Chemical evolution of shallow groundwater along the northeast shore of Mono Lake, California

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Abstract. We attempted to quantitatively discriminate between hypothesized sources and geochemical processes responsible for the chemical evolution of shallow groundwater along the northeast shore of Mono Lake, an alkaline saline lake located in a hydrologically closed basin in east central California. Shallow groundwater samples from 17 sites perpendicular and 11 sites parallel to the lakeshore were analyzed for major ions. The shallow groundwater contains remnant solutes from higher lake stands, which are transported toward the lake by lateral flow and surface runoff. The flow system appears to be segregated into two different regions: a concentrated, highly saline groundwater underlying much of the northeast shore and pockets of more localized lower-salinity groundwater. The saturation state of the groundwater with respect to certain minerals was determined, and simulations for both evaporative concentration of inflow and mixing of lake water with inflow coupled with mineral precipitation were performed. Solute trends in the shallow groundwater result primarily from the degree of mixing with historical lake water; however, evaporative concentration and redissolution cycles along with various chemical fractionation mechanisms including Ca, Mg, and Na carbonate precipitation, sulfate reduction, ion exchange, and potentially Mg silicate formation are also important controls.

Introduction

Groundwater plays an important role in the chemical evolution of waters in hydrologically closed basins. Likewise, chemical and physical processes occurring in closed basins significantly influence groundwater evolution [Jones, 1966]. For example, in arid regions with terminal lakes, fluctuations in lake level and consequent alteration of lake chemistry can affect the chemical composition of surrounding groundwater [Langbein, 1961]. Near-surface groundwaters in exposed lake beds typically experience evaporative concentration resulting in formation of a seasonal salt crust [Jones et al., 1969]. Understanding the processes affecting the groundwater geochemistry in these regions is essential to define the formation mechanism of saline groundwater and related salt crust.

Numerous studies have examined the controls on the chemistry and evolution of groundwater and surface water in hydrologically closed basins [Jones, 1965; Eugster, 1970; Phillips and Van Denburgh, 1971; Smith and Drever, 1976; Yuretich and Cerling, 1983; Spencer et al., 1985a, b; Thomas et al., 1989]. Models for the evolution of closed basin brines were initiated by Garrels and Mackenzie [1967], who quantitatively evaluated the evolution of one inflowing water composition in Mono Basin, California. Hardie and Eugster [1970] used computer simulations to determine the fate of several inflow waters. These models, however, were based solely on evaporative concentration with equilibrium to the atmosphere and only considered mineral precipitation. Eugster and Jones [1979] discussed several other fractionation mechanisms, including dissolution and ion exchange. Using the principles of closed basin brine evolution by Hardie and Eugster [1970] and the aqueous solution model of Harvie and Weare [1980], Spencer et al. [1985b] discussed the geochemical evolution of the Great Salt Lake, Utah, in which waters were evaporated to examine the effects of mineral precipitation on the residual solutions and the sequence of phases to be expected. In addition, Spencer et al. [1985a] provided a more quantitative account of the historical hydrochemistry of the Great Salt Lake using mixing and evaporation curves with mineral precipitation and dissolution.

Rogers et al. [1992] characterized the groundwater system around Mono Lake as comprising different regions depending on recharge, evaporation, response to lake level variation, geomorphology, and subsurface lithology. They documented that the arid northeast shore has the lowest recharge in the basin owing to less rainfall [Vorster, 1985], low-permeability sediments, and low water table elevation and that the groundwater beneath the shore is saline. They attempted to quantify the processes responsible for the distribution of total dissolved solids (TDS) between shoreline sediments, lake, and groundwater through a groundwater flow and solute transport model incorporating field investigation results of water table measurements, seasonal lake level change, and electrical conductance (EC). However, they used EC as a proxy in the absence of chemical analysis, and they did not evaluate the behavior of individual solutes. Rogers [1992a] indicated that knowledge of groundwater chemistry would provide further information on...
the source of saline water and processes the water undergoes. In addition, in a study on the sources of spring water in Mono Basin using major solutes and Sr isotopes, Neumann [1993] was unable to distinguish recharge end-members that influence the northeast shore groundwater chemistry.

