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Description and Evaluation of Legacy Hydrochemical Data for the Big and Little Blue River Watersheds, Nebraska, USA

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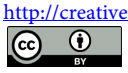

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Abstract

Numerous legacy hydrochemistry data [major cations and anions, pH, total dissolved solids (TDS)] (STORET database, 1968-1975) resulting from collection and analysis by the Nebraska Department of Environment and Energy (NDEE) were statistically, graphically, and hydrogeochemically analyzed for the Big and Little Blue River watersheds in southcentral Nebraska. Interpretation of this large legacy dataset (29 Big and Little Blue River watersheds sampling stations and 13 sampling sites on seven tributaries) revealed low but notably variable TDS concentrations (~100 - 500 mg/L), possessing predominant Ca-HCO_3 hydrochemical facies. Median TDS values range from about 150 - 440 mg/L; slight calcite and dolomite supersaturation exists; and low computer software-generated saturation index values comprise a line of evidence for the near thermodynamic equilibrium of the studied surface waters. Many calculated saturation indices for calcite and dolomite were slightly positive, indicating slightly precipitating conditions. Subjecting Ca-HCO_3 hydrochemical facies sample analyses to Pearson correlation and linear regression evaluation reveals strong covariance for Ca-HCO_3 and Ca-SO_4 pairs and somewhat less strong for Ca-Cl. These statistical analyses suggest primary carbonate weathering [assuming insignificant contribution of HCO_3 originating from silicate (feldspar) weathering], followed closely by gypsum dissolution and less closely by evaporite dissolution in the studied river watersheds.

Keywords

Hydrochemical Facies, Linear Regression Analysis, Stiff Diagram, Visual MINTEQ, Silicate (Feldspar) Weathering

1. Introduction

From the late 1960s through approximately 1990, the Nebraska Department of Environment and Energy (NDEE) and its predecessors the Nebraska Department of Environmental Quality (NDEQ) and the Nebraska Department of Environmental Control (NDEC) sampled numerous river and stream discharges throughout the state, typically monthly, and analyzed the grab samples for all major ions, total dissolved solids (TDS), pH, specific conductance (SC), and temperature. Major-ion analyses allow aqueous geochemical evaluation, encompassing hydrochemical facies determination, identification of probable parent material source(s), and accuracy evaluation of analytical results (Atkinson, 2019). This study evaluates historical major-ion data collected by the NDEC for the Big and Little Blue River watersheds located in southcentral Nebraska. Major-ion data for the two river systems and nine tributaries, collected during the period April 1968-November 1975, were initially evaluated for accuracy, modified where appropriate, and then evaluated hydrochemically using applicable diagrams, x-y plots, and computer software as described below. The Big and Little Blue River watersheds occur in the central Great Plains of North America.

The objective of this study was to comprehensively evaluate and interpret hydrogeochemically the extensive legacy STORET (STORage and RETrieval) data and to integrate pertinent geological and hydrological information for the Big and Little Blue River watersheds in Nebraska. This legacy database, corrected where appropriate by cation-anion balance checks, forms an excellent historical baseline for tracking current and long-term changes in water quality throughout the studied watersheds.

2. Study Area Description

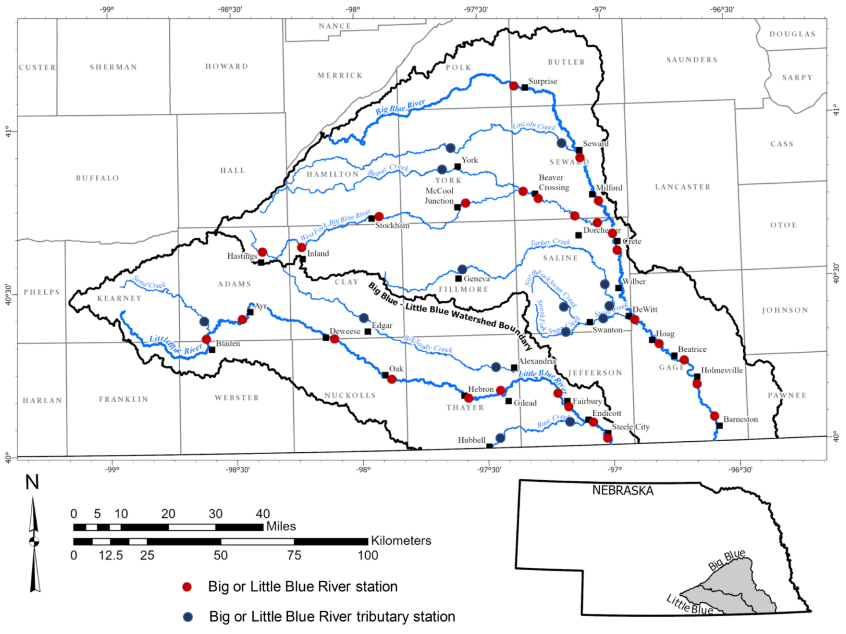

Figure 1. Big and Little Blue River watersheds in Nebraska showing the surface-water sampling locations and tributary streams.

The study area, the Big and Little Blue River watersheds, lies in the southcentral part of Nebraska (**Figure 1**). The Big Blue River was given its name by the Kansa tribe of Native Americans, who lived at its mouth (from 1780-1830), and who called it the Great Blue Earth River.

The Big Blue River is the largest tributary of the Kansas River. The river flows for approximately 480 km (300 mi) from southcentral Nebraska to the Kansas border and 96 km (60 mi) into Kansas, to its confluence with the Kansas River near Manhattan, Kansas. The portion of the Big Blue River watershed residing in Nebraska covers approximately 18,830 km^2 (7270 mi^2). The Little Blue River watershed (Nebraska portion) encompasses about 6970 km^2 (2690 mi^2). The Big and Little Blue River watersheds in Nebraska encompass eight hydrologic unit codes (HUCs) contained collectively in the Big Blue River Basin HUC 102702 subbasin (USGS, 1976).

2.1. Climate

The study area has a temperate, subhumid, midcontinental climate that is characterized by wide seasonal variation in temperature and rainfall amounts. The average annual total precipitation across the study area ranges from approximately 63.5 cm (25 in.) at Minden in the northwest corner of the Basin to approximately 78.7 cm (31 in.) at Beatrice in the southeast corner of the Basin. More than 65 percent of the mean annual precipitation occurs during the growing season from May through September (DNR, 2013). Mean annual Class A pan evaporation near Hastings, Nebraska, is approximately 132 cm/year (52 in./yr), with roughly 114 cm (45 in.) occurring during the May-September growing season (DNR, 2003).

