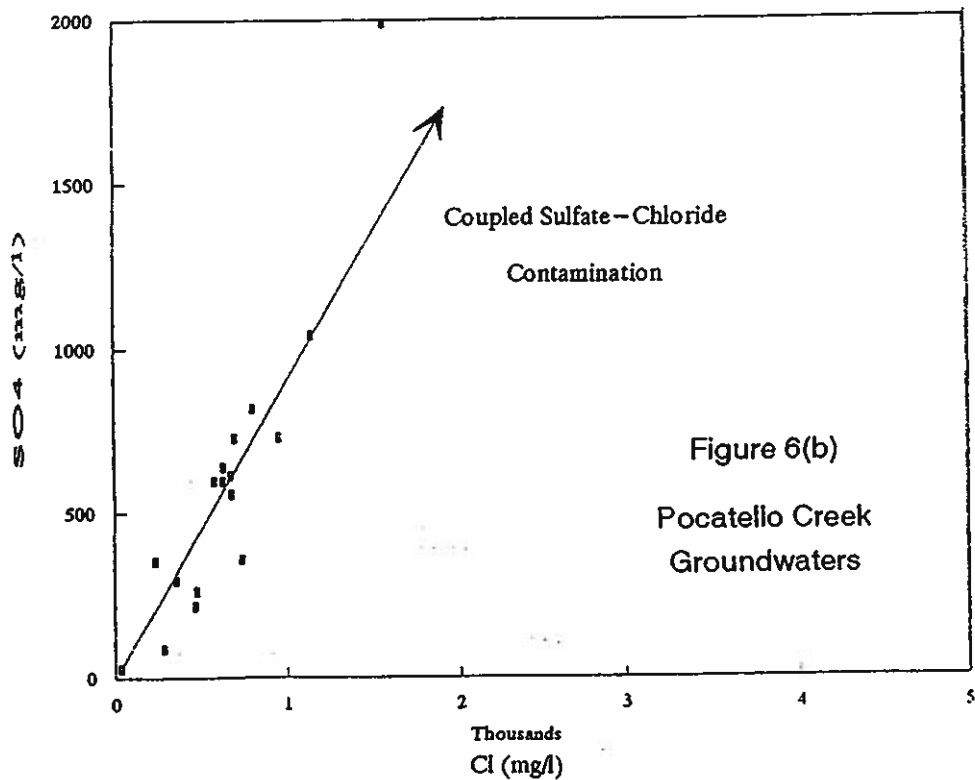
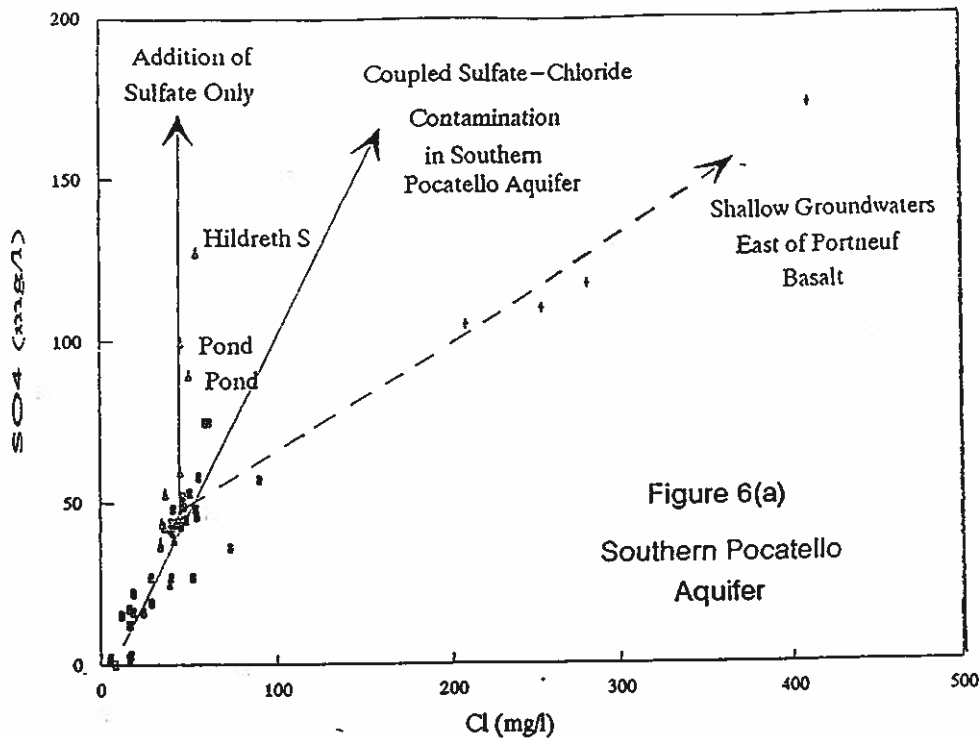