This study is concerned with identifying the possible controls on the chemical evolution of shallow groundwater along the northeast shore of Mono Lake. These include evaporation of recharge, mixing of historical lake water with recharge, and solute fractionation mechanisms. Because this portion of the shore was lake bed before the Los Angeles Department of Water and Power (LADWP) diversions in 1941, the shallow groundwater in the area may contain remnant solutes from higher lake levels. The specific goal of this research was to quantitatively discriminate between evaporation and mixing as processes controlling the groundwater chemistry. These processes, in turn, are affected by a variety of factors such as recharge, surface conditions, stratigraphy, topography, groundwater gradients, and distance to the modern lake. Thus we examined the groundwater chemistry variations along two transects: one perpendicular to the lake and another parallel to the lakeshore. The one perpendicular to the lake, called the Ten Mile Road transect, provides trends in solute concentration with depth and distance to the modern lake. The transect along the lakeshore, called the northeast shore study, permits comparison of the differences in hydrochemistry arising from varying recharge, surface conditions, and stratigraphy. Groundwater samples were analyzed for the major solutes, pH, EC, and temperature. The saturation state of the groundwaters with respect to certain minerals was determined, and factors influencing solute fractionation were evaluated to help determine the processes responsible. Saturation data were also used as a guide to help establish assumptions and phase boundaries in the geochemical modeling, in which we attempted to discriminate between evaporation and mixing conceptual models. This was accomplished with the aid of geochemical computer modeling using the code PHRQPITZ [Plummer et al., 1988] and the chemical data as input.

**Site Description**

Mono Basin, located in east central California, is a hydrologically closed basin with Mono Lake being a regional groundwater sink (Figure 1). Evaporation from the lake and near-surface groundwater provides the main sources of water loss in the basin [National Research Council, 1987]. Snowmelt and rainfall in the adjacent Sierra Nevada provide almost all the bulk inflow to the basin through runoff in perennial streams and by groundwater seepage [Vorster, 1985; National Research Council, 1987]. The Sierra Nevada snowpack accounts for about 85% of the surface and subsurface inflows to the basin, with the majority carried by Lee Vining and Rush Creeks [Vorster, 1985; National Research Council, 1987].

Following the export of water from streams feeding Mono Basin, beginning in 1941 by LADWP, the level of Mono Lake has dropped more than 12 m [Stine, 1987]. This decline in lake level has exposed former lake bottom, creating an extensive area of barren playa along the northeast shore. Groundwater beneath this portion of the shoreline is alkaline and very saline. A shallow water table along with strong capillary forces and evaporative flux causes evaporation of groundwater, which results in the development of a 1-cm seasonal salt crust during the summer [Lee, 1969; Basham, 1988; Groeneveld, 1991; Rogers, 1992a]. Runoff in the winter from snowmelt and rainfall can redissolve the crust. In the arid part of the basin, mountain streams and springs infiltrate permeable alluvial fan and delta deposits, recharging groundwater [Vorster, 1985]. This fresh recharge flows laterally as groundwater underflow downgradient toward the lake where it discharges along the shore or at the lake bottom both in springs and as diffuse seepage [Lee, 1969; Sinclair, 1988; Danskin et al., 1991]. Both the near-shore water table and the lake level are high in late fall, winter, and spring owing to runoff from rainfall and snowmelt and recede in the summer and fall owing to evaporation [Rogers, 1992b].

The stratigraphy along the northern and northeast shore includes a series of sandy and gravelly beach and volcanic ash deposits interlayered with fine-grained lacustrine sediments [Stine, 1987] (Figures 2 and 3). The surface of the shore is covered with sand north and west of Warm Springs, whereas southeast of Warm Springs the surface consists of clay [Rogers, 1992b]. At most sites, sediments deeper than about 0.3 m were black in color and had a strong sulfurous odor [Rogers, 1992b].

**Methods**

At the Ten Mile Road transect, water samples were collected from 17 sites, including 15 piezometers (Figure 2) and two deeper wells (Figure 1). Fifteen piezometers were ar-
Geochemical Results and Interpretation

The solute concentrations, TDS content, pH, EC, and temperature of the groundwater samples collected from the piezometers at the Ten Mile Road site are presented in Table 1 and from the northeast shore seepage pits in Table 2. No significant

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Figure 2. Ten Mile Road transect cross section showing generalized stratigraphy and locations of the 1991 piezometers. Depth of each well's screen is indicated. At each site the shallow, intermediate, and (where present) deep piezometers are designated by letters A, B, and C. Average total dissolved solids (TDS) (grams per liter) values (through March 1991) are posted at the location of the piezometer screen to which they apply. Modified from Rogers [1992b].

Figure 3. Northeast shore transect generalized stratigraphy and approximate elevations of auger sites, along with groundwater and EC values. Site numbers are shown below stratigraphic column. Modified from Rogers [1992b].