2.2. Geology

The uppermost bedrock units range from the oldest in the southeast of the study area to the youngest in the western part. In the Gage County area, the Admire Group of Pennsylvanian age occurs along with the Chase Group and Council Grove of Permian age (**Figure 2**) (DNR, 2013). Moving westward, Cretaceous age formations range from the Dakota Group to the Pierre Shale. The far western portion of the study area is underlain by the Ogallala Group of Tertiary age. Where the Ogallala and Dakota Groups contain significant sand, they provide drinking water to wells.

The Dakota Group (also referred to as the Dakota Sandstone, Dakota Formation, and Dakota Aquifer [Gosselin et al., 2001]) is a sequence of interbedded shale and sandstone units deposited during Late Cretaceous time (Condra & Reed, 1959; Brown et al., 1980; Engberg, 1984). This formation approaches 43 m (98 ft) in thickness in some eastern Nebraska locations (Druliner & Mason, 2001). The Dakota is the uppermost bedrock in parts of Polk, York, Fillmore, and Thayer Counties.

The Carlile Shale is a Late Cretaceous marine unit that consists of shale, limestone, and sandstone. The approximate thickness is 46 m (150 ft) (Condra & Reed, 1959; USGS, 2021).

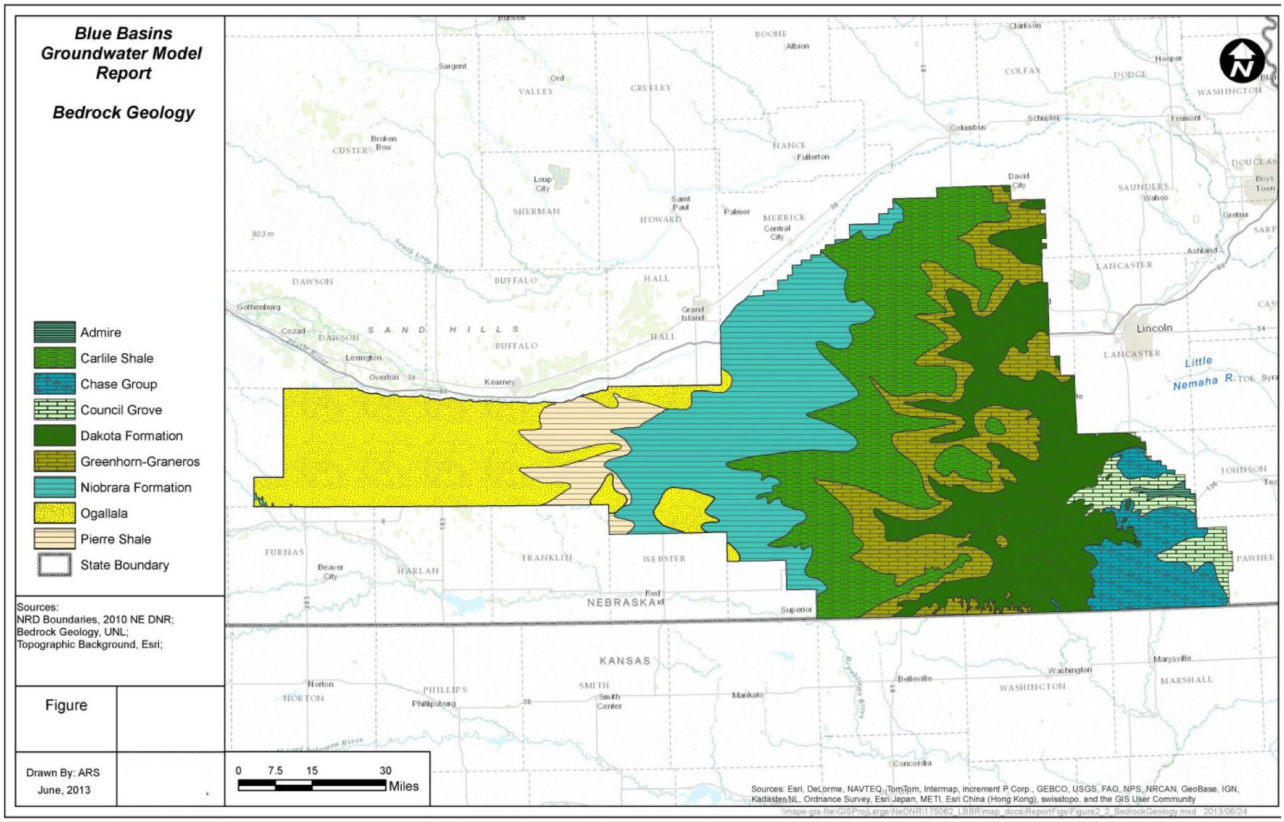

Figure 2. Uppermost geologic units in the Big and Little Blue River watersheds.

The Niobrara Formation is the uppermost bedrock in the study area in Adams, Clay, and Hamilton Counties. It consists primarily of chalk, limestone, and shale with thickness approximating 76 m (250 ft) (Goeke et al., 1992). Bedding planes, commonly marked by thin layers of gypsum, occur at the top of the unit (Condra & Reed, 1959; USGS, 2021).

The Pierre Shale consists mostly of dark-colored marine shale whose weathered top is referred to as *ochre* (Goeke et al., 1992). Locally, it grades to thin beds of calcareous, silty shale, marl, shaly sandstone, and sandy shale and contains thin gypsum seams (USGS, 2021).

The Ogallala Group, a heterogeneous collection of fluvial and aeolian clays, silts, sands, sandstones, gravels, and volcanic ash beds, was deposited on the eroded and weathered Pierre Shale surface in many locations in central and eastern Nebraska during Tertiary time. Much of the Ogallala is cemented by calcium carbonate (Eversoll et al., 1988; Goeke et al., 1992). The Ogallala Group is the primary geologic unit comprising the High Plains Aquifer.