Figure 6(a) is a plot of chloride concentrations vs sulfate concentrations in groundwaters from the main Pocatello Aquifer (squares), the Highway Ponds area (triangles), and the area east of the lava flow (diamonds). The impact of slag derived sulfate can be seen in the Highway Ponds area which deviates from other waters which have a coupled Cl-SO₄ trend. Figure 6(b) shows sulfate and chloride concentrations in Pocatello Creek. The slope of the line shown in 6(b) is that observed in the main Pocatello aquifer in Figure 6(a).

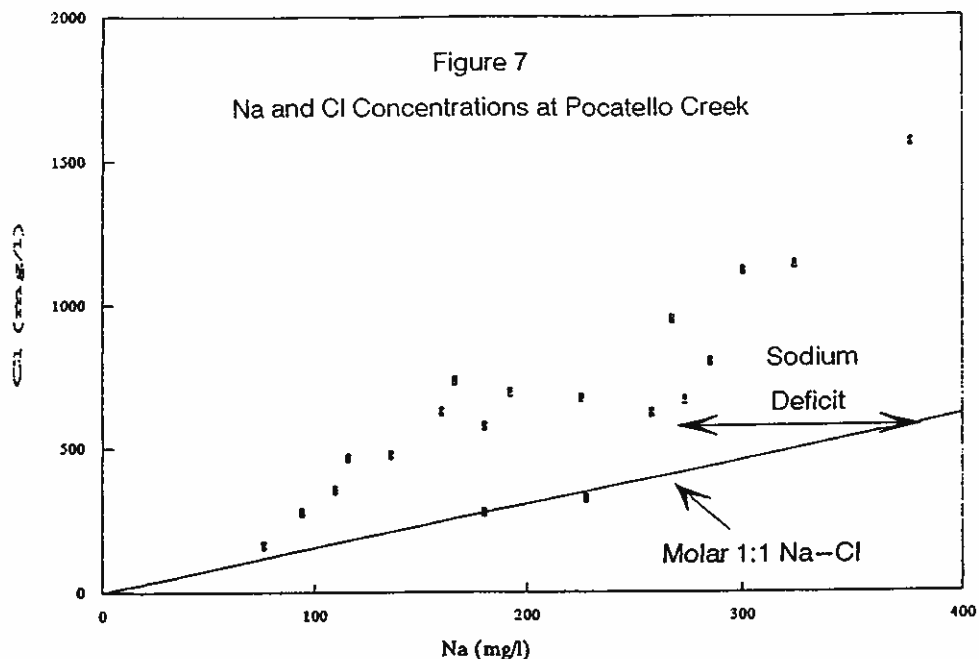


Figure 7: Correlation of sodium and chloride at Pocatello Creek. These concentrations are compared with a molar 1:1 ratio of sodium vs chloride. There appears to be a deficit of sodium, if they are mutually derived from road salt. This may be explained by ion-exchange with clays.