Figure 4. Map of Mono Lake's northeast shore showing approximate locations of May 1992 auger holes. Site numbers are shown beside the auger location. Shading represents elevation contours. Modified from Groeneveld [1991] and Rogers [1992b].
seasonal change in EC readings [Rogers, 1992b] or solute concentration [Connell, 1993] was observed during the monitoring period. The major differences in the chemistry of the waters of Mono Basin are illustrated using Piper plots (Figures 5 and 6). Surface water in Mono Basin varies from a dilute Ca-HCO$_3$ type present in creeks and a Mg-Na-Ca-HCO$_3$ type in mountain springs to a saline Na-C1-HCO$_3$ type present in the lake (Figure 5). At the Ten Mile Road transect, shallow groundwater samples collected from pits along the northeast shore also is a very concentrated Na-C1-HCO$_3$ brine near the lake (Figure 6). Seepage water collected from pits along the northeast shore also is a very saline Na-C1-HCO$_3$ brine (Figure 7). Thus, in this study, C1 is used as a conservative reference of concentration during the evolution of water composition and the behavior of individual solutes. And although we cannot quantify all the various types of fractionation, we nevertheless evaluated the factors influencing solute fractionation to help determine some of the processes responsible for the chemical evolution of the groundwater. Groundwater and lake water samples are undersaturated with respect to halite (Figure 7). Thus, in this study, C1 is used as a conservative reference of concentration during evaporation and mixing simulations.

### Fractionation During Brine Evolution

Chemical fractionation of solutes may significantly influence the evolution of water composition and the behavior of individual solutes. And although we cannot quantify all the various types of fractionation, we nevertheless evaluated the factors influencing solute fractionation to help determine some of the processes responsible for the chemical evolution of the groundwater. Groundwater and lake water samples are undersaturated with respect to halite (Figure 7). Thus, in this study, C1 is used as a conservative reference of concentration during evolution [Eugster and Jones, 1979], and behavior of other solutes can be evaluated relative to that of C1. Figure 8 shows an analysis of possible solute fractionation mechanisms and spatial trends in solute behavior perpendicular to the lake and parallel to shore is presented in the next section. The solute concentrations are then used to quantitatively compare results from evaporation and mixing simulations.

### Table 2. The pH, Electrical Conductance (EC), Temperature, Species Concentration, and Total Dissolved Solids (TDS) of the Groundwater Samples Collected in December 1991 and March 1992 From the Ten Mile Road Site