Unconsolidated silts, sands, and gravels of the Quaternary Period (Holocene and Pleistocene Epochs) overlie the Ogallala Group bedrock in the western portion of the study area. These unconsolidated silt and sand deposits generally range from a depth of 0.6 m (2 ft) to more than 30 m (100 ft) thick. In much of Kearney County, Pleistocene loess (wind-blown silt and clay, predominantly) and under-

lying sand typically rest directly and unconformably on the Pierre Shale (Wilson & Stuebe, 2004; Goeke et al., 1992). Most valley bottoms and terraces in the study area are mantled by Quaternary-age sand, gravel, silt, and clay.

The Laramide Orogeny [Late Cretaceous to Tertiary (Paleogene)] formed the Rocky Mountains of Colorado and surrounding mountainous areas (English & Johnston, 2004). Thousands of years of erosion resulted in fluvial transport of rock and mineral fragments down the eastern slope of the Front Range and into the Great Plains of western Nebraska and eastward (Atkinson, 2018).

2.3. Topography and Physiography

The Big and Little Blue River watersheds reside in the Central Loess Plains, a part of the Great Plains physiographic province (Fenneman, 1946). The land surface generally slopes from west-northwest to east-southeast across the watersheds. The topography is characterized as relatively flat uplands and gently rolling hills with narrow valley regions of low relief found along the major streams and the Big and Little Blue Rivers.

There are three distinct topographic regions within the watersheds. Most of the watersheds are in the Plains topographic region, which consists of relatively flat loess-mantled uplands. Runoff in the Plains topographic region is low.

The portion of the study area that is generally south of the Little Blue River is in the Dissected Plains topographic region. This topographic region consists of hilly land with moderate to steep slopes, sharp ridge crests, and remnants of the old plain. Generally, runoff is high because of the topographic variability.

The eastern portion of the Basin is in the Rolling Hills topographic region, which is characterized by areas of hilly lands with moderate to steep slopes and rounded ridge crests. These topographic features (ridges and valleys) were formed by glaciers and then modified by erosion and more recent deposition. The glacial deposits consist largely of low-permeability glacial till (UNL CSD, 1998).

2.4. Surface-Water and Groundwater Hydrology

Long-term average streamflow for the Big Blue River downstream at Barneston is 22 m^3/s (779 cfs) (USGS, 2026a). For the Little Blue downstream at Fairbury, average flow is 15 m^3/s (536 cfs) (USGS, 2026b). A portion of this calculated streamflow is groundwater inflow (base flow). Approximate base flow for the Big Blue watershed is 2.82×10^8 m^3/year (228,740 ac-ft/year) and is 1.49×10^8 m^3/year (121,080 ac-ft/year) for the Little Blue River watershed. Groundwater recharge from precipitation in the Big Blue is about 23 mm/year (0.9 in./year) and is about 20 mm/year (0.8 in./year) in the Little Blue watershed. Surface runoff is about 7.60×10^8 m^3/year (615,990 ac-ft/year) in the Big Blue watershed and is approximately 3.27×10^8 m^3/year (265,440 ac-ft/year) in the Little Blue River watershed (UNL CSD, 1998).

Sampled tributaries that feed the Big Blue River include: Türkiye Creek, Swan Creek, Lincoln Creek, and Beaver Creek. Sampled tributaries that discharge to the

Little Blue River encompass: Sandy Creek, Big Sandy Creek, and Rose Creek.

3. Materials and Methods

For approximately 40 years, NDEC and NDEQ major-ion and related water-quality analyses were uploaded to the US Environmental Protection Agency (USEPA) STORET (Storage and Retrieval) database, known as the STORET Legacy Data Center. The hydrochemical data for this study were downloaded from the STORET Water Quality Portal (WQP), successor to the Legacy Data Center, in April 2022. The WQP is a cooperative service sponsored by the USGS and USEPA (WQP, 2019).

The author understands that each major ion, pH, specific conductance, TDS, temperature, latitude/longitude value, and sampling date for a sampling site constitutes a data record. Therefore, each sampling event produced 13 digital records. Therefore, if a sampling site is associated with 10 sampling/analysis events, 130 records need to be identified and added to each site's MS Excel file. Consequently, several thousand records for the Big/Little Blue River watersheds were downloaded to sampling site Excel files. Most study-area sampling stations have about 5 - 25 sampling events (SEs); however, the Big Blue River at Crete N has 92 SEs; the Big Blue River at Barneston has 99 SEs; the Little Blue River at Ayr has 98 SEs; and the Little Blue River at Steele City also possesses 98 SEs. Probably only about 100 records were excluded primarily due to incomplete major ion values. Approximately 30% of retained records (principally HCO_3 and Ca) were modified, resulting from cation/anion balance and related accuracy check methods.

To evaluate and enhance major-ion data quality and usefulness, concentrations expressed in milliequivalents per liter (meq/L), cation-anion balance (CAB) errors, and numerous quality-assurance ratios [e.g., calculated:measured TDS, (0.01) * (SC, in µS/cm):sum of anions in meq/L, (0.01) * (SC):sum of cations in meq/L], were used to evaluate major-ion data quality (Hem, 1992; Atkinson, 2011, 2018, 2019). The USGS considers ion balances within the ±6% range to indicate major-ion analyses of useful quality; however, CAB errors up to ±12% are still considered acceptable by the USGS (Bartos & Ogle, 2002).

The quality assurance check (QAC) tool consists primarily of the cation-anion balance method. Sheet 1 of the Excel QAC tool contains the downloaded STORET data. Sheet 2 contains entries for each water-quality parameter and algorithms for calculating meq/L values; sums of major ions (in meq/L); (total cations or anions)/0.01(SC); TDS/SC ratio; and (difference between cations and anions)/(sum of cations and anions), in %, which is cation-anion balance (CAB) error. Changes in CAB error are made by adjusting concentrations of one, several, or all seven major cations and anions. CAB error should be in the range of about ±6%.

For this study, CAB errors range from approximately −47% - +43%. For analyses that exceeded about ±3% CAB errors, ion concentrations were revised appropriately using computer-based algorithms (Atkinson, 2011, 2018, 2019), and revisions were constrained by measured TDS concentrations, SC values, and several

empirical water-quality ratios as described above.

In essentially all cases, corrections of major ion concentrations did not impact hydrogeochemical conclusions or hydrochemical facies classification. Correction of individual-ion values typically did not exceed about 10%. For example, a reported HCO_3 value of 200 mg/L usually was not corrected to more than about 220 mg/L.