Reaction Path Modeling

If the change in water compositions along a hydrologic flow path between arbitrary starting and ending points is due to the effects of chemical reactions or mixing, then the reactions responsible for the change can be quantified by a chemical mass balance model (Plummer and Back, 1980). Such an approach only identifies the possible phases and/or components involved in a set of reactions. In contrast, chemical reaction path modeling is used to determine (1) the conditions under which the reactions have occurred (e.g. open vs. closed system) (2) how the water composition changes in response to perturbations in the system. The modeling of an aqueous system in this fashion is facilitated by calculations of equilibrium speciation and mass balance (Plummer et al, 1983). Two computer programs, NETPATH (Plummer and others, 1991) and MINTEQA2 (Allison and others, 1991), were used to incorporate both of these calculations.

NETPATH was used for the mass balance calculations to determine the amounts of "plausible phases" that must dissolve and/or precipitate to account for the observed water compositions. The mass balance approach consists of balancing a net chemical reaction in the form:

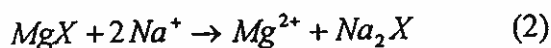
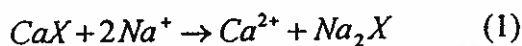
$$\text{Initial solution composition} + \text{"Reactant Phases"} = \text{Final solution composition} + \text{"Product Phases"}$$

"Product Phases" represent those constituents that must physically leave the aqueous phase during the reaction, while "Reactant Phases" represent chemical constituents that must physically

~~"Product Phases" represent those constituents that must physically leave the aqueous phase during the reaction, while "Reactant Phases" represent chemical constituents that must physically enter the aqueous phase.~~ The term "plausible phases" represents the reasonable choices for possible reactants and products based on the modeler's geochemical insight and as constrained by equilibrium speciation calculations (Plummer et al, 1983).

MINTEQA2 is a geochemical equilibrium speciation model for dilute aqueous systems. MINTEQA2 was used to evaluate models suggested by NETPATH and determine if they were plausible in terms of their thermodynamic requirements.

The first step was to determine the "plausible phases" that may be present and responsible for the observed chemical changes at the Highway Ponds and Pocatello Creek. Gypsum (CaSO_4) was used in modeling the sulfate component, since calcium and sulfate were derived from leached aggregate in a 1:1 ratio (Table 1). The addition of NaCl (road salt), was used to account for the level of chloride concentrations observed in the groundwater. Figure 7 shows concentrations of sodium and chloride in wells at Pocatello Creek compared with the trend expected for a molar 1:1 ratio of sodium and chloride. If sodium and chloride are from a single source, namely road salt, there appears to be a sodium deficiency. Ion exchange of sodium with clays may account for this deficiency. Such reactions would be of the form:



Reaction 2 could also account for the magnesium increases observed at both the Highway Ponds and Pocatello Creek (magnesium was not found to be a major constituent in the aggregate leach test). Another plausible source of magnesium may be from the dissolution of dolomite. For these reasons a calcium-sodium and a magnesium-sodium exchanger, along with dolomite, were also considered to be "plausible phases" in the modeling. Calcite and CO_2 gas were also added as phases, considering that carbonate reactions are an important chemical process for these types of ground waters and may help explain the reaction(s) buffering Calcium. A KSO_4 phase was assumed to be a component of the aggregate and was used to model the observed potassium increases.

The initial NETPATH models were run using the June 1993 analyses of Katsilometes well water as the initial background water and Hildreth South as the final endpoint. The elements carbon, sulfur, calcium, magnesium and potassium were used as constraints to fix the masses of the chosen phases that can enter or leave the aqueous solution. Initially, NaCl was not used in model runs, so sodium and chloride were not entered as constraints. NETPATH yielded nine possible models that could account for the chemical signature of the water found at Hildreth South.

Table 3 summarizes the nine possible models calculated by NETPATH. Positive values indicate dissolution of the particular phase, while negative values indicate precipitation. For the exchangers, positive values mean that reactions 1 and 2 are occurring as they are written; a negative value indicates the reaction is occurring in the reverse direction, so that sodium would be released as free ions to solution.