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>EC, mScm at 25°C</th>
<th>Temperature, °C</th>
<th>Ca, mg/kg</th>
<th>Mg, mg/kg</th>
<th>K, mg/kg</th>
<th>Na, mg/kg</th>
<th>Cl, mg/kg</th>
<th>Alkalinity, mg/kg</th>
<th>Sulfate, mg/kg</th>
<th>Boron, mg/kg</th>
<th>Silica, mg/kg</th>
<th>TDS, mg/kg</th>
<th>Density</th>
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<tbody>
<tr>
<td>SS1</td>
<td>9.75</td>
<td>63</td>
<td>11.5</td>
<td>2.7</td>
<td>2.8</td>
<td>950</td>
<td>18,500</td>
<td>20,800</td>
<td>24,600</td>
<td>6,100</td>
<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS2</td>
<td>9.70</td>
<td>39</td>
<td>13.0</td>
<td>1.4</td>
<td>1.53</td>
<td>510</td>
<td>10,400</td>
<td>10,800</td>
<td>1,500</td>
<td>5,800</td>
<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS3</td>
<td>9.65</td>
<td>78</td>
<td>10.0</td>
<td>2.0</td>
<td>2.08</td>
<td>1,300</td>
<td>23,200</td>
<td>25,600</td>
<td>29,600</td>
<td>7,600</td>
<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS5</td>
<td>9.60</td>
<td>116</td>
<td>14.0</td>
<td>2.1</td>
<td>3.48</td>
<td>2,100</td>
<td>38,000</td>
<td>39,200</td>
<td>46,900</td>
<td>11,300</td>
<td>557</td>
<td>26</td>
<td>114,300</td>
<td>1.06</td>
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<tr>
<td>SS6</td>
<td>8.60</td>
<td>107</td>
<td>12.0</td>
<td>1.1</td>
<td>2.53</td>
<td>1,700</td>
<td>32,800</td>
<td>35,300</td>
<td>37,600</td>
<td>10,800</td>
<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS7</td>
<td>9.70</td>
<td>104</td>
<td>13.0</td>
<td>1.6</td>
<td>4.49</td>
<td>1,900</td>
<td>34,100</td>
<td>39,200</td>
<td>44,700</td>
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<td></td>
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<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS8</td>
<td>9.70</td>
<td>62</td>
<td>9.0</td>
<td>1.9</td>
<td>1.02</td>
<td>1,100</td>
<td>19,700</td>
<td>19,400</td>
<td>24,300</td>
<td>6,300</td>
<td>323</td>
<td>23</td>
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<tr>
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<td>38</td>
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<td>2.5</td>
<td>1.01</td>
<td>630</td>
<td>13,300</td>
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<td></td>
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<tr>
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<td>9.70</td>
<td>45</td>
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<td>2.2</td>
<td>1.81</td>
<td>990</td>
<td>19,500</td>
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<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS12</td>
<td>9.70</td>
<td>61</td>
<td>11.0</td>
<td>2.3</td>
<td>1.22</td>
<td>960</td>
<td>19,100</td>
<td>19,300</td>
<td>23,600</td>
<td>6,400</td>
<td></td>
<td></td>
<td>167</td>
<td>40</td>
</tr>
<tr>
<td>SS13</td>
<td>9.50</td>
<td>83</td>
<td>11.0</td>
<td>1.6</td>
<td>1.68</td>
<td>1,250</td>
<td>25,400</td>
<td>26,300</td>
<td>27,200</td>
<td>7,400</td>
<td>328</td>
<td>24</td>
<td>72,000</td>
<td>1.05</td>
</tr>
<tr>
<td>MLK</td>
<td>9.80</td>
<td>98</td>
<td>12.8</td>
<td>3.7</td>
<td>37.10</td>
<td>1,600</td>
<td>31,900</td>
<td>20,500</td>
<td>25,300</td>
<td>12,500</td>
<td>379</td>
<td>12</td>
<td>81,600</td>
<td>1.07</td>
</tr>
<tr>
<td>MUR</td>
<td>8.20</td>
<td>0.107</td>
<td>7.0</td>
<td>8.6</td>
<td>4.70</td>
<td>2.3</td>
<td>9</td>
<td>5.3</td>
<td>599</td>
<td>9.1</td>
<td>0.12</td>
<td>37</td>
<td>98</td>
<td>1.00</td>
</tr>
<tr>
<td>RCR</td>
<td>6.40</td>
<td>0.065</td>
<td>3.0</td>
<td>9.4</td>
<td>2.00</td>
<td>1.2</td>
<td>3</td>
<td>8.2</td>
<td>33.4</td>
<td>24</td>
<td>0.02</td>
<td>6.2</td>
<td>60</td>
<td>1.00</td>
</tr>
<tr>
<td>LCR</td>
<td>6.60</td>
<td>0.057</td>
<td>1.0</td>
<td>5.6</td>
<td>1.20</td>
<td>0.8</td>
<td>2.1</td>
<td>5.3</td>
<td>24.6</td>
<td>4.8</td>
<td>0.03</td>
<td>9.3</td>
<td>44</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Alkalinity expressed as bicarbonate.
that B also behaves conservatively in the groundwater system, however, the other ions do not.

Sodium and potassium. Na generally behaves conservatively in the groundwaters at the Ten Mile Road Site, demonstrating only slight depletion relative to Cl with proximity to the lake (Figure 8). In northeast shore seepage water, Na/Cl decreases even more compared to the Ten Mile Road groundwaters and lake water. These samples, along with the lake water sample, approach saturation with respect to gaylussite (Na₂Ca(CO₃)₆·5H₂O) (Figure 7), whereas the Ten Mile Road samples are undersaturated; therefore mineral precipitation can account for the loss of Na in only the most concentrated waters. Gaylussite is a common mineral in recent muds of alkaline saline lakes [Eugster, 1980]. Bischoff et al. [1991] observed gaylussite crystals on hard substrates below the lake surface, and Bischoff et al. [1993] suggested that gaylussite can form from ikaite. In addition, cyclic deflation of alkali carbonate crusts and dissolution and infiltration resulting in Cl recycling can remove Na relative to Cl.

K is depleted relative to Cl in the groundwater and lake water (Figure 8). Groundwaters collected from the Ten Mile Road Site show a slight enrichment of Na over K as they become more concentrated (Figure 8). K is probably removed from these waters by ion exchange [Jones et al., 1969; Eugster and Jones, 1979], in which K displaces Ca on the exchange sites. Modified from Neumann [1993].

Calcium and the carbonate species. Ca is depleted relative to Cl in groundwater and lake water, and although the carbonate species increase in concentration as water evolves from dilute inflow to concentrated groundwater and lake water, these species are also removed from solution in more concentrated groundwaters and lake water (Figure 8). Groundwater and lake water samples are supersaturated with respect to calcite and approach saturation with respect to gaylussite (Figure 7). Thus the precipitation of calcite is a probable reason for the Ca depletion [Lee, 1969; Eugster, 1980]. The precipitation of calcium carbonate minerals, such as calcite, is well documented for Mono Basin [Russell, 1889], and these minerals are currently the primary precipitate [Cloud and Lajoie, 1980]. Groundwater samples from the Ten Mile Road site increase lakeward from 1.7- to 5.9-fold supersaturation with respect to calcite, and samples from the northeast shore range from 4- to 9-fold supersaturation.