Visual MINTEQ (Gustafsson, 2009), a Microsoft Windows version of the DOS-based computer code MINTEQA2 prepared for USEPA (Allison et al., 1991), is an equilibrium speciation model. This public-domain software, which contains an extensive and updated thermodynamic database, was used to calculate aqueous mineral saturation indices (SIs) for the samples collected at one Big Blue River sampling station (Milford), one representative sampling station on the Little Blue River (Oak) and one on the West Fork of the Big Blue River (McCool Junction). To calculate saturation indices in Visual MINTEQ, all values for major cations and anions plus water temperature and pH were input. The primary model assumption is that all specified reactions and parameter concentrations have reached thermodynamic equilibrium. Additionally, Visual MINTEQ was utilized to calculate partial pressure of CO_2 for these three sampling stations.

The hydrogeochemical composition and classification (i.e., hydrochemical facies) of surface water and groundwater are oftentimes illustrated with a Stiff diagram (Stiff, 1951). Concentrations of major cations and anions are converted to meq/L and plotted relative to a vertical reference line. Cations are plotted to the left of the reference line, and anion concentrations are plotted to the right of the reference line.

Stiff diagrams are useful in comparing the ionic composition (hydrochemical facies) and TDS concentrations. The polygon size comprising the Stiff diagram is a relative indication of the major cation, anion, and TDS concentrations (Bartos & Ogle, 2002; Atkinson, 2018). Stiff diagrams were constructed for four Big and Little Blue River samples.

NDEC established numerous water-quality monitoring stations along the Big and Little Blue Rivers and their tributaries, then collected numerous water samples from June 1968-December 1975 and analyzed them in the field and laboratory. The 29 river stations extend geographically from near Bladen, NE (Webster County, Little Blue River), to near Barneston, Nebraska (Gage County, Big Blue River) (**Figure 1**). Also depicted on **Figure 1** are 13 sampling stations on seven tributary streams.

4. Results and Discussion

Median TDS (calculated) for the Big Blue River ranges from 207 mg/L at Surprise (most upgradient station) to 362 mg/L at the Dewitt sampling station. For these stations, median Ca values range from 34 - 62 mg/L. Median HCO_3 levels vary from 172 mg/L at Surprise to 276 mg/L at Dewitt. These increases in TDS and major ions in the downgradient direction are probably due to increasing streamflow residence time. For the West Fork of the Big Blue River, median TDS ranges

from 273 mg/L at Hastings (most upgradient) to 369 mg/L at the Inland station. Median HCO_3 concentrations for the West Fork range from 195 mg/L at Stockham to 344 mg/L at Crete; Ca ranges from a median of 46 mg/L at Inland and McCool Junction to 65 mg/L at Crete. Median TDS concentrations for the Little Blue River range from 171 mg/L at the Bladen sampling site (most upgradient site) to 322 mg/L at the Steele City site (most downgradient sampling site). Median Ca levels vary from 22 mg/L at Bladen to 61 mg/L at the Oak sampling station. Median HCO_3 concentrations range from 134 mg/L at Bladen to 243 mg/L at the Oak site.

Türkiye Creek at Geneva recorded the lowest Ca and HCO_3 median tributary concentrations, 50 and 229 mg/L, respectively, and Türkiye Creek at Wilber owns the lowest TDS median, 229 mg/L. The highest tributary median concentrations recorded for Ca, HCO_3, and TDS, 85, 387, and 429 mg/L, respectively, belong to the North Fork of Swan Creek at Swanson.

Referencing the Little Blue River, median TDS content ranges from 171 mg/L at Bladen (most upstream station) to 322 mg/L at the Steele City (most downstream) sampling station. Median Ca levels range from 22 mg/L at Bladen to 61 mg/L at the Oak sampling site. Median HCO_3 concentrations vary from 134 mg/L at Bladen to 243 mg/L at the Oak station. For the five sampling stations on three tributaries of the Little Blue River, median TDS values range from 151 mg/L on Sand Creek near Bladen to 461 mg/L at the Hubbell station on Rose Creek. The Bladen sampling station also owns the lowest median Ca and HCO_3 concentrations, 24 and 129 mg/L, respectively. High Ca and HCO_3 median concentrations, 99 and 365 mg/L, respectively, belong to the Hubbell sampling station.

STORET analyses for the Big and Little Blue Rivers and their tributaries fall predominantly in the Ca-HCO_3 hydrochemical facies. The few notable exceptions encompass the West Fork of the Big Blue at Inland; 11 of 12 samples are classified as Na-HCO_3. For the West Fork at Stockham, two samples are Na-Cl, one is Na-HCO_3 and a fourth is Mg-HCO_3. For the Big Blue River at Barneston (n = 99), two samples are Mg-HCO_3 and eight are Na-HCO_3 hydrochemical facies.

The SI values for calcite, dolomite, and gypsum were calculated using Visual MINTEQ (VM). A representative sampling site for the Big Blue (Milford station), for the West Fork of Big Blue (McCool Junction), and for the Little Blue River (Oak station) was chosen. For the Milford station, six of 19 samples yielded negative SI values for calcite (**Figure 3**). For the 13 remaining samples, positive values ranged from 0.03 - 1.35 with a median of 0.58. VM revealed seven samples with dolomite negative SIs. Twelve samples yielded positive dolomite SI values ranging from 0.12 - 2.47 with a median of 0.80. For McCool Junction's 12 samples, four yielded negative calcite SIs; the eight positive SIs ranged from 0.08 - 0.83, with a median of 0.46. VM output for dolomite SIs encompassed six negative values and six positive values, ranging from 0.08 - 1.08 with a median of 0.69. All 20 samples for the Oak station yielded calcite SI values greater than zero. Values range from 0.19 - 1.09, with a median of 0.53. For dolomite, four values were negative; 16 positive values range from 0.28 - 1.64 with a median of 0.72. VM computed SI values for

gypsum are negative for all samples for the three representative sampling sites with values ranging from about −0.5 - −2.5 with a median of −2.0, documenting unsaturated (dissolving) conditions. The relatively low positive SI values for calcite and dolomite suggest that these samples and the associated stream water are only slightly supersaturated. Consequently, only low quantities of calcite and dolomite are precipitating at these river locations.