When NaCl was included as a plausible phase (and sodium and chloride as constraints), only models that contained exchangers were produced. Since sodium and chloride are not in a molar 1:1 ratio at the Hildreth well as they are in the phase NaCl, the exchangers provide the only other sources and or "sinks" for sodium. Table 3 indicates only one model (Model #1) in which no exchangers are required.

Table 3: NETPATH MODELS FOR HIGHWAY PONDS AREA: All values represent the amount of each phase in mmols that enters (+) or leaves (-) the solution. A (+) sign for exchangers means that reactions 1 and 2 occur as they are written above. They are reversed if they are (-).

Phase	Mod. 1	Mod. 2	Mod. 3	Mod. 4	Mod 5	Mod. 6	Mod. 7	Mod. 8	Mod. 9
Gypsum	0.4901	0.4901	0.4901	0.4901	0.4901	0.4901	0.4901	0.4901	0.4901
KSO4	0.3798	0.3798	0.3798	0.3798	0.3798	0.3798	0.3798	0.3798	0.3798
Calcite	-0.6601	-0.2252	-0.5391	0.3306	-0.7810				
CO2 (g)	0.1209	0.5558				-0.5391	0.3306	0.7810	
Dolomite	0.4349		0.4349		0.5558	.4349		-0.2252	0.1653
Ca-Exch			-0.1209	-0.5558		-0.6601	-0.2252		-0.3905
Mg-Exch		0.4349		0.4349	-0.1209		0.4349	0.6601	0.2696

MINTEQA2 can be used to test whether the precipitation/dissolution reactions proposed by NETPATH are feasible given the constraints of thermodynamic equilibrium. The mass balance method is generally an elimination process in which calculations that identify reactions that cannot occur are eliminated. Proof of a reaction is never positive with the mass balance approach, but by the process of elimination there may remain only a limited number of models that are consistent with the observed chemical data (Plummer and Back, 1980).

Initially, one may use geochemical insight to eliminate certain models in Table 3. Both the Hildreth South water and Katsilometes are saturated with respect to calcite. Thus Model 4 in Table 3 can be eliminated since it requires the dissolution of calcite. Model 8 is probably also unreasonable because it requires the precipitation of dolomite, an unrealistic process for these types of waters.

If the same processes influencing the Hildreth South well are also occurring in Pocatello Creek, their impact in the latter's setting is much greater. Groundwater analyses of residential wells by the Division of Environmental Quality and the District Health Department show concentrations of major ions one to two orders of magnitude greater than in waters at the Highway Ponds. Since the combined effects of road salt and road bed leaching seem more pronounced at Pocatello Creek, these waters were also examined to eliminate models that were not consistent with chemical equilibrium requirements.

The samples labeled Buckskin 29 and 26 in Figure 5 refer to wells that are upgradient from other wells in the diagram. Because these waters are upgradient and appear to be an end member type water on the Piper diagram, they were considered to represent the initial background water for Pocatello Creek. The sample labeled Johnson appears to be the other end-member, most heavily impacted by chloride-sulfate addition. The Buckskin 29 and Johnson wells were used as the initial and final wells respectively, for chemical modeling. The water compositions used for the modeling are given in Table 4.

NETPATH was first used without sodium and chloride as constraints, and without NaCl as a phase. This produced only one model as shown in Table 5. MINTEQA2 was then used to

gypsum and 24.12 mmols of dolomite as "finite solids." The partial pressure of CO₂ was fixed at the amount speciated in the original Buckskin water. The assumption here is that the partial pressure of CO₂ at the Buckskin well is the same in the Johnson well, i.e. the system is open with respect to CO₂.