Recent studies by Bischoff et al. [1993] have shown that although calcite is supersaturated in Mono Lake water, precipitation of this mineral is strongly inhibited by high concentrations of orthophosphate. They suggested that during winter months, ikaite (CaCO₃·6H₂O) precipitates as spring water mixes with lake water because of its low solubility at low temperatures and because of the inhibitory effect of high concentrations of orthophosphate in the lake. During warmer seasons, ikaite is either transformed to anhydrous CaCO₃, which is taken up into shoreline tufa, or dispersed throughout the lake by wind to form gaylussite [Bischoff et al., 1993]. Similar processes may be occurring in the groundwater along the northeast shore in which calcite precipitates secondarily. In addition, cyclic wetting and drying of playa sediments followed by subsequent removal of alkaline earth carbonates by deflation [Eugster, 1980; Drever, 1988] may account in part for the loss of Ca and the carbonate species.

Magnesium and silica. The behavior of Mg and silica in waters of Mono Basin, as well as other hydrologically closed basins, is complex and not well understood. Both are depleted relative to Cl in the groundwater and lake water (Figure 8; Tables 1 and 2). These solutes may be removed from solution by incorporation in authigenic layered Mg-silicates [Spencer, 1985b] such as trioctahedral smectite [Yuretich and Cerling, 1983; Jones, 1986]. Another likely sink for Mg includes biogenic or chemical precipitation of Mg carbonate minerals [Eugster, 1980; Sacks et al., 1992]. Silica may also be removed in lake water by diatom uptake [National Research Council, 1987].

Sulfate. SO₄, in general, is concentrated by evaporation during brine evolution. Groundwater and lake water show almost no fractionation, with the exception of one of the Ten Mile Road deep piezometers (5C) (Figures 8 and 2). Groundwater and lake water samples are undersaturated with respect to mirabilite (Na₂SO₄·10H₂O) (Figure 7); they are also undersaturated with respect to gypsum [Connell, 1993], primarily because of the low concentrations of Ca. The most likely mechanism for SO₄ loss in the deeper groundwater at 5C is micro-
bially mediated sulfate reduction. During this process, hydrogen sulfide gas is released [Drever, 1988], and this gas has been found during well installation and sample collection [Rogers, 1992b]. In addition, black sediments were encountered 0.3 m below surface at most sites [Rogers, 1992b], and Domagalski et al. [1990] have documented amorphous FeS precipitation in Mono Lake bottom sediments.

Spatial Trends in Hydrochemistry

Ten Mile Road transect. Along the transect perpendicular to the lake the TDS and concentrations of Cl, B, Na, K, and alkalinity increase toward the lake for the shallower horizons and are uniform with depth (Tables 1 and 2; Figure 2). Values in the deeper C horizon show little spatial variation. These deeper (C) wells bottom in a sandy silt layer (Figure 3), and according to Rogers [1992a] these wells had the longest recovery rates after purging. The recovery rates suggest that this unit has low permeability and isolates deeper groundwater from shallower waters above.

Significantly, the SO₄, Ca, Mg, and silica concentrations differ from these trends. Although the concentration of SO₄ increases toward the lake in the A and B horizons, it decreases lakeward in the deeper horizon. The concentrations of Ca and Mg are extremely low and do not change spatially. The concentration of silica in the groundwater and lake water remains fairly low at generally less than 40 mg/kg. The lack of correspondence of these solutes with the trends mentioned above and the extremely low concentrations of Ca and Mg are explained by the solute fractionation mechanisms discussed earlier.

The shoreline at the Ten Mile Road site slopes gently toward the lake, and the near-surface shallow groundwater flows in the same direction [Rogers et al., 1992]. The lack of recharge in the late summer and fall, along with a shallow water table and fine-grained sediments, enhances capillary evaporation. Seasonal surface conditions indicate that except for winter, the northeast shore is covered with an efflorescent crust. Runoff in the winter redissolves the crust, and this runoff from snowmelt and rainfall has created channels that trend downslope toward the lake. The winter runoff transports solutes downgradient toward the lake, increasing solute concentration with proximity to the lake. In addition, discharging springs and seeps can redissolve the crust at discrete locations. The dissolution of the crust by the dilute runoff causes fractionation, in which soluble constituents, like Na and Cl, dissolve first and the least soluble silica and alkaline earth carbonates remain in the crust. Runoff flows downslope, undergoes further evaporation, becoming even more concentrated with soluble constituents downshore, and mixes with existing groundwater, thereby adding more soluble constituents to downshore groundwaters. This fractionation due to seasonal wetting and drying cycles increases concentrations of more conservative solutes toward the lake in the shallower groundwaters, and in part accounts for the uniformly low concentrations of Ca, Mg, and silica.