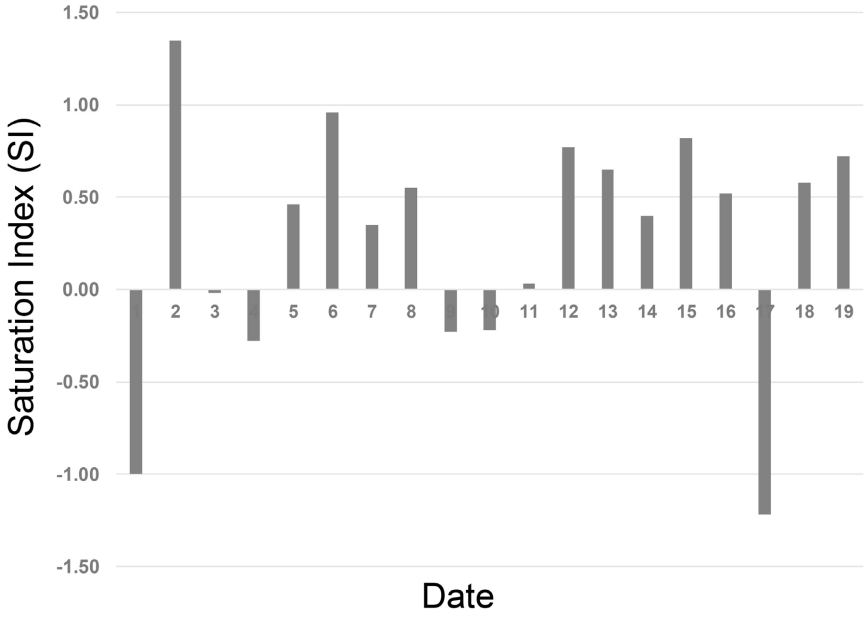

Figure 3. Saturation index values for calcite at Big Blue River Milford sampling site.

VM-calculated partial pressure of CO_2 for the Milford sampling station ranged from 518 - 14400 µatm with a median of 2610 µatm. By comparison, the partial pressure of CO_2 in the atmosphere is approximately 420 µatm. This suggests that the Milford surface water is supersaturated with CO_2. For numerous lakes worldwide, Cole et al. (1994) found most partial pressure values significantly higher than atmospheric, consequently supersaturated with CO_2.

For the McCool Junction sampling station on the West Fork of the Big Blue River, VM-calculated partial pressure of CO_2 ranged from 773 - 4720 µatm with a median of 2185 µatm. At the Oak sampling station on the Little Blue River, CO_2 ranged from 658 - 3020 µatm with a median of 1650 µatm. In summary, surface water in the Big and Little Blue Rivers is supersaturated with CO_2.

To investigate the primary and secondary processes that affect calcium concentrations, the plots and ratios of Ca versus HCO_3 were used. The most common weathering reaction for carbonates is simple dissolution, giving a 1:2 ratio of Ca:HCO_3 (Zhang et al., 1995; Tziritis et al., 2016). According to Drever (1997) and Hounslow (1995), low molar ratios (<0.5) of Ca: HCO_3 indicate exchange of calcium and magnesium in water by sodium and potassium bound in clay or HCO_3 enrichment, possibly from silicate weathering. On the contrary, high ratios (>0.5) suggest other sources for Ca and Mg, such as reverse ion exchange, where sodium

in water is exchanged for Ca and Mg in rocks and minerals. Hence, the origin of calcium is not straightforward and is not solely attributed to the dissolution of carbonate (e.g., calcite and dolomite) and/or other Ca-rich minerals [e.g., anorthite plagioclase ($CaAl_2Si_2O_8$)]. For the Big and Little Blue River watersheds, all but two sampling stations yielded median Ca:HCO_3 ratios less than 0.5. The West Fork of the Big Blue River at Stockham (Hamilton County) recorded a median ratio of 0.51. Rose Creek at Hubbell (Little Blue watershed, Thayer County) scored a median ratio of 0.52. The predominance of low (<0.5) Ca: HCO_3 ratios in the Big and Little Blue River watersheds suggests widespread hydrogeochemical environment(s) of positive ion exchange and possible HCO_3 enrichment originating predominantly from silicate (e.g., feldspar) weathering.

The aqueous hydrochemistry of four representative sample analyses is displayed on Stiff diagrams (Figure 4). Sample analyses for the Big Blue River, West Fork of the Big Blue, and the Little Blue River are depicted in Figures 4(a)-(c), respectively. The high HCO_3 for the Big Blue [Figure 4(a)] distinguishes it from the other two. The Stiff diagram for the West Fork Big Blue River at Inland water sample [Figure 4(d)] depicts the visually higher (Na + K) concentration (3.9 meq/L) (Na-HCO_3 hydrochemical facies) than the other three major ions and higher TDS value than Figure 4(b) and Figure 4(c).

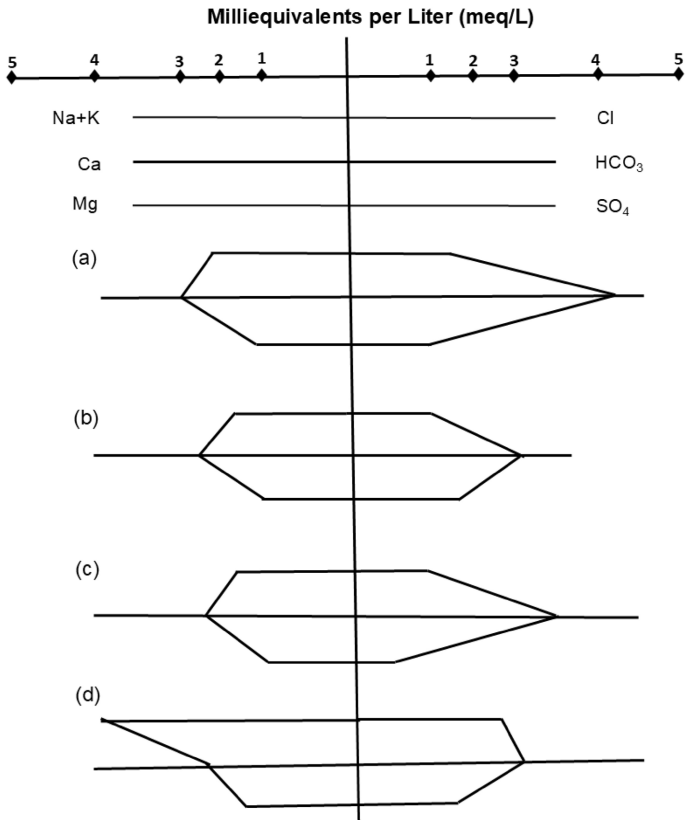

Figure 4. Stiff diagrams for: (a) Big Blue River at Dewitt; (b) West Fork Big Blue River at Stockham; (c) Little Blue River at Endicott; and (d) West Fork Big Blue River at Inland.