Table 4: CHEMICAL ANALYSIS FOR WELLS USED IN CHEMICAL MODELING

All concentrations given as mg/kg of solution. Total alkalinity is given as mg/kg of HCO₃

Sample	Ca	Mg	Na	K	Cl	SO4	Tot Alk	pH	Temp
Buck 29*	49	17	20	1.1	34	27	201	7.0	15°C
Johnson	590	600	376	5.3	1563	1988	590	7.1	15°C

* Note: analysis for Buckskin 29 was obtained from U.S.G.S. Water-Resources Investigations 79-14 Open-File Report

Table 5: NETPATH MODEL FOR POCATELLO CREEK (without NaCl)

All values represent the amount of each phase in mmols that enters (+) or leaves (-) the solution. A (+) sign for exchangers means that reactions 1 and 2 occur as they are written above. They are reversed if they are (-).

Model 1	
Gypsum	20.42
KSO4	0.108
Calcite	-30.96
CO2 Gas	-10.3
Dolomite	24.12

The final concentrations of ions in solution predicted by MINTEQA2 are displayed as Model 1A in Figure 8(a) as a percent of their concentrations in the Johnson well. The final equilibrium pH calculated by MINTEQA2 was 7.04 as compared to 7.1 at the Johnson well. However, figure 8(a) shows that there is a deficit in most of the ions in the model run, compared to the observed concentrations. Not enough gypsum or dolomite was able to dissolve to produce the amount of sulfate, magnesium and calcium observed in the Johnson water. In addition the alkalinity (represented by HCO₃) is much lower in the modeled water than in the Johnson water. Simply stated, this is because insufficient gypsum and dolomite were able to dissolve, as required by the NETPATH model.

An alternative reaction path consisting of two reaction steps had similar results. Model 1B began with Buckskin water with only gypsum added as a finite solid at first. Dolomite was then added to the resultant water as step 2 and allowed to equilibrate. Even less gypsum dissolved in Model 1B as compared to 1A, because with the initial absence of dolomite dissolution, no aqueous CO₃ was added to the solution, and no calcite precipitated in the first step of the model. Therefore there was no "sink" for calcium as the gypsum dissolved. The equilibrium pH for the final model was 7.1.

Additional mass balance models were run using sodium, chloride, and NaCl as constituents. Table 6 displays the results of the NETPATH Models with chloride as the constraint for NaCl. It should be noted that Model 2 in table 6 is the same as Model 1 in Table 5, with the exception of the NaCl phase. Two equilibrium models were again constructed with MINTEQA2 using the same procedures as stated above, this time with 43.38 mmols of NaCl added as a finite solid phase. The results of the one step (Model 2A) and two step model (Model 2B) are displayed in Figure 8(b).