Northeast shore transect. Along the transect parallel to the northeast shore, the TDS and concentrations of Cl, B, Na, K, SO₄, and alkalinity vary considerably from relatively low values near Ten Mile Road (ss9 and ss10) and Warm Springs (ss2) to higher values southeast of Methane Springs (ss5, ss6, and ss7) that generally exceed those in Mono Lake (Table 2; Figure 4). Ca and Mg concentrations are extremely low in all the samples, and silica concentrations remain lower than 40 mg/kg. These results indicate that the same solute fractionation mechanisms discussed earlier occur all along the northeast shore.

Mixing of freshwater appears to be locally important in explaining the waters with low concentration and TDS values. The Cottonwood Creek delta, near ss9 and ss10, and springs associated with the Warm Springs complex, near site ss2, may provide the fresh inflow into the groundwater system (Figure 4; Table 2). A spring mound near site ss2, located northeast of Warm Springs, had an EC of 2.8–1.08 mS/cm [Groeneveld, 1991; Rogers, 1992b].
Figure 8. Plots of solutes as a function of Cl concentrations for the Ten Mile Road and northeast shore groundwater and Mono Lake water samples. Analyses of mountain springs, creeks, shore springs, and warm springs based on data from Neumann [1993].
At sites ss5, ss6, and ss7, with the most concentrated groundwater, the lack of proximity to discrete freshwater discharge areas, along with evaporative concentration and redissolution cycles, contributes to the elevated TDS and solute concentration values (Figure 4; Table 2). In addition, the proximity of concentrated discharge sources such as the Methane Springs complex may also be important. Samples collected by Groeneveld [1991] from seeps at and near Methane Springs had relatively high EC values (11–16 mS/Cm) and B concentrations (120–350 ppm). Oremland et al. [1987] and Groeneveld [1991] observed an increase in the quantity of methane venting at distinct locales along a transect from Ten Mile Road to the Methane Springs complex. Groeneveld [1991] noted that the seepage of methane is accompanied by the occurrence of highly concentrated water. The general southward dip of the topography and underlying strata along this portion of the shore may induce a southward flow of the surface and subsurface water carrying solutes from these concentrated discharge sources through the groundwater system.

Groundwaters from the sites south of Warm Springs (ss1, ss12, and ss13) have intermediate concentrations. The surface of the northeast shore is covered with sand north and west of Warm Springs, whereas south of Warm Springs the surface consists of clay and an additional clay layer is present below surface (Figures 3 and 4). The surficial and deeper clay horizons may prevent mixing of solutes from redissolved salt crust and flushing with fresher recharge.

Computer Modeling

We examined two conceptual models for the hydrochemistry using the computer code PHRQPITZ [Plummer et al., 1988] and measured chemical data: (1) the mixing of compositionally different waters with and without calcite precipitation and (2) the concentration of source waters by evaporation coupled with calcite precipitation. The first, referred to as the mixing model, simulated the effects of mixing inflow waters with remnant Mono Lake water in the pores of the playa sediments. The second, referred to as the evaporation model, simulated the effects of evaporating and thereby concentrating inflowing waters. To compare the model results to the actual measured water composition, we utilize a root-mean-square error (RMSE) in the form

$$\text{RMSE} = \left[ \frac{\sum (C_{\text{measured}} - C_{\text{calculated}})^2}{C_{\text{measured}}^2} \right]^{0.5},$$

where $C$ is the concentration of a single species (moles per kilogram) and $N$ is the number of samples. The RMSE is relative to the measured species concentration, which serves to normalize the magnitude of the error due to differences in the absolute concentrations between species.

In order to determine the model concentration factor (either the mixture ratio of remnant lake water to inflow or the evaporation concentration factor) necessary to produce the observed chemical composition of a particular groundwater sample, the actual measured concentration of Cl was superimposed on the model-simulated Cl mixing curve or evaporation line, and concentration factors were estimated visually from the plot [Connell, 1993]. The molal concentrations of the other nonconservative ions were multiplied by the constant concentration factor for Cl, which allowed for comparison of results of the model simulations to the measured concentration values of pure groundwater samples. Select samples were chosen for simplification.