For sampling stations where samples were collected for several years, concentrations of major ions Ca, Na, HCO_3, Cl, and SO_4 varied substantially at many sampling sites. For example, for the West Fork Big Blue River at Dorchester sampling site (n = 22), HCO_3 varied from 109 - 305 mg/L (Figure 5); sample variance function (SVF) is 3328. For the Big Blue River at Dewitt, SO_4 content varies from 12 - 92 mg/L (n = 9), and the SVF is 533.9.

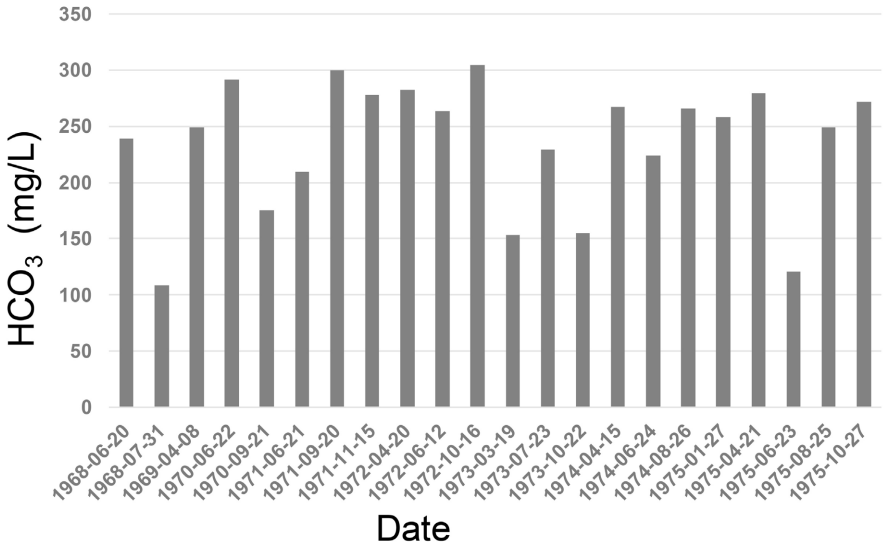

Figure 5. HCO_3 concentrations for the West Fork Big Blue River at Dorchester.

Silicate (feldspar) rock weathering is an important geochemical process universally impacting the major ion chemistry of groundwater and surface waters (Mackenzie & Garrels, 1965; Dehnavi et al., 2011; Vishwakarma et al., 2018; Atkinson, 2019). Specifically, silicate-rock weathering increases the concentration of HCO_3 [and often an alkali metal (e.g., Na) or alkali earth element (e.g., Ca)] in natural waters in accordance with Dehnavi et al. (2011) [Equation (1)]:

$$\begin{aligned} &2\mathrm{NaAlSi_3O_8}\left(\text{albite}\right)+2\mathrm{H_2CO_3}+9\mathrm{H_2O}\Rightarrow \\ &\mathrm{Al_2Si_2O_5}\left(\mathrm{OH}\right)_4+2\mathrm{Na}+4\mathrm{H_4SiO_4}+2\mathrm{HCO_3} \end{aligned} \quad (1)$$

Numerous hydrochemistry researchers have found that in the (Ca + Mg) (y axis) versus (HCO_3 + SO_4) scatter diagram, the ionic concentrations plotting above the 1:1 equiline result primarily from carbonate (calcite and dolomite) weathering and dissolution and/or from reverse ion exchange (Datta & Tyagi, 1996; Gomaa et al., 2013; Vishwakarma et al., 2018; Atkinson, 2019), whereas those falling along the equiline are attributable to carbonate (calcite and dolomite) and sulfate mineral (e.g., gypsum, anhydrite) dissolution. Sample analyses that plot below the 1:1 line reflect silicate (feldspar) weathering/dissolution as the dominant process, and ion exchange is a second potential geochemical process.

Scatter diagrams of (Ca + Mg) versus (HCO_3 + SO_4) for all Big and Little Blue River sampling stations plot below the 1:1 equiline, encompassing the Little Blue

River at Deweese (Figure 6). This hydrochemical ratio ranges from 0.67 for the West Fork of the Big Blue River at Inland to 0.84 along the Little Blue River at Deweese, Gilead, and Endicott sampling stations. These study-area hydrochemical ratio values likely confirm the thesis asserted by Datta and Tyagi (1996), Dehnavi et al. (2011), Gomaa et al. (2013), and other researchers that weathering of silicate minerals (e.g., Ca, Na feldspars) is a dominant hydrogeochemical process. A secondary geochemical process probably occurring throughout the Big and Little Blue River watersheds is cation exchange, decreasing the aqueous concentration of Ca and Mg throughout the watershed. As briefly discussed in the "Geology" section, the Laramide Orogeny provided a source of igneous rocks and minerals (i.e., feldspars) transported by rivers and streams during the Late Cretaceous and Tertiary time eastward into Nebraska and the Big and Little Blue River watersheds.