COMPARISON OF MINTEQ MODELS AT POCATELLO CREEK

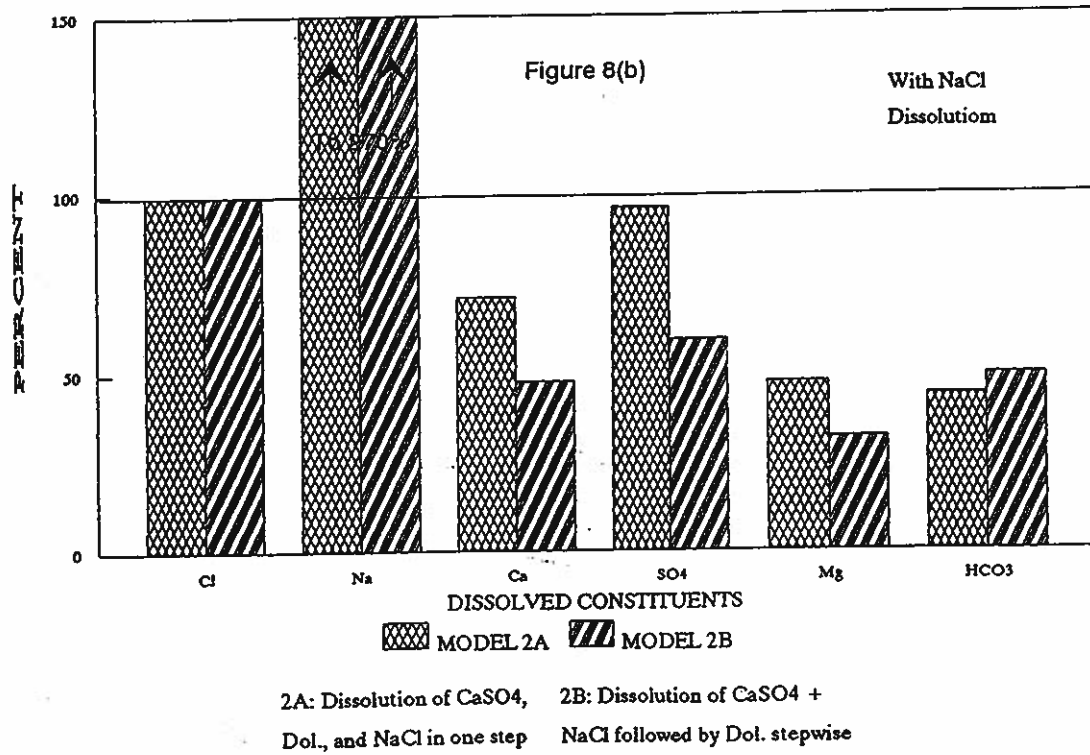
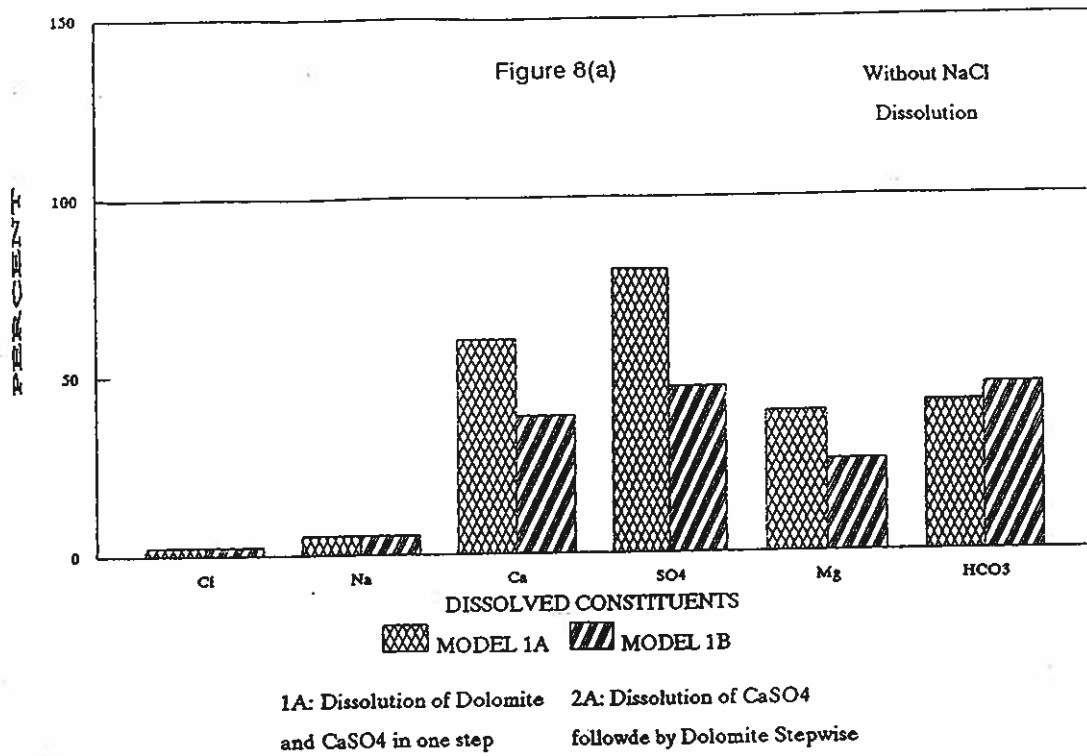


Figure 8 (a) models the dissolution of CaSO4 and dolomite only. Dissolved ion concentrations are represented as a percent of the concentrations of the same ions in the Johnson Well at Pocatello Creek. Figure 8(b) represents the same models and conditions with NaCl added as another phase.