Mixing Simulations

In the mixing simulations the mixing of inflowing water with remnant Mono Lake water was conducted at a constant temperature (25°C) and atmospheric CO$_2$ pressure (log P$_{CO_2} = -3.5$) using the chemical composition of Mono Lake water presented by Neumann [1993]. The input chemical composition, pH, and temperature of the inflowing water used in this study were those for Murphy Spring and Lee Vining Creek, also presented by Neumann [1993]. Two sources were chosen as representative of water that when mixed with Mono Lake composition water, would either directly produce or indirectly affect the chemical composition of the groundwater along the northeast shore. Murphy Spring represents upgradient groundwater recharge from the Bodie Hills (Figure 1). Lee Vining Creek is a representative Sierra Nevada water and, along with Rush Creek, carries the majority of runoff reaching Mono Lake (Figure 1) [Vorster, 1985].

The modeling indicates that by mixing progressively higher percentages of Mono Lake composition water with either Murphy Spring or Lee Vining Creek composition water, the trends observed for some of the absolute concentrations in the shallow groundwater can be duplicated (Figure 9). Individual mixture ratios of Lee Vining Creek to Mono Lake water required to yield the chemical composition of specific groundwater samples are about the same as those observed for Murphy Spring, because the highly concentrated alkaline saline lake water composition dominates the resultant mixture composition at very low percentages regardless of the inflow source [Connell, 1993].

Figure 9 illustrates the results of the Murphy Spring mixing allowing calcite precipitation to equilibrium. The Ca concentration decreases until a mixture ratio of approximately 10% lake water and then remains constant with increasing addition of lake water. Calcite precipitation removes the available Ca from the inflowing spring water as it mixes with the alkaline lake water. The results of the Murphy Spring mixing without calcite precipitation are the same as those with calcite precipitation, except for Ca, which decreases gradually as greater additions of lake water are mixed with the relatively higher Ca content spring water [Connell, 1993]. Carbonate species are
unaffected by calcite precipitation because of the relatively high alkalinity relative to Ca, based on the chemical divide concept by Hardie and Eugster [1970], and because it is an open system (constant P$_{CO_2}$).

Figure 10 presents the comparison between the measured concentrations and the mixture simulation concentrations from the Murphy Spring mixing model. RMSE values for the Lee Vining Creek mixture simulation are nearly the same as those observed for the Murphy Spring mixing model [Connell, 1993]. For groundwater from both the northeast shore seepage pits and the Ten Mile Road site piezometers, Na, K, and B have low relative RMSE values. The carbonate species and Ca are slightly higher, while SO$_4$ is significantly higher, suggesting that these observed solute concentrations cannot be explained by the mixing model alone, and they are higher presumably because of fractionating reactions. The model-predicted CO$_3$ concentrations for the least concentrated groundwaters collected from sites furthest from the modern lakeshore, D5A, 1A, and 1B, are significantly lower than the observed, indicating the model cannot adequately simulate pH effect on carbonate speciation for low lake water additions. The mixing simulation predicts the SO$_4$ concentration to be higher than the observed concentration measured at site 5C, and this discrepancy significantly raises the RMSE value for this solute. As discussed earlier, microbially mediated reduction accounts for the relatively lower measured SO$_4$ concentration at this site.

**Evaporation Simulations**

The choice of the starting water to be evaporated was based on the likelihood that if allowed to evaporate under the model conditions, the chemical composition of the resultant solution along some point of the reaction (path) would resemble that of the groundwater along the northeast shore. If this is valid, the source of the chemical composition of the groundwater may be attributed to the evaporation of waters flowing into the basin.

We selected Murphy Spring and Rush Creek runoff as starting water, assuming a constant atmospheric CO$_2$ pressure (log P$_{CO_2}$ of $-3.5$), a constant temperature of 25°C, and the continuous removal of water vapor. This model only allows equilibration with precipitating calcite and halite; however, the halite phase boundary was not reached during these calculations. Murphy Spring was chosen to represent upgradient groundwater recharge (Figure 1). Rush Creek, along with Lee Vining Creek, carries the majority of runoff from the Sierra Nevada [Vorster, 1985] (Figure 1). In general, the model yielded similar results (RMSE values) for the evaporation simulations of Rush Creek water compared to those of Murphy Spring water, and thus the following discussion applies to the Murphy Spring modeled results.

The results indicate that as evaporation proceeds, the chemistry of the inflow water changes from a Na-Ca-HCO$_3$-Cl water to an alkaline Na-CO$_3$-Cl water (Figure 11). Calcite begins to precipitate at a concentration factor less than 2, and thereafter Ca is continuously removed from solution by precipitation. Concentrations of HCO$_3$ and CO$_3$ and pH rise in the course of evaporation. Concentrations of Na, K, Cl, and SO$_4$ increase as evaporation proceeds because these solutes do not form any solid products in this model. At the Ten Mile Road transect the evaporative concentration factors necessary to produce the observed chemical composition of the groundwater samples...
increase lakeward, as would be expected if evaporation is the dominant process acting to concentrate the dissolved solutes downshore [Connell, 1993].