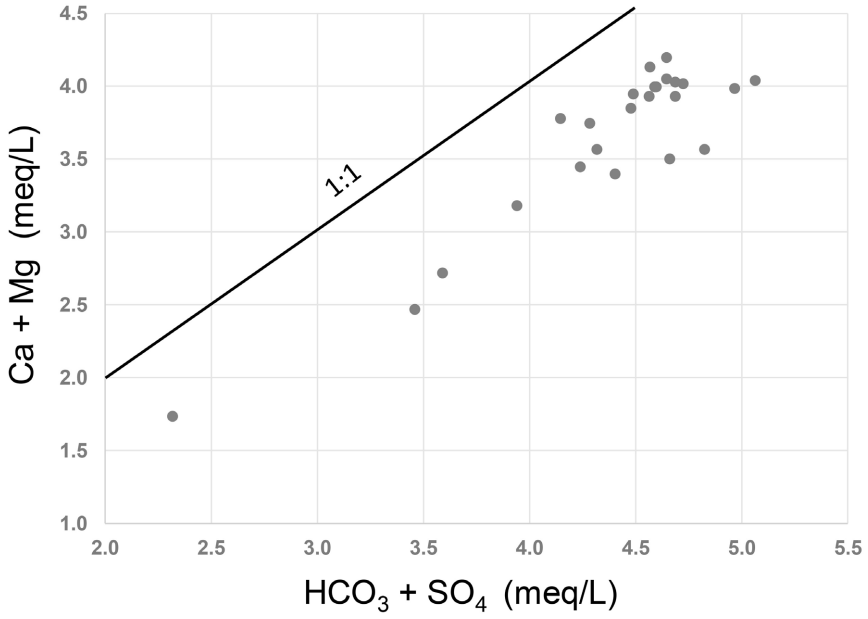

Figure 6. Scatter diagram of (Ca + Mg) versus (HCO_3 + SO_4) for Little Blue River at Deweese.

To explore the possible hydrogeochemical relationship or covariance between the primary cation, Ca, and the major anions, HCO_3, SO_4, and Cl, Pearson correlation analysis was conducted for a representative Big Blue River sampling station, Beatrice (Ca-HCO_3 hydrochemical facies), STORET analytical results for the period July 30, 1968-October 29, 1975. This statistical analysis (n = 20) resulted in notably high r and r^2 values and low *p*-values for Ca versus HCO_3 and Ca versus SO_4 and slightly lower r and r^2 values and higher *p*-value for Ca versus Cl (Table 1(a)). These significantly positive Pearson coefficient values demonstrate that Ca intensely covaries with HCO_3 and SO_4 and slightly less strongly with Cl, suggesting weathering of carbonates, silicates (feldspars), gypsum and probably accompanied by hydrologic mixing, weather conditions, or shared discharge effects.

Joeckel et al. (2005) reported pyrite weathering in the upper Dakota Formation and the lower Graneros Shale in the Fairbury area produces gypsum crust and other SO_4 minerals. The r and r^2 values for Cl may be lower than those for SO_4 and HCO_3, partly because Cl concentrations are lower than those for SO_4 and HCO_3 (medians: $Cl/SO_4/HCO_3$ = 38/53/256 mg/L, respectively).

Linear regression analysis was performed on the three Ca-anion pairs described above to potentially quantify the stoichiometric ratio or slope of the hydrochemical process. The resulting coefficient of determination (R^2) values for all three ion pairs were moderately high (**Table 1(a)**). The slope of the Ca-HCO_3 pair (**Figure 7**) was the highest of the three, 0.91(x) [HCO_3 = 0.91(Ca)]. Milliequivalents per liter is the unit of measurement; therefore, if the mathematical relationship represents calcite dissolution, the theoretical slope would be approximately 1:1. The large positive y intercept (1.47) adds complexity to the regression slope. Statistically, the regression slope measures variation in x(Ca) and y(HCO_3) values, not ratios of the actual values. The regression slope does not accurately portray the stoichiometric ratio; however, it supports the hypothesis that Ca-HCO_3 covariance is dominant, and dissolution of calcite and other minerals (e.g., feldspars) producing HCO_3 is dominant. Additionally, the Ca-HCO_3 zero-intercept R^2 is slightly higher than the Ca-SO_4 one. The Ca-SO_4 ion pair yields a linear regression equation of y = 0.5(x) [SO_4 = 0.5(Ca)], meaning that every 1 meq/L increase in Ca results in a 0.5 meq/L increase in SO_4. This regression slope suggests gypsum or other mineral sources of SO_4 dissolution as a secondary geochemical process. The linear regression slope for Ca-Cl is the lowest of the three, 0.4(x) [Cl = 0.4(Ca)], suggesting only a tertiary, insignificant evaporite/Cl weathering or mixing source exists in the watershed.

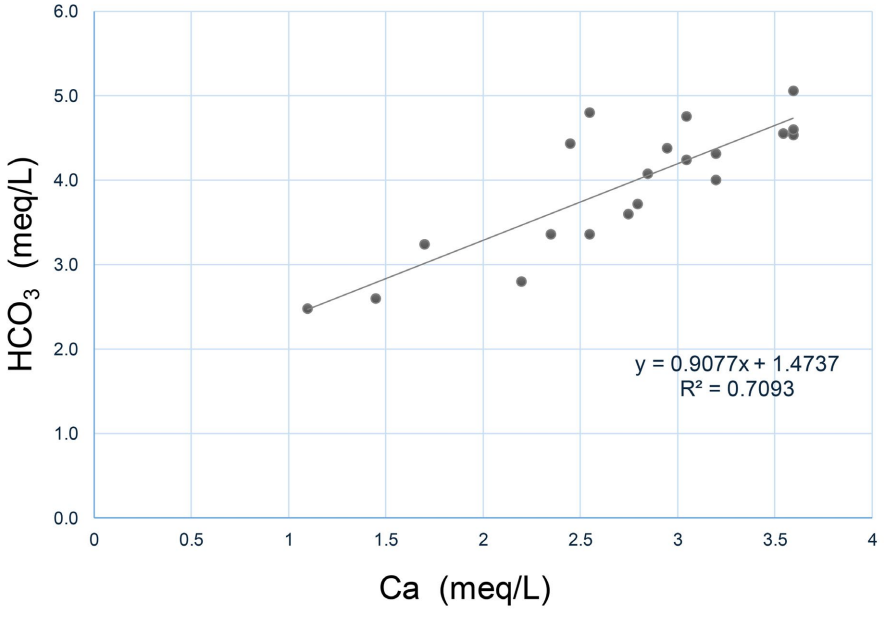

Figure 7. Linear regression for Ca versus HCO_3 for the Big Blue River at Beatrice.

The dataset (Na-HCO_3 hydrochemical facies) for the West Fork of the Big Blue River at Inland also was evaluated for covariance by Pearson coefficient and potential quantification by linear regression analyses. Ca-SO_4 r and r^2 values (Table 1(b)) were significantly higher than those for Ca-HCO_3 and slightly higher than for Ca-Cl. These coefficient values strongly suggest that gypsum/pyrite weathering predominates over the other two major ion pairs. Linear regression also demonstrates, by a high R^2, the apparent preeminence of SO_4 dissolution/weathering or mixing source(s) compared with carbonate and evaporite (Cl) weathering or mixing at this sampling site.