Table 6: NETPATH MODELS FOR POCATELLO CREEK (with NaCl)

All values represent the amount of each phase in mmols that enters (+) or leaves (-) the solution. A (+) sign for exchangers means that reactions 1 and 2 occur as they are written above. They are reversed if they are (-).

Phase	Mod 2	Mod 3	Mod 4	Mod 5	Mod 6	Mod 7	Mod 8	Mod 9	Mod 10
Gypsum	20.42	20.42	20.42	20.42	20.42	20.42	20.42	20.42	20.42
KSO4	0.1081	0.1081	0.1081	0.1081	0.1081	0.1081	0.1081	0.1081	0.1081
NaCl	43.38	43.38	43.38	43.38	43.38	43.38	43.38	43.38	43.38
Calcite	-30.96	-6.84	-41.3	6.93	-20.62				
CO2 Gas	-10.3	13.77				-41.3	6.94	20.62	
Dolomite	24.12		24.12		13.78	24.12		-6.84	3.46
Ca-Exch			10.3	-13.78		-30.96	-6.84		-10.31
Mg-Exch		24.12		24.12	10.34		24.12	30.96	20.65

The results are similar to the previous models with the notable exception of a large surplus of sodium. All four reaction path models indicate that dissolution and precipitation, alone, cannot explain the chemical evolutionary trend of the water at Pocatello Creek. Thus, it is likely that other processes, such as ion-exchange reactions are important, as suggested by the original NETPATH models (Table 6). This would also explain the recognized deficit of sodium in Pocatello Creek waters relative to chloride. Future work on ion-exchange modeling with MINTEQA2 may yield more conclusive models. Laboratory tests are also in progress to empirically evaluate the cation exchange capacity of local soils.

Conclusions

Surface waters at the Highway Ponds borrow pit are the surface expression of local groundwater for that portion of the Southern Pocatello aquifer. Well and surface waters near the borrow pits have been found to have elevated levels of dissolved sulfate. The postulated source for this sulfate is a large pile of crushed slag located in the borrow pits that is used as road aggregate by the State Department of Transportation. Leach tests performed on this aggregate yielded high concentrations of calcium and sulfate in a molar 1:1 proportion, with lesser amounts of potassium. Although the aggregate contains significant amounts of uranium (97 ppm) and other trace metals, none were leached in significant quantities during a prolonged three-week-long leach test. The wide spread use of crushed aggregate in road and rail bed construction throughout Bannock County may be providing a source of readily leachable sulfate to local groundwater.

Sulfate and chloride levels in groundwaters from both the Pocatello Municipal Aquifer and Pocatello Creek are correlated in very similar proportions. The coupled sulfate-chloride enrichments observed in these waters implies a related source for both. Road salt is a likely origin for the chloride considering that sodium and chloride concentrations in these waters also show a direct correlation.

Elevated sulfate in groundwater associated with aggregate and the coupled sulfate-chloride trends may be related by a single process. It is hypothesized that infiltration of salt derived, chloride-rich water along roads in the spring and dissolution of soluble sulfate in roadbed aggregate as this water percolates to the water table is the mechanism by which the coupled chloride-sulfate enrichments originate.

Modeling of some of the possible chemical reactions which may be involved with sulfate addition from aggregate leaching revealed that dissolution/precipitation reactions alone can not

account for the observed groundwater chemistries. Ion-exchange with clays is likely to be an important process and would explain the deficit of sodium concentrations in Pocatello Creek groundwaters. Work is continuing to test the above hypotheses and to understand the nature of the chemical processes involved.

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