Figure 12 presents the comparison between the measured concentrations and the evaporation simulation concentrations. RMSE values for Na, B, Ca, and HCO₃ are all within about the same range, and SO₄, CO₃, and K are significantly higher, suggesting that the observed solute concentrations cannot be explained by the evaporation model alone.

Discussion

The mixing simulations provide a better conceptual model of how the system works than the evaporation simulations, based on the lower RMSE values than the evaporation models. However, because Mono Lake is mainly derived from the evaporation of Sierra Nevada water, it is difficult to distinguish between these processes. In a study of the geochemistry of the Great Salt Lake, Spencer et al. [1985a] found that mixing of different inflow waters dominated, not evaporative concentration and solute loss during inflow. Evidence of a seasonal salt crust covering most of the northeast shore during the summer, combined with the fact that some of the samples collected from shallow pits excavated along the northeast shore have higher TDS and solute concentration values than the sample collected from Mono Lake, strongly supports the idea that evaporative concentration is important. Determination of bromide (Br) and evaluation of Cl/Br ratios might help distinguish evaporation from dissolution, and the volume lost to evaporative flux might be indicated by Δ18O data.

Differences between the solute concentrations predicted by the models and those obtained from analyses of groundwater samples suggest that many of the solutes must be affected by fractionation processes. The saturation indices indicate that precipitation of alkaline and alkaline earth carbonates, such as calcite and gaylussite, may remove Ca, Mg, Na, and the carbonate species from solution. In addition, cyclic wetting and drying of playa sediments resulting in formation and redissolution of salt crust may also remove alkaline and alkaline earth carbonates and concentrate the more soluble salts. However, mineralogical fractional controls on the hydrochemical system, inferred from calculated saturation state data, remain speculative until salt crust samples can be analyzed. Analyses of samples from the northeast shore playa are in progress to help determine mineralogical fractionation controls and redissolution changes with mineralogy. The formation of layered Mg silicates may remove Mg and silica from solution. Reduction processes may remove SO₄ from solution, and K may exchange or adsorb on active surfaces.

Controls on spatial variations in the chemistry of the shallow groundwater perpendicular to the lake include mixing of remnant lake water with dilute inflow, seasonal evaporative concentration of runoff coupled with redissolution, and other solute fractionation mechanisms. Trends in the behavior of the individual solutes and TDS (Table 1; Figure 3) are a function of distance from the modern lakeshore and the recent occupation on the northeast shore during higher lake levels. The decrease in solute concentrations in the shallow groundwater with distance from the lake suggests that solutes are transported toward the lake by lateral groundwater flow and/or surface runoff. The spatial similarity and lower TDS values in the deeper wells indicate at least partial chemical and physical isolation of the deeper stratigraphic unit and the overall dominance of lateral groundwater flow versus vertical flow at any one site.

The spatial patterns observed for the solute concentrations and TDS in groundwater parallel to the northeast shore indicate that the system is segregated into two different regions: a concentrated, highly saline groundwater underlying much of the northeast shore, and pockets of more localized lower-salinity groundwater. The differences in the two areas are caused by differing inflow quantities and compositions. The lower-salinity groundwater may be controlled by localized recharge through distinct flow systems, such as channelized or piped freshwater inflow which discharges at discrete points. According to Cloud and Lajoie [1980], as fresh inflowing groundwater rich in Ca reaches the highly saline groundwater near the lakeshore, calcite is precipitated into vertical tubular structures. These structures may then form discrete flow channels in which the more dilute water rises by density and hydraulic head differences and subsequently discharges at particular locations, typically spring mounds. The less concentrated
discharge from these spring mounds may recharge the shallow groundwater system in nearby areas, or fresh groundwater may mix with nearby concentrated groundwater. The most concentrated groundwater may be attributed to a combination of factors, including the lack of proximity to the discrete freshwater discharge areas, stratigraphic controls on flushing rate, and evaporative concentration and redissolution cycles. In addition, the proximity to concentrated, methane-venting seeps and springs, may also be important. The seepage of methane, accompanied by the occurrence of highly concentrated water with elevated B content, may result from recirculation of older, deeper brines. Oremland et al. [1987] indicate that the source of methane for these seeps originates from a biogenic natural gas deposit of Pleistocene age which underlies the current and former lake bed. Tritium and 36Cl data might help distinguish gas deposit of Pleistocene age which underlies the current and former lake bed. Tritium and 36Cl data might help distinguish

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