Table 1. Results of Pearson correlation and linear regression analyses for: (a) Big Blue River at Beatrice; and (b) West Fork Big Blue River at Inland.

(a)			
Pearson correlation	**Ca versus HCO_3**	**Ca versus SO_4**	**Ca versus Cl**
r	0.842	0.845	0.740
r^2	0.709	0.714	0.548
p-value	3×10^{-6}	3×10^{-6}	1.9×10^{-4}
Linear regression	**Ca versus HCO_3**	**Ca versus SO_4**	**Ca versus Cl**
Regression equation	y = 0.91x + 1.47	y = 0.50x − 0.32	y = 0.40x − 0.07
R^2	0.709	0.714	0.548
p-value	3.2×10^{-6}	2.8×10^{-6}	1.9×10^{-4}
R^2 (0 intercept)	0.982	0.956	0.946
(b)			
Pearson correlation	**Ca versus HCO_3**	**Ca versus SO_4**	**Ca versus Cl**
r	0.603	0.814	0.794
r^2	0.363	0.663	0.630
p-value	0.038	1.3×10^{-3}	2.1×10^{-3}
Linear regression	**Ca versus HCO_3**	**Ca versus SO_4**	**Ca versus Cl**
Regression equation	y = 0.72x + 1.90	y = 1.26x − 1.36	y = 1.73x − 1.91
R^2	0.364	0.668	0.634
p-value	0.038	1.2×10^{-3}	1.9×10^{-3}
R^2 (0 intercept)	0.981	0.933	0.922

5. Conclusion

This study presents analysis and interpretation of the extensive legacy (1968-1975) major ion and related water-chemistry database for the Big and Little Blue River watersheds (encompassing tributaries) in southcentral Nebraska.

The major findings and conclusions associated with this hydrogeochemical study follow:

1) Measured surface-water salinity in the watersheds is relatively low. Median

TDS levels for individual sampling stations range from about 150 - 440 mg/L.

2) The large analytical analyses database reveals that most water samples possess Ca-HCO_3 hydrochemical facies. Na-HCO_3 is the secondary hydrochemical facies.

3) Scatter diagrams of (Ca + Mg) versus (HCO_3 + SO_4) for all Big and Little Blue River watersheds sampling stations plot below the 1:1 equiline. This suggests silicate (feldspar) weathering/dissolution may be a dominant geochemical process, and ion exchange a second potential geochemical process.

4) For sampling stations where samples were collected for several years, concentrations of major ions Ca, Na, HCO_3, Cl, and SO_4 varied substantially at many sampling sites. For one sampling site (n = 22), HCO_3 varied from 109 - 305 mg/L (SVF = 3328).

5) Hydrogeochemical modeling reveals that the SIs for calcite and dolomite for the Big and Little Blue Rivers and their tributaries typically are low positive values (~ 0.1 - 2.5), implying slightly precipitating carbonate environments. All calculated SI values for gypsum are low negative values, suggesting mild dissolving conditions. Low SI values for these three common minerals in rocks and soils comprise a line of evidence for the near thermodynamic equilibrium of the surface waters in the study area.

6) To explore the possible hydrogeochemical relationship or covariance between the primary cation, Ca, and the major anions, HCO_3, SO_4, and Cl, Pearson correlation analysis was conducted for a representative Big Blue River sampling station (Beatrice), yielding Ca-HCO_3 hydrochemical facies water. This statistical analysis (n = 20) resulted in notably high r and r^2 values and low *p*-values for Ca versus HCO_3 and Ca versus SO_4 and slightly lower r and r^2 values and higher *p*-value for Ca versus Cl. These significantly positive Pearson coefficient values demonstrate that Ca strongly covaries with HCO_3 and SO_4 and slightly less strongly with Cl, suggesting weathering of calcite, dolomite, silicates, and gypsum or other SO_4-bearing minerals but less likely dissolution of halite, other Cl-rich evaporite(s), or an anthropogenic source(s). The r and r^2 values for Cl may be lower than those for SO_4 and HCO_3, partly because Cl concentrations are lower than those for SO_4 and HCO_3 (medians: Cl/SO_4/HCO_3 = 38/53/256 mg/L, respectively).

7) Linear regression was performed on the three Ca-anion pairs described immediately above to potentially determine the stoichiometric ratio and quantify the slope of hydrochemical process relationship for the three Ca-anion pairs in Ca-HCO_3 hydrochemistry facies environment. The resulting coefficient of determination (R^2) values for all three cation-anion pairs were moderately high (0.548 - 0.714). The slope of the Ca-HCO_3 pair was the highest of the three, 0.91(x) [HCO_3 = 0.91(Ca) (meq/L)]. The regression slope does not accurately portray the stoichiometric ratio; however, it most likely supports the hypothesis that the dissolution of carbonates and/or silicates (feldspars) is the primary weathering process. Additionally, the Ca-HCO_3 zero-intercept R^2 is slightly higher than the Ca-SO_4 one.

The Ca-SO_4 ion pair yields a linear regression equation of y = 0.5(x) [SO_4 = 0.5(Ca)]. This regression slope suggests gypsum (or other mineral source of SO_4) dissolution as a secondary geochemical process. The linear regression slope (and R^2) for Ca-Cl is lowest of the three, y = 0.4(x) [Cl = 0.4(Ca)], suggesting only a tertiary, insignificant evaporite/Cl weathering or mixing source exists in the watershed.

6. Highlights

- Surface waters in the watersheds are relatively low in TDS; median values typically range from 150 - 440 mg/L. Most river-water samples have Ca-HCO_3 hydrochemistry facies.
- Binary graphs of major ions and hydrochemical ratios suggest that silicate minerals (feldspars) may be the primary source of the watersheds' hydrochemistry.
- Most Big and Little Blue River samples yield low positive calculated saturation index values for calcite and dolomite, documenting low supersaturated aqueous environments and suggesting attainment or near attainment of thermodynamic equilibrium conditions.

Data Availability

Some or all data and computer programs that support the findings of this study are available from the author via email upon reasonable request.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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